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ОБЩАЯ ХИМИЯ

ГОСУДАРСТВЕННОЕ НАУЧНО-ТЕХНИЧЕСКОЕ ИЗДАТЕЛЬСТВО
ХИМИЧЕСКОЙ ЛИТЕРАТУРЫ
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CHAPTER 1

Introduction

1. Matter and Its Motion. Chemistry is one of the natural sciences which treat of the world around us, its wealth of different forms and the diversity of phenomena taking place in it.

All of nature, the whole world, exists objectively outside and independently of the consciousness of man. The world is material; all entities are various kinds of moving matter.

Matter, nature, should not be conceived as something motionless, something in a state of rest. Man's entire socio-historical experience shows that matter is in a state of continuous motion, change, development.

Motion, as constant change, is inherent to matter as a whole and to each of its minutest particles. When we speak of the motion of matter we must not think of it in its narrow mechanical sense, as of a particle travelling through space. The forms of motion of matter are diverse. The heating and cooling of bodies, radiation of light, electric current, chemical changes, vital processes, thought, are no more than various forms of motion of matter.

The different forms of motion of matter can pass into one another. Thus, mechanical motion easily passes into heat or thermal motion, thermal motion into chemical, chemical into electrical, etc. These transitions are evidence of the unity of, and the constant ties between, the qualitatively different forms of motion.

All the various transitions from one form of motion into another are governed by one of the fundamental laws of nature, that of the eternity of matter and its motion. This law covers all the concrete kinds of matter and all the forms of its motion; not a single kind of matter and not a single form of motion can be obtained from nothing or transformed into nothing; the transformation of one kind of matter into another, or one kind of motion into another takes place only in definite quantitative ratios. Matter and its movement can be neither annihilated nor created; they exist eternally and are eternally changing. This is confirmed by the entire development of natural science through the ages.

Now we can define the subject of natural science with sufficient exhaustiveness and accuracy.

The subject of natural science is eternally moving, eternally changing matter. Natural science studies the mutual transformations, changes and development of concrete kinds of matter, brings to light the laws of natural phenomena and the relations between them. Study and knowledge of these laws enable man to control the phenomena of nature and to change it according to his needs.

The different forms of motion of matter are dealt with by various branches of science: physics, chemistry, biology and others. The general laws of development of nature are the subject of materialistic dialectics.

2. Substances and Their Changes. Subject and Method of Chemistry. In chemistry each kind of matter possessing constant physical properties under specific conditions, such as water, iron, sulphur, lime, oxygen, etc., is called a **substance.**

The substances encountered in nature are infinitely diverse. Compare, for instance, sand, water, chalk, sulphur; it will readily be seen that these are all absolutely different substances, bearing even no outward resemblance to one another.

Each substance is distinguished by its properties. Sulphur, for example, possesses a light yellow colour and a crystalline structure; it is brittle and insoluble in water; its specific gravity is 2.07. When heated, sulphur melts at 112.8°C, etc. All these characteristic features of sulphur are its physical properties.

The magnitudes characterizing the physical properties of a substance—its specific gravity, melting point, solubility, etc.—which have constant values under definite conditions, are called physical constants.

To establish the properties of a substance, we must obtain it in as pure a state as possible, since even insignificant impurities may change the numerical values of its constants. Only pure substances possess definite, invariable properties.

Substances are found pure in nature very rarely. In most cases natural substances are mixtures consisting sometimes of a very large number of different substances. For instance, natural water always contains a small amount of mineral salts. When any one substance predominates in a mixture, the whole mixture is called by its name, the other constituents and their content in the mixture sometimes being indicated as impurities. If these are present in such small quantities that they cannot affect the investigation or use of the substance, the latter is called "chemically pure."

Absolutely pure substances are not known. Conventionally we speak of "chemically pure" hydrochloric acid or of "chemically pure" nitric acid, meaning a solution which contains nothing but the acid and water. In contradistinction to "chemically pure" acids, "technical" acids contain various impurities besides water.

A pure substance is always homogeneous; mixtures may be homogeneous or heterogeneous.

A mixture of two or more substances is conventionally called homogeneous if the individual particles of the substances cannot be detected by the naked eye or under the microscope due to their very small size. Gaseous mixtures, many liquids, certain alloys, etc., are examples of such mixtures.

Rocks, soil, turbid water, dusty air, etc., are heterogeneous mixtures.

The heterogeneity of a mixture is not always manifest; sometimes it can be detected only with the aid of a microscope. For instance, at first sight blood is a quite homogeneous red liquid, but when viewed under a microscope it is found to consist of a colourless liquid with red and white corpuscles floating around in it.

Milk is also a heterogeneous mixture, consisting of globules of fat suspended in a colourless liquid (Fig. 1).

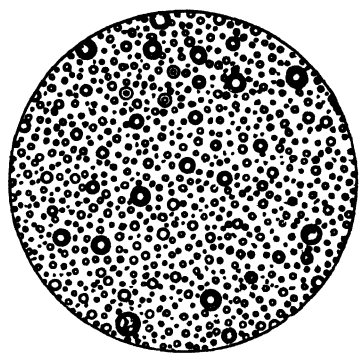


Fig. 1. A drop of milk viewed under the microscope

In everyday life we can observe that substances undergo various changes: water spilled on the floor "dries up," turning into invisible water vapour; an iron article in moist air becomes coated with rust; wood burns in the stove, leaving but a heap of ashes; leaves fallen from the trees gradually decay, turning into a dark mass of humus, etc.

When a lead bullet, fired from a rifle, hits a stone, it grows so hot that the lead melts and becomes a liquid. Here, the mechanical motion of the bullet passes into the thermal motion of the lead particles, but this is not accompanied by any chemical change of the lead, as solid and liquid lead are the same substance in different physical states. No new substance is formed during the transformation.

But when lead turns into lead oxide (litharge) as a result of prolonged heating, an entirely new substance with other properties, i.e., differing qualitatively from the lead, takes its place. The same happens when iron rusts, wood burns, or leaves decay—in all these cases new substances are formed, quite different from the original substances.

Phenomena accompanied by radical changes of substance in which new substances arise in place of the initial ones are called chemical phenomena. The science that treats of such phenomena is called **chemistry**. Hence, *chemistry is the science of the transformation of*

substances. It studies the composition and structure of substances, the relation between the properties of substances and their composition and structure, the conditions and ways of changing substances into one another.

Chemical changes are always accompanied by physical changes. For this reason chemistry is closely related to physics. It is closely related also to biology, since any vital process is accompanied by continuous chemical changes of substances in the organism, by a continuous exchange of substances between the organism and its surroundings (metabolism). However, although chemical phenomena are related to physical, and biological phenomena to physical and chemical, chemistry cannot be reduced to physics, nor biology to physics and chemistry, since each form of motion of matter has its peculiarities.

In chemistry, as in other sciences, the study of any phenomenon begins first of all with observation and description of the phenomenon. But science does not confine itself only to description of observed phenomena; its most important task is to explain them. In seeking to explain phenomena we strive to delve ever deeper into their essence, to ascertain their causes, to establish the conditions under which they occur. For this purpose we reproduce various phenomena artificially, under conditions and in an environment best adapted for their study. The artificial reproduction of a phenomenon is called an **experiment.** Experiments are mostly intended to check the truth of ideas or assumptions which arise in studying a phenomenon. Assumptions put forth to explain a phenomenon, to establish its connection with other phenomena studied earlier, to unite several phenomena under a common idea, are called **hypotheses.** If the conclusions which follow logically from the assumption made are confirmed by experiment, if the hypothesis explains not only the phenomenon in question, but permits general conclusions and prediction of new phenomena as well, the hypothesis becomes a **theory.** If, on the other hand, experiment fails to confirm it, the hypothesis must be discarded.

Theory, which is a broad generalization of experience, greatly facilitates the study of phenomena, enables us to understand them better. Moreover, it points out the trend of further experiments and gives hints for carrying them out, and therefore has an instructive value. Theory makes it possible to carry on investigations without groping in the dark, according to a pre-arranged plan, from a definite standpoint and on the basis of established laws.

Especially important theoretical generalizations in chemistry, which have made for progress in this branch of science are: the theory of atoms and molecules, the theory of chemical structure, the Periodic Law and the periodic system of chemical elements.

3. Importance of Chemistry. Chemistry in the National Economy of the U.S.S.R. Chemistry plays an exceedingly important part in modern life, especially in man's industrial activities. There is hardly a branch of industry but is connected with some application of chemistry. Nature gives us only the raw materials—timber, ore, salt, coal, oil, etc. By subjecting natural materials to chemical treatment, we obtain the various substances we need for agriculture, for the manufacture of industrial products and for domestic use—mineral fertilizers, metals, plastics, dyes, acids, medicinals and pharmaceuticals, soap, soda, etc. Before treating natural raw materials chemically we must know the general laws of the transformation of substances, and it is chemistry that gives us this knowledge.

Chemistry concerns itself also with finding the most economical ways of using natural materials, with the utilization of by-products and industrial wastes; it seeks new, more efficient methods of producting various substances, etc.

Tsarist Russia had no large-scale chemical industry. The few chemical plants that did exist were of a semi-artisan nature, most of them owned by or dependent on foreign capital. The engineers, technicians, foremen and other specialists employed at the plants were mostly foreigners. The lack of progress in the chemical industry told strongly on the state of Russian chemical science, which had no material basis for its development. Scientific activities and research were rarely encouraged by the state. In spite of these extremely unfavourable conditions, however, Russian scientists made some major contributions to chemistry.

The Great October Socialist Revolution of 1917 rooted out the causes that had retarded the progress of Russian science and paved the way for its free development. In the very first years of existence of the new-born Soviet Republic, during the trying years of ruin and Civil War, chemical science received a great deal of aid from the Soviet Government. The first research institutes and laboratories were organized, and they played an outstanding part in the development of Soviet chemical science and industry. Subsequently their numbers began to grow rapidly. The number of chemical schools and colleges also increased many times over. Large-scale research, both theoretical and applied, was launched in all the branches of chemistry at the universities and institutes.

Russia possessed immense mineral resources, but they were insufficiently explored, and the chemical industry of tsarist Russia used mostly imported raw materials. No wonder, therefore, that the first period of development of the Soviet chemical industry was marked by intensive prospecting for chemical raw materials. As a result of the work of the Russian chemist N. Kurnakov and the investigations of the geologist P. Preobrazhensky, enormous deposits

of potassium salts were discovered in the Soviet Union, considerably greater in size than all the European deposits taken together. In 1924 an expedition headed by the Russian scientist A. Fersman discovered vast deposits of mineral phosphates—apatites—on the Kola Peninsula.

A powerful chemical industry supported by home resources of raw materials sprang up in the U.S.S.R. during the pre-war five-year plan periods. The Soviet mining and chemical engineering combines based on the Kola apatites, the Solikamsk potassium salts, the Ural chromium and copper ores, etc., are among the largest in the world. The same years witnessed the erection of such complex enterprises as synthetic ammonia and artificial rubber plants, plants for the electrothermal production of phosphorus, calcium carbide, concentrated fertilizer plants, agricultural pesticide plants, etc. The production of new types of artificial fibres, artificial leather, plastics, organic dyestuffs, pharmaceuticals and cinema film was mastered. The oil refinery industry was developed on a large scale. Production of optical glass, various types of high-quality chemical glass and of glass fibre was started. By 1941 the chemical industry had exceeded its pre-revolutionary level more than twentyfold.

During the Great Patriotic War the chemical industry suffered heavy damage, but already by the end of the first post-war (fourth) five-year plan all the ruined plants had mostly been rebuilt and in 1950 the level of production was 80 per cent above the pre-war level.

In post-war years special emphasis was laid on the expansion of the branches of the chemical industry producing nitrogen and potassium fertilizers, plastics, synthetic rubber, organic synthetic products, chlorine and its derivatives. The production of synthetic fibre, synthetic ethyl alcohol, organic preparations for combating agricultural pests and others was started. The gross output of the chemical industry in 1957 was five times that of 1940. In volume of production the chemical industry of the U.S.S.R. is now the second largest in the world.

The control figures for the economic development of the U.S.S.R. in 1959-1965, approved by the XXI Congress of the C.P.S.U. envisage rapid development of the chemical industry and especially of the production of chemical fibres, plastics, synthetic rubber and other synthetic materials and mineral fertilizers. By the end of this seven-year plan period the production of artificial fibres is to increase fourfold, that of plastics and synthetic resins more than sevenfold, of mineral fertilizers approximately threefold, compared to 1958. The output of sulphuric acid, ammonia, soda, alkalies and other important chemical products is to be increased not less than two- or threefold. Production of automobile tyres, technical rubber goods, rubber footwear, etc., is also to be stepped up considerably.

Further growth of the output of mineral fertilizers will make for their more extensive use in agriculture, and, consequently, for bigger yields of agricultural crops. It is planned to organize the production of new types of concentrated mineral fertilizers and new more effective pesticides. The production of weed-control chemicals will be organized on a large industrial scale, thus effecting a substantial saving of labour in agriculture.

A very important task facing the chemical and oil industries is that of sharply increasing the utilization of natural, casing head and refinery gases for the production of synthetic rubber, ethyl alcohol, detergents and other chemical products. During 1959-1965 the expenditure of foodstuffs for technical purposes must be completely stopped. This will release several million tons of grain and potatoes for the national consumption, as well as a considerable amount of edible fats.

Of no less importance are the tasks of extending the assortment and increasing the output of synthetic materials for machine-building, radio and electrical engineering, for the aircraft, automobile and other industries. The production of high-quality varnishes and dyes, plastics, electrical insulation materials is to be expanded. New synthetic materials will not only substitute natural ones, but will make it possible to raise the technological level of production in many branches of industry. For example, the use of silico-organic insulation materials in the electrical industry will lengthen the lifetime of certain motors eightfold, and increase their power by 35 to 65 per cent without affecting their size. Plastics are not only successful substitutes for non-ferrous metals, but are often independent structural materials, superior to metals in a number of respects.

The use of plastics in machine-building simplifies technologies and reduces the weights of machines and finished goods. Chemical industry products, particularly synthetic materials, are finding ever wider application with each year in the manufacture of textiles, garments, footwear and other consumer goods. Synthetic materials are used to make building parts and pipes, as decorative and insulating materials, etc.

Thus, the development of the chemical industry will make it possible to utilize the natural wealth of the country to the greatest effect and is a necessary condition for the further technical progress of all branches of the national economy.

The decisions of the May (1958) plenary meeting of the C.C. C.P.S.U. outline a truly magnificent programme for rapid development of the chemical industry and especially the production of synthetic materials and goods made of them. This programme envisages the erection and commissioning in the period 1959-1965 of a large number of new enterprises, as well as extension of numerous

enterprises already in operation. According to the seven-year plan the capital investments needed for this purpose will total 100,000 to 105,000 million rubles, which exceeds the investments made in the chemical industry during the previous seven-year period by more than five times.

Accomplishment of the tasks set before the chemical industry will make it possible to increase the total volume of output of the chemical industry almost threefold, which will be of immense importance for the entire national economy of the country.

4. Birth of Chemistry and Initial Stages of Its Development. Chemistry, like other sciences, was born in the process of man's practical activities.

In winning his means of existence man gradually came to know the causes of various phenomena and found practical applications for certain transformations of substances. Thousands of years ago people already knew how to obtain many useful materials. They knew how to smelt metals from their ores, produce and utilize various alloys, manufacture glass and glassware.

In Egypt, technically the most advanced country of the ancient world, many trades based on the use of chemical processes flourished long before our era. The Egyptians smelted iron from its ores, produced stained glass, knew how to tan leather, extract medicines, dyes and perfumes from plants, etc.

Chemical production in India and China dates from still earlier times.

Of course, the scraps of chemical information known at that time could hardly be called a science, but together with observations of natural phenomena they formed a basis for deliberation on the structure of matter and its transformations.

In the writings of ancient Hindu philosophers we read that the universe is built up of a small number of simple substances.

A more comprehensive and integral philosophical conception of nature originated in ancient Greece. It propounded the idea that the foundation of all things is uniform and that all the different substances the world consists of are various forms of a single principle.

Some Greek philosophers taught that all entities came from water. Others were of the opinion that the basic substance of the universe was air. Still others considered fire to be the origin of all things. In the V century B. C. Empedocles combined the ideas of his predecessors and added one more fundamental substance—earth—to the three pointed out by them, thus assuming the existence of four principles, which he called **elements.**

In the same century there arose an entirely new philosophical trend in the attempt to explain the structure of matter. The representatives of this trend were Leucippus and his disciple Democritus—the greatest

materialists of ancient times. According to Democritus, all bodies in nature are built up of minute solid impermeable and indivisible particles, which he called **atoms.** Atoms are so small that they cannot be seen. They may be infinitely different in shape and size, but they all consist of the same matter. There is nothing in the world but atoms and the void between them. The differences between substances depend solely on differences in the number, shape and arrangement of the atoms they consist of. Atoms possess the property of eternal motion. The motion of atoms explains the contraction of bodies when cooled and their expansion when heated, their mixing with water when dissolved and other phenomena. Changes of all kinds consist merely in the combination and separation of atoms.

The materialistic teachings of Democritus were far in advance of the views of his contemporaries, but did not receive general recognition. In its further development philosophy tended to attribute all phenomena to the abstract properties of substance. This philosophy was grounded on the teachings of Aristotle (384-322 B. C.) which greatly influenced the subsequent development of natural science.

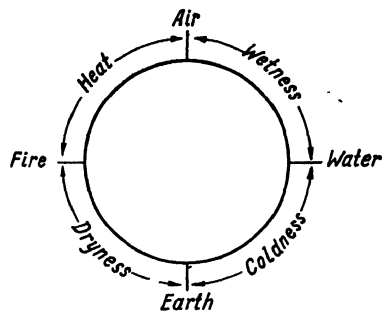


Fig. 2. Aristotle's elements

Aristotle held that the basis of all material being was prima materia, which is eternal and cannot be formed from nothing nor turn into nothing; its quantity in nature is unchangeable. Initial matter has four fundamental qualities, which are perceived by our senses and stand opposite each other by pairs: heat and coldness, dryness and wetness. The diversity of substances depends on combinations of these qualities in different proportions. Combining the qualities by pairs Aristotle arrives at the four elements of Empedocles—earth, water, fire and air (Fig. 2).

According to Aristotle, the fundamental qualities are not connected inseparably with initial matter, but can be taken from or added to it. For instance, when we heat water we take coldness from it and add heat to it; the water evaporates, i. e., turns into air, as Aristotle thought. Hence the conclusion that elements could be transformed into one another. Therefore, the art of creating various substances boiled down to the combining of definite qualities.

The Greek philosophers grounded their general conceptions of natural phenomena only on observation; the productive forces of society at that time were still far from the level at which a precise science based upon experiment could arise.

While in Greece philosophers concentrated mostly on abstract theories, attempting to grasp the intrinsic structure of matter, in other countries practical facts on chemical change were gradually being accumulated.

According to the opinion prevailing today,chemistry, as a collection of various information, often enveloped in mystical form, arose at the beginning of our era (A. D.) in Alexandria, a city on the Nile. Alexandria was an immense commercial and cultural centre that attracted people and goods from all over the ancient world. It concentrated and disseminated the practical knowledge which had existed in Egypt since times immemorial; there the philosophical ideas of ancient Greece found their further development. Treatises written in Alexandria in the first century A. D. contained a great deal of chemical information, many illustrations showing chemical apparatus, descriptions of the operations of calcining, volatilization, filtration, dissolving and crystallization. Here also arose the idea of transmuting base metals into gold, an idea which diverted chemistry for a long time to come to the path of fruitless searchings, thus retarding its progress.

After the Arabian conquest of Egypt and other Eastern countries in the VII century, part of the knowledge accumulated in Alexandria still remained intact. The Arabs made use of this knowledge and subsequently discovered and investigated many new substances, including nitric acid and various salts. The word "chemia," which had been current among Alexandrian scientists, had the Arabian prefix "al" added to it and became "alchemy." The Arabian scientists left a number of books containing descriptions of various chemical experiments and practical information.

The conquest of Southern Spain by the Arabs promoted the penetration of practical chemical knowledge into Western Europe; with the Arabs came the idea of transmuting base metals into gold.

The Middle Ages in Europe passed in fruitless attempts to materialize this idea. In the history of chemistry this period is known as the period of alchemy. Scientific thought was at that time completely under the influence and control of the Catholic Church. The ruling doctrine was the teachings of Aristotle, distorted by the Church. Any doubt as to the truth of this doctrine, as well as of the other dogmas established by the Church, was cruelly persecuted. Complete stagnation in science and the decline of knowledge were characteristic of the Middle Ages.

Instead of true chemistry, this period witnessed the flourishing of alchemy, concerned chiefly with attempts to obtain gold from base metals. All the efforts of alchemists were directed towards the search for the mysterious "philosophers' stone" which, in their opinion, possessed the wonderful properties of healing diseases, restoring youth and prolonging life, as well as transmuting base metals into gold.

Contrary to Arabian alchemy, which had played a positive part in the development of science, alchemy in Western Europe was a reactionary, anti-scientific trend. It was not until the Renaissance that chemistry really began to progress.

During this period, characterized by the formation of capitalist relations in Europe, life confronted chemistry with numerous practical problems. Experiments in the use of chemical preparations for medicinal purposes resulted in a new trend in chemistry, known as iatrochemistry (medical chemistry). It was founded by Paracelsus, a Swiss physician, who held the main object of chemistry to be the preparation of medicines. The positive results which Paracelsus achieved by using chemical preparations in his medical practice brought him wide fame and prompted many physicians to engage in chemical research. The new trend forced back the "problems" of the alchemists and placed the study of chemical change on a sound footing. About this time appeared the works of Agricola, which laid the foundations of metallurgy and opened up a new vast sphere of application for chemistry.

Although the chemists of that period were still under the influence of Aristotle's teachings and shared many of the delusions of alchemy, including the belief in the philosophers' stone, still, their works contributed considerably to the chemical knowledge of their time.

Alchemy was never widespread in Russia. Until the XVII century Russian practical chemistry developed independently of Western Europe. Chemical knowledge was exchanged mainly with the Near East (Byzantium, Armenia, etc.). By their observations and experiments Russian craftsmen added new facts to the chemical knowledge of their time. The experience acquired by Russian chemists was partially reflected in numerous collections of prescriptions known in Russia as travniki (herbals), tsvetniki (flower-books), ustavy (rule-books), lechebniki (cure-books), etc.

Only in the XVII century did chemistry begin to free itself of the scholastic approach to the study of nature, and to found its conclusions on precise experiment. The founder of this new trend in chemistry was the English chemist Robert Boyle (1627-1691).

Boyle was the first to use a new method of investigation in chemistry, based on the idea that knowledge comes from a generalization of experimental data and laws observed in natural phenomena. Boyle held that the task of the chemist is to perform experiments, accumulate observations and not to put forth a single theory without a thorough investigation of the phenomena it embraces. The purpose of chemistry is to ascertain the structure of bodies, and the means of study is chemical analysis, which consists in the breaking down of bodies into their elements. But Boyle's elements had nothing in common with the Aristotelian elements. According to Boyle, elements are

"the simplest bodies, of which complex bodies are composed, and at which we finally arrive by decomposing the latter." Boyle's theoretical views on chemical elements are set forth in his "Sceptical Chemist," in which he sharply criticizes the conceptions of the alchemists and their teachings concerning the transmutation of metals.

Boyle's works, and especially his method of investigation, greatly influenced the further progress of chemistry. However, it took about another 100 years for chemistry to free itself entirely from the yoke of the Aristotelian conception of matter, which had retarded the progress of science for so many years, and to take the path of strict scientific investigation of phenomena. This period is marked by the reign in chemistry of the so-called phlogiston theory, founded towards the end of the XVII century by the German chemist Stahl.

The phlogiston theory owed its origin to the necessity of explaining the combustion, oxidation and reduction of metals—processes which interested chemists primarily in connection with the progress made by metallurgy during the XVII century.

According to Stahl's theory, all combustible substances, including metals, contain a common flammable principle or materia ignea, which he called phlogiston. When combustible substances are burned, or metals calcined, the phlogiston volatilizes, leaving an earthy residue—calx. Hence, combustion is the decomposition of a substance into phlogiston and an earthy residue. For example:

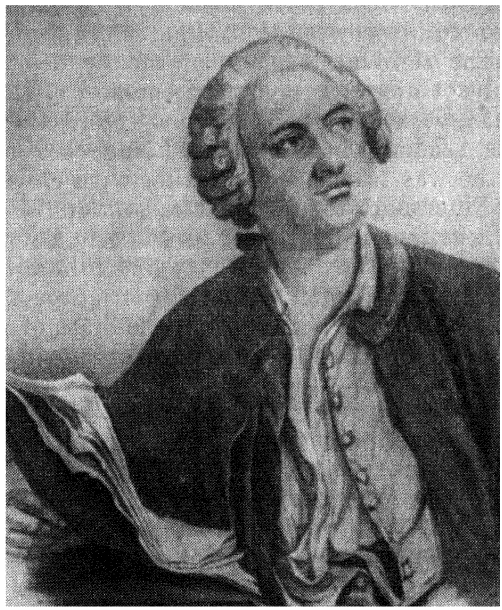
$$\text{zinc} = \text{phlogiston} + \text{zinc calx}$$

Substances which upon combustion leave a very small earthy residue, such as coal, are almost pure phlogiston. Phlogiston can be added to an incombustible substance—a calx—by calcining it with coal, which is rich in phlogiston. Then the calx becomes a metal.

$$\text{zinc calx} + \text{phlogiston} = \text{zinc}$$

Even the increase in the weight of metals during their combustion, which so obviously contradicted the phlogiston theory, was no obstacle to its development. Its adherents attributed this fact to the extreme lightness of phlogiston, which, contrary to other bodies, was not attracted to the earth, but repelled from it. Hence, the more phlogiston a body contained, the lighter it was. On the other hand, when a body lost phlogiston it became heavier. In a similar manner they attempted to get around other contradictions. For instance, the indispensability of air to combustion was explained by the fact that phlogiston did not simply disappear upon combustion, but combined with the air or with some part of it. If there was no air present combustion ceased because there was nothing for the phlogiston to combine with.

Mikhail Vasilyevich
Lomonosov
(1711-1765)



The phlogiston theory was universally recognized for a long time. It made it possible to systematize most of the facts known at that time and to solve new problems put forth by practice. However, like any other false theory which creates illusory explanations instead of revealing the real causes of phenomena, the phlogiston theory finally became an obstacle to the progress of chemistry, preventing it from completely unfettering itself from the remnants of alchemical ideas. Chemistry was freed from the phlogiston theory in the latter half of the XVIII century as a result of the introduction into chemistry of precise methods of investigation, originated by the works of M. Lomonosov.

5. M. Lomonosov. The Russian scientist Mikhail Vasilyevich Lomonosov was born in 1711, in the village of Denisovka near the town of Kholmogory, Arkhangelsk Gubernia, to the family of a fisherman. Taught to read and write by a literate fellow-villager, Lomonosov had soon perused all the books he could obtain in his village. Insatiable inquisitiveness and a passionate thirst for knowledge led him at the age of 19 to leave his native village. In the winter of 1730 Lomonosov left on foot, with hardly any money in his pocket, for Moscow, where he succeeded in getting enrolled in

the Slav-Greek-Latin Academy, the only higher educational institution in Moscow at that time.

The rigid atmosphere of the Academy, and material difficulties did not discourage young Lomonosov. His brilliant capabilities and hard work enabled him to complete the seven-grade curriculum of the Academy in four years. Lomonosov did not finish the last grade, as he was transferred together with eleven others of the best pupils to Petersburg to study at the University of the Academy of Sciences.

Less than a year after he came to Petersburg Lomonosov was sent abroad to study metallurgy and mining.

In 1741, after his return from abroad, Lomonosov was appointed Adjunct of the Academy in the class of physics, and soon became a professor in chemistry and a full member of the Russian Academy of Sciences.

Lomonosov was one of those rare minds whose scientific ideas are scores of years ahead of their time. Delving deep into the nature of observed phenomena, Lomonosov proceeded in his own original way. His tireless scientific and practical activities were striking for their breadth and diversity. "Only now, after two centuries have passed, can we grasp in full and duly appreciate all that was done by this remarkable giant of science," wrote S. Vavilov, late President of the U.S.S.R. Academy of Sciences. "His achievements in the spheres of physics, chemistry, astronomy, instrument-making, geology, geography, linguistics and history would be worthy of the activities of a whole Academy." No wonder Pushkin called Lomonosov "our first university."

One of the main problems which attracted all chemists in Lomonosov's time was that of the nature of fire and the essence of the combustion and roasting of metals. As was mentioned above, the phlogiston theory affirmed that metals lost phlogiston upon roasting. Another widespread theory at that time was that suggested by Boyle in 1673, according to which when metals are roasted a very fine "materia ignea" passes into the metals and combines with them, increasing their weight.

Lomonosov was very sceptical about all kinds of imponderable "matters," which served in his time to explain the phenomena of heat and cold, electricity and light. In his thesis "Deliberations on the Causes of Heat and Cold" presented to the Academy in 1745, he sharply criticized the theory of "thermal matter" or "thermogen", proved the impossibility of existence of such matter and expounded a mechanical theory of heat developed by himself, according to which thermal phenomena were due to the movement of the minute particles, of which all bodies consisted. In this thesis Lomonosov was the first to put forth the idea that the increase in weight of metals when calcined may be due to their combining with the surrounding air, and not to

the penetration into them of "materia ignea", as Boyle supposed. The same idea was expressed in a more categoric form by Lomonosov in 1748 in his letter to the famous mathematician Euler, in which, analyzing Boyle's experiments in the roasting of metals, he wrote: "There is not the least doubt that the particles of air passing continuously over the body being roasted combine with it and increase its weight."

Later, having succeeded through much effort in organizing a chemical laboratory at the Academy of Sciences, Lomonosov undertook a verification of his assumptions by experiment. For this purpose he decided first of all to check Boyle's experiments in the roasting of metals.

Boyle calcined the metals in sealed glass retorts. After a certain quantity of scale had formed on the metal Boyle would unseal the retort, noting the suction of air into it as a proof of the tightness of the seal, after which he would weigh the retort and its contents. Lomonosov performed the same experiments as Boyle, except that he weighed the retorts with the metal in them before and after calcining, *without unsealing them*. The following note by Lomonosov on these experiments has come down to us:

"Made experiments in well-sealed glass vessels, to ascertain whether metals gain weight from pure heat. These experiments revealed that the good Robert Boyle's opinion is false, for, unless the outside air is let in, the weight of the burnt metal remains unaltered."

From Lomonosov's experiments it followed, first of all, that the increase in weight of metals upon roasting could be due neither to the addition of "materia ignea", as Boyle assumed, nor to the loss of phlogiston, as the phlogistonists affirmed. At the same time, unsealing his retorts after the experiments, Lomonosov established that the weight of the vessels increased precisely because air was sucked into them. In this way he proved that the gain in weight of the metal when calcined was due to combination of the metal with air. Thus, Lomonosov was the first chemist to form a corret conception of the nature of combustion processes.

Carrying out experiments in roasting metals in sealed vessels, Lomonosov established the fundamental law of chemical change of substance, formulated in our days as follows:

> *The mass of the substances entering into a reaction always equals the mass of the substances formed as a result of the reaction.*

This law, which is a concrete application of the universal law of the eternity of matter to chemical phenomena, is called the **Law of Conservation of Mass.** It is often called also the Law of Conservation of Weight, as the mass of a substance at any specified point of the globe is proportional to its weight.

The idea that substance in general cannot disappear or be formed anew, that its total quantity in the universe always remains constant, was put forth by the Greek philosophers as far back as the V century B. C. and was accepted by many materialist philosophers of the XVII and XVIII centuries as a thesis which required no proof. However, the chemists of that time did not understand the importance of this thesis for chemistry and paid no attention to the quantitative aspect of chemical processes.

Credit for introducing quantitative determinations into chemistry is due to Lomonosov. In his chemical experiments he invariably used the balance, always determining the quantity of substances taken for the reaction and the quantity obtained after the reaction. With the aid of the balance Lomonosov proved that during chemical changes the total amount of substance remains unaltered. Lomonosov's experiments in calcining metals in sealed vessels confirmed the idea which he first expressed in the above-mentioned letter to the mathematician Euler, and later (in 1760) formulated in much the same way in his "Arguments on the Solidness and Liquidness of Bodies": "...All changes taking place in nature are of such a state that as much of anything as is subtracted from one body is added to another, so that if matter decreases in one place it will increase in another."

Thus the principle of indestructibility of substance, which had up to then been but a philosophical deduction, was proved for the first time by Lomonosov by means of precise quantitative experiments, and thus the brilliant conjecture of the ancient materialists became an experimentally proven law of nature.

The Law of Conservation of Mass is of prime importance for chemistry. It underlies the entire science of transformation of substances. Using this law the chemist can constantly keep a check on the correctness of the investigations he is carring out, as inequality of the weight of the substances taken to the weight of those obtained shows that some error has been made in the experiment.

Lomonosov was the first to define chemistry as a science, while contemporary West-European chemists considered it a description of operations for "decomposing mixed bodies (i. e., complex substances) into their constituent parts or obtaining bodies by combining constituent parts." Lomonosov held that the subject of chemistry is not the chemical operations themselves, but what occurs in "mixed bodies" during chemical operations.

According to Lomonosov, "chemistry is the science of changes occurring in a mixed body...." He regarded this science as chemical facts connected by mathematical exposition and systematized according to the conceptions of the structure of substance.

One who knows the intrinsic nature of substance "can explain all its possible transformations, including separation, combination, etc."

"The true chemist should be both a theoretician and a practical worker," Lomonosov said. Precise experiments with pure substances, using "measures and weights," should be accompanied by theoretical analysis of the results obtained. Lomonosov pointed out the great importance of the conception of the structure of substance in this connection. "Physicists and especially chemists are doomed to grope in the dark if they do not know the internal structure of insensible particles."

Outstripping his contemporaries by decades, Lomonosov developed a corpuscular theory of the structure of substance in which he anticipated the present-day theory of atoms and molecules.

Lomonosov considered chemistry his "main profession," but he was at the same time the first outstanding Russian physicist. He constantly emphasized the necessity of a close connection between chemistry and physics, being firmly convinced that chemistry should be studied with the aid of physics, that chemical phenomena could be treated correctly only on the basis of physical laws. In his "Treatise on the Good of Chemistry" Lomonosov wrote: "A chemist without a knowledge of physics is like a man doomed to grope for everything only by sense of touch. And these two sciences are so closely connected to one another that one cannot be complete without the other."

Explaining chemical phenomena through the laws of physics, Lomonosov founded a new science, namely, physical chemistry. In his "Course of the True Physical Chemistry," he first gave a clear definition of this subject: "Physical chemistry is the science which uses physical laws and experiments to explain what occurs in mixed bodies through the office of chemical operations."

Lomonosov was not only a talented scientist, but a materialist philosopher as well. Examining the phenomena of nature, he came to the materialistic conclusion on the fundamental question of philosophy—that of the relation of thought to being. In a number of theoretical generalizations he refuted the metaphysical conceptions prevailing in his time. Thus, he asserted that nature as a whole, and its separate parts, keep changing, wrote of the development of knowledge as passing from the simplest scientific conclusions to more complex ones, etc.

Lomonosov had deep faith in the might of science and called on the Russian people to conquer the heights of knowledge. As a member of the Russian Academy of Sciences he bent his energies to the propagation of enlightenment in Russia, to the promotion of Russian science.

In 1755 the Moscow University, the first in Russia, was founded thanks to the efforts and after the project of Lomonosov. This university subsequently became a major centre of Russian enlightenment and science.

Lomonosov died in 1765, at the age of 54.

CHAPTER II

Atoms and Molecules

The introduction of the quantitative method of investigation and the establishment of the Law of Conservation of Mass were of immense importance for the progress of chemistry. But only the atomic and molecular theories could provide chemistry with a sound scientific foundation.

6. Origin of the Science of Atoms and Molecules. The fundamentals of the science of atoms and molecules were first expounded by Lomonosov in 1741 in one of his first books, "Elements of Mathematical Chemistry," in which he formulated the main theses of his corpuscular theory of the structure of matter.

According to Lomonosov's conception, all substances consist of minute "insensible" particles, physically indivisible and capable of cohesion with one another. The properties of substances, and primarily their state of aggregation, depend on the properties of these particles; differences in the properties of substances are due solely to the properties of the particles themselves, or to the way they are connected.

Lomonosov distinguished two kinds of particles: smaller ones which he called "elements," corresponding to atoms in the modern sense of the word, and larger ones, "corpuscles," which we now call molecules.

According to Lomonosov's definition, "an element is a part of a body not consisting of any smaller bodies different from it.... A corpuscle is a collection of elements forming a single small mass."

Each corpuscle has the same composition as the substance as a whole. Chemically different substances have corpuscles of different compositions. As Lomonosov put it, "corpuscles are homogeneous if they consist of equal numbers of the same elements, combined identically," and "corpuscles are heterogeneous if their elements are different and are combined differently or in different numbers."

From the above definitions it can be seen that Lomonosov held the difference between substances to be due not only to differences in the compositions of their corpuscles, but to different arrangements of the elements in the corpuscle as well.

In expounding his views on substance being built up of "insensible" particles, Lomonosov emphasized that each corpuscle has a certain

Antoine Laurent Lavoisier
(1743-1794)



finite, though very minute, size, so small that it cannot be seen, and possesses a definite mass. Like all physical bodies, corpuscles can move according to the laws of mechanics; deprived of motion, the corpuscles could not collide with one another, repel or otherwise act on each other and undergo changes. Particularly, such phenomena as the heating and cooling of bodies are due to corpuscular motion. Since all the changes of substances are due to the motion of corpuscles, chemical changes should be studied by physical and mathematical, as well as chemical, methods.

The assumptions put forth in Lomonosov's corpuscular theory could not be verified experimentally at that time for lack of accurate data on the quantitative composition of various complex substances. His ideas were far in advance of the science of that time, and the fundamental theses on the corpuscular theory could not be confirmed until after chemistry had made considerable headway, accumulating a great deal of experimental data and mastering new methods of investigation.

7. The Works of Lavoisier. By the middle of the XVIII century the Aristotelian concepts of elements had already lost their significance, but air, water, various "earths" (calces) and fire under the guise of thermogen or phlogiston were considered elements as before.

Of great importance in establishing the correct conceptions of the chemical elements was the discovery in the latter half of the XVIII century of a number of gaseous substances: hydrogen, nitrogen, chlorine and especially oxygen. On the basis of these discoveries the famous French chemist Antoine Laurent Lavoisier (1743-94) developed the oxygen theory of combustion, which played a very important part in the further progress of chemistry.

In 1773 Lavoisier repeated Lomonosov's experiments on the calcination of metals in sealed vessels, and came to the same results. But Lavoisier made a new, very important observation during these experiments: he found that only part of the air in the vessel is absorbed when the calx forms, and that the difference in weight between the calx and the initial metal equals the weight of air absorbed. Somewhat later Lavoisier showed that the part of the air that disappears upon combustion is oxygen gas (discovered not long before by Priestley) and that air consists of oxygen and another gas which does not support combustion, to which he gave the name azote.* Hence followed the conclusion that combustion was not the decomposition of substance, as the phlogiston theory claimed, but its combination with oxygen, one of the component parts of air.

Lavoisier's explanation of combustion phenomena caused a revolution in chemistry. Disproving the existence of phlogiston, this explanation radically changed the old views on chemical change. Metals, hitherto considered to consist of calx and phlogiston, turned out to be simple substances, and, on the other hand, the "calces" or "earths" which had been taken for elements, now came to be regarded as complex substances. At the same time it was proved that water is also a complex substance, a compound of hydrogen and oxygen, while air is a mixture of oxygen and nitrogen.

Thus, it was established that many substances, which had hitherto been classed as elements (water, air, calx), were really either complex substances or mixtures. The real chemical elements were: the metals, oxygen, hydrogen, nitrogen, sulphur and other substances which could not be decomposed by chemical means.

Having given the correct conception of the nature of combustion and oxidation, Lavoisier was not able, however, to part entirely with the then prevailing view on heat as an "imponderable" element, and even included it under the name of "thermogen" in his list of genuine chemical elements.

Carrying out quantitative analyses of various substances, Lavoisier came to another very important conclusion: in chemical reactions

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* This name is still used in Russian, French and several other languages. The name nitrogen, now current in English, was suggested somewhat later by Chaptal.—*Tr.*

not only the total mass of the substances involved is conserved, as Lomonosov had proved, but the mass of each of the elements contained in the reacting substances also remains constant. Consequently, in chemical reactions elements do not change into one another. This conclusion put an end to all sorts of alchemical attempts at transmutation of the elements. Indirectly it testified also to the existence of atoms and to the conservation of their mass in chemical reactions. On the other hand, the admission that *all* chemical elements (atoms) are unchangeable under *any* circumstances afterwards became an obstacle to the progress of science.

Lavoisier's great merit was that he systematized, on the basis of his oxygen theory of combustion, the immense number of facts accumulated by chemistry. He developed (in collaboration with three other French chemists) a rational chemical nomenclature, drew up an exact classification of all the substances known in his time (elements and chemical compounds). In 1789 Lavoisier published his famous "Elementary Textbook of Chemistry," in which he made a brilliant generalization of all the achievements of chemistry of that time.

Despite a large number of new discoveries, creating the prerequisites for chemical atomics, the science of atoms and molecules made no further progress in the second half of the XVIII century. For its final development this science still lacked knowledge of the laws determining the weight proportions between elements in complex substances. These laws were discovered only at the turn of the XIX century.

8. Law of Definite Proportions. Lomonosov stated at an early date that the corpuscles of a mixed body (complex substance) must be of quite a definite, constant composition, of the same kind as the substance itself. "A mixed body," he wrote, "is one that consists of two or more different principles combined in such a way that each separate corpuscle of the body is in the same ratio to the parts of the principle it is made up of, as the whole mixed body is to the entire separate principles."

Experimental proof of this statement was obtained only in the late XVIII century, after the French chemist Proust had carried out thorough qualitative investigations of the composition of various substances. These investigations led to a conclusion known as the **Law of Definite Proportions:**

> *No matter how a given chemical compound is obtained, its composition is always the same.*

The Law of Definite Proportions appeared as a result of repeated analyses of various chemical compounds. But the composition of a chemical compound can be established by synthesis as well as by analysis. Thus, for instance, when water is decomposed by electric current

eight parts of oxygen by weight are always obtained for each part of hydrogen.* On the other hand, if we mix hydrogen and oxygen in a ratio of 1 : 8 by weight and explode the mixture, the gases will combine without any residue. If one of the gases is taken in greater quantity than this ratio demands, the excess gas will be left out of the compound. Thus, synthesis confirms the results of analysis.

On this basis the Law of Definite Proportions may be formulated alternatively as follows:

> *When any substance forms, its elements always combine with each other in strictly definite proportions by weight.*

For a long time the Law of Definite Proportions was just taken for granted by chemists. No doubt, Lavoisier, who carried out numerous analyses of various substances also took it for granted. But this law was fully recognized only as a result of a prolonged argument between Proust and his countryman Berthollet who held that the composition of a given substance might fluctuate within certain limits, depending on the conditions of its formation and especially on the relative quantities of initial substances taken for its preparation. By way of confirmation Berthollet presented the analyses of certain substances he had obtained under various conditions.

The argument between Proust and Berthollet lasted for about seven years. The final victory went to Proust who proved by a number of precise analyses that in all the cases Berthollet referred to, he had been dealing with mixtures, and not pure substances.

It would be wrong to conclude from the Law of Definite Proportions that compounds of identical composition must necessarily have identical properties. Many substances known to be identical in composition, are different in properties. This phenomenon, called **isomerism**, will be discussed in detail in § 168.

9. Law of Multiple Proportions. Many elements are capable of combining with each other in several different proportions by weight, yielding, of course, different substances in each case. For example, copper forms two compounds with oxygen: one of them is black (cupric oxide) and contains 79.9 per cent copper and 20.1 per cent oxygen; the other is red and contains 88.8 per cent copper and 11.2 per cent oxygen. Similarly, mercury and oxygen, tin and chlorine form two compounds each of different compositions; lead and oxygen give four different compounds, etc.

In 1803 the British chemist Dalton, proceeding from the atomistic conception of the structure of substances, came to the following conclusion, known under the rather inappropriate name of the **Law of Multiple Proportions:**

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* More precisely, for each 1.008 parts of hydrogen.

If two elements form several chemical compounds with one another, the weights of one of the elements corresponding to a fixed weight of the other in these compounds are in a simple integral proportion.

This conclusion was soon confirmed experimentally. Investigating the composition of the two hydrocarbons known at that time—methane

Table 1

Compound	Percentage composition		Composition, parts by weight	
	carbon	hydrogen	carbon	hydrogen
Marsh gas (methane)	75	25	3	1
Olefiant gas (ethylene)	85.71	14.29	6	1

and ethylene—Dalton established (Table 1) that the weights of carbon corresponding to one part by weight of hydrogen in these compounds were to one another as 3 : 6 or 1 : 2.

Dalton found the same simple proportions for compounds of carbon and oxygen. Carbonic acid gas (carbon dioxide) proved to contain half as much carbon as carbon monoxide, in relation to equal amounts of oxygen. Thus, experimental data quite agreed with the conclusion to which Dalton had come theoretically. Later this conclusion was confirmed by the precise experiments of the Swedish chemist Berzelius.

A good illustration of the Law of Multiple Proportions are the five oxides of nitrogen, the compositions of which are given in Table 2.

Table 2

Oxide	Percentage composition		Composition, parts by weight	
	nitrogen	oxygen	nitrogen	oxygen
Nitrous oxide	63.7	36.3	1	0.57
Nitric oxide	46.7	53.3	1	1.14
Nitrogen trioxide	36.9	63.1	1	1.71
Nitrogen dioxide	30.5	69.5	1	2.28
Nitrogen pentoxide	25.9	74.1	1	2.85

The weights of oxygen in these compounds per part by weight of nitrogen are to each other as

$$0.57:1.14:1.71:2.28:2.85$$

If we divide these figures by the least of them we get the ratios:

1:2:3:4:5

Two very important conclusions follow from the Law of Multiple Proportions:

1) Compounds formed of the same elements usually differ sharply in composition by weight. For instance, in the above case each part by weight of nitrogen combines either with 0.57 parts of oxygen or with a quantity from 2 to 5 times greater. Hence, the individual compounds of a series consisting of the same elements differ in composition *jump-wise*.

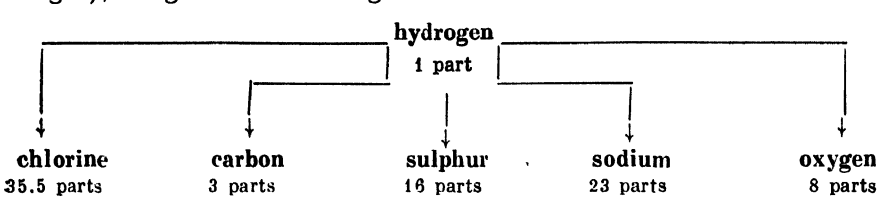
2) Any change in the quantitative ratio of combining elements leads to the appearance of a new quality. Thus, although the oxides of nitrogen consist of the same elements, they all differ qualitatively from one another, i. e., are different substances. This difference is a striking illustration of one of the universal laws of nature—the law of the transition of quantity into quality.

10. Law of Equivalent Weights. A study of the proportions by weight in which various elements combine, led to the discovery of another very important law, best illustrated by actual figures. Consider a series of hydrogen compounds having the percentage compositions shown in Table 3.

Table 3

Compound	Percentage composition					
	chlorine	carbon	sulphur	sodium	oxygen	hydrogen
Hydrogen chloride	97.26	—	—	—	—	2.74
Methane	—	75	—	—	—	25
Hydrogen sulphide	—	—	94.12	—	—	5.88
Sodium hydride	—	—	—	95.83	—	4.17
Water	—	—	—	—	88.89	11.11

Now, if we compute the weights of other elements combined with a fixed weight of hydrogen in these compounds (e. g., with one part by weight), we get the following scheme:



The elements in the above scheme combine not only with hydrogen, but with each other as well, forming compounds in the same proportions by weight with one another as with one part of hydrogen (Table 4).

Table 4

Compound	Composition in parts by weight				
	chlorine	sulphur	oxygen	sodium	carbon
Sodium chloride . . .	35.5	—	—	23	—
Carbon tetrachloride	35.5	—	—	—	3
Chlorine oxide . . .	35.5	—	8	—	—
Sodium sulphide . . .	—	16	—	23	—
Carbon disulphide	—	16	—	—	3
Sodium oxide	—	—	8	23	—
Carbon dioxide . . .	—	—	8	—	3

If we had taken any other element, say, oxygen or chlorine, as the initial one instead of hydrogen, we should have come to the same conclusion.

Thus, for all elements definite numbers can be found expressing the weights in which they combine with one another. These numbers were at first called "combining weights."

Dalton was one of the first to calculate the combining weights for a large number of elements. In doing this he followed the same procedure as above, i. e., assumed the combining weight of hydrogen to be equal to unity.* But as hydrogen forms compounds by no means with all elements, combining weights began to be calculated soon after in relation to oxygen, the combining weight of oxygen being taken equal to eight. Thereupon the combining weights calculated with respect to hydrogen retained their former values, but the combining weight of hydrogen became 1.008.

Subsequently the name "combining weight" was substituted by "equivalent weight" meaning a quantity of equal value. Elements not only combine with one another, but also displace one another in their compounds in equivalent weights.

By the present-day definition, *the equivalent weight of an element is the weight of that element which will combine with eight parts by weight of oxygen (or 1.008 parts of hydrogen) or will displace those amounts from their compounds.*

* Dalton assumed the combining weight of hydrogen to be unity, because hydrogen is the lightest of all the elements and always enters into the composition of various compounds in the least amount. This was done to avoid fractional combining weights.

The introduction of the concept "equivalent weight" made it possible to formulate the following law, called the **Law of Equivalent Weights:**

> *Elements combine with one another in quantities proportional to their equivalent weights.*

Equivalent weights are usually found either from analysis data on various compounds or from the results of displacement of one element by another. It should be stressed that in determining equivalent weights there is no need to proceed necessarily from compounds with oxygen or hydrogen. Making use of the Law of Equivalent Weights *we can calculate the equivalent weight of any element from its compound with any other element of known equivalent weight.*

Example. 3.5 gr. of iron combine with sulphur, giving 5.5 gr. of iron sulphide. Find the equivalent weight of iron if the equivalent weight of sulphur equals 16.

The information stated in the problem shows that in iron sulphide 3.5 parts by weight of iron are combined with 2 parts of sulphur (5.5 — 3.5 = 2). Since the equivalent weight of iron is the weight of it that combines with one equivalent weight of sulphur, then

$$\text{equivalent weight of iron} = \frac{3.5 \times 16}{2} = 28.$$

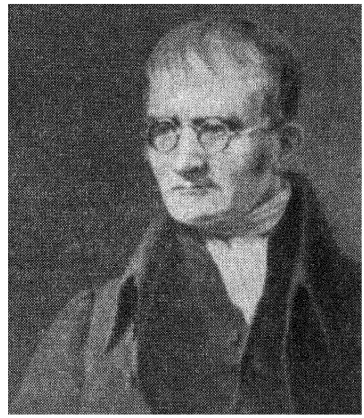
As the same elements often combine in different proportions to form several different compounds, the equivalent weight of an element may obviously have several values, depending on the compound by which it was calculated. But in all such cases the various equivalent weights of the same element are in proportion of small whole numbers. For example, the equivalent weights of carbon calculated from the composition of its compounds with oxygen equal 3 and 6 and are in proportion of 1 : 2.

The conception of equivalent weights has been extended also to complex substances.

The equivalent weight of a complex substance is the weight of the substance which will react without residue with one equivalent weight of hydrogen (1.008 parts by weight) or oxygen (8 parts by weight) or, in general, with one equivalent weight of any substance.

Thus, for instance, if hydrogen is passed over strongly heated cupric oxide, 1 gr. of hydrogen will reduce 40 gr. of cupric oxide. The latter number is the equivalent weight of cupric oxide. The equivalent weight of sulphuric acid equals 49, since 49 parts by weight of sulphuric acid react without residue with one equivalent weight of magnesium, zinc and other metals. In their turn, cupric oxide and sulphuric acid react with one another without residue if

John Dalton
(1766-1844)



49 parts by weight of sulphuric acid are taken for every 40 parts of cupric oxide.

11. Development of Atomics by Dalton. Introduction of the Atomic Weight Concept into Chemistry. The discovery of the laws governing the combination of elements permitted the English chemist Dalton to develop the quantitative aspect of the atomic theory and to explain a number of chemical facts, unknown in Lomonosov's times, on the basis of the atomic concept.

John Dalton was born in 1766, in Cumberland (England). The son of a poor weaver, Dalton went to work at an early age, but spent all his spare time in studying mathematics, the natural sciences and Latin.

In 1793 Dalton was invited to Manchester to instruct in mathematics and natural philosophy at college. In Manchester Dalton was elected Secretary and then President of the Philosophical Society.

Of the natural sciences Dalton was especially interested in meteorology. From 1787 to his very death he daily wrote down his observations of the weather and thus made no less than 200,000 observations. His interest in meteorology led him to investigate the properties of gases. He discovered the Law of Partial Pressures of Gases and from it deduced, as a corollary, that the solubility of a gas in mixture with other gases is proportional to its partial pressure. From 1803 Dalton began to develop the atomic theory in application to chemistry. He established the Law of Multiple Proportions, introduced the conception of relative atomic weights and drew up the first table of atomic weights consisting of 14 elements. He was also the first to use various signs to denote atoms; later these signs were replaced by the chemical symbols we employ today.

Dalton's works brought him world recognition. Dalton was an honorary member of many scientific societies, in particular, the Moscow Society of Natural Science Fans.

Dalton's views were essentially as follows:

1) All substances consist of minute particles—atoms, bound together by forces of mutual attraction.

2) Each substance consists of its own atoms. Simple substances consist of simple indivisible atoms, complex substances—of "complex atoms," capable of breaking down during chemical reactions into atoms of simple substances.

3) All the atoms of the same substance are identical in shape and weight, but differ from the atoms of any other simple or complex substance. The weight of a complex atom equals the total weight of the simple atoms it consists of.

4) When complex substances form, their "complex atoms" are built up of a small number of simple atoms. Thus, for instance, two simple substances consisting of atoms A and B may form complex substances with particles of the composition A+B or 2A+B or A+2B, etc. This accounts for the fact that several different compounds can be formed from the same two elements.

Comparing the views of Lomonosov and Dalton on the structure of substance, we find that Lomonosov's generalizations were in many respects closer to the present-day theoretical ideas accepted in chemistry. Thus, Dalton did not see the qualitative difference between simple and complex atoms. In his conception a complex atom (molecule) was a mechanical combination, a mere sum of simple atoms, and not a new qualitative formation, as Lomonosov considered it. Besides, Dalton was strongly against the assumption that simple substances may consist of molecules, or complex atoms, by his terminology. According to Dalton, atomic motion was due to thermogen. To his opinion atoms themselves had no motion.

Despite the fact that Dalton's atomics was somewhat limited, his atomic hypothesis, together with the data on the quantitative composition of the substances known at that time, served as a basis for the introduction into chemistry of the concept of atomic weight of an element.

Having formulated his views on the structure of substance, Dalton undertook the task of determining the weight of the atoms of the individual elements. Taking into account that the absolute weights of the atoms are exceedingly small and cannot be determined by direct weighing, Dalton decided to determine *relative atomic weights*, taking the weight of the hydrogen atom, the lightest of all atoms, as unity.

Thus, Dalton defined the atomic weight of an element as the ratio between the weight of the atom in question and that of a hydrogen atom.

To determine the atomic weight of any element Dalton would proceed from the results of analysis of a complex substance consisting of hydrogen and the element in question. The weights of the elements

in such a substance must obviously be to one another as the weight of the hydrogen atoms contained in the complex atom of the substance is to the weight of the atoms of the other element. For instance, in water the weight ratio of hydrogen to oxygen is 1 : 8; hence, the weights of the hydrogen and oxygen atoms in the complex water atom are in the same proportion. But to calculate the atomic weight of oxygen, we must know how many atoms of hydrogen and oxygen the complex water atom consists of. Indeed, if the hydrogen atom in the complex water atom is combined with one oxygen atom, the atomic weight of oxygen will be eight; if there are two oxygen atoms to each hydrogen atom, the atomic weight of oxygen is four; if, on the contrary, there are two hydrogen atoms for each oxygen atom, the atomic weight of the latter will equal 16, etc. Having no data at his disposal to solve this question, Dalton made the simplest assumption that the water atom consisted of one atom of hydrogen and one of oxygen; hence the atomic weight of oxygen equalled eight (this value was accepted in chemistry for a long time). Thus, the atomic weight of an element was identified with its equivalent weight. But this identification, aside from its arbitrariness, led to new difficulties. For instance, it was established by analysis that ammonia contains $4^2/_3$ parts by weight of nitrogen to each part of hydrogen, and nitric oxide—7 parts of nitrogen to 8 parts by weight of oxygen. If, proceeding from the composition of ammonia, the atomic weight of nitrogen were accepted as being equal to $4^2/_3$, it would have to be assumed that in the complex atom of nitric oxide the oxygen atom (8 parts by weight) is combined with $1^1/_2$ atoms of nitrogen ($4^2/_3 + 2^1/_3 = 7$ parts by weight), i.e., that the nitrogen atom can be divided in half.

Difficulties arose also in determining the atomic weights of elements with several equivalent weights, there being no way of deciding which of them to accept as the atomic weight.

All this showed that the atomic hypothesis was in itself insufficient for determining the number of simple atoms in the complex atom of a chemical compound and establishing their true atomic weights.

These difficulties were overcome only after the atomic hypothesis was supplemented by the conception of molecules as the smallest particles of substance capable of independent existence. This conception arose from a study of reactions between gaseous substances.

12. Relations Between Combining Volumes of Gases. The first quantitative investigations of reactions between gases belong to the French scientist Gay-Lussac, the author of the well-known Law of Thermal Expansion of Gases. Between 1804 and 1808 he measured the volumes of gases entering into and resulting from reactions between gaseous substances. Gay-Lussac enunciated the results of

his investigations in the form of the following generalization, known as the **Law of Combining Volumes**, or Gay-Lussac's "Chemical" Law.

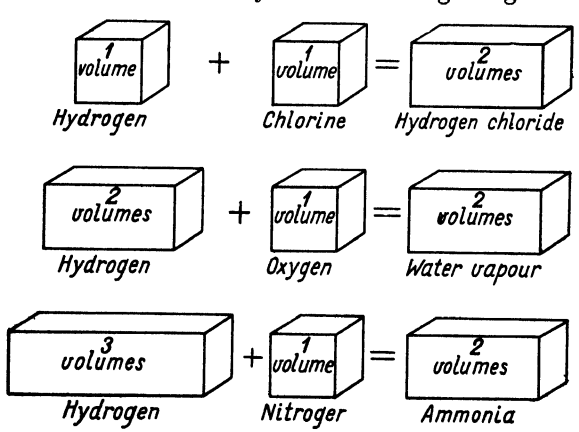
> *The volumes of interacting gases are always in a ratio of small whole numbers to one another and to the volumes of the gaseous reaction products.*

Of course it is taken for granted that the volumes of all the gases taking part in the reaction are measured at equal pressures and temperatures. To verify Gay-Lussac's Law, let us examine several reactions between gaseous substances. As we know, when water is decomposed by electricity, the volume of hydrogen liberated is always twice as large as that of oxygen. These gases have to be mixed in the same two-to-one ratio for them to combine without residue into water. The volume of water vapour they form in this case is equal to $^2/_3$ of the initial volume of the gaseous mixture, i.e., three volumes of detonating gas, or two volumes of hydrogen and one of oxygen, give two volumes of water vapour. Thus, in the reaction between hydrogen and oxygen the proportion between their volumes and that of the resulting water vapour is very simple.

Now let us turn to another well-known reaction between gaseous substances. If we mix equal volumes of chlorine and hydrogen and pass an electric spark through the mixture or expose it to bright sunlight, an explosion will take place, resulting in a new gaseous substance—hydrogen chloride. The gases combine without residue if their volume ratio is one to one, and exactly two volumes of hydrogen chloride are formed.

The same regularity is observed in the formation of ammonia from nitrogen and hydrogen. One volume of nitrogen and three of hydrogen form exactly two volumes of ammonia.

All this is well illustrated by the following diagram:



13. Avogadro's Law. Gay-Lussac's investigations attracted the general attention of chemists. The simplicity of the relation between the volumes of reacting gases showed that here was a manifestation of some fundamental property of gases, another expression of which was their identical behaviour when subjected to changes of pressure and temperature. In the opinion of Berzelius, one of the most authoritative chemists of that time, this property consisted in the fact that equal volumes of gases under identical conditions contain equal numbers of atoms. Hence it seemed that the atomic weights of gases could be determined by comparing the weight of the gas with the weight of an equal volume of hydrogen. However, this assumption immediately came up against a number of contradictions. Indeed, if the number of atoms in equal volumes of gases is the same, then one volume of chlorine and one volume of hydrogen, for instance, cannot give more than one volume of hydrogen chloride, as the complex hydrogen chloride atom must consist of at least one atom of chlorine and one of hydrogen. Meanwhile, in Gay-Lussac's experiments two volumes of hydrogen chloride were formed. Similar contradictions arose when other reactions between gases were examined.

The key to the explanation of Gay-Lussac's laws was found by the Italian physicist Avogadro, who pointed out in 1811 that all these contradictions could easily be eliminated by introducing the conception of the **molecule** as the smallest particle of any substance capable of independent existence, at the same time retaining the conception of the atom as the smallest amount of an element in molecules of various compounds. Avogadro emphasized the fact that *molecules of simple substances are not necessarily identical with elemental atoms*; on the contrary, they usually consist of several identical atoms, as Lomonosov had affirmed at an earlier date.

Avogadro's main thesis was as follows:

> *Equal volumes of any gases at the same temperature and the same pressure contain equal numbers of molecules.*

Avogadro's hypothesis not only explained the simple proportions between the volumes of reacting and resulting gases, but also permitted some very important conclusions regarding the number of atoms in the molecules of simple and complex gases, opening the way to the determination of true atomic weights.

14. Triumph of the Molecular Theory. The conception of the molecular structure of simple substances did not by any means receive immediate recognition. Its adversaries were Dalton and Berzelius, the main chemical authorities of that time, who stubbornly would not admit the possibility of molecules consisting of like atoms.

It was not until the late forties of the XIX century that Avogadro's hypothesis began to gain footing in chemistry. But it was finally recognized only in the sixties as a result of the work of Avogadro's countryman, the Italian scientist Cannizzaro. In 1858 there appeared a booklet by Cannizzaro entitled "Synopsis of a Course in Chemical Philosophy" in which, proceeding from Avogadro's conceptions of molecules, he set forth his views on the fundamental problems of chemistry with remarkable clarity and pointed out methods of determining molecular and atomic weights which excluded all possibility of arbitrariness in their selection. Cannizzaro sent his booklet to many prominent chemists of Europe. On the initiative of some of them two years later (in 1860) a congress of chemists of all countries was called in Karlsruhe to discuss the current problems of chemistry. Here Cannizzaro's views received general approval. As regards the main question, concerning the difference between atoms and molecules, it was resolved to distinguish strictly in the future between these two most important conceptions of chemistry. The congress adopted the following definitions:

A molecule is the ultimate particle of a substance capable of existing independently and incapable of being further broken down without loss of the essential chemical properties of the substance.

*An atom is the smallest particle of an element in the molecule of a simple or complex substance.**

Today Avogadro's hypothesis as to the equality of the number of molecules in equal volumes of gases has been confirmed by so many facts in the sphere of physics and chemistry that it may be considered a law.

15. Molecular Theory and Chemical Elements. The theory of atoms and molecules brought considerable clarity and distinctness into one of the most important concepts of chemistry—that of the chemical element.

The term "element" was introduced into chemistry by Boyle to denote simple substances, i.e., substances which cannot be decomposed by chemical means. For a long time these two conceptions were considered equivalent.

D. Mendeleyev was one of the first chemists to point out the necessity of distinguishing clearly between the notion of a **simple body**, as an individual homogeneous substance, and of the same simple body as a substantial part or **element** in complex substances.

Indeed, a simple substance possesses definite physical and chemical properties, but when it combines with another substance it loses

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* At present these definitions cannot be considered exhaustive. The reader will receive a more complete idea of molecules and atoms after a study of their structure.

most of them. For example, when iron combines with sulphur, it loses its metallic lustre, malleability, magnetic properties, etc. Hence, iron sulphide does not contain iron as such, as we know it in contradistinction to other substances. But since metallic iron can be obtained again from iron sulphide by means of chemical reactions, chemists say that iron sulphide contains the *element* iron, meaning the material which goes to make up metallic iron. Like iron, the sulphur in iron sulphide is not in the form of the brittle yellow combustible substance, but in the form of the *element* sulphur. Similarly, the hydrogen and oxygen contained in water are not the gaseous hydrogen and oxygen with their characteristic properties, but the *elements* hydrogen and oxygen. In their "free state" these elements are simple substances.

When in the sixties of last century the views of Cannizzaro began to take root among chemists, the simple substance and the chemical element were compared with the molecule and the atom: a simple substance, like any substance, consists of molecules, while a chemical element consists of atoms. Subsequently, the chemical element was gradually identified more and more with the atom as the smallest particle of the element, existing in molecules and carrying all the properties of the element. Thus, from the standpoint of the theory of atoms and molecules, *a chemical element is a kind of atoms possessing a definite set of properties.* Each separate atom is a chemical element, but any combination of atoms is no longer an element; if atoms of the same element unite they form simple substances; combinations of different elements result either in a mixture of simple substances or in a complex substance.

The difference between a simple substance and an element becomes especially vivid when we have to do with different simple substances consisting of the same element.

Take, for instance, a piece of phosphorus. It is a white translucent substance, melting at 44.2° C, and very poisonous; phosphorus glows in the dark and is capable of igniting spontaneously in the air; for this reason it is always kept under water. Phosphorus is a simple substance; it cannot be decomposed into other substances. However, if we heat phosphorus without access of air almost to the boiling point, its properties will change sharply after some time: it becomes red-violet in colour, ceases to glow in the dark, becomes unpoisonous and no longer ignites spontaneously in the air; moreover, these properties do not disappear when the source of heat is removed. Thus, we unquestionably have to do with the transition of one substance into another, but with a transition of quite a peculiar nature: the initial substance has not decomposed, nor has anything combined with it. This circumstance makes us regard both the initial substance and that obtained after heating as various forms of existence

of the same element, phosphorus, in its free state: the first is called white, and the second—red phosphorus.

The best proof of the fact that white and red phosphorus are actually different forms of the same element and consist of the same atoms, is their attitude towards oxygen: when heated in oxygen, both white and red phosphorus combine with it, yielding the same substance, phosphoric anhydride. Hence, phosphorus can exist in the elemental state as two simple substances. There are many other elements which,

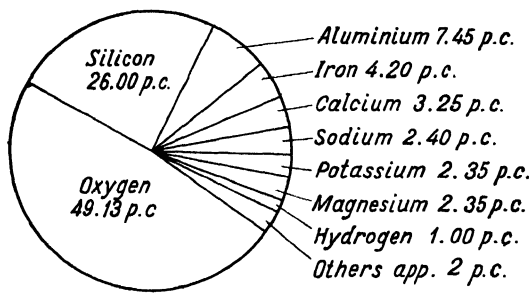


Fig. 3. Weight percentages of the elements in the earth's crust (after Fersman)

like phosphorus, exist as several different substances. Thus, the familiar simple substances, charcoal, graphite and diamond, though of widely different properties, are nevertheless various forms of the element carbon. Combining with any other simple substance, they all form the same complex substance; for example, when any of them combines with oxygen, the result is carbon dioxide.

The existence of a chemical element in the form of several simple substances is called **allotropy,** and the simple substances formed by one and the same element are called its **allotropic modifications.**

Any change in the number or arrangement of the same atoms in the molecule results in a qualitatively new substance with different properties. This was pointed out by Lomonosov, who claimed that molecules (corpuscles) could differ not only in qualitative composition but in the number or order of combination of their atoms as well.

Thus, a molecule is not simply the sum of the atoms constituting it, and, therefore, the properties of a complex substance are not a simple sum of the properties of the elements in it. *When atoms combine chemically, they do not remain absolutely unchanged, but exert a certain influence on one another, so that the same atoms in different molecules are in different states.* For instance, the state of the sulphur and iron atoms in iron sulphide differs from that of the simple substances sulphur and iron.

Vladimir Ivanovich Vernadsky
(1863-1945)



16. Occurrence of the Elements on the Globe. The abundance of the different elements on the globe is far from equal. The study of their occurrence in the earth's crust is the subject of a special branch of science called geochemistry, founded largely due to the works of the Soviet scientists, Academicians V. Vernadsky and A. Fersman.

Vladimir Ivanovich Vernadsky, one of the world's greatest mineralogists, devoted many years to investigations in the field of mineral formation and to studies of the composition of the earth's crust. He established the percentage content in the latter of many elements, including rare and disseminated elements (rubidium, caesium, thallium, etc.). His works on radioactive metals and on the ores of the rarer metals were the scientific basis for the development of the rare metals industry of the U.S.S.R.

Vernadsky was the first to draw attention to the role of live matter in the history of the chemical elements on the earth. In this connection he devoted the latter 15-20 years of his life to a study of the chemical composition and occurrence of animal and plant organisms. Vernadsky investigated their participation in reactions between and the migration of chemical elements in the earth's crust (the biosphere), and founded a new important branch of geochemistry known as *biogeochemistry*.

At present the composition of the earth's crust is quite well known. The most abundant element is oxygen, which constitutes 49.13 per cent of the part of the earth's crust accessible to investigation (see Fig. 3). Second in abundance is silicon (26.0 per cent), and then come aluminium, iron, calcium, sodium, potassium, magnesium and hydrogen. The nine elements named account for over 98 per cent of the earth's crust, leaving less than 2 per cent for all the rest. These

two per cent include such economically important elements as copper, zinc, lead, nickel, sulphur, phosphorus, etc.

It should be pointed out that our usual ideas of the abundance of an element often do not rally with the total percentage content of that element in the earth's crust. Such long-known and well-studied elements as mercury, arsenic, gold, iodine, etc., occur in the earth's crust in quantities many times smaller than titanium, zirconium and vanadium, which are ordinarily considered "rare" elements.

This contradiction may be explained as follows. Some of the elements, despite their small total content in the earth's crust, form separate, though rather rare, workable accumulations (deposits) at the earth's surface, occuring sometimes in their native state (gold, mercury, platinum and others). Owing to the comparative accessibility of these elements they became known to mankind in ancient times, and for this reason are not considered rare. Other elements, on the other hand, are greatly disseminated through the minable layer of the earth's crust, and are therefore referred to as rare elements to this day.

Alexander Yevgenyevich Fersman, a pupil of Vernadsky's, was the founder of the modern school of geochemistry and the author of a number of major works in geochemistry.

Like his teacher, Fersman devoted much of his time and effort to the establishment of the so-called clarks—numbers expressing the relative content of the individual elements in the earth's crust. Of prominent interest are his investigations of the occurrence of the elements in earth's crust in relation to their position in Mendeleyev's Periodic Table. Fersman did a great deal by way of exploration and study of the mineral wealth of the U.S.S.R. and discovered a number of deposits of most valuable minerals.

The conception "rare element" should not be regarded as established once and for all. Growth of the demand for special steels and alloys due to the rapid development of machine building, electrical engineering and transport, as well as continuous progress in the methods of mining and extraction of minerals, make many "rare" elements well known and accessible. For instance, a few decades ago, aluminium and magnesium, now widely used metals, were considered rare elements and were very expensive.

To characterize the abundance of the elements in the earth's crust Fersman introduced the concept of atomic percentage, i.e., the percentage content of the atoms of elements in the earth's crust. The atomic percentage and percentage by weight of the same element are different figures. For instance, by the number of its atoms in the earth's crust hydrogen comes third among the elements (15.6 per cent), but is ninth by weight (1 per cent).

Alexander Yevgenyevich Fersman
(1883-1945)



The following elements play an especially important part in the life of plants and animals: carbon, oxygen, hydrogen, nitrogen, sulphur, phosphorus, chlorine, silicon, potassium, calcium, magnesium and iron.

17. Determination of Molecular Weight of Gaseous Substances. Avogadro's Law is the underlying principle of a very important method of determining the molecular weights of gaseous substances. But before turning to this method, a few words should be said about the units in which molecular and atomic weights are expressed.

At first the accepted unit for calculating atomic weights was the hydrogen atom, it being the lightest of all the elements; the atomic weights of the rest of the elements were referred to that of hydrogen. But since the atomic weights of most of the elements were determined from their oxygen compounds, the calculations were actually made in relation to the atomic weight of oxygen, which was considered to equal 16. The relation between the atomic weights of oxygen and hydrogen was accepted as equal to 16 : 1. Subsequently, more precise investigations showed this relation to be 15.88 : 1 or 16 : 1.008. Therefore, if the atomic weight of hydrogen were considered equal to 1, the atomic weight of oxygen would be 15.88. But for practical reasons it was resolved to leave the atomic weight of oxygen equal to 16 and accept 1.008 as the atomic weight of hydrogen.

Thus, at present the atomic weight unit is $^1/_{16}$ of the weight of the oxygen atom. This unit is known as the **oxygen unit.** The weight of the hydrogen atom equals 1.008 oxygen units, that of the sulphur atom—32.06 oxygen units, etc.

The atomic weight of an element is the weight of its atom, expressed in oxygen units.

Since the weight of a molecule of any substance equals the total weight of the atoms it consists of, molecular weights must obviously be expressed in the same units as atomic weights. For example, the weight of the hydrogen molecule, which consists of two atoms, equals 2.016 oxygen units; the weight of the oxygen molecule, also consisting of two atoms, is 32 oxygen units; the weight of the water molecule, which contains two atoms of hydrogen and one of oxygen, is equal to $16+2.016=18.016$ oxygen units, etc.

The molecular weight of a simple or complex substance is the weight of its molecule expressed in oxygen units.

Now let us see how the molecular weights of gaseous substances can be determined.

According to the Law of Avogadro, equal volumes of gases at the same pressure and the same temperature contain equal numbers of molecules. Hence, it follows that the weights of equal volumes of two gases should be to each other as their molecular weights.

Take, for instance, one litre each of two different gases. Let there be N molecules in each volume. We denote the weight of one litre of the first gas by g, and of the second gas by g_1, and the molecular weights of the gases, respectively, by M and M_1. Since the weight of a litre of gas equals the total weight of the molecules in it,

$$g=N\cdot M, \text{ and } g_1=N\cdot M_1$$

Dividing the first equation by the second, we get:

$$\frac{g}{g_1}=\frac{M}{M_1} \tag{1}$$

The ratio of the weight of a given gas to the weight of the same volume of another gas at the same temperature and pressure is called the **density of the first gas with respect to the second.** Thus, for instance, if 1 l. of carbon dioxide weighs 1.98 gr., and 1 l. of hydrogen under the same conditions weighs 0.09 gr., the density of carbon dioxide with respect to hydrogen will be $1.98 : 0.09=22$.

Denoting the gas density by D, we may rewrite equation (1) as:

$$D=\frac{M}{M_1}$$

hence

$$M=D\cdot M_1 \tag{2}$$

The molecular weight of a gas is equal to its density with respect to another gas multiplied by the molecular weight of the latter.

The densities of various gases are determined very often with respect to hydrogen, as the lightest of all gases. Since the molecular weight of hydrogen is 2.016, the formula for calculating molecular weights then becomes:

$$M = 2.016 \cdot D$$

or, rounding off the molecular weight of hydrogen to 2:

$$M = 2 \cdot D$$

Using this formula, for instance, to calculate the molecular weight of carbon dioxide, the density of which with respect to hydrogen is 22, as was indicated above, we find:

$$M = 2 \cdot 22 = 44$$

The molecular weight of a gas is often calculated also from its density with regard to air. Although air is a mixture of several gases, still, we can speak of the *mean molecular weight of air* determined from the density of air with regard to hydrogen. The molecular weight of air found in this way equals 29.

Denoting the density of the gas in question with respect to air by D_1, we get the following formula for calculating molecular weights:

$$M = 29 \cdot D_1$$

It is useful to remember the number 29 which is often employed in calculations.

Practically, the determination of the molecular weight of a gas reduces to measurement of the weight and volume of a certain quantity of the gas in question to find its density, after which the molecular weight is calculated directly according to the formula. The density of the gas may be computed with respect to any other gas whose molecular weight and weight per unit volume are known. But since the weights of gases are given in handbooks at standard conditions, while in practice the weight and volume of the gas in question usually have to be measured under other conditions, the measured volume of the gas has to be reduced to standard temperature and pressure (S.T.P.) (0°C and 760 mm. Hg) before the density of the gas can be calculated.

The volume is reduced to S.T.P. by means of the following equation combining the gas laws of Boyle-Mariotte and Gay-Lussac:*

$$p \cdot v = \frac{p_0 \cdot v_0 \cdot T}{273}$$

* Gay-Lussac's Gas Law dealing with the dependence between the volume and the temperature of a gas at constant pressure, should not be confused with Gay-Lussac's Chemical Law mentioned above (see p. 42). In English and American literature the former is more commonly known as Charles's Law.—*Tr.*

where p and v are respectively the pressure and volume of the gas under the conditions of the experiment; p_0—the standard pressure; v_0—the volume of the gas at S.T.P.; T—the absolute temperature of the gas.

Solving this equation for v_0, we get a formula for calculating the volume of a gas at 0°C and 760 mm. Hg:

$$v_0 = \frac{p \cdot v \cdot 273}{p_0 \cdot T}$$

Example of calculation of molecular weight. It was found by experiment that 380 ml. of a gas at 27° C and 800 mm. Hg weighed 0.455 gr. Find the molecular weight of the gas if 1 l. of air at S.T.P. weighs 1.293 gr.

Reducing the volume found to S.T.P. we get:

$$v_0 = \frac{800 \cdot 380 \cdot 273}{760 \cdot (273 + 27)} = 364 \text{ ml.}$$

Now we find the weight of 1 l. of this gas (g) at S.T.P.:

$$g = \frac{0.455 \cdot 1{,}000}{364} = 1.25 \text{ gr.}$$

Since 1 l. of air weighs 1.293 gr., the density of the gas in question with respect to air

$$D_1 = \frac{1.25}{1.293} = 0.97$$

and the molecular weight

$$M = 29 \cdot 0.97 \approx 28$$

It should be noted that determination of the molecular weight of a gas by the above method requires no knowledge whatsoever of the chemical composition of the gas; but its density has to be known.

18. Gram-Molecular Volume of a Gas. The molecular weight of a gas can be calculated in another, simpler way. This method is based on the conception of gram-molecular volume of a gas.

Besides the gram, another specifically chemical measure of quantity of substance is used in chemistry; this measure is called the **gram-molecule** or **mole**, for short.

A gram-molecule is a quantity of a substance, the weight of which in grams is numerically equal to the molecular weight of the substance.

For instance, a gram-molecule of hydrogen weighs 2 grams (approximately), a gram-molecule of oxygen—32 gr., one of water—18 gr., etc. Similarly, a gram-atom is the quantity of an element, the weight of which in grams numerically equals the atomic weight of the element. For example, a gram-atom of oxygen weighs 16 gr., a gram-atom of hydrogen—1 gr., etc .

From the definition of the gram-molecule it follows that the number of molecules in a gram-molecule (mole) of any substance must always be the same. Indeed, suppose one mole of hydrogen (2 gr.) contains

n molecules, i.e., n molecules of hydrogen weigh 2 gr. Since the oxygen molecule is 16 times as heavy as that of hydrogen, obviously, the weight of n molecules of oxygen should be $2 \times 16 = 32$ gr., or one mole of oxygen. For the same reason n molecules of water should weigh 18 gr., which makes one mole of water, etc. In other words, *gram-molecules of various substances, though they differ in weight in the majority of cases, contain equal numbers of molecules.* It is clear that gram-atoms of all the elements also contain equal numbers of atoms.

At present the number of molecules in one gram-molecule has been determined quite accurately (see p. 78). It equals 6.02×10^{23}.

According to Avogadro's Law, an equal number of molecules of any gas occupies an equal volume under identical conditions. Hence it follows that the *gram-molecules of all substances in the gaseous state occupy equal volumes provided their temperatures and pressures are the same.* There is no difficulty in calculating the volume occupied by one mole of gas at S.T.P. For instance, it was established by experiment that 1 l. of oxygen at S.T.P. weighs 1. 429 gr. Therefore, the volume of one mole of oxygen (32 gr.) under the same conditions will be equal to 32 : 1.429 = 22.4 l. We should have obtained the same figure, had we calculated the volume of one mole of hydrogen, one mole of carbon dioxide, etc.

A gram-molecule of any gas at S.T.P. occupies a volume of 22.4 l.

This volume is called the **gram-molecular** or **molar** volume of a gas.

Using the molar volume* we can easily calculate the molecular weight of gaseous substances. To do so, it is necessary only to find how many grams 22.4 l. of the substance in question weigh in the gaseous state at S.T.P. The result will be the molecular weight.

Example. 0.7924 gr. of chlorine occupies 250 ml. at 0° C and 760 mm. Hg. What is the molecular weight of chlorine?

The weight of 22.4 l. (22,400 ml.) of chlorine can be found from the proportion

$$250 : 22{,}400 = 0.7924 : x$$

$$\text{Hence, } x = \frac{22{,}400 \cdot 0.7924}{250} = 71 \text{ gr.}$$

Therefore, the molecular weight of chlorine is 71.

As in calculating molecular weights by gas densities, calculations based one the molar volume become a little more complicated if the temperature and pressure of the gas differ from the standard values. In such cases the equation

$$pv = \frac{p_0 v_0}{273} \cdot T \qquad (1)$$

must be used.

* The exact value of the molar volume is 22.414 l., but in practical calculations it is usually considered 22.4. l.

This equation, combining the laws of Boyle-Mariotte and Gay-Lussac, was first deduced by Clapeyron (1834). The value of the factor $\frac{p_0 v_0}{273}$ in the equation depends both on the mass of the gas in question and on its nature; the value of v_0 is different for equal masses of different gases.

If, however, this equation is referred to the quantity of gas equal to one gram-molecule, the factor $\frac{p_0 v_0}{273}$ acquires a quite definite value, equal for all gases, since a gram-molecule of any gas at 0°C and 760 mm. Hg occupies the same volume. In this case the value $\frac{p_0 v_0}{273}$ is the *universal gas constant* and is denoted by the letter R. Introducing the denotation R in equation (1), D. Mendeleyev obtained the following equation in 1876, referring to one gram-molecule of gas:

$$pv = RT \tag{2}$$

In this form expression (2) is called the *equation of state of a gas.*

The numerical value of the gas constant R depends on the units used for the pressure and the volume. If p_0 is in atmospheres and v_0 in litres we get:

$$R = \frac{p_0 v_0}{273} = \frac{1 \cdot 22.4}{273} = 0.082 \frac{\text{l.} \cdot \text{atm.}}{\text{deg.}}$$

In chemical computations the pressure is usually expressed in millimetres Hg, and the volume in millilitres. Then

$$R = \frac{760 \cdot 22{,}400}{273} \approx 62{,}400 \frac{\text{ml.} \cdot \text{mm. Hg}}{\text{deg.}}$$

Since equation (2) refers to one gram-molecule of gas, then denoting the molecular weight of the gas by M, we get for one gram of gas:

$$pv = \frac{1}{M} \cdot RT \tag{3}$$

and for m grams of gas:

$$pv = \frac{m}{M} \cdot RT \tag{4}$$

Equation (4) makes it possible to calculate the molecular weight of a gas if the weight, volume, temperature and pressure of a definite amount of the gas are known.

Example. 304 ml. of a gas at 25° C and 745 mm. Hg weigh 0.78 gr. Find the molecular weight of the gas

Substituting the values given in the problem into equation (4) and putting R=62,400, we get:

$$745 \cdot 304 = \frac{0.78}{M} \cdot 62,400\,(273+25)$$

$$M = \frac{0.78 \cdot 62,400 \cdot 298}{745 \cdot 304} = 64$$

It should be noted that molecular weights determined by the above methods are not quite accurate. Besides the experimental error, the accuracy of the results is affected by the fact that all gases and vapours deviate somewhat from the laws of Boyle-Mariotte and Gay-Lussac. Molecular weights are determined more precisely on the basis of careful analyses of the compounds in question, as will be discussed below.

19. Partial Pressure of a Gas. In determining the molecular weights of gaseous substances it is very often necessary to measure the volume of gases collected over water, in which case they are saturated with water vapour. When ascertaining the pressure of such a gas it is necessary to make corrections for the *partial pressure* of the water vapour.

The partial pressure of a gas is the part of the total pressure exerted by a gaseous mixture, which is due to the gas in question.

It should be remembered that the pressure of a gas at constant temperature depends only on the number of molecules contained in a unit volume of the gas. Therefore, in a mixture of different gases, evenly distributed throughout the entire volume of its container, each gas exerts the same pressure as if it alone occupied the container. Suppose, for instance, that 250 ml. of hydrogen and 750 ml. of nitrogen are placed in an empty vessel with a capacity of 1 l., each of the gases having been under a pressure of 1 atm. before mixing. If we first let only the hydrogen into the vessel, its pressure will decrease fourfold due to the fourfold increase in its volume, and will become $^1/_4$ atm. The subsequent introduction of nitrogen will not change the number of molecules of hydrogen in the vessel, and therefore will not change its pressure, which will remain $^1/_4$ atm. This pressure is the partial pressure of the hydrogen in the mixture.

In its turn, the nitrogen upon being let into the vessel will increase in volume from 750 ml. to 1,000 ml., and the pressure it exerts will become $^4/_3$times less than before mixing. In other words, its partial pressure will be $^3/_4$ atm. The total pressure of the gaseous mixture will obviously be 1 atm., i.e., the sum of the partial pressures of the separate gases. Thus *the partial pressure of a gas in a mixture equals the pressure it would exert if it alone occupied the volume of the whole mixture.*

Suppose we collected 570 ml. of moist gas over water at a temperature of 15°C and a pressure of 780.8 mm. Hg. This pressure is the sum of two values, namely, the partial pressure of the gas itself and that of the saturated water vapour. The latter has a definite value for each temperature; in particular, at 15° C it equals 12.8 mm. Hg. Hence, the partial pressure of the gas in this case equals 780.8 — 12.8 = 768 mm. To reduce the measured volumes of the gas to S.T.P. we substitute its partial pressure (768 mm.) and not the total pressure (780.8 mm.) into the formula:

$$v_0 = \frac{768 \cdot 570 \cdot 273}{760 \cdot (273 + 15)} = 546 \text{ ml.}$$

Not taking into account the correction for the moisture content, we should have obtained instead:

$$v_0 = \frac{780.8 \cdot 570 \cdot 273}{760 \cdot (273 + 15)} = 555.1 \text{ ml.}$$

The error is 9.1 ml., i.e., about 1.5 per cent, which is tolerable only in very rough calculations.

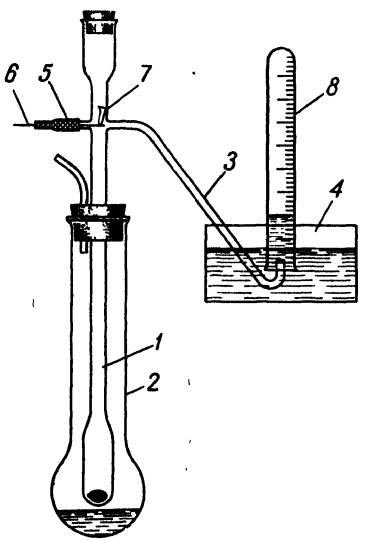


Fig. 4. Apparatus for determining molecular weight of vapours:
1—glass tube; *2*—flask used as steam bath; *3*—gas delivery tube; *4*—dish; *5*—rubber sleeve; *6*—glass rod; *7*—test tube with specimen; *8*—measuring tube.

20. Determination of Molecular Weight of Vapours. On the basis of Avogadro's Law we can determine the molecular weights not only of gases, but of all substances which pass into the gaseous state (without decomposing) when heated. For this purpose a certain quantity of the substance under investigation is converted to vapour and the weight, volume, temperature and pressure of the latter are measured. Then the molecular weight is calculated as in the case of gases.

The molecular weights of the vapours of liquids or of easily volatilized solids can be determined conveniently with the apparatus shown in Fig. 4.

The apparatus consists of a long glass tube *1*, with a bulb on its end, inside a glass flask *2*, containing a liquid which boils at a temperature high enough to vapourize the substance under investigation. Tube *1* is stoppered at the top and a bent gas delivery tube *3* is fused into its upper part. The other end of tube *3* is under the surface of the water in dish *4*. A short glass arm is fused into the wall of tube *1* opposite tube *3* and contains a glass rod *6* in a rubber sleeve *5*. The rod supports a tiny test tube (ampule) *7* containing the sample.

The liquid in the flask *2* is heated to boiling, the air in tube *1* expanding and being partly expelled through tube *3* as bubbles. When the stream of air bubbles ceases, indicating that the temperature has become constant, a measur-

ing tube (eudiometer) *8* filled with water is brought over the end of tube *3*. Then, by slightly withdrawing the glass rod *6*, the test tube holding the precisely weighed sample is allowed to fall to the bottom of tube *1*, containing some mercury to protect the bottom from the impact. The substance vapourizes and its vapours displace a certain volume of air into the measuring tube where it acquires room temperature. There is no need to know the temperature at which the substance vapourized, since the volume of air in the measuring tube equals the volume which the vapours of the substance would occupy at room temperature if it could be vapourized at that temperature. The third value determined by the experiment is the pressure of the imaginary vapour, which is equal to the pressure of the air in the measuring tube. This value is found by subtracting the pressure of the water column in the tube *8* from the pressure of the atmosphere.

21. Kinetic Theory of Gases. At present the Law of Avogadro can be deduced theoretically from the so-called Kinetic Theory of gases. The deduction is not given here, as it can be found in any textbook of physics. We shall discuss only the essence of the theory, which gives an excellent explanation of many of the properties of gaseous substances.

One of the most remarkable properties of gases is their easy compressibility. Any gas can be compressed to a very great extent. Thus, for instance, the volume of oxygen taken at ordinary conditions can be decreased 200-fold and more by means of pressure. Hence it follows that the molecules of gases are separated from one another by large spaces, and when we compress the gas we only decrease the free space between them. Calculations show that the volume of the molecules proper is only from $\frac{1}{4,000}$ to $\frac{1}{1,800}$ of the total volume occupied by the gas at S.T.P.

The molecules of a gas are in constant motion; they move in straight lines in all directions. The motion of the molecules accounts for diffusion, as well as the tendency of gases to occupy the greatest possible volume.

When a gas is enclosed in a vessel of any kind, its molecules in their motion keep constantly striking against the walls of the vessel and thus cause what we call the pressure of the gas.

Let a certain volume of gas be enclosed in a cylinder under a piston. Moving in all directions, the molecules of the gas strike against the walls of the cylinder and against the piston. Suppose the piston receives 500 impacts per second. If we move the piston down to the middle of the cylinder we thereby halve the space occupied by the molecules. The number of molecules per unit volume will now be twice as large; therefore the piston will now be receiving 1,000, and not 500 impacts per second; hence, the pressure will be doubled. If we decreased the volume threefold, then, reasoning along the same lines, we should come to the conclusion that the pressure should increase threefold, etc. This throws light on the experimentally established Law of Boyle and Mariotte, according to which the

pressure of a given mass of gas at constant temperature is in inverse proportion to the volume occupied by the gas.

When a gas is heated the velocity of its molecules increases, and therefore their kinetic energy, equal to one half the product of the mass by the velocity squared, also increases. Hence, the force of the impacts of the molecules against the walls of the vessel becomes greater, and the pressure of the gas increases.

One of the chief conclusions of the Kinetic Theory says that *the molecules of all gases at the same temperature possess the same mean kinetic energy*. This means that as the mass of the molecule changes, its velocity changes in such a way that the product of the mass by the velocity squared remains constant. Therefore, *the pressure of a gas at a given temperature, stipulated by the impacts of its molecules, depends on the number of molecules per unit volume of the gas, but does not depend on the mass of the molecule, i.e., on the nature of the gas.*

If we denote the masses of the molecules of two gases by m_1 and m_2, and their respective mean velocities by v_1 and v_2, then, on the basis of the foregoing, we may write:

$$\frac{m_1 v_1^2}{2} = \frac{m_2 v_2^2}{2} \tag{1}$$

hence,

$$\frac{v_1}{v_2} = \frac{\sqrt{m_2}}{\sqrt{m_1}} \tag{2}$$

i.e., *the mean velocities of molecules are inversely proportional to the square roots of their molecular weights.*

The Kinetic Theory makes it possible to calculate the mean velocity of molecules. This velocity is very high and differs for different gases. Thus, at 0° C the hydrogen molecule moves at an average rate of 1,695 m. per sec., that of oxygen at 430 m. per sec., etc.

Convincing proof of the difference in the velocities of the molecules of different gases can easily be obtained by performing the following experiment. The apparatus needed for the experiment is shown in Fig. 5. A porous clay cylinder is closed tightly by means of a stopper carrying a glass tube which connects the cylinder with a double-necked bottle containing some water. A glass tube reaching down almost to the bottom of the bottle is inserted through the other neck. If we cover the clay cylinder with an inverted beaker preliminarily filled with hydrogen, the latter immediately begins to diffuse into the air, and the air into the hydrogen. But owing to their greater velocity the hydrogen molecules penetrate into the cylinder faster than the heavier molecules of oxygen and nitrogen can leave it.

As a result, the pressure within the cylinder and the doublenecked bottle increases and the water begins to fountain out of the bottle.

22. Determination of Atomic Weights. Dalton first attempted to determine atomic weights by analysing various compounds of the elements with hydrogen. However, to calculate the atomic weight from the data of analysis, the number of atoms of each element in the compound analysed had to be known. Dalton did not know these numbers, and for that reason many of the atomic weights he calculated turned out afterwards to be incorrect.

When in 1811 Avogadro suggested his hypothesis concerning the equality of the number of molecules in equal volumes of gases, he at the same time pointed out a method of determining the atomic composition of molecules of simple gases. A study of interacting volumes in reactions involving hydrogen, oxygen, nitrogen and chlorine showed that the molecules of these gases are diatomic. Hence, the atomic weight of any of the gases mentioned could be found directly by determining its molecular weight and dividing it by two. For instance, the molecular weight of chlorine was found to be 71; hence, it followed that the atomic weight of chlorine equalled $\frac{71}{2} = 35.5$.

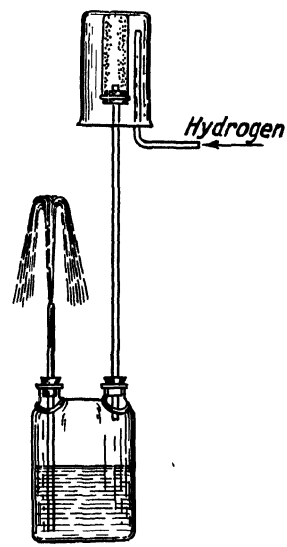


Fig. 5. Apparatus for demonstrating diffusion of hydrogen

Another method of determining atomic weights, which found wider application, was suggested in 1858 by Cannizzaro. According to this method, the molecular weights are first found for the greatest possible number of gaseous or volatile compounds of the element in question by their vapour densities. Then the number of weight (oxygen) units of the element in the molecule of each of the compounds is calculated from the results of analysis of the same compounds. The smallest of the numbers found is accepted as the atomic weight.

To illustrate this method, we shall employ it to determine, for example, the atomic weight of carbon. Table 5 gives the molecular weights of a number of carbon compounds and the percentage content of carbon in each of them. The last column of the table shows the quantity of carbon in the molecule of each of the compounds as calculated from the percentage composition.

The least weight of carbon in the molecules of the compounds in Table 5 equals 12. Hence, it is clear that the atomic weight of carbon

Table 5

Compound	Molecular weight	Carbon content per cent	Number of oxygen units of carbon in one molecule
Carbon dioxide	44	27.27	12
Carbon monoxide	28	42.86	12
Acetylene	26	92.31	24
Carbon disulphide	76	15.76	12
Benzene	78	92.31	72
Ethyl ether	74	64.86	48
Acetone	58	62.07	36
Naphthalene	128	93.75	120

cannot be greater than 12 (for instance, it cannot be 24 or 36). Otherwise, it would have to be assumed that the molecules of carbon dioxide, carbon monoxide and carbon disulphide contain a fraction of an atom of carbon. On the other hand, there are no grounds to assume the atomic weight of carbon to be less than 12. Twelve oxygen units is the smallest quantity of carbon contained in any of its known compounds. In chemical reactions this quantity passes from one molecule to another without dividing. All the other quantities of carbon are whole multiples of 12; therefore, this number is the atomic weight of carbon.

The above method of determining atomic weights has a shortcoming. The authenticity of the atomic weight found depends on the number of compounds of the element investigated. The more compounds investigated, the smaller the probability that any compound will be found containing a fraction of the accepted atomic weight in its molecule. Besides, Cannizzaro's method can be used to find the atomic weights only of elements which form gaseous or easily volatilized compounds. But most metals do not form such compounds. Therefore, in determining the atomic weights of metals, another method was used in its time, based on the relation between the atomic weight of the element and the specific heat of the corresponding simple substance in its solid state.

In 1819, determining the specific heats of various metals, the French scientists Dulong and Petit found that the product of the specific heat of a simple substance (in the solid state) by the atomic weight of the corresponding element is approximately the same for most elements and averages 6.3. Since this product is the amount of heat needed to raise the temperature of one gram-atom of the element one Centigrade degree, it is called the **atomic heat. This relationship is known as the Rule of Dulong and Petit.**

The atomic heat of the elements equals approximately 6.3.

Table 6 illustrates this Rule.

From the Rule of Dulong and Petit it follows that the atomic weight of an element can be found approximately by dividing 6.3 by the specific heat of the corresponding simple substance, a value which can be easily determined by experiment.

The above methods of determining atomic weights do not give quite accurate results; the accuracy of determination of the molecular weight by the vapour density is rarely above 1 per cent while the Rule of Dulong and Petit permits determination of the atomic weight only *approximately*. However, the atomic weight found by one of these methods can easily be corrected by comparing it with the equivalent weight of the element.

Table 6

Specific Heats of Some of the Elements

Element	Atomic weight	Specific heat	Atomic heat
Magnesium	24.3	0.248	6.0
Sulphur	32.0	0.175	5.6
Iron	55.8	0.112	6.3
Copper	63.6	0.095	6.0
Zinc	65.4	0.093	6.1
Tin	118.7	0.054	6.4
Iodine	126.9	0.052	6.6
Gold	197.0	0.031	6.1
Lead	207.2	0.031	6.4

The equivalent weights of the elements can be found very accurately from the data of analyses of various compounds. There is a definite relation between the equivalent and atomic weights of an element, viz.: *the atomic weight of an element is always a multiple of its equivalent weight*, i. e., either equals the equivalent weight or is a whole number of times greater than it. This relation follows directly from the atomic theory and the definition of "equivalent weight." Indeed, if the atom of an element can combine with or displace only one atom of hydrogen weighing 1.008 oxygen units, the equivalent weight of that element, obviously, equals its atomic weight. But if an atom of the element combines with two or more hydrogen atoms, its atomic and equivalent weights cannot coincide; however, the latter will infallibly be a *whole* number of times smaller than the atomic weight. For example, the equivalent weight of oxygen (8) equals one half

of its atomic weight, since the oxygen atom combines with two hydrogen atoms, that is, $^{16}/_{2}$ parts by weight of oxygen combine with 1.008 parts by weight of hydrogen. The equivalent weight of aluminium, the atom of which displaces three hydrogen atoms, equals $^{1}/_{3}$ of the atomic weight of aluminium, etc.

Thus, to find the equivalent weight of an element we must divide its atomic weight by the number of hydrogen atoms that can combine with or be displaced by that element. The divisor in this case is the valency of the element; hence it follows that the equivalent weight of an element equals its atomic weight divided by its valency:

$$\text{equivalent weight} = \frac{\text{atomic weight}}{\text{valency}}$$

Using this relation we can easily establish the exact atomic weight of an element if we know its approximate atomic weight and equivalent weight. For this purpose we first find the valency of the element by dividing the approximate atomic weight by the equivalent weight. Since the valency is always a whole number, we round the quotient to the nearest whole number. Then we find the exact value of the atomic weight by multiplying the equivalent weight by the valency.

Example. The equivalent weight of indium equals 38.25; its specific heat is 0.053. Find the exact atomic weight of indium.

First of all, applying the Rule of Dulong and Petit, we find the approximate atomic weight of indium:

$$6.3 : 0.053 = 118.9$$

Then, dividing the approximate atomic weight by the equivalent weight, we find the valency of indium:

$$118.9 : 38.25 = 3.1, \text{ or, roundly, } 3$$

Multiplying the equivalent weight by the valency we get the exact atomic weight of indium:

$$38.25 \cdot 3 = 114.75$$

There are other methods of determining atomic weights besides those just described. Some of them will be dealt with in the following chapters.

23. Chemical Symbols. Our modern system of chemical symbols was introduced into science in 1813 by Berzelius. He suggested denoting the elements by the initial letters of their Latin names. For instance, oxygen (Oxygenium) is designated by the letter O, sulphur (Sulfur) by S, potassium (Kalium) by K. When the names of several elements begin with the same letter, one of the subsequent letters is added to the initial one. Thus, for instance, carbon (Carboneum) has the symbol C. calcium (Calcium), the symbol Ca, copper (Cuprum), the symbol Cu, etc.

Chemical symbols are not merely abbreviated names of the elements, but have a definite quantitative meaning as well. Each symbol denotes either one atom of the element or a weight of the element numerically equal to its atomic weight. Thus, O denotes either one atom or 16 parts by weight of oxygen, Cl—either one atom or 35.5 parts by weight of chlorine, etc.

Combining chemical symbols, we get the chemical formulas of various complex substances. Just as the symbol of an element represents its atom, so the formula of a substance represents either one molecule or a weight of the substance numerically equal to its molecular weight. For instance, the formula H_2O stands for either one molecule or 18 parts by weight of water.

Simple substances are also denoted by formulas which show how many atoms the molecule of the simple substance consists of. For example, the formula of hydrogen is H_2. If the atomic composition of the molecule of the simple substance is unknovn, it is designated by the simplest possible formula, i. e., simply by the symbol of the element.

Thus, the symbols of elements and the formulas of substances are employed in chemistry for two purposes: 1) to designate atoms or molecules and 2) to denote weights corresponding to atomic or molecular weights. When we express reactions by chemical equations the symbols and formulas stand for the atoms and molecules of the reacting substances, and in all chemical calculations they stand for weights proportional to their atomic and molecular weights (usually gram-atoms and gram-molecules).

24. Derivation of Chemical Formulas. To derive the formula of a complex substance the elements it consists of, and the proportions by weight in which they are combined, must first be determined by analysis. Usually the composition of a complex substance is expressed as percentages, but it may be expressed in numbers of any other kind showing the proportion between the weights of the constituent elements in the substance. For example, the composition of aluminium oxide, which contains 52.94 per cent aluminium and 47.06 per cent oxygen, is quite defined if we say that the aluminium and oxygen have combined in a ratio by weight of 9 : 8, i. e., that there are 8 parts by weight of oxygen for every 9 parts by weight of aluminium. Of course, the ratio 9 : 8 must equal the ratio 52.94 : 47.06.

Knowing the composition by weight of the complex substance and the atomic weights of the elements forming it, we can easily find the relative number of atoms of each element in the molecule of the substance, and thus establish its simplest formula.

Suppose, for instance, we wish to derive the formula of calcium chloride, which contains 36 per cent calcium and 64 per cent chlorine. The atomic weight of calcium is 40 and that of chlorine 35.5

Let the number of calcium atoms in the calcium chloride molecule be x and the number of chlorine atoms be y. Since an atom of calcium weighs 40, and an atom of chlorine 35.5 oxygen units, the total weight of calcium atoms in the calcium chloride molecule will be $40x$, and the weight of the chlorine atoms $35.5y$. The ratio of these numbers, obviously, must equal the ratio of the weights of calcium and chlorine in any quantity of calcium chloride. But the latter ratio is 36 : 64.

Equating both ratios we get:

$$40x : 35.5y = 36 : 64$$

Then we free the unknowns x and y of their coefficients by dividing the first terms of the proportion by 40 and the second by 35.5:

$$x : y = \frac{36}{40} : \frac{64}{35.5} = 0.9 : 1.8$$

The numbers 0.9 and 1.8 express the relative number of atoms in the calcium chloride molecule, but they are fractions, whereas a molecule can contain only a whole number of atoms. In order to express the ratio $x : y$ by two integers, we divide both terms of the second ratio by the smaller of them and obtain:

$$x : y = 1 : 2$$

Therefore, there are two chlorine atoms in the calcium chloride molecule for each atom of calcium. This condition is satisfied by a whole series of formulas: $CaCl_2$, Ca_2Cl_4, Ca_3Cl_6, etc. Since we have no data to tell which of the above formulas corresponds to the actual atomic composition of the calcium chloride molecule, we select the simplest of them, $CaCl_2$, which indicates the smallest possible number of atoms in the molecule of calcium chloride.

However, if the molecular weight of the substance is known besides its composition by weight, there can be no arbitrariness in selecting its formula. In this case there is no difficulty in deriving the formula which expresses the true composition of the molecule.

Consider the following example.

Analysis showed that glucose contains 4.5 parts of carbon, 0.75 parts of hydrogen and 6 parts of oxygen by weight. Its molecular weight was found to equal 180. Derive the formula of glucose.

As in the previous case, we first find the ratio between the number of atoms of carbon (atomic weight 12), hydrogen and oxygen in the glucose molecule. Denoting the number of atoms of carbon by x, of hydrogen by y and of oxygen by z, we write the proportion:

hence,

$$x:y:z=\frac{4.5}{12}:\frac{0.75}{1}:\frac{6}{16}=0.375:0.75:0.375$$

Dividing all three terms on the right side of the equation by 0.375, we get:

$$x:y:z=1:2:1$$

Hence, the simplest formula of glucose would be CH_2O. But the molecular weight calculated according to this formula would be 30, whereas the actual molecular weight of glucose is 180, i.e., six times as large. Obviously, the formula of glucose should be $C_6H_{12}O_6$.

Formulas based not only on the data of analysis, but on determinations of the molecular weight as well, and showing the actual number of atoms in the molecule are called **true** or **molecular** formulas; formulas derived only on the basis of analytical data are called **simplest** or **empiric** formulas.

Now that we are acquainted with the derivation of chemical formulas, we can easily understand how exact molecular weights are established. As was mentioned above, the existing methods of determining molecular weights do not in the majority of cases give quite accurate results. But if we know at least the approximate molecular weight and the percentage composition of the substance, we can establish the formula which expresses the atomic composition of its molecule. Since the weight of the molecule equals the total weight of the atoms in it, we can determine this weight in oxygen units, i.e., the molecular weight of the substance, by adding up the weights of the atoms constituting the molecule. The accuracy of the molecular weight found in this manner will be the same as that of the atomic weights.

The determination of the formula of a chemical compound can in many cases be greatly simplified by making use of the concept of **valency** of the elements.

It will be remembered that the valency of an element is the property of its atoms to combine with or displace a definite number of atoms of another element.

The valency of an element is defined as a number showing how many atoms of hydrogen (or any other univalent element) the element in question will combine with or displace.

The more profound sense put into the valency concept by modern chemistry will be discussed in Chapter V.

The valency concept pertains not only to individual atoms, but also to whole groups of atoms entering into the composition of chemical compounds and participating in chemical reactions as an integral whole. Such groups of atoms are known as **radicals**. The

most important radicals in inorganic chemistry are: 1) the hydroxyl radical OH; 2) acid radicals; 3) basic radicals.

The *hydroxyl radical* results if one atom of hydrogen is removed from a water molecule. In the water molecule the hydroxyl radical is combined with one atom of hydrogen; hence, the OH group is univalent.

Acid radicals are groups of atoms (or sometimes single atoms) of acid molecules which "remain" if one or several of the hydrogen atoms displaceable by metals are imaginarily removed. The valency of these groups depends on the number of hydrogen atoms removed. For instance, sulphuric acid yields two acid radicals, one of them bivalent, SO_4, and the other univalent, HSO_4, forming part of various acid salts. Phosphoric acid, H_3PO_4, can give three acid radicals: trivalent PO_4, bivalent HPO_4 and univalent H_2PO_4, etc.

Basic radicals is the term given to atoms or groups of atoms which "remain" if one or several hydroxyl radicals are imaginarily removed from molecules of bases. For instance, if we abstract hydroxyl radicals successively from the molecule $Fe(OH)_3$, we get the following basic radicals: $Fe(OH)_2$, FeOH and Fe. Their valencies are determined by the number of hydroxyl groups subtracted from each: $Fe(OH)_2$ is univalent, FeOH is bivalent and Fe is trivalent.

Basic radicals, containing hydroxyl groups, are constituent parts of so-called **basic salts**. The latter may be regarded as bases in which some of the hydroxyls are replaced by acid radicals. Thus, if two of the hydroxyls in $Fe(OH)_3$ are displaced by the acid radical SO_4, the basic salt $FeOHSO_4$ results; the result of replacing one hydroxyl in $Bi(OH)_3$ by the acid radical NO_3 is the basic salt $Bi(OH)_2NO_3$, etc.

Knowledge of the valencies of individual elements and radicals makes it possible in simple cases to derive the formulas of a great many chemical compounds very rapidly, relieving the chemist of the necessity of memorizing them.

Since the derivation of the simplest formulas, namely those of oxides, bases and normal salts, is generally dealt with in detail in elementary chemistry, we shall confine ourselves to a few examples in deriving the formulas of acid and basic salts.

Example 1. Derive the formula of calcium bicarbonate, an acid salt of carbonic acid.

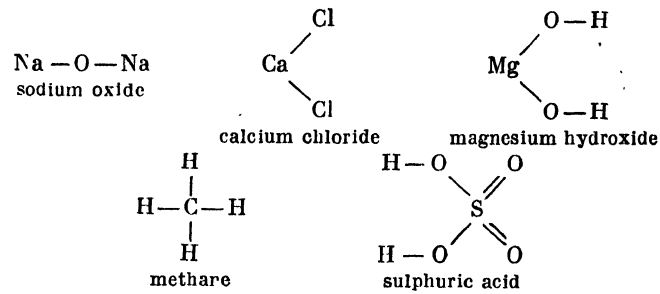
The composition of this salt must include calcium atoms and the univalent acid radicals HCO_3. Since calcium is bivalent, two acid radicals should be taken for each calcium atom. Therefore, the formula of the salt will be $Ca(HCO_3)_2$.

Example 2. Derive the formula of basic copper carbonate, the basic copper salt of carbonic acid.

This salt must consist of univalent basic CuOH radicals and the bivalent acid radical CO_3. Therefore the formula of the salt is

$$(CuOH)_2CO_3 \text{ or } Cu_2(OH)_2CO_3$$

The rule for deriving formulas according to valency becomes more vivid if the composition of the molecules is depicted by their so-called *structural* or *constitutional formulas*. The following are structural formulas of some of the simplest compounds:



Structural formulas show not only which atoms the molecule of the compound consists of, but also how these atoms are linked together in the molecule. In many cases these formulas make it possible to explain various properties of the compound, to comprehend the valencies of its constituent atoms, etc. They play an especially important part in organic chemistry, where substances often consist of very complex molecules.

25. Using Formulas for Calculations. The chemical formula of a substance, made up of a few letters and figures, contains very much important information for the chemist. First of all, it shows directly what elements the substance consists of and how many atoms of each element its molecule contains. Then it permits a number of values characterizing the substance to be computed. The most important types of calculations are given below.

1. The *molecular weight* of the substance is calculated from the formula as the total weight of the atoms constituting its molecule. The accuracy of molecular weights so found was mentioned in the previous paragraph.

2. The *composition by weight of a complex substance.* The composition of any substance can be expressed as a ratio of the weights of its constituent elements. This ratio follows directly from the formula of the substance. For example, the formula of soda Na_2CO_3 shows that there is one atom of carbon and three of oxygen for every two atoms of sodium. Since the atomic weight of sodium is 23, and that of carbon and oxygen, 12 and 16, respectively, the ratio between the weights of these elements in any quantity of soda must be equal to:

$$23 \cdot 2 : 12 : 16 \cdot 3 = 46 : 12 : 48$$

The percentage composition of each element in any substance can be computed just as easily.

3. The *density of the substance in the gaseous state.* This computation is made by means of the formula $D=\frac{M}{M_1}$, where D is the density of the substance, M its molecular weight and M_1 the molecular weight of the gas with respect to which the density is being determined.

4. The *weight of 1 litre of gas at 0°C and 760 mm. pressure.* A gram-molecule of any gas at S.T.P. occupies a volume of 22.4 l., hence, the weight (g) of 1 litre of gas under the same conditions will equal the gram-molecular weight (M) divided by 22.4:

$$g=\frac{M}{22.4}$$

5. The *volume occupied by any weight of gas.* If the gas is taken at 0° C and 760 mm. pressure, the computation can be made very simply by proceeding from the gram-molecular volume.

If, however, the gas is at other temperatures and pressures, the volume can be calculated according to the equation:

$$pv=\frac{m}{M}\cdot RT$$

The same equation may be employed to calculate the weight of any volume of gas under any given conditions.

26. Chemical Equations and Calculations Based on Them. According to the atomic and molecular theory, any chemical reaction consists in the molecules of one set of substances turning into the molecules of another set of substances composed of the same atoms as the reacting molecules. Knowing the molecular composition of the reacting substances and of the substances formed as a result of the reaction, we can express any reaction by a *chemical equation.*

A chemical equation is a short way of recording a reaction by means of chemical formulas. In such an equation the formulas of the initial substances (reactants) are written to the left, and the formulas of the reaction products (resultants), to the right of the equality sign. Since the total number of atoms remains unchanged in the reaction, the number of atoms of each element on the left and right sides of the equation should always be equal, provided the equation is written correctly.

In order to write out the equation of a reaction, we must know precisely which substances react with each other, and which are produced as a result of the reaction. A chemical reaction is an expression of experimentally established facts. We cannot, after writing down the formulas of the reactants on the left side of the equation, rearrange them at our own discretion into new substances on the right side.

If analogical reactions have been studied thoroughly, the products of the reaction can sometimes be predicted. It is known, for instance,

that when an acid reacts with a base or with the oxide of a metal, the result is always a salt and water, that the action of an acid on a salt usually leads to the formation of a new salt and a new acid, etc. However, even in these cases unexpected things are likely to spring up. Thus, the action of hydrochloric and dilute sulphuric acids on many metals leads to the liberation of hydrogen and the formation of salts of the metals taken, such as:

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

But if we were to write out a similar equation for the reaction between nitric acid and zinc, we would be making a gross mistake, because the action of nitric acid on metals does not, as a rule, lead to the liberation of hydrogen. This example shows that conclusions made "by analogy" are not always reliable and therefore should be avoided as far as possible.

When writing equations it must always be kept in mind that we are not at liberty to alter the formulas of the substances to balance the number of atoms on the left and right sides of the equation. Equations can be balanced only by selecting the correct coefficients.

Sometimes a reaction is recorded as an unbalanced equation, showing only which substances are the reactants and which the resultants of the reaction. In such cases the equality sign will be replaced by an arrow, showing the direction of the chemical transformation. For instance, the combustion of hydrogen sulphide can be represented schematically as follows:

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

In practice chemical equations are used for carrying out various calculations connected with the reactions they represent. We remind the reader that each formula in a chemical equation stands not only for the molecule, but for a definite weight of the substance as well, corresponding to its molecular weight, for instance one gram-molecule. By substituting the weights of the substances for their formulas we find the weight ratios of all the substances taking part in the reaction. For instance, the equation of the reaction of formation of water from hydrogen and oxygen may be interpreted as follows:

$2H_2$	+	O_2	=	$2H_2O$
2 moles		1 mole		2 moles
$2\times2=4$ gr.		32 gr.		$2\times18=36$ gr.

It can be seen from the equation that 4 gr. of hydrogen combine with 32 gr. of oxygen to give 36 gr. of water.*

* Of course the weights of the reacting substances may be expressed in other units besides grams, e.g., kilograms, tons, etc.; this does not alter the proportions by weight.

Having written out the equation of a reaction and having determined by its means the gram-molecular weights of the reacting substances, we can carry out all kinds of calculations needed to reproduce that reaction in the laboratory or in industry.

When a reaction takes place between gaseous substances, its equation gives an idea of the relative volumes of the reacting gases, besides their quantities by weight, as is evident from the following example:

	$2\ CO$	$+$	O_2	$=$	$2\ CO_2$
Weight of gases	56 gr.		32 gr.		88 gr.
Volumes at S.T.P. . . .	44.8 l.		22.4 l.		44.8 l.
	(2 vol.)		(1 vol.)		(2 vol.)

Therefore, if it is required in the problem to find the volume of gas taking part or formed in a reaction, there is no need to calculate its weight. The volume can be calculated directly from the equation of the reaction.

Example. How many litres of oxygen can be produced by decomposing 100 gr. of potassium chlorate?

Writing out the equation of the reaction, we put down under the formula of potassium chlorate its doubled molecular weight, and under the formula of oxygen, its volume in litres:

$$2KClO_3 = 2KCl + 3O_2$$
$$2.122.5 \qquad 3.22.4$$
$$245 \text{ gr.} \qquad 67.2 \text{ l.}$$

Then, as usual, we write a proportion from which we find the volume directly, without calculating the weight of oxygen and then converting it to litres:

$$245:100 = 67.2:x;\ \ x = \frac{67.2 \cdot 100}{245} = 27.4 \text{ l.}$$

The volume found is, of course, at 0° C and 760 mm. Hg; if any other temperature or pressure is specified, a corresponding re-calculation must be made.

27. Transformation of Energy During Chemical Reactions. Many chemical reactions, such as combustion, combination of metals with sulphur or chlorine, neutralization of acids by alkalis, etc., are accompanied by the evolution of considerable amounts of heat. Such reactions as the decomposition of calcium carbonate, the decomposition of mercury oxide and a number of others, on the contrary, require a continuous influx of heat, and stop immediately if heating is discontinued. Evidently, in these cases the chemical change is accompanied by absorption of heat. In some reactions light is emitted together with the heat.

A thorough study of various chemical processes showed that chemical change is always connected with the evolution or absorption of energy. These phenomena are an essential peculiarity of chemical

changes; in practice they are often more important than the formation of new substances which they accompany. For this reason we shall deal with the evolution and absorption of energy during chemical changes in greater detail.

The evolution of energy in the form of heat upon the combination of various substances shows that these substances had already possessed a certain supply of energy in latent form before their combination. This form of energy, which is concealed in substances and "liberated" only during chemical transformations, is called internal or *chemical energy*.

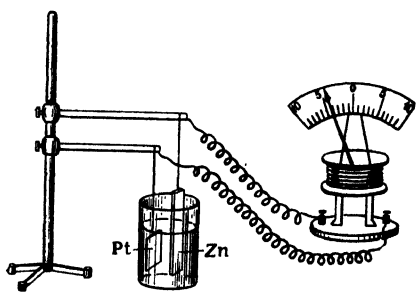


Fig. 6 Arrangement for demonstrating transformation of chemical energy into electrical

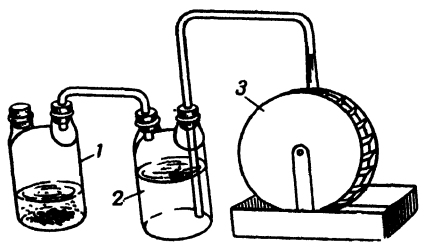


Fig. 7. Arrangement for demonstrating transformation of chemical energy into mechanical:
1—bottle with zinc and sulphuric acid; *2*—bottle with water; *3*—bladed wheel

The liberation of chemical energy is connected with its transformation into other forms of energy. Thus, for instance, when hydrogen combines with oxygen, the chemical energy of these substances is transformed into thermal energy and manifests itself as heat given off during the reaction. It is clear that the water formed no longer contains the same amount of energy as hydrogen and oxygen together before their combination. But this does not at all mean that there is no chemical energy left in the water. Water, in its turn, can react with other substances to evolve energy; hence, it still has a supply of chemical energy. In general, during chemical transformations only part of the energy contained in the substances is liberated; we cannot exhaust all the chemical energy and do not know how large its supply is in various substances. By measuring the thermal effect of a reaction we can judge only of the change the supply undergoes.

Very many chemical reactions are accompanied by the evolution of heat, as chemical energy is most readily transformed into thermal energy. The conversion of chemical energy into luminous energy is much rarer. Usually when light is emitted during chemical reactions the chemical energy is not transformed into light directly, but

through thermal energy. For instance, the emission of light during the combustion of coal is a result of the coal being brought to a high temperature by the heat evolved due to the reaction. The same effect can be obtained by heating the coal by purely physical means, for example, by passing current through the carbon filament of an electric light bulb. But there are also such processes, rare though they may be, in which chemical energy is transformed directly into luminous. These include the glow of phosphorus in the air, the glow of rotten wood, etc. In all these cases the emission of light takes place without any perceptible rise in temperature.

Chemical energy can also be transformed into electricity. To demonstrate this by experiment, two plates, one of platinum and one of zinc, are placed in a beaker with dilute sulphuric acid and their top ends are wired to a galvanometer (Fig. 6). The indicator of the galvanometer is immediately deflected, showing that an electric current is passing through the wire. At the same time bubbles of hydrogen escape from the liquid, while the zinc and sulphuric acid are gradually used up. It should be noted that only the zinc and the sulphuric acid undergo chemical change, the platinum remaining unaltered and serving but as a conductor of electricity.

Thus, under these conditions the chemical energy of zinc and sulphuric acid is transformed into electrical energy. Under other conditions chemical energy can be transformed into mechanical. This can be easily demonstrated by means of the arrangement shown in Fig. 7. The bottle *1* contains sulphuric acid and a few pieces of zinc. The hydrogen generated by the reaction between the zinc and the sulphuric acid exerts pressure on the water in bottle *2* and forces it up the tube. The chemical energy of the zinc and the sulphuric acid in this case is transformed into the bulk energy of a compressed gas, and the latter—into the potential energy of elevated water; if a bladed wheel is placed under the end of the tube, the water flowing out of the latter will put the wheel into motion, thus doing a certain amount of work.

When explosives decompose, their chemical energy also turns into mechanical energy—some of it directly, and some of it after first passing into thermal energy.

Thus, the chemical energy liberated during chemical changes may pass into thermal, luminous, electrical and mechanical energy. And, conversely, all these forms of energy can be transformed into chemical. The most frequent case is the transformation of thermal into chemical energy. As we know, the decomposition of many substances requires continuous heating. The heat thus administered is absorbed during the reaction and transformed into the chemical energy of the decomposition products. Therefore, for instance, the mercury and oxygen produced by the decomposition of mercury oxide, together

contain more chemical energy than the mercury oxide from which they originated.

Some reactions of combination are also accompanied by the absorption of heat. For instance, the production of nitric acid from air is based on the fact that at high temperatures nitrogen unites with oxygen, absorbing heat and forming nitric oxide, NO, which can then be converted into nitric acid. In this case the complex substance—nitric oxide—possesses a greater supply of energy than the simple substances nitrogen and oxygen from which it was formed.

Electrical energy is transformed into chemical energy during the decomposition of substances by means of electricity. One of the examples of such a transformation is the decomposition of water by electricity. Many metals are obtained from their compounds nowadays in a similar way, as well as various chemical products, such as potassium chlorate, chlorine, caustic soda, etc.

The transformation of luminous energy into chemical, accompanying the assimilation of carbon dioxide from the air by green plants, plays a very important part in nature. This process, which sustains all organic life on the earth, requires a continuous influx of energy from the outside. The energy is supplied by the sun's rays, which are absorbed by plants and changed into the latent chemical energy of the substances formed in the plants.

The decomposition of certain substances under the action of light is also accompanied by the absorption of luminous energy and its transformation into chemical energy. Thus, for example, silver chloride or bromide can be kept in the dark practically indefinitely, but under the action of light they gradually decompose into their constituent parts, the silver forming minute black grains. The use of silver chloride and bromide in photography is based on this fact.

Since energy is absorbed or evolved during chemical changes most frequently in the form of heat, all reactions during which energy is liberated are called **exothermal.** Reactions in which energy is absorbed are termed **endothermal.** Accordingly, chemical compounds produced from simple substances with the evolution of energy are called *exothermal*, in contradistinction to *endothermal* compounds, during the formation of which energy is absorbed. Endothermal compounds are much rarer than exothermal; they form from simple substances only at high temperatures, contain a larger quantity of energy in comparison with the latter and decompose with relatively greater ease, i.e., are more or less unstable. On the contrary, exothermal compounds usually form at low or moderate temperatures, are more stable and decompose with much greater difficulty than endothermal compounds.

From the Law of Conservation of Energy it follows directly that:

If a certain quantity of heat is evolved (or absorbed) during the formation of a chemical compound from simple substances, the same quantity of heat will be absorbed (or evolved) upon the decomposition of that compound into its simple substances.

Indeed, if more heat were evolved during the formation of a complex substance than is expended on the decomposition of the same substance, we could, by first uniting the simple substances and then decomposing the compound formed, obtain a certain heat surplus from nothing, which, according to the Law of Conservation of Energy, is impossible. Hence, it is clear that the more the heat given off during the formation of a chemical compound, the more energy has to be expended to decompose it. That is why exothermal compounds are more stable and decompose with greater difficulty than endothermal compounds.

28. Thermochemical Equations. The amount of heat evolved or absorbed during a reaction can be measured and included in the equation of the reaction. All measurements are conventionally referred to gram-molecular quantities of the substances formed, since from a chemical standpoint only such quantities are comparable.

The amount of heat evolved or absorbed during the formation of one gram-molecule of a chemical compound from its simple substances is called the heat of formation of the compound. For instance, the expression "the heat of formation of water equals 68.4 Cal." means that so many large calories are liberated upon the formation of 1 gram-molecule, i.e., 18 grams of water from 2 grams of hydrogen and 16 grams of oxygen.

If the heat of formation of a substance is indicated with a minus sign, it means that during the formation of the substance heat is not evolved, but absorbed. For example, the heat of formation of nitric oxide equals —21.6 Cal.

Chemical equations in which the quantity of heat evolved or absorbed during the reaction is indicated are called **thermochemical** equations. In such equations the chemical symbols and formulas always stand for gram-atoms or gram-molecules, and the thermal effect of the reaction is usually expressed in large calories, having a plus sign if the reaction is exothermal and a minus sign if it is endothermal. For instance, the thermochemical equation of the reaction of formation of water from hydrogen and oxygen is as follows:

$$2H_2 + O_2 = 2H_2O + 136.8 \text{ Cal.}$$

$$H_2 + \frac{1}{2} O_2 = H_2O + 68.4 \text{ Cal.}$$

2 gr. 16 gr. 18 gr.

This equation shows that the total internal energy contained in 2 gr. of hydrogen and 16 gr. of oxygen is higher than that of 18 gr.

of water by a value equivalent to 68.4 Cal. Fractional coefficients are quite admissible before the formulas in thermochemical equations, as in this case the formulas denote gram-molecules, and not molecules.

Unlike the formation of water, the formation of nitric oxide from nitrogen and oxygen is accompanied by absorption of heat and is expressed by the following thermochemical equation:

$$\frac{1}{2}N_2+\frac{1}{2}O_2=NO-21.6\ Cal.$$

In this case, as can be seen from the equation, the initial substances, nitrogen and oxygen, contain less energy than the nitric oxide they form.

The thermal effects of other chemical reactions are recorded in a similar manner. For example, consider the thermochemical equation of combustion of acetylene, C_2H_2:

$$C_2H_2+2\frac{1}{2}O_2=2CO_2+H_2O+312.4\ Cal.$$

This equation shows that the combustion of acetylene is an exothermal reaction and that 312.4 Cal. of heat are liberated when 1 gram-molecule of acetylene is burned.

The thermal effect of each chemical reaction is a strictly definite value, which depends, however, on the physical states of the reactants and resultants. For instance, the heat of formation of water vapour equals 57.8 Cal., while that of liquid water is 68.4 Cal. The difference of 10.6 Cal. represents the latent heat of evaporation of water, evolved when the water passes from the gaseous into the liquid state.*

In writing thermochemical reactions the physical state of the substances is indicated by the following letters placed in parentheses after the formulas of the corresponding substances: (s)—solid, (l)—liquid, (g)—gas. For example:

$$C\,(s)+O_2\,(g)=CO_2\,(g)+97.7\ Cal.$$

$$H_2\,(g)+\frac{1}{2}O_2\,(g)=H_2O\,(g)+57.8\ Cal.$$

If there is no doubt as to the state of the substances the letters are omitted.

Thermochemical equations reflect the changes taking place in substances during reactions more fully than ordinary chemical equations. Besides indicating the reactants and resultants of the reaction, they give an idea of the energy transformations accompanying it.

* The latent heat of evaporation is given for 25° C, since all the formation heat values also refer to this temperature.

29. Reality of Atoms and Molecules. The theory of atoms and molecules was of immense importance for chemistry, which began to make rapid progress under its influence and in a short time had achieved brilliant results.

However, in the late XIX century, when this theory had already given such valuable results, there arose a reactionary trend which completely denied the very existence of atoms and molecules. Under the influence of the idealistic philosophy in Germany there appeared the so-called "energy" school of chemists headed by the prominent German scientist Ostwald. This school based its theoretical views on an abstract conception of energy, divorced from matter. Its adherents considered that all external phenomena could be attributed to processes taking place between energies, and categorically denied the existence of atoms and molecules, as particles inaccessible to direct sensual perception.

Ostwald's energetics was one of the varieties of idealistic philosophical trends aimed against materialism in science. In divorcing energy, i.e., motion, from matter, in assuming the existence of nonmaterial motion, Ostwald's followers tacitly admitted that our conscience, thought, senses exist independently, as something primary, not connected with matter. They regarded chemical elements as various forms of chemical energy, and not as definite substances.

The reactionary essence of Ostwald's teachings was brilliantly revealed by V. I. Lenin in his book "Materialism and Empiriocriticism." In Chapter V of this work, dealing with the connection between philosophical idealism and certain new trends in physics, Lenin dwells, among others, on the "philosophy" of Ostwald, proves its complete groundlessness and shows the inevitability of its defeat in the fight against materialism.

Lenin not only completely revealed the idealistic basis of Ostwald's arguments, but pointed out the internal contradictions in them as well. In advancing the philosophical idea of the existence of motion without matter, Ostwald rejects the objective existence of matter, but at the same time, as a physico-chemist, he himself treats energy materialistically at every step, leaning upon the Law of Conservation and Transformation of Energy.

Soon the new striking discoveries of the beginning of the XX century so irrefutably proved the reality of atoms and molecules that at length even Ostwald was obliged to admit their existence.

Among the experimental investigations devoted to the question of the existence of atoms and molecules, of especial interest are the works of the French physicist Perrin, who studied the distribution and movement of the particles of so-called suspensions.*

* Suspensions are systems consisting of liquids with minute solid particles suspended in them.

Perrin prepared a suspension containing particles of equal size visible under the microscope and investigated the distribution of particles in it. As a result of numerous experiments, carried out with extreme care, he proved that the vertical distribution of the suspension particles was in exact agreement with the Law of Vertical Decrease of the Concentration of Gases deduced from the Kinetic Theory of Gases. Thus, Perrin showed that suspensions are virtual models of gases; hence, individual molecules exist also in gases, only they are invisible owing to their minute size.

Even more convincing were the results obtained by Perrin in observing the movement of the suspended particles.

If a drop of a liquid with particles suspended in it is observed under a powerful microscope, it can be seen that the particles are not at rest, but keep moving incessantly in all directions. Their motion is extremely unorderly. If the path of a separate particle is traced under the microscope, the result is a very complex zigzag line showing the absence of any regularity in the movement of the particles (Fig. 8). This movement may continue indefinitely without weakening or changing its character.

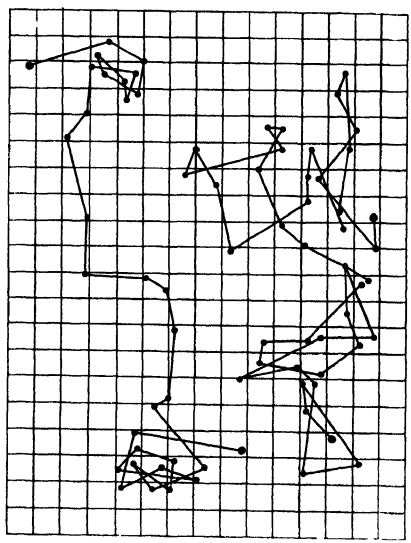


Fig. 8. Brownian movement

The above phenomenon was discovered in 1827 by the British botanist Brown and is called the Brownian movement. However, it found explanation only in the sixties following the development of the molecular-kinetic conceptions. According to this explanation, the visible movement of the suspended particles is due to the invisible thermal movement of the liquid molecules surrounding them. The impacts of the liquid molecules colliding with the suspension particles on all sides cannot, of course, exactly neutralize one another; at each moment the equilibrium is disturbed in favour of one direction or another, accounting for the fanciful path of the particles. Thus, the very fact of the Brownian movement is evidence of the reality of molecules and gives the picture of their unorderly movement, since the suspended particles repeat, in general, the same movements as the molecules of the liquid. But Perrin went still further in his investigations: by prolonged observation of the movement of the

particles under the microscope, he succeeded in determining the mean velocity of migration of the particles. Hence, knowing the mass of the particles in the suspension, Perrin calculated their mean kinetic energy. The result he obtained was astounding. He found that the kinetic energy of the particles corresponded exactly to that of a gas, calculated for the same temperature on the basis of the Kinetic Theory. The particles in Perrin's experiments were about 10^{12} times as heavy as a hydrogen molecule, but the kinetic energy of the two was equal. After the establishment of these facts the objective reality of molecules could no longer be denied.

At present the Brownian movement is regarded both as a result of the thermal movement of the molecules of the liquid and as the thermal movement of the suspension particles themselves. The latter may be likened to giant molecules taking part in the thermal movement together with the invisible molecules of the liquid. There is no difference, in principle, between the one and the other.

Besides proving that molecules really exist, Perrin's experiments made it possible to calculate the number of molecules in one gram-molecule of gas. This number, of universal significance, is called **Avogadro's number.** According to Perrin's calculations, it was found to equal, approximately, 6.5×10^{23}, which was very close to the values of this magnitude found earlier by other methods. Since then Avogadro's number has been determined many times by different physical methods, but the results have always been very close. Such a coincidence of results testifies to the correctness of the number found and is irrefutable proof of the real existence of molecules.

At the present time the accepted value of Avogadro's number is

$$6.02 \cdot 10^{23}$$

The colossal magnitude of Avogadro's number is beyond the powers of imagination. We can get some idea of it only by comparison.

Let us assume, for instance, that 1 mole, i.e., 18 gr. of water, is distributed evenly over the entire surface of the globe. A simple computation shows that there would then be about 100,000 molecules on every square centimetre.

Or another comparison. Suppose we were able in some way to label all the molecules in 18 grams of water. If that water were then poured into the sea and mixed evenly with all the water on the globe, we should, upon taking a glass of water from any point, find in it about 100 labeled molecules.

Since the gram-molecule of any gas occupies a volume of 22.4 l. under standard conditions, 1 ml. of gas under the same conditions contains 2.7×10^{19} molecules. If we should evacuate a vessel of any kind to the extreme limit attainable with the best pumps (approximately to one-ten thousand millionth of an atmosphere), i.e., obtain

what we practically consider an "airless void," the number of molecules in 1 cm. of this void would still be considerably larger than the human population of the globe. This gives us an idea of how infinitesimal the dimensions of molecules and atoms must be, since such an immense number of them can fit into 1 cm. Nevertheless, physicists have calculated these dimensions by various methods. If we imagine molecules in the form of very tiny spheres, their diameter will measure

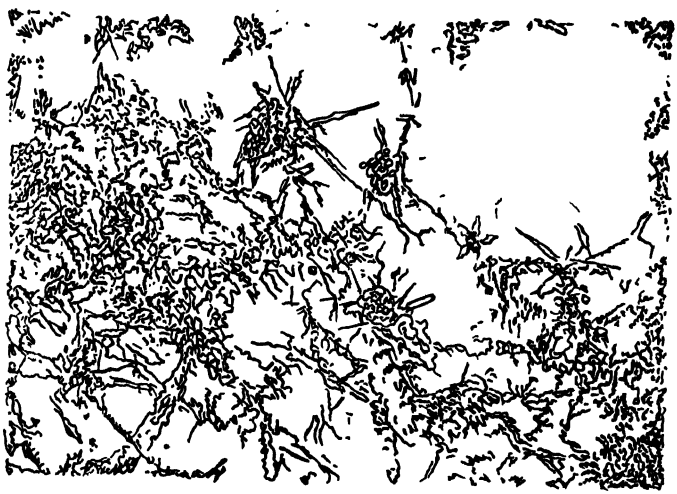


Fig. 9. Zinc oxide smoke particles magnified 20,000X

a few hundred millionths of a centimetre. For example, the diameter of an oxygen molecule is about 3.2×10^{-8} cm., that of a hydrogen molecule is 2.6×10^{-8} cm. and of a hydrogen atom, 1×10^{-8} cm.

To express such small values it is very convenient to accept as a unit of length one one-hundred millionth part of a centimetre (10^{-8} cm.). This unit was suggested by the Swedish physicist Ångström for measuring the lengths of light waves, and is called the **Ångström unit** after him. It is denoted by the symbol Å or A. The linear dimensions of atoms and molecules are usually a few Ångström units.

Knowing the number of molecules in one gram-molecule, and hence, the number of atoms in one gram-atom, we can compute the weight of an atom of any element in grams. For instance, if we divide a gram-atom of hydrogen by Avogadro's number, we get the weight of the hydrogen atom in grams:

$$\frac{1.008}{6.02 \times 10^{23}} = 1.67 \cdot 10^{-24} = 0.000,000,000,000,000,000,000,001,67 \text{ gr.}$$

It is just as easy to express the weights of other atoms and molecules in grams. It should be noted, for the sake of comparison, that the smallest difference of weight we can still detect with the aid of the most sensitive micro-balance is about 3×10^{-10} gr., with a maximum weight of 5 mg. on the balance.

At present science has at its disposal the means of determining the exact arrangement of atoms and molecules in space, the distance between them and in some cases even of photographing individual molecules. Modern electron microscopes, employing electron beams instead of light rays, make it possible to obtain images magnified tens and hundreds of thousands of times (Fig. 9).

CHAPTER III

Periodic Law of Mendeleyev

After the consolidation of the atomic and molecular theories, the most important event in chemistry was the discovery of the Periodic Law of Chemical Elements. This discovery, made in 1868 by the Russian scientist D. Mendeleyev, ushered in a new epoch in chemistry and determined the trends of its development for many decades to come. The classification of chemical elements based on the Periodic Law and expressed by Mendeleyev in the form of a periodic table became the guiding principle in the study of the properties of chemical elements and played a very important part in the further development of the science of the structure of substance. Therefore, before turning to a consideration of the modern theory of atomic structure we must first acquaint ourselves with the Periodic Table of Elements.

30. Early Classifications of the Elements. Comparison of the properties of the chemical elements has long since led to their division into two large groups—metals and non-metals or metalloids.* This division was based primarily on differences in the external, physical properties of simple substances.

Metals are distinguished by their characteristic "metallic" lustre, malleability and ductility; they can be rolled into sheets or drawn into wire, are good conductors of heat and electricity. At ordinary temperatures all metals (except mercury) are solids.

Non-Metals do not possess these properties. They do not have the characteristic lustre of metals, are brittle and very poor conductors of heat and electricity. Many of them are gases under ordinary conditions.

But the main criterion for referring an element to one group or the other is its chemical properties, especially the nature of its oxides: oxides of metals are predominantly of a basic nature; oxides of non-metals are acidic.

However, not all the representatives of the above two groups have distinctly metallic or non-metallic properties. As a matter of

* The term metalloids was introduced into chemistry by Berzelius (1808) to denote simple substances of non-metallic nature. It should be noted that this name is incorrect, as the word metalloid means, literally, resembling a metal.

fact, there is a gradual gradation from typical metals to typical non-metals, making it impossible to draw a sharp line between the two groups. In classing an element as a metal or a non-metal we only indicate which of its properties—metallic or non-metallic—are more pronounced in it.

The division of the elements into metals and non-metals was essentially their first and simplest classification. But as time went on this classification became insufficient for chemists.

Attempts were made to arrange the elements in smaller groups, according to similarities in their properties. Most investigators involuntarily came to the idea of establishing a relation between the chemical properties of the elements and their atomic weights and basing their classification on this principle.

In 1829 the German chemist Döbereiner published an attempt to group elements according to chemical resemblances. He found that elements with similar properties can be grouped by threes, whereupon the atomic weight of one of them turns out to be approximately the arithmetical mean of the atomic weights of the other two, as, for example:

Lithium . .	7	
Sodium . .	23	$\frac{7+39}{2}=23$
Potassium .	39	
Chlorine . .	35.5	
Bromine . .	80.0	$\frac{35.5+126.5}{2}=81$
Iodine . . .	126.5	

Döbereiner called these groups **triads.** He considered that the relationships he had found could serve as a basis for a systematic classification of the elements. However, among all the elements known at that time he succeeded in finding only four triads.

Without dwelling on a number of other attempts of a similar nature, we shall mention only the direct predecessors of Mendeleyev.

In 1863 Newlands, an English scientist, arranged the elements in order of increasing atomic weights and noticed that every eighth element, starting from any point, approximately repeated the properties of the first, like the eighth note in music. Newlands called this relationship the "Law of Octaves" and attempted to divide all the elements known to him into groups (octaves) on the basis of this law.

Newlands's first three octaves are given below as an illustration of his system:

H	Li	Be	B	C	N	O
F	Na	Mg	Al	Si	P	S
Cl	K	Ca	Cr	Ti	Mn	Fe

Newlands's arrangement of the elements in octaves was rather arbitrary: in some cases he would switch their positions to artificially accommodate them in his scheme; in others, he would put two elements in the same position, and he made no allowance whatsoever for the possibility of new elements being discovered. Newlands's system had many contradictions; however, it was based on the correct assumption that the properties of the elements gradate periodically with increasing atomic weights.

The next year, in 1864, Lothar Meyer published a table of some of the chemical elements arranged according to their valencies into six groups. Pointing out that the difference between the atomic weights of consecutive elements in each group displays a definite constancy, Meyer concluded his paper with the words: "There can be no doubt that a certain relationship exists between the numerical values of the atomic weights." However, Meyer did not draw any more definite conclusions as to the nature and importance of this relationship.

Döbereiner, Newlands, Meyer and the other predecessors of Mendeleyev in the systematic arrangement of the chemical elements were concerned only with their classification and went no further than to arrange the individual elements into groups based on chemical resemblances. They regarded each element as something quite individual and not related in any way with the other elements.

31. Mendeleyev's Periodic Law. Unlike his predecessors, Mendeleyev was firmly convinced that all the chemical elements must be regularly interrelated. He approached the problem of their systematization by attempting first of all to find the property which would most accurately reflect the relation between the elements, and came to the conclusion that the most likely property in this respect was their atomic weight, a value which characterized the relative mass of the atom and might therefore serve as a basis for systematization.

"... According to the sense of all exact information on natural phenomena," wrote Mendeleyev in his "Principles of Chemistry," "*the mass of a substance is precisely the property on which all its other properties must depend.* ... Therefore, it is most natural to expect to find a relation between the properties and similarities of elements on the one hand and their atomic weights on the other."

Indeed, arranging all the elements in order of increasing atomic weights, Mendeleyev found that elements chemically similar to each other occur at regular intervals and that identical properties thus repeat themselves periodically throughout the series of the elements.

This remarkable relationship was expressed in the **Periodic Law** which Mendeleyev formulated as follows:

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

To illustrate the regularities found by Mendeleyev, the first twenty elements are written out below in order of their atomic weights.

Beneath the symbol of each element stands the formula of its highest oxide, corresponding to the highest valency of the element:

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_2P_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
—	—	—	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	etc.
P_2O_5	SO_3	Cl_2O_7	—	K_2O	CaO	

The only exception in this series has been made for potassium, which should have come before argon. As we shall see later on, this exception is fully justified by the present-day theory of atomic structure.

Leaving hydrogen and helium aside for the time being, let us trace the order in which the properties of the rest of the elements change.

Lithium is a univalent metal which decomposes water vigorously, forming a strong alkali. It is followed by beryllium which is also a metal, but is bivalent and decomposes water slowly at ordinary temperatures. After beryllium comes boron, a trivalent element with slightly non-metallic properties, but at the same time manifesting certain properties of a metal. The next in the series is carbon, a tetravalent non-metal. Then come: nitrogen—an element with quite pronounced non-metallic properties, pentavalent in its highest oxide N_2O_5; oxygen—a typical non-metal. The seventh element, fluorine, is the strongest of all non-metals, and until recently no oxygen compounds of fluorine were known.

From this cursory examination of the properties of the above seven elements we see that the metallic properties, pronounced ir

lithium, gradually weaken as we pass from one element to another, giving way to non-metallic properties, which reach their highest degree in fluorine. At the same time, as the atomic weights grow, the valencies of the elements with respect to oxygen, beginning with 1 in lithium, increase regularly by one unit for each consecutive element.

If the properties kept changing further in the same direction fluorine should have been followed by an element with even more pronounced non-metallic properties; actually the next element after fluorine—neon—is an inert gas which does not unite with other elements and displays neither metallic nor non-metallic properties. Neon is followed by sodium, a univalent metal resembling lithium. Here we seem to have returned to the beginning of the series of properties just enumerated. Indeed, sodium is followed by magnesium, an analogue of beryllium; then comes aluminium which, although it is a metal and not a non-metal like boron, is also trivalent and possesses some of the properties of non-metals. After aluminium come silicon, a tetravalent non-metal, in many respects similar to carbon; pentavalent phosphorus, which resembles nitrogen in chemical properties; sulphur, an element with pronounced non-metallic properties; chlorine, a very strong non-metal belonging, as is known, to the same group of halogens as fluorine; and, finally, again an inert gas, argon.

If we trace the gradation in properties of all the rest of the elements we find that they change in the same general order as the first sixteen (not counting hydrogen and helium): argon is again followed by a univalent alkali metal, potassium, then a bivalent metal, calcium, which resembles magnesium, etc.

Thus the gradation of properties in the chemical elements with increasing atomic weight does not progress continuously in one direction but is of a periodic nature. After a definite number of elements there is a kind of relapse to the starting point, after which the properties of the preceding elements are repeated, to a certain extent, in the same succession, but with definite qualitative differences.

32. Periodic Table of Elements. Series of elements with consecutively gradating properties, such as the series of eight elements from lithium to neon or from sodium to argon, Mendeleyev called periods. If we write the two periods named one beneath the other, putting 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

Now the vertical columns contain elements with similar properties and the same valency, for example lithium and sodium, beryllium and magnesium, etc.

Dividing all the elements into periods and arranging the latter in horizontal rows with elements of similar properties, forming similar types of compounds, directly beneath one another, Mendeleyev drew up a table which he called the **Periodic Table of Elements by Groups and Series.** This Table in its present-day form, supplemented by the elements discovered after Mendeleyev's time, is given on pages 90-91. It consists of ten horizontal series and nine vertical columns or **groups,** containing similar elements.

To begin with, let us turn our attention to the horizontal series. The first series contains only two elements—hydrogen at the beginning of the series and helium at its end. These two extreme elements make up the first period in which all the intermediate members are to be regarded as absent.

The second and third series consist of the elements we have considered above and form two periods of eight elements each. Both periods begin with an alkali metal and end with an inert gas. These three periods are called the **short periods.** The fourth series also begins with an alkali metal, potassium. Judging by the gradation of properties in the two preceding series, it might be expected that they would change in the same sequence in this case as well, and that the seventh element in the series will again be a halogen and the eighth an inert gas. But this is not so. Instead of a halogen, the seventh position is occupied by manganese, which has very little in common with the halogens. Manganese is a metal, albeit of a transitional nature, forming both basic and acidic oxides, of which the highest, Mn_2O_7, is analogous to chlorine oxide, Cl_2O_7. Next to manganese in the same series come three more elements—iron, cobalt and nickel which are very similar to one another but have nothing in common with the inert gases. And only the next, the fifth series, beginning with copper, finally ends in the inert gas krypton. The sixth series again begins with the alkali metal rubidium, etc.

Thus, following argon, the properties of the elements repeat themselves more or less fully only every eighteen elements and not every eight, as in the second and third series. These eighteen elements form a **long period** consisting of two series.

The next two series, the sixth and seventh, also form one long period. This period begins with the alkali metal rubidium and ends with the inert gas xenon.

The eighth series brings a new complication. Here after lanthanum come fourteen elements called the **rare-earth metals** or **lanthanides,***

* Sometimes they are also called lanthanoids.

which occur in very small quantities and are very similar to lanthanum and to each other. Owing to this similarity, which is due to the peculiarities of their atomic structure (see § 55), the lanthanides are now placed outside the general Table, their position in the system being indicated in the box allotted to lanthanum.*

Since the next inert gas after xenon, radon, is only at the end of the ninth series, the eighth and ninth series also form one long period embracing thirty-two elements.

In the long periods, not all the properties of the elements change as consistently as in the second and third short periods. Here the usual gradation of properties is supplemented by a certain periodicity within the periods themselves. Thus, for instance, the valency first increases regularly from element to element, but after reaching a maximum in the middle of the period, drops abruptly to one, and then increases again to seven at the end of the period. In connection with this, the long periods are divided into two parts (two series), each of which forms a kind of separate period.

The tenth series contains only fifteen elements, the last nine of which were produced comparatively recently by artificial means. These nine elements, as well as the three preceding elements, uranium, protactinium and thorium, are very similar in atomic structure to actinium, for which reason they, like the lanthanides, are placed outside the general Table under the name of **actinides.**

Thus, the ten horizontal series of the Table constitute three short periods, three long and one incomplete period. The first period begins with hydrogen and the rest with one of the alkali metals. Each period ends in an inert gas.

The vertical columns of the Table, or the groups, as indicated above, contain elements with similar properties. Therefore each vertical group is a kind of natural family of elements. There are altogether nine such groups in the Table. The numbers of the group are indicated at the top by Roman numerals. At the bottom of the Table are given the types of the highest salt-forming oxides characteristic of each group.

The first group includes elements forming oxides of the type R_2O; the second, of the type RO; the third, of the type R_2O_3, etc. Thus, the highest valency of the elements of each group in their oxygen compounds corresponds, with very few exceptions, to the number of the group.

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* In Mendeleyev's original Table there was a large blank interval between cerium and tantalum, including the latter part of the eighth series, the ninth series and the beginning of the tenth series, the total number of series being twelve. At present, the lanthanides having been included in a single group, the Table consists only of ten series.

The group may also be characterized by valency with respect to hydrogen. The elements of the first, second and third groups are almost exclusively metals which either do not combine with hydrogen, or combine with it to form solid substances decomposable by water. On the other hand, the non-metals situated in the fourth, fifth, sixth and seventh groups, give characteristic *gaseous* hydrogen compounds, the types of which are indicated at the bottom of the Table. It can be seen that while the valency of the non-metals with respect to oxygen keeps growing continuously, their valency with respect to hydrogen, equal in the fourth group to 4, decreases, the sum of both valencies (with respect to oxygen and to hydrogen) always equalling 8. This makes it possible to determine one of the valencies if we know the other. For instance, if we remember that nitrogen is trivalent with respect to hydrogen (NH_3), we find that its highest valency with respect to oxygen equals 5 ($8-3=5$).

Comparing elements belonging to the same group, it will readily be seen that, beginning with the fourth horizontal series, each element bears less resemblance to the elements directly above and directly below it, than to its neighbours in the same horizontal series. For instance, bromine in the seventh group is not adjacent to chlorine and iodine but is separated from each of them by one element; the similar elements selenium and tellurium in the sixth group are separated by molybdenum, which has very little in common with them. Potassium, a metal of the first group, bears a great resemblance to rubidium in the sixth series but has very little in common with copper, which is situated directly below it, etc.

This is due to the fact that the fourth series marks the beginning of the long periods, each of which consists of two series, an even and an odd one, situated one above the other. For this reason, each group includes one element from the first half of the period (the even series) and one from the second half (odd series). Since the metallic properties weaken within the period from left to right, it is clear that in the elements of the even series they are stronger, generally, than in those of the odd series. To indicate this difference between the series, the even series elements of the long periods are written in the Table at the left side of their boxes and the elements of the odd series—at the right side.

Thus, beginning with the fourth series, each group of the periodic system, except the eighth and zero groups, can be subdivided into two subgroups: an "even" subgroup, embracing the even series elements of the long periods and an "odd" subgroup constituting the elements of the odd series. As to the elements of the second and third periods, which Mendeleyev called **typical**, in some groups they are closer in properties to the elements of the even series and in others to the elements of the odd series. For this reason the typical

elements are usually combined with the elements of the even or odd series which resemble them into the main subgroup which is more characteristic of the given group; the remaining subgroup is accordingly called the **secondary** subgroup. In connection with this, the typical elements of the first and second groups are written at the left side of their columns and those of the other groups at the right.

The difference between the main and secondary subgroups is most pronounced in the extreme groups of the Table (not counting the eighth and zero groups). Thus, in the first group the main subgroup is made up of the even series elements of the long periods—potassium, rubidium, caesium and francium, and lithium and sodium of the second and third series. They all possess pronounced metallic properties and decompose water violently to form strong alkalis. The secondary subgroup consists of copper, silver and gold which bear very little resemblance to the elements of the main subgroup. In the seventh group the main subgroup consists of the non-metals—fluorine, chlorine, bromine and iodine, while the secondary subgroup constitutes elements of the even rows—manganese, technetium and rhenium which have predominantly metallic properties.

In the main subgroups it can readily be seen that the metallic properties of the elements become more pronounced with increasing atomic weight.

The eighth group of elements occupies a unique position in the Periodic Table. It contains only nine elements, three very similar elements being situated in each horizontal series. These "triads" are transitional between the end of one horizontal series and the beginning of the next in each long period. The elements of the eighth group might be expected to have the highest valency with respect to oxygen, equal to 8. However, so far the highest oxides of the type RO_4 have been obtained only for a few of them.

Mendeleyev's original Table contained only eight groups, as the inert gases argon, helium, etc., were unknown at the time he compiled it. Afterwards, when the inert gases were discovered, a new group had to be set apart for them. Mendeleyev placed them before the first group and called them the *zero* group, which, besides the order, indicated the unique chemical nature of the group: its members do not combine with other elements, i.e., are of zero valency. However, at present, for a reason which will be explained later, the zero group is usually placed in the last column at the right side of the Table.

It should be noted that as far back as 1883, eleven years before the discovery of the first of the inert gases, argon, a Russian revolutionary and scientist, N. Morozov, imprisoned by the tsarist government for his revolutionary activities, predicted the existence of the inert gases, theoretically calculated their atomic weights and indicated their exact places in the Mendeleyev Table. But Morozov's remarkable

MENDELEYEV'S PERIODIC TABLE OF ELEMENTS

Periods	Series	Groups of Elements								
		I	II	III	IV	V	VI	VII	VIII	0
I	1.	1. H Hydrogen 1.0080								2. He Helium 4.003
II	2.	3. Li Lithium 6.940	4. Be Beryllium 9.013	5. B Boron 10.82	6. C Carbon 12.011	7. N Nitrogen 14.008	8. O Oxygen 16	9. F Fluorine 19.00		10. Ne Neon 20.183
III	3.	11. Na Sodium 22.991	12. Mg Magnesium 24.32	13. Al Aluminium 26.98	14. Si Silicon 28.09	15. P Phosphorus 30.975	16. S Sulphur 32.066	17. Cl Chlorine 35.457		18. Ar Argon 39.944
IV	4.	19. K Potassium 39.100	20. Ca Calcium 40.08	21. Sc Scandium 44.96	22. Ti Titanium 47.90	23. V Vanadium 50.95	24. Cr Chromium 52.01	25. Mn Manganese 54.94	26. Fe Iron 55.85 27. Co Cobalt 58.94 28. Ni Nickel 58.69	36. Kr Krypton 83.80
	5.	29. Cu Copper 63.54	30. Zn Zinc 65.38	31. Ga Gallium 69.72	32. Ge Germanium 72.60	33. As Arsenic 74.91	34. Se Selenium 78.96	35. Br Bromine 79.916		
V	6.	37. Rb Rubidium 85.48	38. Sr Strontium 87.63	39. Y Yttrium 88.92	40. Zr Zirconium 91. 22	41. Nb Niobium 92.91	42. Mo Molybdenum 95.95	43. Tc Technetium [99]	44. Ru Ruthenium 101.1 45. Rh Rhodium 102.91 46. Pd Palladium 106.7	
	7.	47. Ag Silver 107.880	48. Cd Cadmium 112.41	49. In Indium 114.76	50. Sn Tin 118.70	51. Sb Antimony 121.76	52. Te Tellurium 127.61	53. I Iodine 126.91		54. Xe Xenon 131.3

VI	8.	55. Cs Caesium 132.91	56. Ba Barium 137.36	57. La* Lantha-num 138.92	72. Hf Hafnium 178.6	73. Ta Tantalum 180.95	74. W Tungsten 183.92	75. Re Rhenium 186.31	76. Os Os-mium 190.2	77. Ir Iridium 192.2	78. Pt Plati-num 195.23
	9.	79. Au Gold 197.0	80. Hg Mercury 200.61	81. Tl Thallium 204.39	82. Pb Lead 207.21	83. Bi Bis-muth 209.00	84. Po Polo-nium 210	85 At Astatine [210]			86. Rn Radon 222
VII	10.	87. Fr Francium (233)	88. Ra Radium 226.05	89. Ac** Actinium 227	(Th)	(Pa)	(U)				
					Highest Salt-Forming Oxides						
		R_2O	RO	R_2O_3	RO_2	R_2O_5	RO_3	R_2O_7	RO_4		
					Gaseous Hydrogen Compounds						
					RH_4	RH_3	RH_2	RH			

* Lanthanides

58. Ce Cerium 140.13	59. Pr Praseo-dymium 140.92	60. Nd Neody-mium 144.27	61. Pm Prome-thium [145]	62. Sm Sama-rium 150.43	63. Eu Euro-pium 152.0	64. Gd Gadoli-nium 156.9	65. Te Terbi-um 158.93	66. Dy Dyspro-sium 162.46	67. Ho Holmium 164.94	68. Er Erbium 167.2	69. Tu Thulium 168.94	70. Yb Ytter-bium 173.04	71. Lu Lutetium 174.99

** Actinides

90. Th Thori-um 232.05	91. Pa Protactin-ium 231	92. U Urani-um 238.07	93. Np Neptu-nium [237]	94. Pu Pluto-nium [242]	95. Am Ameri-cium [243]	96. Cm Curium [245]	97. Bk Berkel-ium [245]	98. Cf Califor-nium [248]	99. En Einstein-ium [253]	100. Fm Fermium [255]	101. Mv Mende-levium [256]		

prediction became known only after his liberation from prison in 1905 and the publication of his works written in solitary confinement.

In building up the periodic system, the guiding principle by which Mendeleyev arranged the elements was their atomic weights. However, as can be seen from the Table, this principle was transgressed in three cases. Argon (at. wt. 39.944) stands before potassium (at. wt. 39.100) although its atomic weight is greater than that of potassium, cobalt

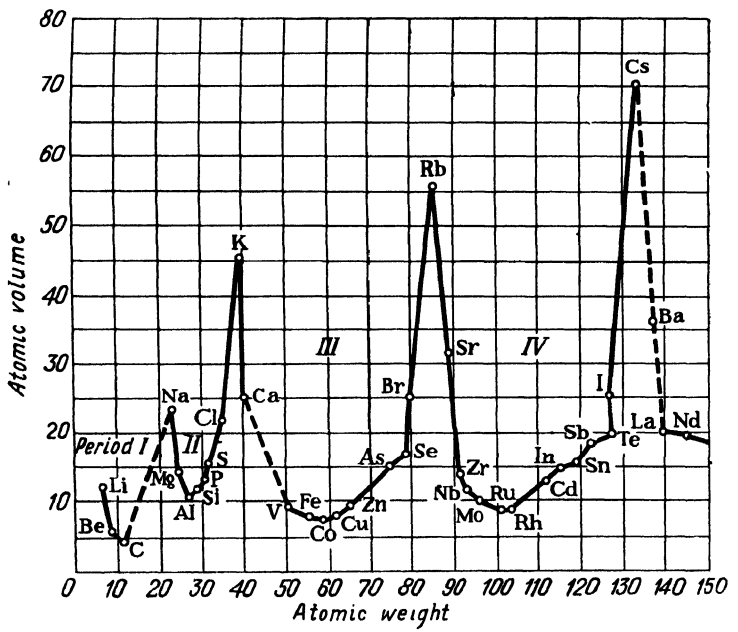


Fig. 10. Atomic volume curve

(at. wt. 58.94) comes before nickel (at. wt. 58.69) and tellurium (at. wt. 127.61) precedes iodine (at. wt. 126.91). In these cases Mendeleyev departed from the usual order because the properties of these elements required precisely the sequence indicated. Thus he did not regard the atomic weight as the decisive factor, but in establishing the position of each element in the Table took into account all its individual properties.

Later investigations showed that Mendeleyev's arrangement of the elements in the periodic system was perfectly correct and corresponded to the structure of their atoms. This will be dealt with in greater detail in Chapter VII.

Thus, in the periodic system the properties of the elements, their atomic weights, valency, chemical nature, etc., vary in a definite

order both horizontally and vertically. The position of each element in the Table is therefore determined by its properties and vice versa, each position is occupied by an element possessing a definite set of properties. Therefore, we can predict the properties of any element quite accurately from its position in the Table.

Suppose, for instance, that we have to find the properties of the element situated in the third horizontal series between magnesium and silicon. The very fact that the element is in the third group shows that it forms an oxide of the type R_2O_3, i.e., that it is trivalent. Then, since the element magnesium at its left, in the second group, is a typical metal, and silicon at its right, in the fourth group, is a weak non-metal, the element in question will most probably be a metal, but a less typical one than magnesium. This conclusion is confirmed also by the fact that directly above it in the same group is boron with very weak metallic properties and directly below it scandium, whose properties are already distinctly metallic. Thus the element in question is a metal. Hence, it either does not combine at all with hydrogen or forms a solid compound with it; its oxide, as the oxide of an element transitional between the metal magnesium and the non-metal silicon, must possess weakly basic properties or be amphoteric, i.e., form salts both with acids and bases. Such, actually, are the properties of the element aluminium which occupies the position under consideration.

The atomic weight of aluminium can also be easily computed by its position in the Table, as the arithmetical mean of the atomic weights of its neighbours.

It should be noted that not only the chemical properties of the elements but very many physical properties of simple substances as well, change periodically if regarded as functions of their atomic weights. The periodicity of the change in the physical properties of simple substances becomes especially clear-cut if the atomic volumes of the simple substances, that is, the volumes occupied by one gram-atom of each in the solid or liquid state, are compared. The curve of atomic volumes shown in Fig. 10 illustrates the variation of their values as the atomic weights increase. The highest points of the curve are occupied by the alkali metals which possess the largest atomic volumes.

Periodic changes are also observed in the specific gravities, melting and boiling points and other physical constants of simple substances.

33. Significance of the Periodic Table. The Periodic Table of Elements greatly influenced the subsequent development of chemistry. Besides being the first natural classification of chemical elements, showing that they form a regular system and are closely related to one another, it has proved a mighty tool for research.

At the time Mendeleyev drew up his Table on the basis of his Periodic Law, many elements were still unknown; for instance, the element scandium in the fourth series was one of these unknown elements. The element following calcium according to its atomic weight was titanium. But titanium could not be placed next to calcium, because this would put it in the third group, whereas titanium is tetravalent, forming TiO_2 as its highest oxide; besides, all its other properties show that it should be in the fourth group. For this reason Mendeleyev skipped one box, that is, left a blank space between calcium and titanium. On the same grounds two blank spaces were left in the fifth series between zinc and arsenic, these spaces now being occupied by the elements thallium and germanium. Blank spaces had to be left also in other series. Mendeleyev was not only certain that there existed elements then unknown which would fill these spaces, but even went so far as to predict the properties of three of these elements in accordance with their positions among the other elements of the periodic system.

He called one of them, which was to take its place between calcium and titanium, eka-boron (as its properties would resemble those of boron); two others, for which blank spaces were left in the Table in the fifth series between zinc and arsenic, were called eka-aluminium and eka-silicon.

In predicting the properties of these unknown elements, Mendeleyev wrote: "I take the liberty to do this in order that in time at least, when any one of these predicted bodies is discovered, I may fully reassure myself and be able to convince other chemists of the truth of the assumptions on which the system I have suggested is based."

In the course of the next fifteen years Mendeleyev's predictions were brilliantly confirmed: all three elements were actually discovered. First the French chemist Lecoq de Boisbaudran discovered a new element, gallium, which possessed all the properties predicted by Mendeleyev for eka-aluminium; soon after, in Sweden, Nilson discovered scandium with the properties of eka-boron and finally, several years later, in Germany, Winkler discovered the element germanium, identical to Mendeleyev's eka-silicon.

To give an idea of the remarkable accuracy of Mendeleyev's predictions, a comparison of the properties predicted by him for eka-silicon in 1871 with those of germanium, discovered in 1886, is given below:

Properties of eka-silicon	*Properties of germanium*
Eka-silicon Es—a fusible metal, capable of volatilizing when strongly heated.	Germanium Ge—a grey metal, melting point about 960° C; volatilizes at higher temperatures.
Atomic weight of Es—about 72.	Atomic weight of Ge—72.6.
Specific gravity of Es—about 5.5.	Specific gravity of Ge—5.35 at 20° C.

EsO_2 should be readily reducible.
Specific gravity of EsO_2 will be close to 4.7.
$EsCl_4$ is a liquid, b.p. about 90°C. Specific gravity close to 1.9.

GeO_2 is easily reduced to the metal by coal or hydrogen.
Specific gravity of GeO_2 equals 4.703 at 18° C.
$GeCl_4$ is a liquid, b.p. 83° C. Specific gravity 1.88 at 18° C.

The discovery of gallium, scandium and germanium was a real triumph of the Periodic Law. News of the predictions of the Russian chemist which had come true spread all over the world, and after this Mendeleyev's Periodic Law received universal recognition.

Mendeleyev himself received these discoveries with great satisfaction. "When in 1871 I wrote an article on the application of the Periodic Law for determining the properties of undiscovered elements," he said, "I did not think I would live to see this deduction from the Periodic Law proved, but reality has ruled otherwise. I then described three elements, eka-boron, eka-aluminium and eka-silicon, and before twenty years had passed I had the joy of seeing all three discovered. . . ."

The periodic system was of great importance also in deciding the question of the valency and atomic weights of several of elements.

For instance, for a long time the element beryllium was considered an analogue of aluminium and the formula of its oxide was considered to be Be_2O_3. Analysis showed that beryllium oxide contained nine parts by weight of beryllium to every sixteen parts of oxygen. But no volatile compounds of beryllium being known at that time, the atomic weight of this element could not be determined accurately enough. On the basis of the percentage composition and the assumed formula of beryllium oxide, its atomic weight was considered to equal 13.5. But there was only one position for beryllium in the Periodic Table—that above magnesium, according to which its oxide must have the formula BeO; the atomic weight of beryllium, therefore, must be 9. This conclusion was soon borne out by determinations of the vapour density of beryllium chloride which made it possible to calculate the atomic weight of beryllium.

In a similar way the Periodic Table incited investigators to correct the atomic weights of several rare elements. For instance, caesium had earlier been thought to have an atomic weight of 123.4. But in arranging the elements in the Table Mendeleyev found that according to its properties the place of caesium was in the left column of the first group, under rubidium, and that its atomic weight must equal about 130. Recent determinations have shown the atomic weight of caesium to be 132.91.

At first, the Periodic Law was received very coldly and with distrust. When, on the basis of his discovery, Mendeleyev questioned a number of experimental data concerning atomic weights and ventured

to predict the existence and properties of elements, which had not yet been discovered, many chemists were more than sceptical towards his daring statements. Thus, for instance, L. Meyer wrote in 1870 concerning the Periodic Law: "It would be hasty to undertake an alteration of the conventional atomic weights on such shaky grounds."

However, Mendeleyev's predictions came true and the Periodic Law was universally recognized. The problem, so brilliantly solved by Mendeleyev, had troubled the minds of many scientists, and there had been attempts in several countries to found the Periodic Law. For this reason other chemists besides Mendeleyev claimed to have discovered the law. In this connection Mendeleyev wrote in his "Principles of Chemistry":

"A law can be confirmed only by making deductions which are impossible and unexpected without it, and by proving these deductions experimentally. That is why, after discovering the Periodic Law, I, on my part (1869-71), made logical deductions capable of proving its truth. ... Not a single law of nature can be confirmed without such a test. Neither Chancourtois to whom the French attribute the honour of discovering the Periodic Law, nor Newlands, credited by the English, nor L. Meyer, whom others have called its founder, dared to guess at the *properties of undiscovered* elements, to alter 'conventional atomic weights' or to regard the Periodic Law as a new, strictly decreed law of nature, capable of embracing facts still ungeneralized, as I did at the very start (1869)."

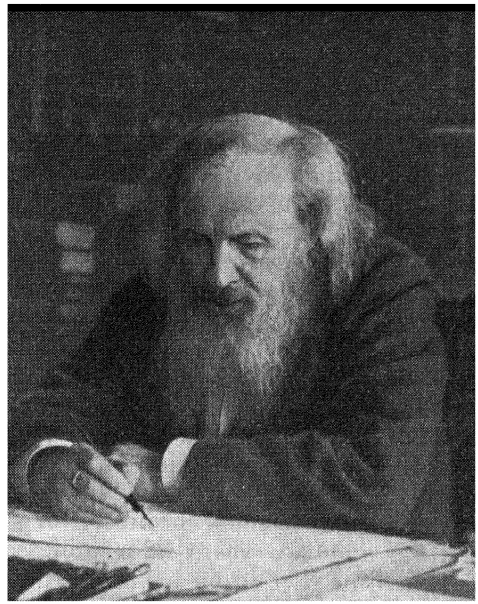
The discovery of the Periodic Law and the founding of a system of chemical elements were of immense importance not only for chemistry and other natural sciences, but for philosophy as well, for the materialistic world outlook. Revealing the relationship between the properties of the chemical elements and the quantity of substance in their atoms, the Periodic Law presented a striking proof of the universal law of development of nature, the Law of Transformation of Quantity into Quality.

According to F. Engels, "By means of the—unconscious—application of Hegel's law of the transformation of quantity into quality, Mendeleyev achieved a scientific feat which it is not too bold to put on a par with that of Leverrier in calculating the orbit of the until then unknown planet Neptune."*

But the periodic system not only reflects the transformation from quantity to quality; it reveals also the unity of opposites manifested in the properties of the elements. It testifies to the fact that there are contradictions in the very nature of the elements, as a result of which one and the same element under different conditions may show directly opposite properties.

* F. Engels, "Dialectics of Nature", Foreign Languages Publishing House, Moscow, 1954, p. 90.

Dmitry Ivanovich
Mendeleyev
(1834-1907)



Before Mendeleyev chemists used to group the elements according to their chemical resemblances, striving to bring only similar elements together. Mendeleyev's approach to the elements was entirely different. He brought together dissimilar elements placing next to each other chemically different elements with close atomic weights. It was this arrangement that made it possible to reveal the profound organic relation between all the elements and led to the discovery of the Periodic Law.

The Periodic Law was one of the greatest generalizations of all the knowledge on the chemical elements available in Mendeleyev's time. Mendeleyev showed that the chemical elements are a regular system based on a fundamental law of nature.

Though he attached great importance to the Periodic Law, Mendeleyev pointed out more than once that much hard work and many new investigations would still be needed to get to its bottom. "The Periodic Law," he wrote, "is pictured now as a new, only partly revealed secret of nature." The subsequent progress of science opened the way for a much deeper penetration into the structure of matter on the basis of the Periodic Law, than was possible in Mendeleyev's time. The theory of atomic structure developed in the early XX century revealed the inner meaning of the Periodic Law and threw

a new light on Mendeleyev's system, making it even more harmonious and significant.

The history of the discovery of the Periodic Law and its further development is a striking example of how human thought delves into the innermost secrets of nature and gradually solves its "riddles".

34. D. Mendeleyev. The father of one of the greatest generalizations in chemistry—the Periodic Table of Elements—Dmitry Ivanovich Mendeleyev, was born in 1834 in the town of Tobolsk (Siberia), in the family of the director of the town Gymnasium. He received a secondary education at the Tobolsk Gymnasium and then entered the Petersburg Pedagogical Institute, from which he graduated with a gold medal in 1857. After graduation he worked as a teacher for two years, first in the Simferopol and then Odessa Gymnasiums.

After receiving his master's degree in 1859 for a thesis presented under the title "On Specific Volumes," Mendeleyev went abroad on a two-year scientific commission, during which he took part in the World Chemical Congress in Karlsruhe (1860). Upon his return to Russia he was elected professor of the Petersburg Technological Institute and two years later professor of the Petersburg University where he carried on his scientific and pedagogical activities for twenty-three years. In 1893 Mendeleyev was appointed Director of the Bureau of Weights and Measures. At the same time he carried on a great deal of scientific and literary work. In 1906 he issued a book under the title "Contribution to the Knowledge of Russia" which contained profound thoughts as to the trends for the further development of Russian industry and the Russian national economy.

In 1907 D. Mendeleyev died of pneumonia.

The greatest result of Mendeleyev's creative effort was the discovery of the Periodic Law and the drawing up of the Periodic Table of Elements.

Of other works by Mendeleyev, the most important are: "Investigation of Aqueous Solutions by Their Specific Gravity," his Doctor's thesis "On the Combination of Alcohol with Water" and "A Conception of Solutions as Associations." The so-called "chemical" or hydrate theory of solutions developed by Mendeleyev laid the foundation for the present-day theory of solutions.

To Mendeleyev we owe the discovery of the "absolute boiling point" (now called "critical temperature"), i.e., the temperature above which no pressure can stop a given liquid from vapourizing or condense a given vapour into a liquid.

One of Mendeleyev's prominent works is his book "Principles of Chemistry" in which inorganic chemistry was for the first time expounded entirely from the standpoint of the Periodic Law. "The 'Principles' are my favourite offspring," wrote Mendeleyev in 1905. "They contain my image, my experience as a teacher and my bosom

ideas." Mendeleyev's scientific and practical activities were broad in scale and exceedingly versatile. His works embrace various fields of science—chemistry, physics, physical chemistry, geophysics. Dozens of his major works were devoted to economic and social problems.

Organically combining theory and practice Mendeleyev gave a great deal of attention throughout his life to the development of the industry of his country. "Science and industry—there lie my dreams!" wrote Mendeleyev. Profoundly interested in problems of petroleum technology, he took up petroleum engineering in Baku, zealously advocated the necessity of maximally increasing the output and chemical treatment of oil, and suggested the construction of an oil line from Baku to the Black Sea. In 1887 Mendeleyev suggested the idea of underground coal gasification. Afterwards, taking an interest in the Urals iron industry, he studied it on the spot and raised the question of the utilization of the Kuznetsk Basin coal for iron and steel production in the Urals. He offered a number of suggestions concerning the development of metallurgy in the East and posed the problem of "direct production of iron and steel from the ore, by-passing pig iron." A great scientist, Mendeleyev was a remarkable citizen and patriot as well, who devoted his life and energies to the progress of his country's science and industry.

CHAPTER IV

Atomic Structure

The existence of a relationship between all the chemical elements, so strikingly manifested in the Periodic Table, suggests that the atoms have something in common at their foundation, that they are all closely akin to one another. However, until the end of the XIX century the predominant conviction in chemistry was the metaphysical conception that the atom is the smallest particle of a simple substance, the ultimate limit of divisibility of matter. In all chemical changes only molecules are broken down and built up again, but atoms remain unchanged and cannot be divided into smaller particles.

Only a few scientists understood the one-sidedness and restrictedness of such conceptions. For instance, the Russian scientist A. Butlerov wrote in 1886: "...The now so-called 'atoms' of certain elements may perhaps, as a matter of fact, be capable of chemical division, i.e., they are not indivisible by nature, but indivisible only by the means to which we have access today and ... may become divisible by processes which will be discovered at some time in the future." Similar ideas were put forth almost at the same time by another Russian scientist, N. Morozov. "Can it be assumed," he wrote, "that atoms never decompose to still more primal particles under some other cosmic conditions, such as the heavenly fires observed from time to time during spectral investigations of flashing stars? Of course not! There is a great deal of evidence that the atoms of chemical elements are going through their evolution in the eternal history of the universe."

But at that time none of these assumptions could be confirmed by experimental data. It was not until the end of the XIX century that discoveries were made revealing the complexity of atomic structure and the possibility of breaking down atoms under certain conditions to form other atoms. These discoveries greatly accelerated the progress of the science of atomic structure.

35. Discovery of Electrons. The first indications of the complex structure of atoms were obtained through a study of the cathode rays resulting from electrical discharges in highly rarefied gases. To observe these rays, as much of the air as possible is pumped out of

a glass tube with two metallic electrodes fused into it and then high-voltage current is passed through. Under these conditions "invisible" *cathode rays* are emitted from the cathode of the tube perpendicular to the cathode plate. These rays cause the glass of the tube to glow bright green at the spot they fall upon.

Cathode rays can move light mobile bodies placed in their path and are deflected from their original direction in magnetic (Fig. 11) and electrical fields (in the latter case, towards the positively charged

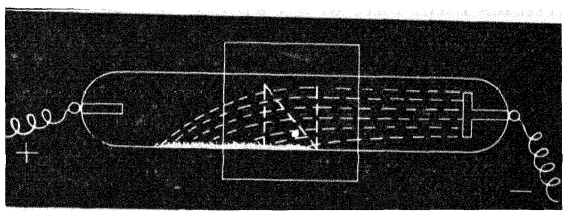


Fig. 11. Deflection of cathode rays in a magnetic field

plate). The action of cathode rays can be detected only inside the tube because glass is impermeable to them, and they cannot emerge from the tube.

A study of the properties of cathode rays led to the conclusion that they are a stream of minute particles charged with negative electricity and travelling at a rate equal to about half the velocity of light. By special methods scientists succeeded in determining the mass of the cathode-ray particles and the magnitude of their charge.

It was found that the mass of each particle equals 0.00055 of an oxygen unit, or only $^1/_{1,840}$ of the mass of a hydrogen atom, the lightest of all atoms. The charge of a cathode-ray particle equals $1.60 \times \times 10^{-19}$ coulombs or 4.80×10^{-10} electrostatic units. It is especially remarkable that neither the mass of the particles, nor the magnitude of their charge depends on the nature of the gas in the cathode tube, on the substance of the electrodes, or on any other conditions of the experiment. Besides, cathode-ray particles are known only in the charged state and cannot be deprived of their charges, cannot be converted into neutral particles: the electrical charge constitutes, so to say, the very essence of their nature. These particles are known as **electrons.**

According to present-day conceptions, the charge of the electron is the ultimate electrical charge, the smallest quantity of electricity that can exist. Electricity consists of separate particles—"atoms" of

electricity, any charged body invariably containing a whole number of such particles.

In cathode-ray tubes the electrons are torn away from the cathode under the influence of an electrical discharge. However, they may arise also out of any connection with electrical discharges. Thus, for instance, all metals emit electrons when strongly heated; electrons are found also in the flame of a candle or gas burner; many substances throw off electrons under the action of ultra-violet or X-rays, etc.

The emission of electrons by a great variety of substances shows that these particles form part of all atoms; hence atoms are complex formations consisting of still smaller structural units.

36. Discovery of X-Rays. In 1895 the German physicist Röntgen, when studying the fluorescence of glass under the influence of cathode rays, discovered a new type of radiation—X-rays, sometimes called also **Röntgen rays.** These rays were detected by their action on a photographic plate and by their property of causing luminescence (fluorescence) in many substances. The most remarkable property of X-rays is their tremendous penetrating power. They can pass almost unhindered not only through glass, but also through cardboard, wood, fabrics and various other substances impermeable to ordinary light rays. Only metals, especially heavy metals, can stop them to any considerable extent.

Any solid can serve as a source of X-rays if subjected to the action of cathode rays, but platinum emits them especially intensively. That is why special X-ray (Röntgen) tubes (Fig. 12) made for the production and study of X-rays are so designed that the beam of cathode rays falls upon a platinum plate, called **anticathode.** Under the impacts of the fast cathode-ray particles (electrons) this plate emits X-rays. In contradistinction to cathode rays, X-rays are not deflected by magnetic or electrical fields; hence, they do not carry electrical charges of any kind.

Besides the above properties, X-rays are capable of ionizing gases. When X-rays pass through a gas, the latter becomes a conductor of electricity. Investigations have shown that the conductivity of the gas is due to the formation of positively and negatively charged gas particles, called **ions,** therefore it is said that the gas is ionized.

The formation of ions is another confirmation of the presence of the electrons in atoms. Under the influence of X-rays electrons are torn out of the neutral atoms and molecules of the gas, as a result of which the atoms or molecules become positively charged. At the same time other molecules combine with the liberated electrons and become negatively charged ions.

The capacity of X-rays to ionize gases was utilized for direct measurement of the charge on an electron. The measurement was carried out with the arrangement shown diagrammatically in Fig. 13. The apparatus is a small chamber

with several windows. The two plates of a condenser are mounted on insulators inside the chamber.

The method of measurement was as follows. Very minute droplets of oil were sprayed into the chamber through port *A* and they began to settle slowly under the influence of gravity. The falling droplets were observed through a microscope opposite the window in the front wall of the chamber, the inside of the chamber being illuminated by means of an electric arc *B*. The weight of the droplets was determined by their rate of descent. Subjected for a short time to the action of X-rays (through window *C*), the air between the condenser plates breaks up partly into ions which are captured by individual droplets and thus charge the latter electrically. As long as the plates of the condenser are not charged these droplets continue to descend at the usual rate under the influence of

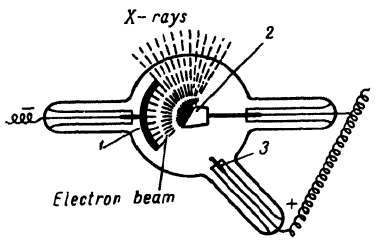


Fig. 12. X-ray tube:
1—cathode; *2*—anticathode; *3*—anode

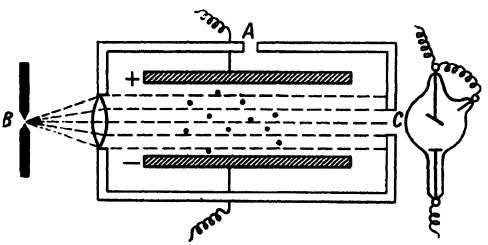


Fig. 13. Diagram of apparatus for determining charge on electron

gravity. But as soon as a charge is applied to the condenser, the movement of the drops changes: if, for instance, a certain droplet is charged negatively and the upper plate of the condenser positively, the droplet will be attracted to the upper plate; its descent is retarded or it may even begin to reascend. By regulating the charge of the condenser any droplet can be stopped altogether and will hang suspended in the air. Obviously, under such conditions the weight of the droplet is exactly neutralized by the attraction of the plate. Hence, knowing the voltage of the electric field and the weight of the droplet, we can calculate its charge.

Numerous observations of individual droplets show that their charges vary, but they are always equal to or multiples of a definite least charge which, according to present-day data, equals 4.803×10^{-10} electrostatic units. Since the droplet cannot absorb less than one electron this least charge is the charge of an electron.

For a long time the nature of X-rays was a point of controversy. Finally physicists came to the conclusion that X-rays are electromagnetic oscillations of the same kind as the rays of visible light, but with a much smaller wave length. Investigations of X-ray spectra played a very important part in the development of the theory of atomic structure.

37. Discovery of Radioactivity. A year after the discovery of the new type of rays by Röntgen, the French physicist Becquerel noticed that salts of the metal uranium, the heaviest of all chemical elements known at that time (atomic weight 238.07), possess the property

of emitting certain rays which, like X-rays, could penetrate various substances and darken photographic plates protected from the action of ordinary light.

Somewhat later Marie Curie-Sklodowska discovered the same property in compounds of thorium, an element close to uranium in atomic weight. At Curie's suggestion this property was called **radioactivity** (which means literally ray-emitting activity), and the substances emitting rays like those emitted by uranium and thorium salts were termed **radioactive.**

Marie Curie-Sklodowska was born in Warsaw in 1867. In her youth Marie Sklodowska took an active part in the revolutionary movement as member of a circle organized by the students of the college where her father lectured in mathematics and physics. After this circle collapsed owing to police persecution, she was obliged to leave Warsaw, and settled in Paris where she entered the university.

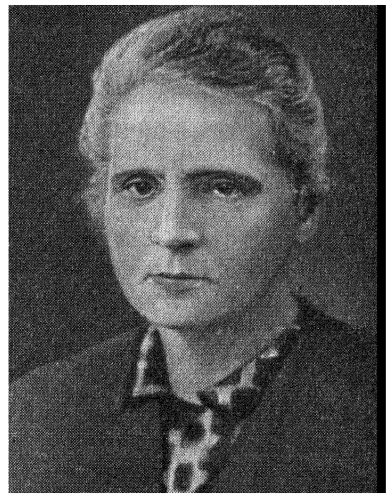
After graduating the university Sklodowska, together with her husband Pierre Curie, undertook a study of radioactivity. For her brilliant discoveries in this field she was awarded the degree of Doctor of Physical Science. After the death of her husband (in 1905) Curie-Sklodowska continued her scientific activities in the study of radioactive elements. In 1910 she obtained metallic radium for the first time. Curie-Sklodowska twice received the Nobel Prize for her discoveries.

The discovery of the radioactive properties of uranium salts moved Mme. Curie to undertake an extensive investigation of all uranium compounds. This investigation showed that radioactivity is a property belonging to the atoms of uranium, as its degree depends exclusively on the quantity of uranium in its compounds and is quite independent of the elements the uranium is combined with. Undertaking a study of the natural compounds of uranium, Curie found that despite the lower uranium content in them they were more radioactive than pure uranium salts or than uranium itself. It was natural therefore to assume that the uranium ores contained an admixture of some other radioactive substance and since this substance could not be detected by usual methods of analysis it followed that its content in the ore was very minute.

Indeed, by successively isolating the substances contained in uranium pitchblende ore, Curie succeeded in establishing the presence of two new highly radioactive elements. She called one of them *polonium* and the other *radium.*

The percentage of both elements in the ore was exceedingly small. Therefore, to obtain them in their pure form it was necessary to treat enormous quantities of ore. This work was carried out by Marie Curie together with her husband Pierre Curie. The initial material was not the pitchblende itself but the waste left over after uranium had been extracted from the ore. After more than half a year's painstaking work, in the course of which they treated several tons of waste,

Marie Curie-Sklodowska
(1867-1934)



the Curies obtained only a few hundredths of a gram of radium in the form of the pure chloride salt. However, this amount was sufficient to cause a complete revolution in science. Due to the practically imperceptible content of polonium in the ore they were unsuccessful in extracting it in its pure form.

Subsequently a third radioactive element—*actinium*—was discovered in uranium ore.

38. Radium and Its Properties. At present the properties of radium have been studied thoroughly. It is a silvery metal, rather soft, decomposing water at room temperatures. Its chemical behaviour greatly resembles that of barium with which it occurs together in the pitchblende ore. Radium and barium are very difficult to separate, owing to the great resemblance of their salts. Like barium, radium belongs to the second group of the Periodic Table. The atomic weight of radium (Ra) equals 226.05. Radium is usually obtained in the form of the chloride or the bromide ($RaCl_2$ or $RaBr_2$).

Radium is quite widespread in nature; it occurs in many minerals and mineral springs, but always in very minute quantities. Radium is obtained from uranium ores, in which it is always present. Even the richest uranium ore contains only about 0.2 gr. of radium per ton of ore. That is why radium preparations are so costly and difficult to obtain.

The most remarkable property of radium is its high radioactivity, which is several million times greater than that of uranium. Radium

salts glow in the dark, emitting rays which darken photographic plates, as mentioned above, and are capable of causing many other chemical reactions as well. Water containing a dissolved radium salt gradually decomposes into hydrogen and oxygen; under the action of radium rays ammonia decomposes into hydrogen and nitrogen, hydrogen chloride into hydrogen and chlorine, and oxygen turns into ozone. It should be noted that these reactions are endothermal, that is, require an influx of energy from the surroundings.

Many substances begin to glow when acted on by radium rays; some non-conductors (for instance paraffin) become perceptibly conductive. Finally, radium displays a high physiological activity, destroying tissues in the organism, killing bacteria, etc.

Especially striking is the capacity of radium to continuously emit large quantities of energy. Calorimetric measurements have shown that one gram of radium emits about 137 cal. of heat per hour, and observations over a period of many years have detected no perceptible decrease in the quantity of energy emitted.

These "wonderful" properties of radium seem to challenge the very Law of Conservation of Energy. Radium appeared to be a perpetual source of energy which could be obtained without expending any other kind of energy. Hence it is not surprising that many scientists undertook investigations of radium and radioactive radiations. The results of these investigations were so important that they radically changed the former conceptions of chemical elements and of the immutability of atoms.

39. Rays of Radioactive Substances. If a radium preparation, say, a few hundredths of a gram of $RaBr_2$, is placed in a small lead box with an opening in its top, only a narrow beam of vertical rays will be emitted from it; all the other rays will be stopped by the lead. If we place a photographic plate over the opening a dark spot will appear where the rays strike it.

Now let us bring the north pole of a strong magnet near the opening in the box. The picture changes abruptly. Instead of a single dark spot on the plate, there will now be three: one in the same place as before, another to the right of it and a third to the left.

This experiment shows that the radiation observed is not homogeneous, since the vertical beam decomposes under the influence of a magnetic field into three kinds of rays (Fig. 14): the rays that do not change their direction in the magnetic field are called gamma rays; those that are deflected to the left are known as beta rays and those which swerve to the right, as alpha rays.*

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* Radium itself emits only alpha and gamma rays. The emission of beta rays by radium preparations is due to the fact that these preparations always contain impurities of other radioactive substances which emit them.

Gamma rays greatly resemble X-rays. Like the latter, they are of the same nature as ordinary light rays, but have a much shorter wave length and an immense penetrating power; their action can be detected even after passing through an iron plate 30 cm. thick.

Beta rays resemble cathode rays. They are streams of fast particles charged with negative electricity and having a mass equal to only $\frac{1}{1,840}$ of the mass of a hydrogen atom. Such particles, as we already know, are called electrons.

The only difference between beta rays and cathode rays is in the velocities of their constituent particles. While the fastest cathode

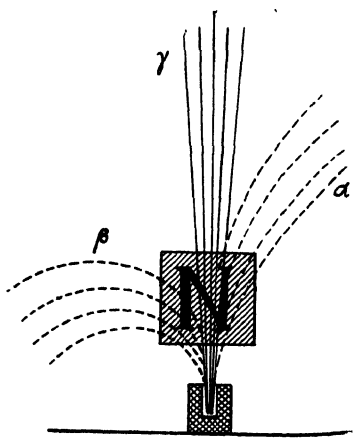


Fig. 14. Split-up of radioactive radiation in magnetic field

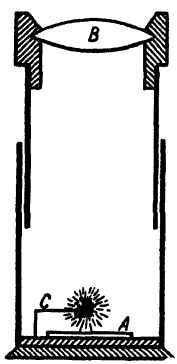


Fig. 15. Spinthariscope

particles have a velocity of 150,000 km. per sec., the velociy of some beta particles is almost equal to that of light (300,000 km. per sec.). Beta rays are capable of passing through aluminium sheets up to 3 mm. thick.

Alpha rays. The most interesting are the alpha rays. Like beta rays, they are streams of particles, but their charge is positive instead of negative. Their velocity is much smaller than that of beta particles, but is still quite high—20,000 km. per sec.; alpha particles are absorbed by substance much more easily than the others: an aluminium sheet 0.1 mm. thick is enough to stop them entirely.

By measuring the deflection of alpha particles in magnetic and electrical fields it has been possible to calculate the ratio of the charge of each alpha particle to its mass; this ratio was found to equal 1 : 2, if the charge on an electron is accepted as the unit of charge and $^1/_{16}$ of the mass of an oxygen atom as the unit of mass. Direct

measurement of the charge on alpha particles showed, besides, that its value equals twice the charge on an electron; hence it follows that the mass of an alpha particle equals four. But this is the mass of the helium atom. Thus, alpha particles proved to be nothing but atoms, or rather ions, of helium, bearing a double positive charge.

The identity between alpha particles and helium was proved by direct experiment. A radium preparation fused into a glass tube thin enough for the alpha particles to penetrate its walls was placed inside another thick-walled glass tube. After some time helium could be detected in the outer tube by means of a spectroscope.

If a screen coated with zinc sulphide is placed in the path of alpha rays, it will be observed to glow in the dark. Such observations can be conveniently made with an apparatus called **spinthariscope** (Fig. 15). This apparatus consists of a brass cylinder with a magnifying glass *B* at its top and a screen *A* at its bottom, coated with zinc sulphide. A needle *C* with some radioactive substance on its point is placed in front of the screen. If the screen is observed through the magnifying glass the glow can easily be seen to consist of a large number of separate flashes or scintillations, each of which is the result of one alpha particle striking the screen. Hence, by counting the number of flashes we can determine the number of alpha particles striking the screen during a definite period of time.

These light flashes were the first visible action of individual atoms and are the most irrefutable proof of the reality of their existence. That a single infinitesimally small atom is capable of causing a perceptible light effect when it collides with the screen becomes quite credible if we take into account the huge kinetic energy of an alpha particle, which is high enough to produce a visible luminous effect. By counting up the number of scintillations it was established that one gram of radium ejects 3.5×10^{10} alpha particles per second.

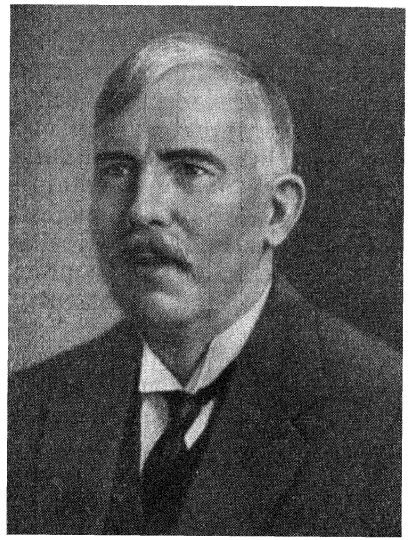
40. Radioactive Decay. Radium emits not only alpha and gamma rays, but also a new gaseous radioactive substance which was at first called **radium emanation.** Although this gas forms in exceedingly small quantities, it has been collected and its properties have been studied. From a chemical standpoint, emanation is an inert gas incapable of reacting with any substances. It is a chemical element. Subsequently this element received the name of *radon* (Rn).

The atomic weight of emanation, or radon, was found to equal 222. Since the atomic weight of radium is 226 and the atomic weight of helium 4 there is no doubt that the irradiation of radium is accompanied by decay of its atoms into radon and helium atoms.

In other words, radium keeps continuously changing into two new elements—radon and helium:

$$\underset{226}{\mathrm{Ra}} \longrightarrow \underset{222}{\mathrm{Rn}} + \underset{4}{\mathrm{He}}$$

Ernest Rutherford
(1871-1937)



A subsequent study of radon showed that it is very short-lived. Emitting alpha rays, it decomposes into helium and a solid radioactive substance called *radium* A. In its turn, radium A passes consecutively into a whole series of radioactive elements. One of them is *polonium* which was discovered at the same time as radium.

The discovery of radioactivity left no doubt as to the fact that the atoms of the chemical elements are complex systems capable of breaking down into new atoms. The transmutation of radium into radon and helium, as well as the further transmutations of radon have been proved irrefutably. Hence, the chemical elements, or at least some of them, are capable of being transmuted into one another.

These changes, however, differ essentially from ordinary chemical reactions. While the velocity of chemical reactions is affected by the temperature, the pressure and other conditions, no external factors known to present-day science have any perceptible influence on radioactive transformations. At the very lowest and very highest temperatures, in vacuum and under immense pressure, in the dark and in the light, these changes take place in exactly the same way. They occur, so to say, "of their own accord." We can neither accelerate, nor decelerate them.*

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* Many radioactive elements have been obtained lately by artificial methods. "Artificial" radioactivity will be dealt with in Chapter XXVI.

41. Nuclear Model of the Atom. The study of atomic structure began practically in 1897-98, after the nature of cathode rays had been established finally as a stream of electrons, and the charge and mass of the electron had been determined. The emission of electrons by a great variety of substances suggested that electrons are contained in all atoms. But the atom as a whole is electrically neutral; hence, it must contain some other component part bearing a positive charge large enough to balance the total negative charge of all the electrons. This positively charged part of the atom was discovered in 1911 by the prominent English scientist Rutherford in investigating the movement of alpha particles through gases and other substances.

As was mentioned above, the alpha particles emitted by the atoms of radioactive elements are positively charged helium ions with velocities up to 20,000 km. per sec. Due to this tremendous velocity, alpha particles knock electrons out of the gas molecules they collide with as they travel through the air. The molecules which lose electrons acquire a positive charge, whereas the electrons knocked out of them are immediately captured by other molecules and impart a negative charge to them. In this way positively and negatively charged gas ions are formed in the air along the path of the alpha particles.

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

Beginning with 1900 Rutherford occupied himself with radioactive phenomena. He discovered the three types of rays emitted by radioactive substances; suggested (together with Soddy) a theory of radioactive decay; gave a precise proof of the formation of helium during many radioactive processes. In 1911 he discovered the atomic nucleus and worked out the planetary model of the atom, thus initiating the present-day science of atomic structure. In 1919 he brought about the first artificial transmutation of several stable elements by bombarding them with alpha particles.

The ability of alpha particles to ionize air was utilized in a very clever manner by the English physicist Wilson to make the paths of individual particles visible and to photograph them.

Wilson's method was as follows: If air saturated with water vapour is cooled quickly, the vapour will condense into minute drops of fog. However, if the air is entirely free of dust the fog will not appear in spite of such a cooling; to form the fog there must be dust particles present, around which the vapour can condense. Electrically charged gas molecules have the same effect as dust particles. If we pass alpha particles through a chamber containing air supersaturated with water vapour, the ions formed along the path of alpha particles will cause droplets of water to condense around them, and if the chamber

is illuminated laterally the path of each particle becomes visible as a fine trail of fog.

The Wilson Chamber, used for experiments of this kind (its diagram is shown in Fig. 16), is a cylinder A with a glass cover B; the bottom of the cylinder is a movable piston C. If the piston is lowered rapidly, the moist air in the chamber will cool due to expansion and become supersaturated with water vapour.

Fig. 17 shows one of the photographs of the fog-tracks made by alpha particles. Examining this photograph we see that the paths of alpha particles are rectilinear. At the same time theory shows that each particle must collide with hundreds of thousands of atoms

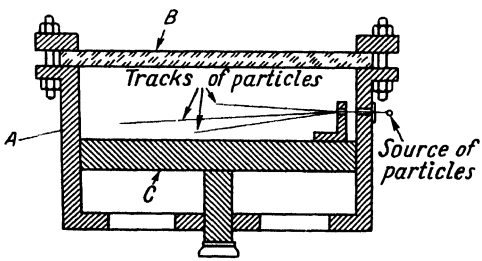


Fig. 16. Diagram of Wilson Chamber

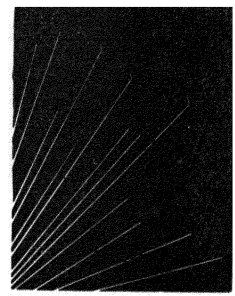


Fig. 17. Photograph of fog-tracks made by alpha particles

along its path, which in air may be as long as 11 cm. If, nevertheless, its path remains rectilinear, this can be attributed only to the fact that the alpha particle flies right *through* atoms.

A more thorough investigation of this phenomenon showed that if a beam of parallel rays is passed through a layer of gas or a thin metal plate, the rays lose their parallelism and become slightly divergent; we say that the alpha particles are scattered, that is, are deflected from their original path. True, the angles of deflection are generally not large, but there is always a small number of particles (about one in 8,000) which are deflected very strongly; some particles are even thrown back, as if they had collided with something solid, impenetrable in their path. These sharp deviations of alpha particles can be clearly seen on some photographs (Fig. 18).

What can be the reason for the abrupt change in direction of the alpha particles? It is easy to see that the deflection in general is caused by electrical interaction between the alpha particles and the charged parts of atoms. These charged parts can hardly be electrons. The mass of the electron is almost 7,500 times less than that of an alpha particle; hence, even if an alpha particle passed very

close to an electron, it would deflect the electron but itself would hardly change the direction of its flight. It remains to assume that the deflection is caused by interaction between the alpha particles and the positively charged parts of atoms, the mass of which is obviously a value of the same order as the mass of the alpha particles. Besides, it must be assumed that this mass occupies an infinitesimally small volume as otherwise its charge would not be able to create a strong electric field and large deflections would be impossible.

On the basis of these considerations Rutherford suggested the following scheme of atomic structure. In the centre of the atom is a positively charged nucleus, about which electrons whirl in different

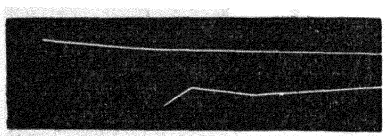


Fig. 18. Photograph of fog-tracks made by two alpha particles

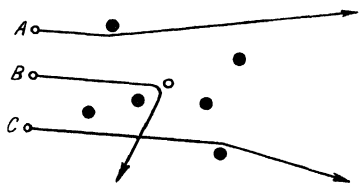


Fig. 19. Paths of alpha particles through an atom

orbits. The centrifugal force due to their rotation is neutralized by the attraction between the nucleus and the electrons, keeping the latter a certain distance away from the nucleus. Since the mass of the electron is infinitesimally small, almost the entire mass of the atom is concentrated in its nucleus. The size of the atom and its separate parts can be expressed approximately by the following figures: the diameter of the atom* is a magnitude of the order of 10^{-8} cm., the diameter of an electron 10^{-13} cm. and the diameter of the nucleus from 10^{-14} to 10^{-12} cm. Hence it is clear that the nucleus and the electrons, the number of which, as we shall see below, is comparatively small, take up but a negligible part of the total space occupied by the atomic system.

The scheme of atomic structure or, as it is usually called, the atomic model suggested by Rutherford easily explains the above described phenomena of deflection of alpha particles. Indeed, the nucleus and the electrons are very small compared to the atom as a whole, bounded by the outermost electron orbits; that is why most of the alpha particles pass through atoms without perceptible deflection. Only when the alpha particle comes very close to the

* By the diameter of an atom we mean the diameter of the sphere enclosing the entire atomic system.

nucleus does electrical repulsion cause it to deviate sharply from its original course.

Fig. 19 shows the paths of alpha particles as they pass through an atom. The black dots denote electrons and the white dot in the centre of the figure, the atomic nucleus. Particles *A* and *C* are deflected only slightly when they collide with electrons; particle *B* is sharply deflected after colliding with the positively charged nucleus.

Thus, investigation of the scattering of alpha particles laid the foundation for the nuclear theory of the atom. Since then this theory has been confirmed in so many diverse ways that at present its truth is beyond doubt.

42. Nuclear Charges. Moseley's Law. One of the problems that stood before the theory of atomic structure at the beginning of its development was determination of the nuclear charge on the different atoms. Since the atom as a whole is electrically neutral, determination of the charge on the nucleus would make it possible to establish the number of electrons surrounding it. A great aid in the solution of this problem were investigations of X-ray spectra.

Let us first recall what ordinary optical spectra, that is "visible" light spectra are.

If a flat beam of white light emitted by a white-hot solid body is passed through a glass prism a so-called **continuous** spectrum will appear on a screen placed on the other side of the prism as a coloured band containing all the colours of the rainbow from red to violet in continuous succession. This phenomenon is known to be due to the fact that white light consists of coloured rays of various wave lengths, which are deflected differently when they pass through the prism and fall on different parts of the screen forming a spectrum.

A diffraction grating may be used instead of the prism to produce the spectrum. This grating is a glass plate with fine parallel lines ruled on its surface very close to each other by means of a diamond (perhaps 1,500 lines to the millimetre). These non-transparent lines play the part of the "rods" of a grating. In passing through a grating of this kind light decomposes and forms a spectrum similar to that obtained by means of the prism, but the order of the colours in this case is reversed.

Strongly heated solid bodies or liquids always give continuous spectra. An entirely different picture is observed upon the decomposition of light emitted by a heated gas or vapour. The light of the latter contains only certain definite rays. Therefore, instead of the continuous coloured band a number of individual coloured lines appear on the screen, separated by dark intervals. The number, colour and arrangement of these lines depend on the nature of the heated gas or vapour. Thus, for instance, potassium vapours give a spectrum consisting of three lines, two red and one violet; the

spectrum of calcium vapours contains several red, yellow and green lines, etc. Such spectra are called **discontinuous** or **line** spectra.

Optical spectra are studied by means of special instruments, spectroscopes and spectrometers, which not only reveal the number and arrangement of the spectral lines, but make it possible to measure the wave lengths of the corresponding rays as well.

Now let us consider X-ray spectra and the conclusions their study has led to.

It will be recalled that X-rays arise when fast electrons collide with a solid body, and are distinguished from the rays of visible light only by their much shorter wave length. While the shortest visible light waves have a length of about 4,000 Ångströms (violet rays) the wave lengths of X-rays are between 20 and 0.1 Ångström units.

An ordinary prism or the diffraction grating described above cannot be used to produce X-ray spectra. Theoretically for rays with such short wave lengths as X-rays we should have to rule a diffraction grating with 1 million lines per mm. As no such grating could be made artificially, X-ray spectra could not be produced for a long time.

In 1912 the German physicist Laue came upon the idea of using crystals as diffraction gratings for X-rays. The regular arrangement of the atoms in crystals and the very small distances between them gave grounds to assume that a crystal would be the very thing to play the part of the required diffraction grating. Laue's assumption was brilliantly confirmed by experiment and soon instruments were constructed, making it possible to obtain the X-ray spectra of almost all the elements.

To produce X-ray spectra the anticathode in an X-ray tube is made of the metal whose spectrum is to be studied, or some compound of the element in question is applied to a platinum anticathode. The screen for the spectrum is a photographic plate or sensitized paper; after development all the lines of the spectrum become clearly visible.

X-ray spectra are much simpler than the line spectra of vapours and gases. The spectrum of each element consists of several lines or groups of lines denotes K-, L- or M-series, the arrangement of which for the different elements is perfectly analogous. The influence of the substance emitting the rays tells only on the wave lengths of the spectral lines.

In 1913, in a study of X-ray spectra, the English scientist Moseley found that *as the atomic numbers of the elements increase* (atomic numbers are numbers showing the position occupied by the element in the Periodic Table) *the lines of each series shift regularly in the direction of decreasing wave lengths.*

Fig. 20 shows the displacement of the two brightest lines α and β of the K-series for the elements from arsenic to strontium. It can be

seen that the displacement of the first three elements is approximately equal. In passing from bromine (No. 35) to rubidium (No. 37) the displacement is twice as large, showing that one element has been skipped.

The relationship between the atomic numbers of the elements and the wave lengths of their X-rays is called **Moseley's Law,** which may by stated as follows:

> *The square roots of the inverse wave lengths are in linear relation to the atomic numbers of the elements.*

This means that if the atomic numbers of the elements are plotted along the abscissa axis and the square roots of the inverse wave lengths along the ordinate axis, the relation between them will be represented graphically by a straight line.

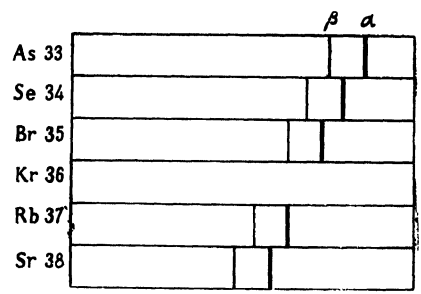


Fig. 20. Shift of K-series lines in X-ray spectra of elements arranged according to their atomic numbers

Moseley's discovery played a very important part in elucidating the structure of atoms. The close relation between the X-ray spectra of the elements and their atomic numbers indicated that atomic numbers do not simply register the position of the elements in the Periodic Table but have a definite physical sense, i.e., express a certain property of the atoms.

Even before Moseley certain theoretical considerations had made possible the assumption that the atomic number of an element indicates the number of positive charges on the nucleus of its atom. At the same time, Rutherford, in studying the scattering of alpha particles when they pass through thin metal plates, found that if the charge on an electron is taken as a unit, the charge on the nucleus expressed in the same units is approximately equal to one half the atomic weight of the element. The atomic numbers, at least of the lighter elements, also equal approximately half their atomic weight. All this taken together led to the conclusion that *the charge on the nucleus of an element is numerically equal to its atomic number.*

This conclusion was finally confirmed in 1920 by the English physicist Chadwick by direct measurement of the charges on copper, silver and platinum atoms.

	Copper	Silver	Platinum
Nuclear charge	29.3	46.3	77.4
Atomic number	29	47	78

Taking into account the inevitable errors of experiment, the agreement of the figures obtained with the atomic numbers of the elements may be considered very good.

Thus Moseley's Law made it possible to determine the charges on atomic nuclei. At the same time, owing to the neutrality of atoms, this established the number of electrons revolving around the nucleus in the atom of each element.

43. Line Spectra of the Elements. Bohr's Theory. Rutherford's nuclear atomic model was further developed by the Danish scientist Niels Bohr, who related the theory of atomic structure to the theory of the origin of spectra.

As indicated in the previous paragraph, line spectra are obtained by resolving the light emitted by hot vapours or gases. Each chemical element has its own corresponding spectrum, differing from the spectra of other elements. Most elements give very complex spectra containing large numbers of lines (for instance, the spectrum of iron has as many as 5,000 lines), but comparatively simple spectra are also known.

Developing Rutherford's nuclear theory, scientists came to the conclusion that the complex structure of line spectra is due to the oscillation of the electrons within the atoms. According to Rutherford's theory, each electron rotates around the nucleus, the attractive force of the latter being neutralized by the centrifugal force due to the rotation of the electron. The rotation of the electron is quite analogous to rapid oscillations and should give rise to electromagnetic waves. Therefore, it may be assumed that a rotating electron emits light of a definite wave length, depending on the frequency of rotation of the electron in its orbit. But in emitting light the electron loses part of its energy, thus disturbing the equilibrium between itself and the nucleus; in order to restore its equilibrium, the electron would have to gradually approach the nucleus, upon which the frequency of rotation of the electron and the nature of the light it emits would change just as gradually. Finally, after exhausting all its energy, the electron should "fall" on to the nucleus and the radiation of light should stop.

If such a continuous change in the movement of the electron really took place, the spectrum would also be always continuous and would not consist of rays of a definite wave length. Besides, the "fall" of the electron onto the nucleus would mean destruction of the atom and the end of its existence. Thus, Rutherford's theory was not only unable to explain the laws of arrangement of the lines in the spectrum, but even the very existence of line spectra.

In 1913 Bohr suggested a new theory of atomic structure which very cleverly reconciled spectral phenomena with the nuclear model of the atom, by applying to the latter the quantum theory of radiation

introduced into science by the German physicist Planck. Essentially, the quantum theory boils down to the statement that radiant energy is not emitted and absorbed in continuous streams as was thought previously, but in separate very minute, but quite definite, portions called energy **quanta.** The supply of energy of a radiating body changes in jumps, quantum by quantum; fractional number of quanta cannot be emitted or absorbed.

The magnitude of an energy quantum depends on the number of oscillations of the energy radiated: the greater the number of oscillations, the larger the quantum.

If we denote an energy quantum by ε and the number of oscillations by γ we may write

$$\varepsilon = h\gamma$$

where h is what is known as the **Planck constant,** equal to 6.624×10^{-27} erg $\times$sec. Quanta of radiant energy are also called **photons.** Applying quantum conceptions to the rotation of electrons around the nucleus, Bohr founded his theory on three rather daring assumptions or postulates. Although these postulates contradict the laws of classical electrodynamics they are justified by the striking results to which they lead and by the full agreement between the theoretical results obtained and a vast number of experimental facts.

Bohr's postulates consist in the following.

An electron cannot revolve about the nucleus in any chosen orbit, but only in such as satisfy definite conditions following from the quantum theory. These orbits are known as **stable** or **quantum** orbits.

When an electron moves along one of its possible stable orbits it does not radiate energy at all.

By applying the laws of elementary mechanics it can be shown that the supply of internal energy of an atom, consisting of a nucleus and one electron, will be the greater the farther away the electron is from the nucleus. With the atom in its normal state, each electron occupies the orbit closest to the nucleus and the atom has the least supply of energy. If energy is conveyed to the atom from the surroundings the electron may pass to one of the more distant orbits and the father the orbit to which it passes is from the nucleus, the greater its supply of energy. In other words, it may be said that such and such an electron is at a higher **energy level.** If the external influence is strong enough, the electron may be thrown altogether beyond the limits of the atom converting the latter into an ion. *The passage of an electron from a more distant orbit to a less distant one is accompanied by a loss of energy. During each such passage the energy lost by the atom is converted into one quantum of radiant energy. The frequency of the light thus radiated is determined by the radii of the two orbits between which the electron passes.* If we denote the supply of energy

of an atom with its electron on the more distant orbit by I_2 and with its electron on the less distant orbit by I_1, and divide the energy lost $I_2 - I_1$, by the Planck constant, we get the frequency of the light radiated:

$$\nu = \frac{I_2 - I_1}{h}$$

The greater the distance between the orbit on which the electron is and that to which it passes, the higher the frequency of the radiation.

The simplest of all atoms is the hydrogen atom which has only one electron revolving about its nucleus. On the basis of the above postulates Bohr calculated the radii of the possible orbits of this electron and found that they were to each other as the squares of the natural numbers:

$$1^2 : 2^2 : 3^2 \ldots\ldots\ldots n^2$$

The value n afterwards came to be known as the principal quantum number.

The radius of the orbit closest to the nucleus in the hydrogen atom equals 0.53 Ångström units. The frequencies of the radiations accompanying the passage of the electron from one orbit to another calculated on the basis of this figure proved to coincide exactly with the frequencies found experimentally for the lines of the hydrogen spectrum. This showed that the stable orbits had been computed correctly, and that Bohr's postulates were applicable to such computations. Subsequently the Bohr theory was extended to the atomic structure of other elements.

44. Structure of the Electron Shells of Atoms. Bohr's theory made it possible to solve the very important question of the arrangement of the electrons in the atoms of various elements and to establish the dependence between the properties of the elements and the structure of the electron shells of their atoms.

Today the schemes of atomic structure of all the chemical elements have been worked out. In drawing up these schemes scientists proceeded from the enormous amount of experimental data accumulated during the study of optical and X-ray spectra, as well as from general considerations as to the stability of various combinations of electrons. But their main guide was D. Mendeleyev's Periodic Law.

It must, however, be kept in mind that these schemes are by no means complete and firmly established; they are but a more or less true hypothesis, which enables us to explain many of the physical and chemical properties of the elements.

We have already seen that the number of electrons revolving around the nucleus of the atom is equal to the atomic number of

the element in the Periodic Table. It was assumed at first that the electrons move in groups along the same circular orbits forming several concentric rings. Afterwards it became necessary to assume that each electron has an orbit of its own, which may be a circle or an ellipse, and that these orbits are arranged differently in space, i.e., are at various angles to one another all around the nucleus. Instead of being arranged in rings, the electrons are now assumed to be grouped in electron layers. Each layer is filled or saturated by a definite number of electrons. Electrons of the same layer are characterized by almost equal supplies of energy, i.e., are approximately at the same *energy level*. The entire electron shell of the atom is divided up into several layers or energy levels, denoted by the letters K, L, M, N, ..., the letter K denoting the layer closest to the nucleus. The electrons of each subsequent layer are at a higher energy level than the electrons of the preceding one. The orbits of all the electrons belonging to the same layer have elliptical orbits with equal long axes, but different short axes. The greatest number of electrons N which can be contained in any given layer (i.e., at any given energy level) equals twice the square of the layer number

$$N = 2n^2$$

where n is the layer number. Thus, the first layer, K, that closest to the nucleus, can hold no more than two electrons, the second layer, L, no more than eight, the third, M, no more than eighteen, etc. It has been established, besides, that the number of electrons cannot exceed eight in the outermost layer of any of the elements, except palladium, and cannot exceed eighteen in the second last layer.

The electrons of the outermost layer, which are the farthest from the nucleus and therefore the least strongly connected with it, can break away from the atom and be captured by other atoms, taking up a position in their outer layers. Atoms which have lost one or several electrons become positively charged, as the charges on their nuclei will then exceed the total charge of the remaining electrons. On the contrary, atoms which have gained extra electrons become negatively charged. The charged particles formed in this way differ qualitatively from the corresponding atoms and are called **ions.**

The charge of an ion depends on the number of electrons the atom has lost or gained. For instance, if an aluminium atom, which has a total of 13 electrons in its shell, loses the three electrons in its outer layer, the resulting aluminium ion will have a charge of $+3$, since the loss of electrons does not alter the charge on the nucleus which equals $+13$, but the total charge of the remaining electrons will now be -10 (the charge of the ion will be $-10+13=+3$). A sulphur atom has a total of 16 electrons, six of which are in the outer layer. If it acquires two more electrons the result is a negative

doubly charged sulphur ion, since the total charge of the electrons becomes -18 while the charge on the nucleus equals $+16$ (the charge on the ion will be $-18+16=-2$).

Ions are conventionally denoted by the same symbols as the atoms with a superscript consisting of the same number of plus or minus signs as there are units in the charge on the ion. For instance, the triply positively charged aluminium ion is denoted by the symbol Al^{+++} or Al^{3+} and the doubly negatively charged sulphur ion by the symbol S^{--} or S^{2-}, etc.

Many ions can in their turn lose or gain electrons, whereupon they become either electrically neutral atoms or other ions with other charges.

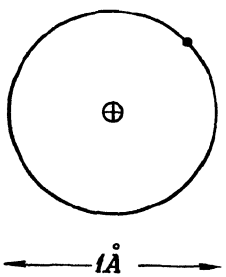


Fig. 21. Structure of hydrogen atom

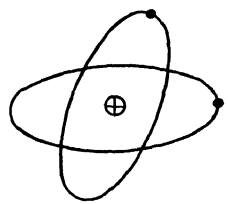


Fig. 22. Structure of helium atom

When an ion loses an electron its positive charge increases or its negative charge decreases or becomes zero (i.e., the ion becomes an electrically neutral atom). On the other hand, the addition of electrons to an ion decreases its positive or increases its negative charge. For instance, if the doubly positively charged iron ion Fe^{++} loses one electron it becomes a triply charged ion Fe^{+++}, or if it gains two electrons it turns into an electrically neutral atom Fe; if the doubly negatively charged sulphur ion S^{--} loses two electrons, it turns into a sulphur atom S, etc.

Outer electrons may pass from one atom to another in a great variety of chemical processes; this will be dealt with in greater detail in the next chapter. The number of such electrons is the principal factor determining the differences in the chemical properties of atoms. Only the electrons of the outer layer take part in the emission and absorption of visible light rays, as well as infra-red and ultra-violet rays, which are close to them in wave length.

Now let us examine the arrangement of the electrons in the atoms of some of the elements.

The hydrogen atom has only one electron, travelling about the nucleus in a circle, as shown in Fig. 21. The hydrogen atom can easily

give its electron away to other atoms to become a singly positively charged hydrogen ion consisting only of a nucleus, called a **proton.**

The next element after hydrogen, helium, has two electrons, forming the first layer *K*. Both electrons revolve in circular orbits at a certain angle to each other (Fig. 22) and possess equal energies, i.e., are at the same (first) energy level. Such an arrangement of electrons is very stable, so that helium is inclined neither to give away its electrons nor to acquire the electrons of other atoms. That is why helium is chemically inert.

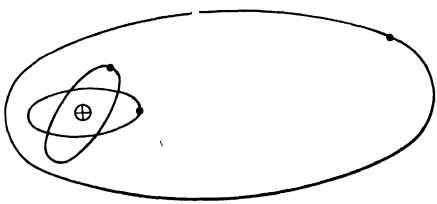


Fig. 23. Structure of lithium atom

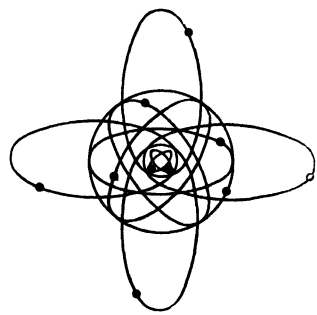


Fig. 24. Structure of neon atom

After helium comes lithium with three electrons. The helium electron layer, being very stable, remains intact in this atom; the third electron is situated on a considerably elongated elliptic orbit and starts the second electron layer (Fig. 23). This electron is less strongly attached to the nucleus than the first two, and the lithium atom easily gives it away, changing into a positively charged ion.

The elements following lithium, namely, beryllium, boron, carbon, etc., retain the helium layer of two electrons, but the number of electrons in their second, *L* layer increases successively by one in each element until the number reaches 8 in the neon atom. Then we get a very stable symmetrical arrangement of electrons (Fig. 24), as a result of which neon, like helium, can neither lose nor gain electrons. On the contrary, in the atoms of the elements situated between helium and neon the electrons of the *L* layer are weakly attached and can be split off, turning these atoms into ions.

Neon is followed by sodium. Ten of its electrons are arranged in the same way as in the neon atom (two on the first energy level and eight on the second), while the eleventh electron occupies a greatly elongated elliptic orbit and is on the third energy level (Fig. 25). Thus, the sodium atom has a structure resembling that of the lithium atom, which accounts for the chemical resemblance of these elements. In passing from sodium to magnesium, aluminium and the subsequent elements, just as in passing from lithium to neon, the number of electrons keeps successively increasing, but now in the third layer,

and in argon (Fig. 26) we again have a stable structure with an electron octet in the third layer.

The further growth of the electron layers and their saturation with electrons will be considered in detail in Chapter VII.

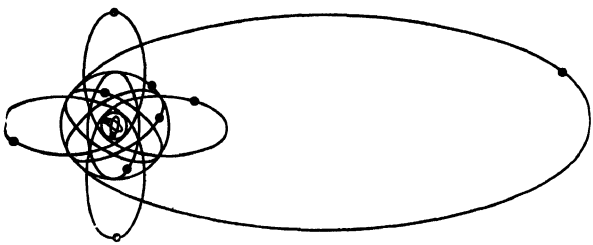


Fig. 25. Structure of sodium atom

The atomic models shown in Figures 21-26 representing the arrangement of the electron orbits in the atoms of various elements are very clumsy and inconvenient. For chemical purposes the simplified diagrams of atomic structure schemes shown in Fig. 27 are quite sufficient. It must only be remembered that these schemes give no idea of the actual arrangement of the electrons in the atoms, but only indicate the number of electrons in each layer. Each circle corresponds to one layer of electrons, i.e., one energy level.

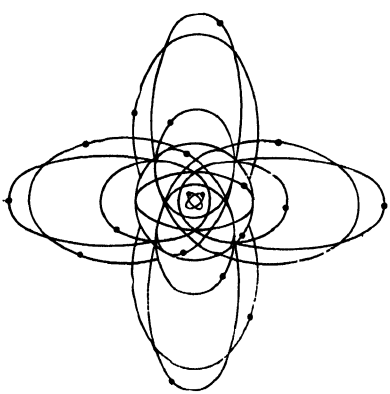


Fig. 26. Structure of argon atom

45. State of the Electrons in Atoms. Elements of Wave Mechanics. The Bohr theory was of great service to physics and chemistry, approaching the discovery of the laws of spectroscopy and an explanation of the mechanism of radiation on the one hand, and a revelation of the structure of individual atoms and the establishment of the relation between them on the other. However, there were still many phenomena in this field, which the Bohr theory could not explain.

Bohr pictured the motion of the electrons in the atom to a certain extent as simple mechanical motion, whilst actually it is very complex and peculiar. The peculiarity of the motion of the electrons was revealed by a new theory, the **quantum theory** or **wave mechanics.**

This theory proceeds from the idea that the Newtonian laws of mechanics, which are true for bodies of sufficiently large mass (i.e., for those we usually have to do with in practice), are inapplicable to the motion of electrons in atoms and should be replaced by new laws conforming with the peculiarities of this motion.

Quantum mechanics shows that the laws of motion of electrons have very much in common with the laws of wave propagation, and that is why it is otherwise called wave mechanics. Thus, according to the principles of quantum mechanics, the scattering of electrons by

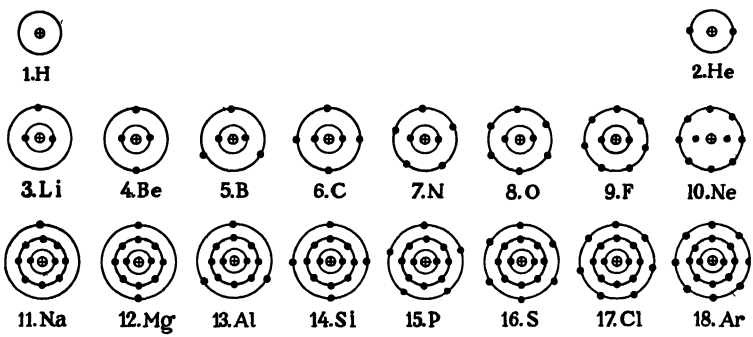


Fig. 27. Atomic structure of elements of I to III periods (simplified schemes)

crystals should give rise to diffraction phenomena, just like the scattering of X-rays. Electron diffraction was actually observed soon after and is used at present for the study of the structure of substance just as widely as X-ray diffraction. Particularly, electron diffraction is the underlying principle of the electron microscope.

As the mathematical aspect of this new theory is very complicated, we shall not dwell upon it. It should be noted only that the fundamental equation of wave mechanics is an equation relating the wave length λ of a stream of electrons to their velocity v and mass m:

$$\lambda = \frac{h}{m \cdot v}$$

where h is the Planck constant, equal to 6.624×10^{-27} erg $\times$ sec.

Wave mechanics embraces a broader sphere of phenomena than the Bohr theory and therefore can solve a number of problems which are beyond the scope of the latter.

For instance, wave mechanics explains why only certain definite electron orbits are stable. Only those orbits are "stable" which can accommodate a whole number of waves. Since the length of a circular

orbit of radius r equals $2\pi r$, the stability of the orbit is determined by the equation

$$2\pi r = \frac{nh}{m \cdot v}$$

where n is an integer. This is the mathematical expression of Bohr's first postulate, on which he based his calculation of the motion of the electron in the hydrogen atom in 1913.

In the above equation the factor n, called the principal quantum number, can take the value of any whole number from 1 to infinity.

The principal quantum number defines the energy level corresponding to any given orbit and the distance of the latter from the nucleus. The value $n=1$ corresponds to the lowest energy level, designated by the letter K; the value $n=2$, to the energy level L, etc.

It should be noted that present-day wave mechanics puts a different meaning into the word "orbit" than it had in the Bohr theory. Wave mechanics considers only the higher or lower probability of a swiftly moving electron being at any given point of space; therefore in wave mechanics the word "orbit" means the field (sphere) around the nucleus in which the electron is found most often *on the average*.

The probability of an electron being at a certain point can also be expressed by the conception of the electron atmosphere. The electron revolves around the nucleus so swiftly that its electrical charge can be imagined as "diffused" into an atmosphere of negative electricity. The density of the atmosphere is higher where the probability of the electron being present is greater.

Thus, the conception of the electron orbit as of a definite line is substituted in wave mechanics by the conception of the electron sphere or the electron atmosphere. For instance, the circular electron orbit in the hydrogen atom having the principal quantum number $n = 1$ corresponds to an electron atmosphere in which the density is greatest near a spherical layer of radius $r = 0.53$ Ångström units, equal to the radius of the first Bohr orbit. The electron may be at a greater or smaller distance from the nucleus, but the probability of its being there will be lower. With $n=2$ the density of the electron atmosphere is greatest farther away from the nucleus, and so forth.

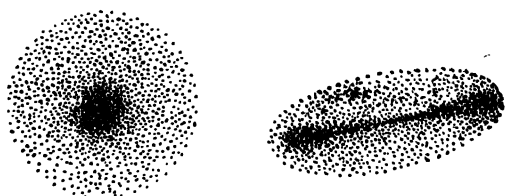
Thus, the principal quantum number determines the mean radial arrangement of electron density around the nucleus.

The state of the electron in the atom is characterized by three more quantum numbers, besides the principal one; these numbers are denoted by l, m and s.

The *secondary (azimuthal) quantum number* l characterizes the moment of momentum of the electron with respect to the centre of its orbit. It determines the shape of the electron atmosphere (the

shape of the orbit), its continuity or discontinuity and its elongation.

With each given principal quantum number n the secondary quantum number l can take all the values of the whole numbers from 0 to $n-1$. Thus, if the principal quantum number n equals 1, the secondary quantum number l can equal only 0. In this case the electron atmosphere has the shape of a sphere (Fig. 28*a*).



a *b*

Fig. 28. Electron clouds:
a—hydrogen atom; *b*—hydrogen molecule

If the principal quantum number equals 2, the secondary quantum number may have the values 0 and 1. With the principal quantum number equalling 3 the possible values of l are 0, 1, 2, and so forth.

Quite often instead of denoting l by the figures 0, 1, 2, 3, 4, the literal designations *s*, *p*, *d*, *f*, *g*, are used; then we speak of the *s*, *p*, *d*, etc., states of the electrons, or the *s*-, *p*-, *d*-, etc., orbits.

The *magnetic quantum number m* defines the position of the electron orbit plane in space or, according to the conceptions of wave mechanics, the direction in which the electron atmosphere is elongated. This number can take all the values of the whole numbers, both positive and negative, but only within the limits of the l value. For instance, with l equalling zero, m also equals zero; if l equals three, m may equal $-3, -2, -1, 0, 1, 2, 3$.

However, the electron in the atom rotates not only around the nucleus, but around its own axis as well, two opposite directions of rotation being possible. This rotation of the electron (called "spin") is characterized by the fourth, *spin quantum numbers*. The latter can take only two values—positive or negative—in accordance with the two possible directions of rotation of the electron.

With the four quantum numbers indicated the entire aggregate of complex motions of the electron in the atom can be characterized. However, they do not give an exhaustive idea of the arrangement of the electrons in the atom, since the number of their random combinations with each other is unlimited.

By analysing spectra and taking account of the positions of the elements in the Periodic Table, the physicist Pauli discovered a general

rule by which the combinations of quantum numbers corresponding to reality could be selected. According to this rule not a single atom can contain electrons identical in all respects. In other words, no two electrons in the atom can have all their four quantum numbers equal.

Thus, for instance, only two electrons of different spins can be present on the first energy level ($n = 1$; $l = 0$; $m = 0$).

The second energy level, corresponding to the quantum number 2, can contain two electrons with opposite spins in the *s* state or on the *s*-orbit ($l = 0; m = 0$) and two electrons on each of the *p* states or *p*-orbits ($l = 1$, $m = -1, 0, +1$). Thus, altogether the second energy level can contain 8 electrons (see Table 7).

Table 7

Arrangement of Electrons in Atoms of the Short Period Elements

Layer		*K*	*L*		*M*		
Principal quantum number *n*		1	2		3		
Secondary quantum number *l*		0	0	1	0	1	2
Literal designation of *l*		*s*	*s*	*p*	*s*	*p*	*d*
1. Hydrogen	H	1					
2. Helium	He	2					
3. Lithium	Li	2	1				
4. Beryllium	Be	2	2				
5. Boron	B	2	2	1			
6. Carbon	C	2	2	2			
7. Nitrogen	N	2	2	3			
8. Oxygen	O	2	2	4			
9. Fluorine	F	2	2	5			
10. Neon	Ne	2	2	6			
11. Sodium	Na	2	2	6	1		
12. Magnesium	Mg	2	2	6	2		
13. Aluminium	Al	2	2	6	2	1	
14. Silicon	Si	2	2	6	2	2	
15. Phosphorus	P	2	2	6	2	3	
16. Sulphur	S	2	2	6	2	4	
17. Chlorine	Cl	2	2	6	2	5	
18. Argon	Ar	2	2	6	2	6	

With the principal quantum number $n = 3$ the secondary quantum number l can take the values 0, 1 and 2 (s, p and d) which correspond to the following values of m:

with $l=0$ $m=0$
with $l=1$ $m=-1, 0, +1$
with $l=2$ $m=-2, -1, 0, +1, +2$

Since there can be two electrons in each m state, the total number of electrons that can be accommodated at the third energy level, corresponding to $n=3$, is 18 (Table 10 on pp. 163-5). In the same way it can easily be calculated that the fourth energy level ($n = 4$) cannot hold more than 32 electrons. In general, the maximum number of electrons N which can be contained at a given energy level n, is determined, according to Pauli's Rule, by the formula $N=2n^2$, which we already know.

The arrangement of the electrons in the atoms can be conveniently written in the form of short formulas as follows. First we write the figure indicating the principal quantum number; this is followed by a letter denoting the secondary quantum number, the number of electrons on each corresponding orbit being written as a superscript to this letter. Thus, for instance, the "electron formula" of the hydrogen atom is $1s^1$, that of the helium atom—$1s^2$, of the lithium atom—$1s^2$, $2s^1$, of the oxygen atom—$1s^2$, $2s^2$, $2p^4$, of the neon atom—$1s^2$, $2s^2$, $2p^6$, of the aluminium atom—$1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^1$, etc.

CHAPTER V

Structure of Molecules

46. Chemical Bonds and Valency. As we know, the atoms of chemical elements differ in their ability to combine with a definite number of other atoms. To characterize this property, in the middle of the XIX century the conception of valency of the elements was introduced into chemistry. The meaning of this conception was indicated in § 24. However, the nature of the forces governing the bond between atoms and molecules was for a long time unknown. Only after the development of the science of atomic structure did theories begin to appear explaining, on the basis of electronic conceptions, why elements have different valency and how chemical compounds are formed. All these theories are grounded on the existence of a relation between chemical and electrical phenomena.

Let us first consider the relation of substances to electrical current.

Some substances are conductors of electricity in both the solid and the liquid states; such, for instance, are all the metals. Other substances do not conduct current in the solid state, but are electrical conductors when melted. These include the great majority of salts, as well as many oxides and hydroxides. Finally, there is a third group of substances which conduct current neither in the solid, nor in the liquid state. These are almost all the non-metals, their compounds with oxygen and other non-metals, anhydrous acids and most organic substances.

The passage of current through fusions of salts and compounds resembling them is essentially different from the passage of current through metals. Whereas metallic conductors are only heated by the current, without their substance undergoing any chemical change, in fusions current causes profound changes, manifested by the appearance of decomposition products of the salt or salt-like compound at the electrodes immersed in the fusion.

For instance, when current is passed through molten table salt the metal sodium is liberated at the cathode (the electrode connected to the negative pole of the source of electricity) and the gas chlorine at the anode (the electrode connected to the positive pole).

It has been established by experiment that the electrical conductivity of metals is due to the motion of electrons, while the conductivity of fused salts and similar compounds is due to the motion of ions with opposite charges. For instance, when current is passed

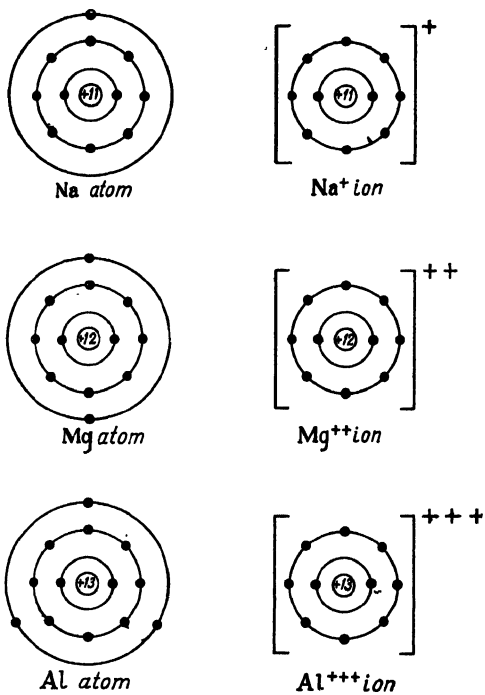


Fig. 29. Structure of atoms and ions of sodium, magnesium and aluminium

through molten table salt, positively charged sodium ions Na^+ move towards the cathode and negatively charged chloride ions Cl^- towards the anode; at the electrodes the ions are discharged and converted into electrically neutral atoms of sodium and chlorine. It is evident that in salts and salt-like compounds the ions exist in the solid substance, and fusion merely creates the conditions for them to move freely. Therefore such compounds are known as *ionic compounds.* Substances which practically do not conduct current, contain no ions; they are made up of electrically neutral molecules or atoms. Thus, the different attitude of substances to electric current is a consequence of different electrical states of the particles making up these substances.

The three above types of substances respond to three different types of chemical bonds, namely, a) *metallic bonds* (between particles forming metals); b) *ionic bonds*, otherwise called *electrovalent bonds* (between oppositely charged ions in ionic compounds); c) *atomic*, or *covalent*, *bonds* (between electrically neutral atoms in the molecules of all other substances).

The nature of metallic bonds will be considered later in describing the metals. Here we shall dwell in greater detail on the other two types.

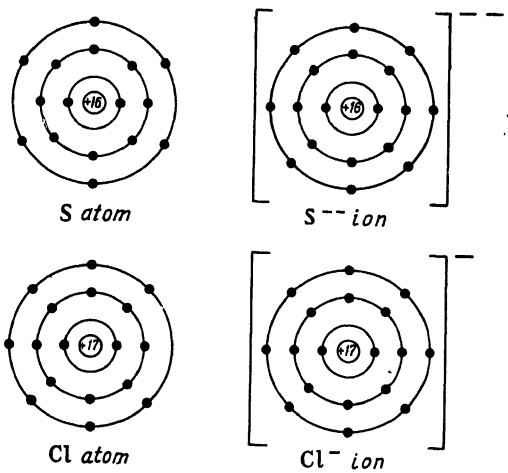


Fig. 30. Structure of atoms and ions of sulphur and chloride

Ionic Bonds. This type of bond occurs between oppositely charged ions and is due to simple electrostatic attraction between the ions.

As stated in § 44, positive ions are formed by atoms losing electrons, while negative ions result when atoms gain electrons.

Thus, the ion Na^+ forms when one electron is abstracted from a sodium atom. Since there is only one electron in the outermost layer of the sodium atom, it is only natural to suppose that precisely this electron, which is the farthest from the nucleus, is split away from the sodium atom when the latter is converted into an ion. In a similar manner, magnesium ions Mg^{++} and aluminium ions Al^{+++} form as a result of the loss of two and three outer electrons by the atoms of magnesium and aluminium, respectively.

The structure of the atoms Na, Mg, Al, and the ions Na^+, Mg^{++} and Al^{+++} is shown diagrammatically in Fig. 29.

In Fig. 30 the electronic structure of sulphur and chlorine atoms is compared with that of the negative ions of these elements formed

by the addition of electrons to the corresponding elements. As the inner electron layers of the chlorine and sulphur atoms are filled, the additional electrons in the ions S^{--} and Cl^{-} must evidently take up their positions in the outer layer, as shown in the figure.

Comparing the composition and structure of the electron shells of the ions Na^{+}, Mg^{++} and Al^{+++}, we find that they are identical in all these ions, namely, the same as in the atom of the inert gas neon Ne, and therefore can be expressed by the same electron formula:

$$1s^2,\ 2s^2,\ 2p^6$$

At the same time the ions S^{--} and Cl^{-} formed as a result of the capture of electrons by sulphur and chlorine atoms have the same electron shells as the argon atom. Therefore their electron formula is the same as for the argon atom:

$$1s^2,\ 2s^2,\ 2p^6,\ 3s^2,\ 3p^6$$

Thus, in the above cases of conversion of atoms into ions the electron shells of the ions become similar to those of the inert gases closest to them in the Periodic Table.

The present-day theory of valency attributes this to the fact that the electron groupings in the atoms of the inert gases (two electrons in the outer layer of the helium atom and eight electrons in the atoms of the rest of the inert gases) are especially stable. The stability of these groupings accounts for the inert gases not being capable of combining with other elements. Atoms with less than eight electrons in their outermost layer tend to acquire the structure of inert gases by losing their "excessive" electrons or by supplementing them at the expense of the electrons of other atoms to form an octet in their outer layer. This is what happens during the formation of the majority of chemical compounds consisting of ions.

The formation of a chemical compound of the ionic type from its constituent atoms can be pictured as follows.

First the atoms are converted into oppositely charged ions as a result of electrons of one atom passing over to the other, after which the ions attract one another, forming a compound with ionic bonds.

Suppose, for instance, that sodium atoms, which have only one electron in their outermost shell, encounter chlorine atoms which contain seven electrons in their outer shell. The sodium atoms yield their excessive electrons to the chlorine atoms, turning into singly positively charged ions with the electron configuration of the inert gas neon. Simultaneously, the chlorine atoms, having gained one electron each in their outer layers, become singly negatively charged ions with the structure of argon atoms. After this the ions thus formed are brought together by electrical attraction between the unlike charges, resulting in the salt sodium chloride (Fig. 31).

Denoting electrons by the letter e with a superscript minus sign (e^-), the processes taking place during the formation of sodium chloride can be expressed by the following "electronic" equations:

$$Na - e^- = Na^+$$
$$Cl + e^- = Cl^-$$
$$Na^+ + Cl^- = Na^+Cl^- \text{ (or NaCl)}$$

The formation of other ionic compounds can be explained in a similar manner. For instance, in the formation of magnesium sulphide, MgS, each magnesium atom gives away two electrons to a sulphur

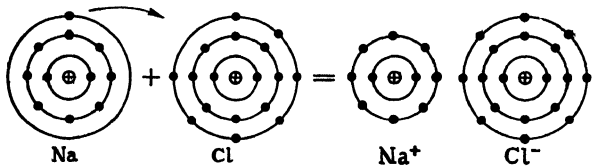


Fig. 31. Formation of sodium chloride

atom. The result is a doubly positively charged magnesium ion Mg^{++} and a doubly negatively charged sulphide ion S^{--}. The ions thus formed attract each other, giving magnesium sulphide:

$$Mg - 2e^- = Mg^{++}$$
$$S + 2e^- = S^{--}$$
$$Mg^{++} + S^{--} = Mg^{++}S^{--} \text{ (or MgS)}$$

In the formation of aluminium oxide Al_2O_3 each aluminium atom gives three electrons away to oxygen atoms. Having only two deficiencies in its outer shell, each oxygen atom accepts two electrons. The result is triply positively charged aluminium ions Al^{+++} and doubly negatively charged oxide ions O^{--} with two aluminium ions for every three oxide ions. Attracting each other, these ions form aluminium oxide:

$$(Al^{+++})_2(O^{--})_3 \text{ (or } Al_2O_3)$$

It should be noted that while the electron shells of all negatively charged ions resemble the shells of inert gas atoms, positively charged ions may have shells which differ from those of the atoms of inert gases. Such, for instance, are the electron shells of Fe^{++}, Fe^{+++}, Zn^{++} and many other positively charged ions.

Valency of Elements in Ionic Compounds. The above conceptions of the mechanism of formation of ionic compounds lead to the conclusion that the *valency of elements in ionic compounds is characterized by the number of electrical charges on their ions.* This is otherwise called **electrovalency.**

The electrovalency number is equal to the number of electrons lost by an atom in forming a positive ion or gained by it in forming a negative ion. In the first case the electrovalency is considered **positive,** and in the second **negative.**

The ability of atoms to turn into positive or negative ions depends on the position of the corresponding elements in the Periodic Table. Atoms of the elements at the beginning of any period have a smaller nuclear charge than atoms of elements at the end of the period. In the first case the electrons are attracted less strongly than in the second; therefore, the tendency of atoms to change into positive ions decreases in each period, generally speaking, from left to right. Only atoms containing more than five electrons in their outer layer (atoms of non-metals) can become negative ions. Atoms with less than four electrons in their outer layer (with the exception of the hydrogen atom) can only give away electrons but, as far as we know, can never accept them. Such are the atoms of the elements we call metals.

Electrons capable of splitting away from the atom during chemical reactions are called valency electrons. The number of valency electrons in an atom, as a rule, equals the group number of the corresponding element in the Periodic Table.

Structure of Ionic Compounds. In considering the formation of ionic compounds it should be remembered that all ions, with the exception of the hydrogen ion H^+, which is a "naked" nucleus, i.e., one entirely devoid of electrons, possess a certain negatively charged electron shell. Consequently, when oppositely charged ions are brought very close together they begin to repel each other. At a certain distance the attraction is balanced by the repulsion and the ions remain at some distance from one another.

If a large number of positive and negative ions are brought close together, the result is a crystal in which each ion of one sign is surrounded by ions of the opposite sign. Obviously, the conception of molecules is inapplicable to crystals made up of ions, i.e., to ionic compounds in general. For instance, in the case of common salt we can say that it consists of NaCl molecules only in a very conventional sense. Actually there are no such molecules in its crystals. The entire crystal consists of a large number of Na^+ and Cl^- ions. NaCl molecules appear only in the vapours of common salt. Hence, strictly speaking, the formula NaCl does not depict the molecule of sodium chloride; it shows only that in this substance each atom or, more precisely, each ion of sodium, has one corresponding chlorine atom (chloride ion), which quite defines the composition of common salt by weight. However, in the future we shall conventionally use the term "molecule" for salts whenever we have to indicate the ratio between the number of positive and negative ions forming the salt.

All that has been said about NaCl crystals pertains also to the crystals of other ionic compounds.

Atomic Bonds. The assumption of electrostatic attraction between oppositely charged ions being the reason for the appearance of chemical bonds is obviously inapplicable to molecules of simple substances (hydrogen H_2, oxygen O_2, etc.) as well as to molecules of substances formed from elements of close chemical properties, as it is difficult in such a case to assume the formation of oppositely charged ions. Therefore, with respect to such substances a different theory of formation was suggested, known as the **theory of covalency.** In developing this theory the chemical stability of inert-gas atoms was also taken into account, as well as the fact that the total number of valency electrons in the great majority of molecules is even (for example, in the molecule O_2 it equals 12, in the molecule CO_2, 16, etc.).

According to the theory of covalency, when a molecule forms (just as in the case of ionic compounds), the atoms of the chemical elements acquire stable electron shells similar to those of inert gas atoms. However, this stability is not attained by transferring electrons from one atom to another, but by the formation of one or more electron pairs which become common to the combined atoms, i.e., belong to the electron shells of both the atoms simultaneously. It may be imagined that these "paired" electrons travel in orbits embracing the nuclei of both atoms, and in this way link the atoms into a molecule.

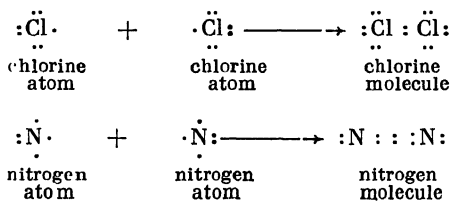
A chemical bond which is due to the presence of electron pairs is called a covalent or atomic bond in contradistinction to the electrovalent or ionic bond based on electrostatic attraction between oppositely charged ions.

The supposition that pairs of electrons "serving" both nuclei are the reason for the formation of covalent bonds has found a proof in wave mechanics. The two positively charged nuclei may be considered a single nucleus with a larger charge than either of the original ones. An electron moving about such a combined nucleus is retained more strongly than if it were moving about either of the original nuclei. This accounts for the fact that energywise the formation of covalent bonds is more advantageous. The new orbit of the electron in the molecule is called a molecular orbit. The motion of electrons in molecular orbits obeys the same Pauli's Rule as their motion in atomic orbits. Therefore, there can be no more than two electrons on the same molecular orbit and these must have opposite spins. Electrons with the same spins cannot be on the same orbit. That is why each covalent bond is formed by one pair of electrons only.

From the point of view of wave mechanics, the formation of a molecular orbit is a consequence of the "overlapping" of atomic

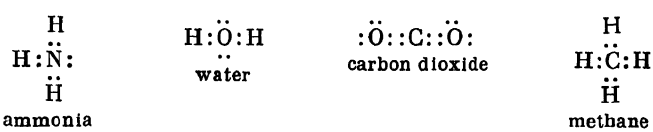
orbits. As a result of this overlapping the electron density in the molecular orbit (conceiving the latter as an electron atmosphere) is greatest between the nuclei. This means that in moving along their molecular orbit the electrons report most often in the space between the nuclei. This results in a kind of layer of negative electricity arising between the nuclei which helps them to approach one another. Therefore, the more the atomic orbits "overlap" in forming the molecular orbit, the stronger the bond.

Covalent bonds in chemical formulas are denoted in the following manner. Around the symbol of each atom are placed as many points as the atom has valency electrons. The common electrons are indicated by points placed between the chemical symbols; a double or triple bond is designated respectively by two or three pairs of points. Using these designations, we can graphically depict the formation of stable shells by means of common electrons, as well as the structure of various molecules. By way of example we give below the schemes of formation of molecules of chlorine and nitrogen:



The outer shell of the chlorine atoms contains seven electrons. When chlorine atoms combine into a molecule two of their electrons become common; as a result, each atom acquires a stable outer shell of eight electrons, six belonging to each atom separately and two being common to both atoms. In the formation of a nitrogen molecule three pairs of electrons become common. Thus, the outer shell of each atom is filled to make eight electrons in each.

The following formulas show the molecular structure of several complex substances—ammonia, water, carbon dioxide and methane.



In the ammonia molecule each of the three hydrogen atoms is bound to the nitrogen atom by a pair of common electrons (one electron from the hydrogen atom and one from the nitrogen). Thus,

the nitrogen acquires an eight-electron outer shell, while the nucleus of each hydrogen atom is now surrounded by two electrons, forming a stable "helium" shell. Hydrogen atoms have similar shells in the molecules of water and methane. In the carbon dioxide molecule, where the carbon atom is connected with each of the oxygen atoms by two pairs of electrons, all three atoms have octet outer shells.

It will be noted that in the above formulas each pair of electrons linking two atoms corresponds to one line indicating a valency bond in ordinary structural formulas. Therefore, *the valency, or to be more precise, the covalency of an element in a given compound is determined by the number of electrons of its atom used to form common or "linking" electron pairs.*

Quantum-mechanical computations show that only electrons with opposite spins can become "paired" in the electric field of a nucleus (or nuclei). Hence, to form a covalent bond, each of the combining atoms must have at least one electron with a spin opposite to the spin of the electron of the other atom. But in free atoms part of the valency electrons, namely, the electrons on one and the same orbit, are already "paired", as their spins are opposite, according to Pauli's Rule (see p. 126). Obviously, such electrons cannot take direct part in the formation of a covalent bond. Therefore the valency (covalency) of a free atom does not equal the total number of its valency electrons, but only the number of "unpaired" electrons.

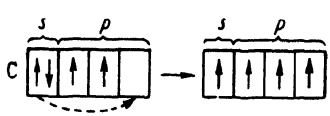
A study of the spectra of the elements has made it possible to establish which of the valency electrons in the atoms are "unpaired" and which "paired". By way of example, the structure of the outer electron layer of the atoms of some of the second period non-metals (nitrogen, oxygen, fluorine) may be pointed out. We remind the reader beforehand that the energy level of the electrons in these atoms is determined by the main quantum number 2, and that with $n=2$ there can be only one *s*-orbit and three *p*-orbits. It should also be noted that the electrons in the *p*-orbits are always arranged singly, unless their number exceeds the number of orbits possible for the electron level in question.

Denoting each of the above orbits conventionally by a rectangular cell and the electrons by arrows pointing in opposite directions in the case of paired electrons, the orbital arrangement of the outer electrons in the atoms N, O, and F will be as follows:



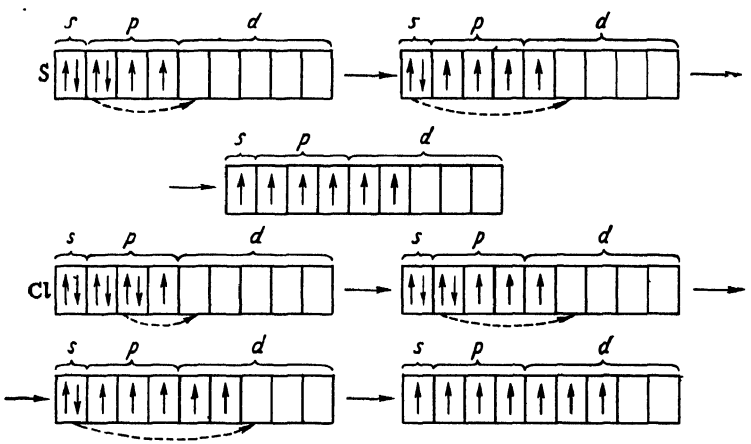
These diagrams show that from the standpoint of the spin theory of valency a nitrogen atom can form three covalent bonds, an oxygen atom—two, and a fluorine atom only one covalent bond.

The orbital arrangement of the valency electrons in the carbon atom is shown in the diagram below (left). According to this diagram carbon should be only a bivalent element. However, if the atom loses only a relatively small amount of energy, the pair of *s*-electrons separates, one of them passing over to a *p*-orbit at the same energy level:



The energy loss is amply covered by the energy liberated during the formation of four covalent bonds. That is why carbon is tetravalent in the great majority of its compounds.

Now let us consider the orbital arrangement of the valency electrons in the atoms of sulphur and chlorine, belonging to the third period. The valency electrons in these atoms are at an energy level corresponding to the principal quantum number 3, for which five *d*-orbits are possible, besides one *s*-orbit and three *p*-orbits. But the *d*-orbits are energywise less advantageous than the *s*- and *p*-orbits, so that all the valency electrons in "unexcited" sulphur and chlorine atoms are situated on the *s*- and *p*-orbits. It follows from the diagram given below that with such an arrangement the sulphur atom would be able to form only two, and



the chlorine atom only one covalent bond. However, if a certain amount of energy is expended (compensated by the energy liberated during the formation of the covalent bonds) the sulphur atom may pass into an "excited" state with four or six separated electrons, and the chlorine atom into a state with three, five or seven separated electrons.

The corresponding valency values are actually observed in sulphur (2, 4 and 6) and chlorine atoms (1, 3, 5 and 7).

Thus, covalent bonds between atoms in molecules are due to the presence of one or several pairs of common electrons. Since the formation of a covalent bond is not, as a rule, accompanied either by loss or gain of electrons in the atoms, it is evident that molecules with covalent bonds do not contain ions. However, if the atoms in the molecule are heterogeneous the common electron pairs may be more intimately associated with one atom than with the other. For instance, in the compound of chlorine and hydrogen the common electrons are drawn towards the chlorine, as towards the element possessing the stronger non-metallic properties, in consequence of which the chlorine atoms acquire a partial negative charge and those of hydrogen a partial positive charge.

In such cases the covalent bond is called "polar" in contradistinction to the "non-polar" covalent bond when the common electrons are equidistant from both atoms. If the combining atoms possess directly opposite chemical properties the electron pair may pass entirely over to one of the atoms, converting it into a negative ion and the other atom into a positive ion, thus forming an ionic compound.

The following scheme illustrates these three cases:

$: \ddot{\underset{\cdot\cdot}{Cl}} : \ddot{\underset{\cdot\cdot}{Cl}} :$ The bonding electrons are shared equally by both atoms.

$H : \ddot{\underset{\cdot\cdot}{Cl}} :$ The bonding electrons are drawn towards the chlorine atom.

$[Na]^{+} [:\ddot{\underset{\cdot\cdot}{Cl}} :]^{-}$ The electron pair has passed entirely over to the chlorine atom.

The state of atoms linked by a polar covalent bond approaches that of an ionized atom. For instance, in the HCl molecule the states of the atoms H and Cl are close to those of the ions H^+ and Cl^- respectively.

Thus, all substances (except metals) may be divided according to the nature of the chemical bond between their atoms into two main groups:

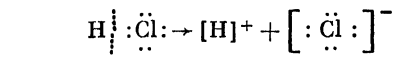
1) *Substances with electrovalent* or *ionic bonds* consisting of positively and negatively charged ions, held together by electrostatic attraction.

2) *Substances with covalent* or *atomic bonds*, the molecules of which do not contain ions. In such molecules the bond between the atoms is a result of interaction between electrons which become common to both atoms.

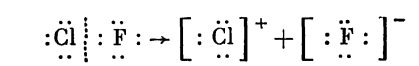
Typical representatives of substances with ionic bonds are, as we have mentioned above, salts, basic oxides, etc.; the simple gases—hydrogen, nitrogen, oxygen—are typical representatives of substances with atomic bonds. No sharp line can be drawn between these two groups of substances. Firstly, there are many compounds which contain both atomic and ionic bonds at the same time. Secondly, in compounds with atomic bonds the shared electron pairs may be drawn strongly towards one of the atoms, making these compounds similar in some properties to typical ionic compounds. Therefore, the nature of the bond in any given compound can be determined only by examining a considerable number of its properties and even then the nature of the bond remains disputable in many cases.

Positive and Negative Valency of the Elements in Atomic Compounds. The chemical behaviour of covalently linked atoms is determined to a great extent by their relative charges. Thus, for instance, in very

many reactions involving hydrogen chloride, the bond between the hydrogen and the chlorine is ruptured in such a way that the linking pair of electrons passes wholly over to the chlorine, which is split off as a negative ion. This may be expressed schematically in the following manner:



(the dotted line indicates the point of rupture of the bond). On the contrary, in compounds of chlorine with fluorine, the bond between the chlorine and the fluorine may be so split that the chlorine is converted into a positive ion:



In chemical practice it is often necessary to estimate not only the covalency of a given atom in compounds with atomic bonds, but also its relative charge due to displacement of electrons towards one or the other of the nuclei. This fact is indicated by stating, for instance, that the valency of chlorine in hydrogen chloride equals —1 and in chlorine fluoride, +1.

Thus the conception of positive and negative valency is not limited to ionic compounds but can be extended to compounds with atomic bonds as well.

The magnitude of the positive or negative valency of elements in atomic compounds depends on the charge their ions would acquire if each of the bonds broke up in such a way that the electrons forming the bond were transferred completely from one of the atoms to the other in accordance with the position of those atoms in the Periodic Table.

In deciding the direction in which the electrons are drawn, the following guiding principles should be used:

1) Within the same period the electrons are drawn towards the element closer to the right end.

2) Within the main subgroups the electrons are drawn towards the element closer to the top.

3) If two identical atoms are combined directly the electrons will be divided equally between them when the bond is ruptured.

4) Oxygen always displays negative valency (except when in combination with fluorine).

5) In compounds with non-metals the valency of hydrogen is positive.

To illustrate the use of these rules let us consider the valency of sulphur in several of its compounds.

In sulphuric anhydride SO_3, the electrons are drawn towards the oxygen, as oxygen is above sulphur in the sixth group of the Periodic

Table. If all the valency electrons are transferred from the sulphur to the oxygen, each oxygen atom gains two electrons and becomes an O^{--} ion, while the sulphur atom loses six electrons. Thus, the valency of sulphur in this compound equals +6 and that of oxygen, —2.

In sulphur dichloride SCl_2 the electrons are also drawn away from the sulphur towards the chlorine, as chlorine is at the right of sulphur in the same period and the charge on its atomic nucleus is one unit larger than that of sulphur. Each chlorine atom can gain only one electron. Therefore if all the common electrons are transferred from the sulphur to the chlorine, the sulphur atom will become an S^{++} ion and the chlorine atom, a Cl^- ion. Hence, the valency of sulphur in sulphur dichloride equals +2 and that of chlorine equals —1.

In phosphorus pentasulphide P_2S_5 the electrons are drawn from the phosphorus to the sulphur, inasmuch as sulphur is in the same period as phosphorus, but at its right. Since each sulphur atom can acquire two electrons, the transition of all the electrons forming the bond to the sulphur atoms converts the latter into negative S^{--} ions. At the same time, two phosphorus atoms lose ten electrons and form positive P^{5+} ions with five charges each. Thus, the valency of sulphur in phosphorus pentasulphide equals —2 and that of phosphorus +5.

Now let us see how to calculate the magnitude and sign of the valency of an element in a complex substance consisting of several elements, if the valencies of the other elements in the substance are known. Suppose, for instance, we have to determine the valency of boron in borax, the formula of which is $Na_2B_4O_7$. In this compound there are four boron and seven oxygen atoms for every two atoms of sodium. The valency of the sodium atom is +1, that of the oxygen —2. As the algebraical sum of positive and negative valency units of all the constituent atoms in any chemical compound must equal zero, we may write the following equation, denoting the number of valency units of the boron atom by x:

$$2+4x-7\cdot 2=0$$

whence

$$4x=12, \text{ and } x=+3.$$

In a similar manner we can easily calculate the valency of phosphorus in phosphoric acid H_3PO_4, the valency of nitrogen in saltpetre KNO_3, etc.

The valency of the elements in simple substances is considered to equal 0.

47. Polar and Non-Polar Molecules. All molecules contain both positively charged particles—atomic nuclei—and negatively charged —electrons. For each type of particle (or rather charge) a point

can be found to represent a sort of "electrical centre of gravity" of these charges. Such points are called the poles of the molecule. If the electrical centres of gravity of the positive and negative charges in the molecule coincide, the molecule is *non-polar*. Such, for instance, are the molecules H_2, N_2, consisting of identical atoms in which the common electron pairs are shared equally by both atoms, and also many molecules of symmetrical structure with atomic bonds, such as methane CH_4, carbon tetrachloride CCl_4. But if the molecule is asymmetrical, for instance consists of two heterogeneous atoms,

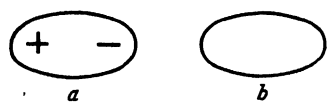


Fig. 32. Polar and non-polar molecules:
a—polar molecule; *b*—non-polar molecule

the common electron pair, as we have already mentioned, may be drawn more or less towards one of the atoms. Obviously, in this case the electrical centres of gravity in the molecule do not coincide due to the non-uniform arrangement of positive and negative charges, and the result is a polar molecule (Fig. 32).

Polar molecules are **dipoles.** This term denotes any electrically neutral system, i.e., any system consisting of positive and negative charges so arranged that their electrical centres of gravity do not coincide.

The distance between the electrical centres of gravity of the different charges (between the poles of a dipole) is called the **dipole length.** The length of a dipole characterizes the degree of polarity of the molecule. Obviously, different polar molecules have different dipole lengths; the greater this length, the more pronounced the polarity of the molecule.

In practice the degree of polarity of any given kind of molecule is established by measuring the so-called **dipole moment** of the molecule m, which is defined as the product of the length of the dipole l by the charge on its pole e:

$$m = l \cdot e$$

Dipole moment values are related to some of the properties of substances and can be determined experimentally. The order of m is always 10^{-18}, since the charge of an electron equals 4.80×10^{-10} electrostatic units and the dipole length is a value of the same order as the diameter of a molecule, i. e., 10^{-8} cm. The table below gives the dipole moments of the molecules of some inorganic substances.

Dipole Moments of Certain Substances

	$m \cdot 10^{18}$		$m \cdot 10^{18}$
Hydrogen	0	Water	1.85
Nitrogen	0	Hydrogen chloride	1.03
Carbon dioxide	0	Hydrogen bromide	0.79
Carbon disulphide	0	Hydrogen iodide	0.38
Hydrogen sulphide	1.1	Carbon monoxide	0.12
Sulphur dioxide	1.6	Hydrocyanic acid	2.1

Determination of dipole moment values allows many interesting conclusions to be drawn regarding the structure of various molecules. Some of these conclusions are examined below.



Fig. 33. Structure of CO_2 and CS_2 molecules

As might have been expected, the dipole moments of the molecules of hydrogen and nitrogen equal zero; the molecules of these substances are perfectly symmetrical, and therefore the electrical charges in them are arranged uniformly. The absence of polarity in carbon dioxide and carbon disulphide shows that their molecules are also symmetrical. The structure of the molecules of these substances is shown schematically in Fig. 33.

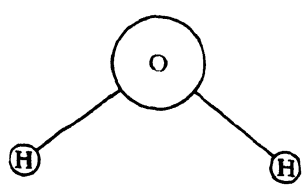


Fig. 34. Structure of a water molecule

The presence of a fairly large dipole moment in water is rather unexpected. The formula of water being analogous to the formulas of carbon dioxide and carbon disulphide, it might be expected that its molecules would be symmetrical in structure, just like those of CS_2 and CO_2. However, in view of the experimentally established polarity of the water molecule this assumption must be discarded. At present an asymmetrical structure is attributed to the water molecule (Fig. 34). The two hydrogen molecules are connected to the oxygen molecule with their bonds at an angle of about 105° to each other.

There are other molecules of the same type (H_2S, SO_2) which possess dipole moments with their atomic nuclei similarly arranged.

The polarity of water molecules explains many of its physical properties.

48. Polarization of Molecules and Ions. When considering the structure of polar and non-polar molecules in the foregoing, we proceeded from the assumption that these molecules are not under

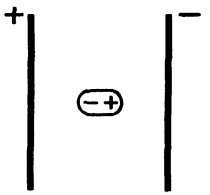


Fig. 35. Polarization of non-polar molecule in electric field

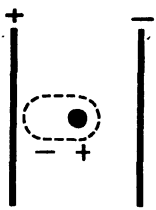


Fig. 36. Polarization of ion in electric field

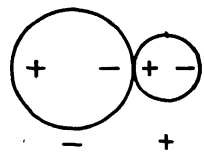


Fig. 37. Mutual polarization of ions

the action of any outside electrical forces. Such forces may change the internal structure of the molecules considerably, and therefore also their properties. Particularly, under the action of an external electrical field molecules which are themselves non-polar become temporarily polar.

Indeed, suppose a non-polar molecule is placed between the two plates of a condenser (Fig. 35). Obviously, the charges of the plates will affect the arrangement of the charges within the molecule: the positively charged nuclei are attracted to the negative plate and the electrons to the positive. The result is a shift of the electrons with regard to the nuclei, and if prior to this the centres of gravity of the positive and negative charges coincided, they will now separate, making the molecule a dipole with a certain dipole moment. This phenomenon is called **polarization** of the molecule, and the dipole formed is called **induced.** If the external field is removed, the dipole disappears and the molecule again becomes non-polar. Ions can be polarized in an electrical field just like molecules (Fig. 36).

Each ion bears an electrical charge, as a result of which it is itself at the same time an electrical field source. Therefore, in molecules consisting of oppositely charged ions the latter mutually polarize one another: the positively charged ion draws the electrons of the negatively charged ion towards itself and at the same time the negative ion repels the electrons of the positive ion (Fig. 37). The ions are thus *deformed*, i.e., the structure of their electron shells changes. It follows, therefore, that the structure of ions combined in a molecule must differ considerably from that of the free ions.

The larger the charge on an ion, the greater its polarizing action, and with constant charge the polarizing action increases rapidly as the radius of the ion grows smaller; on the other hand, the deformability of the ion thereupon decreases. Since positive ions are generally smaller than the negative ones, it is chiefly the negative ion that deforms upon the mutual polarization of two ions within a single molecule (Fig. 38).

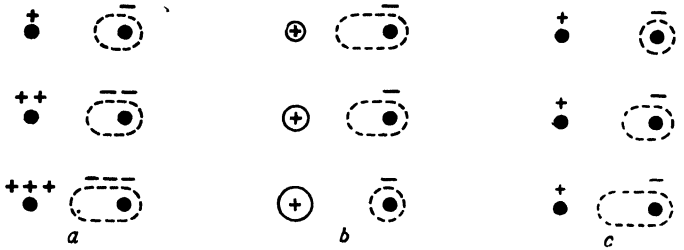


Fig. 38. Polarization of negative ions:
Effect on polarization: *a*—of charge on positive ion; *b*—of size of positive ion; *c*—of size of negative ion

The positive hydrogen ion has a strong polarizing action, as it is a nucleus (proton) of a very small radius entirely free of electrons. Due to the absence of an electron shell the proton is not repelled from negative ions and can approach them very closely. The deformation of the negative ions due to this proximity results in the proton penetrating, in a sense, into the electron shell of the negative ion, i. e., to the formation of a covalent bond. As we shall see in the following, a proton can penetrate the electron shell of certain electrically neutral molecules as well, converting them into complex positive ions.

Investigation of the deformation of electron shells of ions has made it possible to get a deeper insight into the structure of chemical compounds and to explain a number of their physical and chemical properties. For example, the unequal deformation of negative ions accounts for the differences in the dipole moments of molecules of analogical structure, such as HCl, HBr and HI, the instability of certain acids and salts and a number of other chemical phenomena. A close relationship has also been found to exist between the deformation of ions and the colour of their corresponding salts.

CHAPTER VI

Structure of Solid Substances

49. Physical States of Substance. In the foregoing chapters we have become acquainted with the structure of atoms and molecules, the minutest particles, of which all substances consist. In order to get a complete picture of the structure of substance we have still to see how these particles are arranged in various substances, whether their arrangement follows any relationship or is haphazard and unorderly. For this purpose we must first consider the three physical states of substance, namely, the gaseous, liquid and solid states.

Gases are characterized by their ability to fill uniformly any volume placed at their disposal. This property of gases is due to the extraordinary mobility of their particles. That the particles of gases are at great distances from one another is confirmed by the high compressibility of gases. Under such conditions the mutual attraction between particles is very small and does not keep them from flying in all directions. The particles move so swiftly and unorderly that any regular arrangement is out of the question.

Liquids differ from gases in that they occupy a definite volume at any given temperature. The very slight compressibility of all liquids shows that their particles are much more crowded than those of gases. Therefore, the mutual attraction between the particles is much more manifest and keeps them from flying apart. This accounts for the constancy of the volume of liquids. However, these forces are not large enough to keep the particles fixed. Liquids spread under the influence of gravity and thus have no shape of their own, always taking the shape of the vessel they occupy. Only when in very small quantities (drops) are liquids capable of retaining their own shape. Due to their incessant motion the mutual arrangement of the particles of a liquid is always changing and is generally just as unorderly as in a gas.

Solids, contrary to liquids and gases, have a definite, independent shape and retain it regardless of their position. The particles of a solid are so rigidly connected to one another that they cannot move from place to place. True, even in solids the particles retain some

motion, but in this case it is of the character of minute vibrations about definite points.

From this brief review of the properties of substance in its various states it follows directly that the particles forming a substance can be expected to have a regular arrangement only in the solid state.

50. Crystalline and Amorphous Substances. Most solids are crystalline in structure. This can easily be verified by breaking a piece of substance and examining its fracture. Usually (for example in sugar,

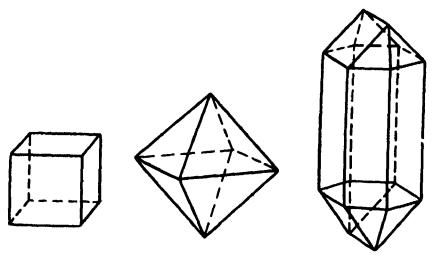


Fig. 39. Forms of crystals:
a—common salt; *b*—alum; *c*—saltpetre

sulphur, metals) tiny crystalline faces at various angles to each other can easily be detected on the fracture, sparkling due to various reflection of light. If the crystals are very small the crystalline structure of the substance can be established by means of a microscope. There are solid substances whose fracture gives no indications of crystals. For example, if we break a piece of ordinary glass, its fracture will be found to be smooth and bounded, unlike the fractures of crystalline substances, by curved instead of plane surfaces. A similar picture is observed if pieces of pitch, glue and certain other substances are broken. All such substances are called **amorphous** (i. e., formless).

Each crystalline substance usually gives crystals of quite a definite form. For instance, common salt crystallizes in the form of cubes (Fig. 39*a*), alum as octahedrons (Fig. 39*b*), saltpetre as prisms (Fig. 39*c*), etc. Crystalline form is one of the characteristic properties of substances.

The classification of crystalline forms is based on determination of the degree of symmetry of crystals. Various cases of symmetry of crystalline polyhedrons are discussed in detail in books on crystallography. It will suffice here to mention that all the varieties of crystalline forms can be classed into six groups or **crystal systems**, which in their turn are subdivided into classes. These systems are known as: 1) regular (cubic), 2) tetragonal or rectangular; 3) orthorhombic, 4) hexagonal, 5) monoclinic and 6) triclinic.

The system a crystal belongs to is determined by the relative arrangement of its crystallographic axes (coordinate axes drawn in a definite fashion within the crystal) and by the length of the intercepts of their faces.

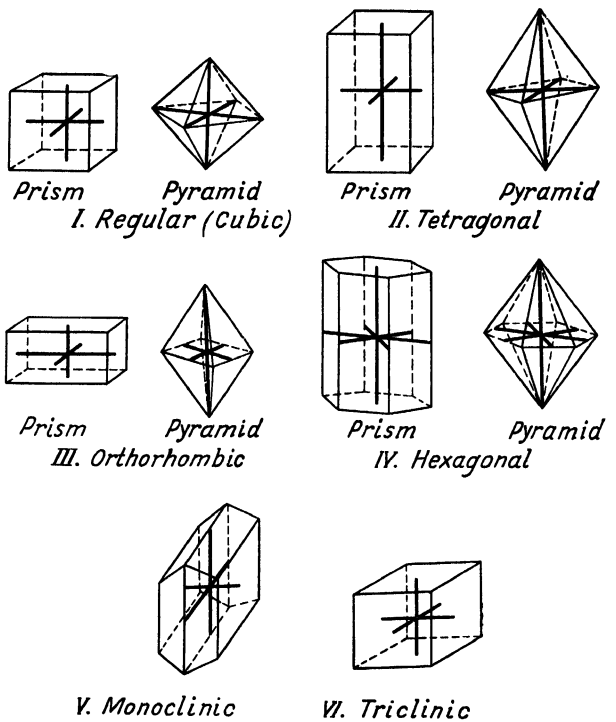


Fig. 40. Crystal systems

Fig. 40 shows the simplest crystal forms, the prisms and pyramids of the various systems.

In crystals of the *regular system* all three crystallographic axes, shown in Fig. 40 by bold lines, are at right angles to each other and the intercepts of their crystal faces are equal in length. This system includes the most symmetrical forms, such as cube, octahedron, etc.

In crystals of the *tetragonal system* the crystallographic axes are also at right angles to each other; of the three intercepts of the faces two are equal in length, while the third is shorter or longer. Crystals of the tetragonal system are somewhat less symmetrical; they are usually drawn out in one direction.

The *orthorhombic system* is characterized by three axes at right angles and by unequal lengths of the intercepts on these axes. This system received its name from the fact that crystals belonging to it often have rhombic cross-sections.

The *hexagonal system* differs from all the rest in its having four axes, three of which are in the same plane and inclined to each other at equal angles; the fourth axis is perpendicular to the first three; the intercepts on the axes in the same plane are equal. The cross-section of such crystals is often a hexagon.

Crystals of the *monoclinic system* have three crystallographic axes, one of which is perpendicular to the other two, the latter forming an oblique angle. The intercepts of the axes are of unequal length. Crystals of this system are much less symmetrical than those of the foregoing systems. They can be divided into two symmetrical halves only by one plane. The greatest number of all the crystals investigated (above 42 per cent) belong to the monoclinic system.

The *triclinic system* is characterized by three axes at different angles to one another and by different lengths of the intercepts on these axes. The forms belonging to this system are very diverse and the least symmetrical.

Natural crystals, as well as crystals obtained by artificial means, rarely correspond exactly to the forms shown in Fig. 40. Usually during the solidification of a melted substance the crystals grow together and thus turn out to be incomplete. When a solid substance is crystallized out of solution the result is also mostly irregular crystals, distorted due to non-uniform growth during crystallization. However, no matter how unevenly the crystal has developed, no matter how its shape is distorted, the angle between the faces of a crystal of any definite substance is always constant. This is one of the fundamental laws of crystallography, known as the **Law of Constancy of Interfacial Angles.** Therefore, by the value of the interfacial angles in a crystal we can always establish its crystalline system and the class to which the crystal belongs.

A thorough study of the properties of crystalline substances has shown that their peculiarities are not confined merely to external form. Although the substance in a crystal is quite homogeneous, many of its physical properties, such as cohesion, thermal conductivity, attitude towards light, etc., are not always manifested identically in various directions inside the crystal; in other words, the properties of a crystal are *vectorial.**

For instance, if we cut two bars of equal thickness from a cubic crystal of common salt, one at right angles to the faces of the cube (see Fig. 41*a*), the other along the diagonal of one of its faces (see Fig. 41*b*), and test the tensile strength of these bars, we shall find that if the first bar can be ruptured by force of 1 kg., the second bar will require a force of 2.5 kg. to rupture it. Obviously, in crystals

* A vector is a value depending on the direction.

of common salt the cohesion between particles in the direction perpendicular to the cube faces is two and a half times less than in the direction of the diagonals.

In many crystals the difference between the cohesion in various directions is so great that when struck or broken they split along planes perpendicular to those in which the cohesion is the smallest. This property of crystals is called *cleavage*. A good example of cleavage are mica crystals which split, as is commonly known, into very thin flakes.

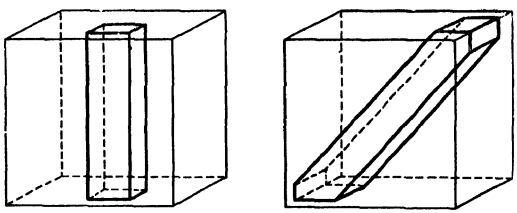


Fig. 41. Bars cut out of crystals of common salt: *a*—at right angles to cube faces; *b*—diagonally to one of the cube faces

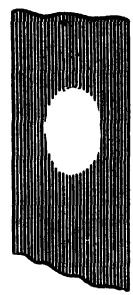


Fig. 42. Plate of mica coated with wax

The attitude of crystals towards light is also an interesting point. In crystals of the regular system light is propagated in all directions at the same rate; in crystals of all the other systems the velocity of light varies, depending on the direction.

A similar relation is observed with regard to thermal conductivity. If, for instance, a plate of mica is covered with a layer of wax and then touched with the sharp point of a hot metal rod, the wax around the point will begin to melt, soon forming an ellipse-shaped melted spot (Fig. 42). This experiment shows that the mica plate conducts heat in different directions at different rates. Thus, one of the important peculiarities of crystalline substances is the vectoriality of their properties.

The difference between crystalline and amorphous substances is especially pronounced in their attitude towards heating. While each crystalline substance melts at a strictly definite temperature and passes back from the liquid to the solid state at the same temperature, amorphous substances have no constant melting point. When an amorphous substance is heated it gradually softens, then begins to flow and finally becomes quite liquid. Upon cooling it hardens just as gradually. It is impossible to establish the moment of transition of an amorphous substance from one state into the other.

Amorphous substances have another peculiarity related to the absence of a constant melting point: many of them are fluid just like liquids, i.e., are capable of gradually changing their shape under the prolonged influence of comparatively small forces. For instance, a piece of pitch placed on a flat surface in a warm room will flow in several weeks and acquire the shape of a disk; a glass

tube supported by the ends gradually sags, etc. The internal structure of amorphous substances is also similar to that of liquids. It is characterized by an unorderly arrangement of its molecules. For this reason, amorphous substances are now regarded as liquids whose viscosity increases greatly upon cooling. Only crystalline substances are considered solids.

In conclusion it should be noted that one and the same substance may be both crystalline and amorphous, depending on the conditions under which it passes into the solid state. In nature, for instance, silicon dioxide SiO_2 occurs as well-formed crystals of the mineral quartz (Fig. 43), but is found also in the amorphous state (the mineral flint). If glass is repeatedly heated and cooled slowly it passes

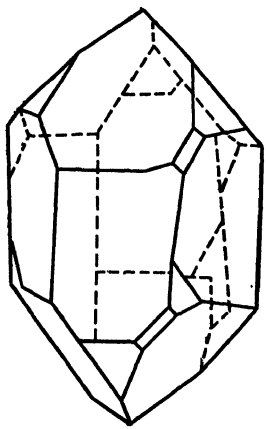


Fig. 43. Quartz crystal

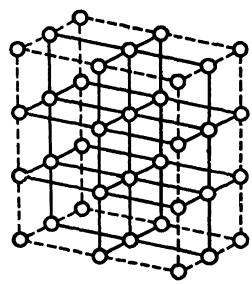


Fig. 44. Space lattice

from the amorphous state to the crystalline or, as we say, it "devitrifies"; such typically amorphous substances as glue have been obtained in distinctly crystalline form, etc.

51. Internal Structure of Crystals. It was assumed long since that the external form of a crystal is but a reflection of its concealed internal structure, being due to regular arrangement of its particles—the molecules or atoms making up the crystal—at strictly definite points of space.* All these points taken together make up a so-called *space* (crystal) *lattice* of one form or another, which is the geometrical expression of the structure of a crystalline substance (Fig. 44). The points at which the particles are arranged are called *lattice points.*

The truth of these conceptions was proved comparatively recently, only after it was established that X-rays are deflected upon passing through a crystal and that the arrangement of the particles in the crystal can be judged by the extent of their deflection. After that

* This idea was put forth by M. Lomonosov in his work "On the Birth of Saltpetre" (1749).

very accurate and convenient methods of investigating crystals by means of X-rays were developed, and these methods are now widely used at research laboratories and industrial plants, especially in the field of metallurgy.

The use of X-rays for the study of crystals made it possible to determine the character of the space lattices of many crystals. An important result of these studies was the discovery that *the lattice points of many complex substances* (for instance salts) *are occupied by separate positively and negatively charged ions and not by molecules.*

In this connection four main types of lattices are distinguished: molecular, atomic, ionic and metallic.

Molecular lattices are distinguished by the fact that their points are occupied by molecules. Such lattices are formed by compounds of non-polar or slightly polar types and generally by compounds with atomic bonds.

The structural units of the *atomic lattice* are neutral atoms, covalently linked together. Lattices of this type are peculiar to certain simple substances, such as diamonds.

Ionic lattices, in which positive and negative ions alternate in the lattice points, are characteristic of compounds of ionic build; they include almost all the salts, many oxides and some other substances.

Metallic lattices are of a special structure. The points of such lattices are occupied by positive ions instead of neutral atoms, with free, very mobile electrons in the spaces between them. Metallic lattices will be dealt with in greater detail when considering metals.

The difference between molecular, atomic and ionic lattices is not only due to the type of particles in them but to the nature of their interaction as well. The Coulomb forces acting between positively and negatively charged ions in ionic structures give rise to a much stronger bond between the particles than the forces linking electrically neutral atoms and molecules. That is why the melting point and hardness of ionic compounds are usually much higher than those of substances made up of polar or non-polar molecules.

The strength of the bond between the particles forming a crystal is characterized by the work that has to be done to destroy the lattice and to remove its constituent particles to such distances from one another at which their interaction is negligible. This work is called the *energy of the crystal lattice*. It is referred to one mole of substance and is expressed in large calories.

Thus, for instance, to decompose one mole of NaCl into free gaseous ions 185 Cal. must be expended:

$$[NaCl] = [Na]^+ + [Cl]^- - 185\,\text{Cal}.$$

Obviously, during the formation of one mole of NaCl from free gaseous ions the same amount of energy should be liberated.

The physical properties of a solid are in close relation to its crystal lattice type, i.e., to the type and nature of the bond between its structural units. This relation is shown in Table 8.

Lattices may be very diverse in structure. The least part of a lattice which still retains all the characteristic features of its structure is called a **unit cell.** In the general case this cell is in the shape of a parallelepiped and contains a definite number of particles. The entire crystal consists of a huge number of such cells adjacent to one another. Just as when bricks are laid next to one another the external shape of the building does not necessarily repeat the shape of the brick, so in the case of the crystal its shape does not at all necessarily determine the form of its unit cell. However, the form of the unit cell can be judged by the nature of its crystallographic axes.

Crystal lattices belonging to the regular system, in which the unit cell is a cube, have the simplest structure.

Fig. 45 shows part of the cubic lattice of sodium chloride NaCl, namely, its unit cell, cut out of a crystal to give an idea of how its ions are arranged inside the crystal. The chloride and sodium ions are situated at the lattice points in such a way that each chloride ion is surrounded by six sodium ions and each sodium ion by six chloride ions. This will easily be seen if we imagine the lattice continued in all directions. It is a characteristic feature that the sodium and chloride ions are not connected to one another by pairs: there is nothing in the crystal which might correspond to a NaCl molecule. The crystals of other salts are of a similar structure. Hence, it follows that the conception of molecules of gaseous substances, which has a strictly definite meaning in chemistry, is inapplicable to solid crystalline substances forming ionic lattices.

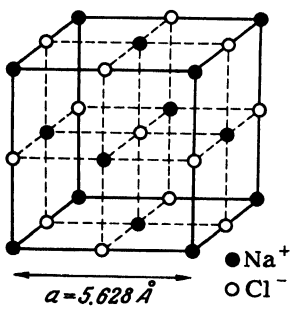


Fig. 45. Lattice of sodium chloride

In considering the structure of salts and other compounds forming ionic lattices, we involuntarily begin to wonder whether these compounds can exist as molecules at all, seeing that their crystals consist of ions. In this connection it should be pointed out that determination of the vapour densities of various salts at high temperatures shows that these vapours consist of molecules and not of ions.

A very important value characterizing crystals is the lattice constant *d*, indicating the least distance between the centres of two adjacent particles in the unit cell and determined usually by X-ray methods. The lattice constant of a cubic lattice can easily be calculated if the edge length of the unit cube is known. For instance, the

Table 8

Properties of Solid Substances with Various Types of Crystal Lattices

Crystal lattice type	Structural units	Melting and boiling points	Electrical conductivity of fused substance	Other properties of crystals	Examples
Ionic	Positive and negative ions	High	High	Hard, brittle; dissolves more readily in polar than in non-polar solvents	NaCl, KBr, CaF_2, BaO
Molecular, formed by polar molecules	Polar molecules	Low	Low	Low hardness; usually soluble in polar solvents	H_2O, PCl_3, HCl, NH_3
Molecular, formed by non-polar molecules	Non-polar molecules	Very low	Extremely low	Very soft; soluble in non-polar and very slightly polar solvents	O_2, Cl_2, N_2, CO_2
Atomic	Atoms connected covalently with one another	Very high	Low	Usually very hard; insoluble in most solvents	Diamond, SiC, AlN, B_4C

edge length a of the cube of a sodium chloride crystal, determined by X-ray methods, equals 5.628 Ångström units, while the least distance between the sodium and chloride ions equals half this value, i.e., $d=2.814$ Ångström units.

52. Determination of Radii of Atoms and Ions. The use of X-rays in the study of crystals makes it possible not only to establish the inner structure of the latter, but to determine the size of the atoms or ions forming the crystal as well.

To make these calculations clear, suppose the particles constituting the crystal are spherical in shape and contact each other. It may then be considered that the distance between the centres of

two adjacent particles equals the sum of their radii (Fig. 46). If the particles are atoms of a simple substance, the radius of an atom can be determined by measuring the distance between them, and will obviously be equal to one half the distance found. For instance, if we know that the lattice constant d of a metallic sodium crystal equals 3.72 Ångström units, we can find that the radius of a sodium atom $r = \frac{d}{2} = 1.86$ Ångström units.

Determination of the radii of various ions is somewhat more complicated. In this case, the distance between the ions can no longer be divided in half, as the sizes of the ions are different. But if the

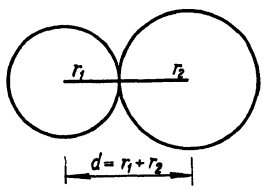


Fig. 46. Adjacent particles in crystal

radius of one of the ions r_1 is known, the radius of the other r_2 can easily be found by subtraction: $r_2 = d - r_1$.

Hence, it follows that to calculate the radii of various ions from their crystal lattice constants we must know the radius of at least one ion. Then there is no difficulty in determining the radii of all the rest of the ions.

The radii of fluoride and oxide ions (F^- and O^{--}) have been determined quite accurately by optical methods, and have been found to equal, respectively, 1.33 Å and 1.32 Å; these radii serve as the initial values for calculation of the radii of other ions. Thus, for instance, the lattice constant of magnesium oxide MgO was found to be 2.1 Ångström units. Subtracting the radius of the oxide ion, we find that of the magnesium ion:

$$2.1 - 1.32 = 0.78 \text{ Å}$$

The lattice constant of sodium fluoride equals 2.31 Å; since the radius of the fluoride ion is 1.33 Ångström units, the radius of the sodium ion must be:

$$2.31 - 1.33 = 0.98 \text{ Å}$$

Knowing the radius of the sodium ion and the lattice constant of sodium chloride, we can easily calculate the radius of the chloride ion, etc.

In this way, the radii of almost all atoms and ions have been determined.

Table 9 gives a general idea of the magnitude of these values.

These data show that the atomic radii of the metals are larger than those of their ions; with non-metals the opposite is true, the radii of the ions being larger than those of the atoms.

However, the ionic radius values determined by X-ray measurement cannot be considered the true radii of the ions. Ions in crystals do not touch one another, but remain fixed at a certain distance from each other, at which the attraction and repulsion forces acting between them are balanced. Therefore, ionic radii determined by X-ray methods are known as *apparent* or *effective radii*: they show only how close the centres of the ions can approach one another in the formation of crystals.

Table 9

Radii of the Atoms and Ions of Some of the Elements

Element	Radius of atom	Radius of ion	Symbol of ion
Sodium	1.92	0.98	Na^+
Potassium	2.38	1.33	K^+
Rubidium	2.51	1.49	Rb^+
Caesium	2.70	1.65	Cs^+
Magnesium	1.60	0.78	Mg^{++}
Calcium	1.97	1.06	Ca^{++}
Barium	2.24	1.43	Ba^{++}
Fluorine	0.67	1.33	F^-
Chlorine	1.07	1.81	Cl^-
Bromine	1.19	1.96	Br^-
Iodine	1.36	2.20	I^-
Sulphur	1.04	1.74	S^{--}

Similarly, if the crystal consists of uncharged atoms, we find the *effective atomic radii.*

Since the effective radii must be approximately proportional to the true radii, they can be used successfully to explain many of the properties of atoms and ions.

In some of the simplest cases the radii of atoms or ions can be calculated from the specific gravity of the solid substance.

The relative size of the ions forming a crystal greatly influences the structure of the space lattice. For instance, CsCl and NaCl, though very similar chemically, nevertheless form lattices of different

types, each positive ion in the first compound being surrounded by eight negative ions, and in the second compound only by six. This difference is due to the difference in size of caesium and sodium ions. Certain considerations lead us to assume that the ions in a crystal must be arranged in such a way that each smaller sized ion fills the space between the larger ions, surrounding it as completely as possible, and vice versa; in other words, the negative ions, which are almost always larger than the positive, should be gathered as closely as possible around the positive ions; otherwise the system would be unstable. Since the radius of the caesium ion Cs^+ equals 1.65 Å, and that of the sodium ion Na^+ only 0.98 Å, more Cl^- ions can gather around the first than around the second.

The number of negative ions surrounding each positive ion in a crystal is called the **coordination number** of the lattice. A study of the structure of various crystals shows the following coordination numbers to be the most common: 2, 3, 4, 6, 8 and 12.

The coordination number depends on the ratio between the radii of the positive and negative ions: the nearer this ratio is to unity, the larger the coordination number. If we regard the ions as spheres arranged in the crystal so as to attain the densest packing possible, we can calculate the coordination number for each radius ratio between the positive and negative ions.

The maximum coordination numbers calculated theoretically for several radius ratios are given below:

Radius ratio	Coordination number
0.15 to 0.23	3
0.23 to 0.41	4
0.41 to 0.73	6
0.73 to 1.00	8

It can easily be seen that the coordination numbers found by this table for NaCl and CsCl correspond exactly to the actual arrangement of ions in the crystals of these substances.

For instance, in the case of NaCl the ratio of the radius of the sodium ion (0.98 Å) to that of the chloride ion (1.81 Å) equals $0.98 : 1.81 = 0.54$. This ratio is in the range 0.41 to 0.73; hence, the coordination number in the NaCl lattice must be equal to six.

53. Isomorphism. Some substances of similar chemical nature, though different in composition, give crystals of exactly the same form, characterized by identical or almost identical space lattice constants. Such substances are called **isomorphous** (i.e., possessing the same form) and the phenomenon of the formation of identical crystals by substances having different compositions is called **isomorphism.**

A characteristic feature of isomorphous substances is their ability to crystallize jointly out of solution to form so-called *mixed crystals.*

The latter contain variable quantities of the initial substances, depending on the concentration of each in the solution. Of course, other substances absolutely unakin to each other may also crystallize simultaneously from solution, but in this case the result will not be mixed crystals but a mechanical mixture of pure crystals of each of the substances present in the solution.

A typical example of isomorphous substances are the various alums, double salts of sulphuric acid containing one univalent and one trivalent metal. If we dissolve a mixture of colourless aluminium alum, $KAl(SO_4)_2 \cdot 12\ H_2O$, and intensively violet-coloured chrome alum, $KCr(SO_4)_2 \cdot 12\ H_2O$ (Fig. 47), in water and leave the solution

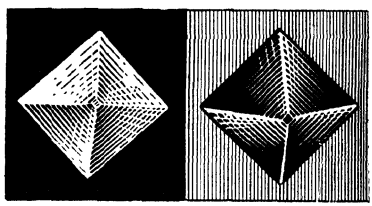


Fig. 47. Isomorphous crystals of aluminium and chrome alum

to crystallize, mixed crystals will result containing both kinds of alum and having a pale or deep purple colour, depending on the proportion of the alums dissolved. Since mixed crystals are quite homogeneous, though of variable composition, they are known also as *solid solutions.*

Another example of isomorphous substances are the salts $KClO_4$ and $KMnO_4$, which form crystals in the orthorhombic system with almost identical corresponding angles between their faces. Many sulphate salts of bivalent metals containing equal numbers of molecules of hydration water are also isomorphous, for instance: $MgSO_4 \times \times 7H_2O$, $ZnSO_4 \cdot 7\ H_2O$, $NiSO_4 \cdot 7\ H_2O$. Isomorphism is rather widespread among minerals as well. For instance, galena PbS and silver glance Ag_2S are isomorphous: natural galena crystals often contain Ag_2S, i.e., are essentially mixed crystals or solid solutions.

If a green crystal of nickel sulphate $NiSO_4 \cdot 7\ H_2O$ is suspended by a thread in a saturated solution of magnesium sulphate, these two compounds being isomorphous, the crystal will continue to grow in the solution and will become covered with a layer of colourless $MgSO_4 \cdot 7\ H_2O$, just as if it were growing in a solution of nickel sulphate. The growth of the crystals of one substance in the solution of another is a very characteristic feature of isomorphous substances.

The phenomenon of isomorphism was discovered in 1819 by the German chemist Mitscherlich, who noticed that salts of phosphoric and arsenic acids containing equal quantities of water of hydration, such as $Na_2HAsO_4 \cdot 12H_2O$ and $Na_2HPO_4 \cdot 12H_2O$, have almost identical crystal forms. Mitscherlich observed the same phenomenon in the case of other salts of similar types and came to the conclusion that substances containing equal numbers of atoms in their molecules and similar in chemical properties form identical crystal forms.

The discovery of isomorphism played an important part in its time for the determination of the atomic weights of some of the elements. Since, according to Mitscherlich, isomorphous substances should contain equal numbers of atoms in their molecules, then, knowing the formula of one of a pair of isomorphous substances we can determine the formula of the other, provided the composition of the latter has been ascertained. For instance, from the fact that potassium sulphate K_2SO_4 and potassium selenate are isomorphous, Mitscherlich concluded that the formula of the latter is K_2SeO_4. Knowing the percentage composition of potassium selenate, Mitscherlich found the atomic weight of selenium. On the basis of the isomorphism of aluminium salts with salts of ferric oxide, the formula of which is Fe_2O_3, it was concluded that the formula of aluminium oxide must be Al_2O_3. On the basis of this formula and the composition of aluminium oxide it was established that the atomic weight of aluminium equals 27.

The explanation of isomorphism and the formation of mixed crystals is that atoms or ions of approximately equal size and with equal charges can substitute one another in the crystal lattice without affecting its stability. The nature of the lattice depends to a considerable extent on the size of the ions constituting it. Hence, it is not surprising that, for instance, KCl and KBr have almost identical lattices, since the radii of chloride and bromide ions are quite close to one another (1.81 Å and 1.96 Å, respectively). When dissolved in water, the crystals of KCl and KBr break up into separate ions (see Chapter XII). Therefore, a mixture of the solutions of both salts contains K^+, Cl^- and Br^- ions. If water is evaporated from such a solution crystallization will set in at a certain moment: the ions recombine to form crystals, both negative ions Cl^- and Br^- taking part simultaneously in the building of each crystal. The result will be mixed crystals containing both Cl^- and Br^- ions (or, which is the same, KCl and KBr) in quantities depending on their relative contents in the solution. Thus, by varying the relative amounts of KCl and KBr in the solution, we can achieve a continuous transition from crystals consisting only of potassium chloride to crystals consisting only of potassium bromide.

Ions with very different radii cannot substitute one another in crystals. For instance, sodium chloride and potassium chloride have lattices of the same type and are very similar chemically, but do not form mixed crystals because the radius of the potassium ion (1.33 Å) is much larger than that of the sodium ion (0.93 Å), and their lattice constants are absolutely different. Therefore, sodium chloride and potassium chloride are not isomorphous.

Thus, isomorphism consists in the fact that certain chemically similar substances form crystals of exactly identical form. The opposite phenomenon, when one and the same substance, depending on the conditions, crystallizes in different forms is called **polymorphism**, and substances possessing these properties are called **polymorphous.** Each crystal form of a polymorphous substance is stable only within a definite range of temperatures and pressures.

A good example of polymorphous substances is sulphur. When melted sulphur solidifies slowly, long needle-like or prismatic crystals of the monoclinic system result. However, these crystals can exist for a long time only at temperatures above 96° C; at lower temperatures they gradually change into the orthorhombic crystals of which natural sulphur consists. In their turn, if the orthorhombic crystals are heated slowly above 96° C they change into monoclinic crystals (see § 120).

There are also many salts which can crystallize in various systems. For instance, at ordinary temperatures ammonium nitrate forms crystals in the orthorhombic system; above 85° C these crystals absorb heat and change into crystals of one of the classes of the hexagonal system, and above 125° C, into crystals of the regular system.

The phenomenon of polymorphism is widespread in nature. For instance, titanium dioxide TiO_2 occurs as the minerals rutile, brookite and anatase of different crystal structure; calcium carbonate forms the minerals: calcite, crystallizing in the hexagonal system, and aragonite, which belongs to the orthorhombic system, etc.

CHAPTER VII

Development of the Periodic Law

All the theories of atomic structure and chemical valency, beginning with the theories of Rutherford and Bohr, are grounded directly or indirectly on Mendeleyev's Periodic Table. However, the reverse is also true. The facts and relationships discovered in the process of the experimental and theoretical study of atomic structure have made it possible to get a deeper insight into the Periodic Law and the periodic system of elements.

From the present-day point of view Mendeleyev's Table gives a natural classification of the chemical elements, based on the structure of the electron shells of their atoms. Therefore, to appreciate the great importance of the Periodic Table for chemistry, we must consider the electron structures of all the elements in greater detail, as well as the determinant influence of these structures on their chemical properties. Furthermore, we must establish the relation between the positions of the elements in the Periodic Table and the structure of their atoms and ascertain the structural peculiarities of the atoms of the elements of the even and odd series. Finally, we must become better acquainted with the phenomenon of isotopy and with the modern definition of the concept "chemical element."

54. Atomic Numbers of the Elements. In discussing the theory of atomic structure we mentioned the relationship between the X-ray spectra of the elements and their atomic numbers. An investigation of this relationship led to the conclusion that the atomic number, determined by the position of the element in the Periodic Table, is one of the most important constants of the element, showing the number of positive charges on the nucleus of its atom. The nuclear charges on the atoms of all the elements were determined by means of X-ray spectra. The results of these determinations showed that *in the Periodic Table the elements are arranged in strict sequence in order of increasing charges on the nuclei of their atoms.*

This discovery was additional proof of the correctness of the Periodic Table. At the same time, it removed the apparent contradiction in Mendeleyev's system, namely, the fact that some elements with higher atomic weights had been placed before other elements with lower atomic weights (tellurium and iodine, argon and potassium,

cobalt and nickel). There proved to be no contradiction at all, as the position of each element in the Table is not determined by its atomic weight but by the charge on its atomic nucleus. Evaluation of the nuclear charges of tellurium and iodine showed that the charge on the first equalled 52 and on the second 53, so that tellurium should actually be before iodine, despite its greater atomic weight. Similarly, the nuclear charges of argon and potassium, nickel and cobalt were found to be in full agreement with the sequence of their arrangement in the Table.

Thus, the charge on the atomic nucleus is the basic value on which all the properties of any element, as well as its position in the Periodic Table, depend. Therefore Mendeleyev's Periodic Law is now formulated as follows:

> *The properties of the elements are a periodic function of the nuclear charges on their atoms.*

The evaluation of the atomic numbers of the elements from their X-ray spectra was very important in one more respect. It made it possible to establish the total number of positions in the Periodic Table between hydrogen, the atomic number of which is one, and uranium (atomic number 92), which at that time was considered the last member in the Periodic Table. When the theory of atomic structure was in its initial stage of development, the positions 43, 61, 72, 75, 85, and 87, remained unoccupied, indicating the possible existence of still undiscovered elements. Indeed, in 1922 a new element hafnium was discovered which occupied the 72nd position; then, in 1925 the 75th position was filled with the element rhenium. As to the elements which were to occupy the remaining four blank positions in the Table, it must be said that despite several communications in literature as to their discovery, there is no reliable proof of the existence of these elements in nature. Lately, however, all four elements were produced artificially and their chemical properties studied, in spite of the fact that the quantities obtained did not exceed 10^{-10} to 10^{-14} gr. The new elements were called: *technetium* (No. 43), *promethium* (No. 61), *astatine* (No. 85) and *francium* (No. 87). Thus, it may be considered that at present all the positions in the Periodic Table between hydrogen and uranium are filled.

However, the periodic system itself is not complete, as is evident from the discovery of the so-called transuranium elements, i. e., elements following uranium according to the nuclear charge on their atoms. These elements will be discussed in greater detail in § 266.

The substitution of atomic weights for nuclear charges or atomic numbers not only failed to break up the system, but, on the contrary, made it even stronger. At the same time, the sequence of elements

established by Mendeleyev remained unaltered, as it was in full agreement with the new basis of the system, namely the charges on the atomic nuclei.

55. Electronic Structure of Atoms and the Periodic Law. The gradation in properties from element to element, as well as the seeming irregularities in the Periodic Table (such as the unequal numbers of elements in the periods, the close similarity of the fourteen so-called rare-earth elements and others), are consequences of the change in structure of the electron shells of the atoms. Therefore, before proceeding any further we must become acquainted with the arrangement of electrons in the atoms of all the chemical elements and see by Table 10 how the electron layers grow and are gradually filled with electrons as the atomic numbers of the elements increase.

In Chapter IV we discussed the arrangement of the electrons in the atoms of the first eighteen elements of the Periodic Table, i. e., the elements of the three short periods, and examined the schemes of their atomic structure (Fig. 27). It will be remembered that the electron layers in the atoms of these elements were filled up regularly with increasing atomic numbers: each subsequent element acquired one additional electron in its outer layer, or if that layer was already full, the new electron began the next layer. Thus, in the eighteenth element, argon, the first or K layer contains two electrons, the second, L layer, eight electrons and the third, M layer, also eight electrons; this information may be briefly recorded as follows:

$$\left\{\begin{array}{cccc} & K & L & M \\ \oplus & -2 & -8 & 8 \end{array}\right\}^{*}$$

Spectroscopic data show that the electron layers of the atoms of long period elements are filled in a more complex manner (see Table 10).

As the limit number of electrons in the outer layer equals eight, the first element of the fourth period, namely, potassium (No. 19), acquires a new layer, N, with one electron, although the M layer is capable of holding eighteen electrons.

In the calcium atom (No. 20) one more electron is added to the N layer. Thereupon the addition of electrons to the N layer is temporarily discontinued.

From scandium (No. 21) to copper (No. 29), which marks the beginning of the second half of the fourth period, electrons are gradually added to the M layer, while the number of electrons in the outer, N layer, remains equal to two, and in the atoms of chromium and copper even drops to one.

* The symbol $\oplus$ denotes the atomic nucleus.

Table 10

Electron Arrangement in the Atoms of the Chemical Elements

Period	Atomic number and name of element	Chemical symbol	Number of electrons in layer						
			K	*L*	*M*	*N*	*O*	*P*	*Q*
I	1. Hydrogen	H	1						
	2. Helium	He	2						
II	3. Lithium	Li	2	1					
	4. Beryllium	Be	2	2					
	5. Boron	B	2	3					
	6. Carbon	C	2	4					
	7. Nitrogen	N	2	5					
	8. Oxygen	O	2	6					
	9. Fluorine	F	2	7					
	10. Neon	Ne	2	8					
III	11. Sodium	Na	2	8	1				
	12. Magnesium	Mg	2	8	2				
	13. Aluminium	Al	2	8	3				
	14. Silicon	Si	2	8	4				
	15. Phosphorus	P	2	8	5				
	16. Sulphur	S	2	8	6				
	17. Chlorine	Cl	2	8	7				
	18. Argon	Ar	2	8	8				
IV	19. Potassium	K	2	8	8	1			
	20. Calcium	Ca	2	8	8	2			
	21. Scandium	Sc	2	8	8+1	2			
	22. Titanium	Ti	2	8	8+2	2			
	23. Vanadium	V	2	8	8+3	2			
	24. Chromium	Cr	2	8	8+5	1			
	25. Manganese	Mn	2	8	8+5	2			
	26. Iron	Fe	2	8	8+6	2			
	27. Cobalt	Co	2	8	8+7	2			
	28. Nickel	Ni	2	8	8+8	2			
	29. Copper	Cu	2	8	18	1			
	30. Zinc	Zn	2	8	18	2			
	31. Gallium	Ga	2	8	18	3			
	32. Germanium	Ge	2	8	18	4			
	33. Arsenic	As	2	8	18	5			
	34. Selenium	Se	2	8	18	6			
	35. Bromine	Br	2	8	18	7			
	36. Krypton	Kr	2	8	18	8			

Table 10 (continued)

Period	Atomic number and name of element	Chemical symbol	Number of electrons in layer						
			K	*L*	*M*	*N*	*O*	*P*	*Q*
V	37. Rubidium	Rb	2	8	18	8	1		
	38. Strontium	Sr	2	8	18	8	2		
	39. Yttrium	Y	2	8	18	8+1	2		
	40. Zirconium	Zr	2	8	18	8+2	2		
	41. Niobium	Nb	2	8	18	8+4	1		
	42. Molybdenum	Mo	2	8	18	8+5	1		
	43. Technetium	Tc	2	8	18	8+5	2		
	44. Ruthenium	Ru	2	8	18	8+7	1		
	45. Rhodium	Rh	2	8	18	8+8	1		
	46. Palladium	Pd	2	8	18	8	0		
	47. Silver	Ag	2	8	18	18	1		
	48. Cadmium	Cd	2	8	18	18	2		
	49. Indium	In	2	8	18	18	3		
	50. Tin	Sn	2	8	18	18	4		
	51. Antimony	Sb	2	8	18	18	5		
	52. Tellurium	Te	2	8	18	18	6		
	53. Iodine	I	2	8	18	18	7		
	54. Xenon	Xe	2	8	18	18	8		
VI	55. Caesium	Cs	2	8	18	18	8	1	
	56. Barium	Ba	2	8	18	18	8	2	
	57. Lanthanum	La	2	8	18	18	8+1	2	
	58. Cerium	Ce	2	8	18	18+2	8	2	
	59. Praseodymium	Pr	2	8	18	18+3	8	2	
	60. Neodymium	Nd	2	8	18	18+4	8	2	
	61. Promethium	Pm	2	8	18	18+5	8	2	
	62. Samarium	Sm	2	8	18	18+6	8	2	
	63. Europium	Eu	2	8	18	18+7	8	2	
	64. Gadolinium	Gd	2	8	18	18+7	8+1	2	
	65. Terbium	Tb	2	8	18	18+9	8	2	
	66. Dysprosium	Dy	2	8	18	18+10	8	2	
	67. Holmium	Ho	2	8	18	18+11	8	2	
	68. Erbium	Er	2	8	18	18+12	8	2	
	69. Thulium	Tu	2	8	18	18+13	8	2	
	70. Ytterbium	Yb	2	8	18	18+14	8	2	
	71. Lutetium	Lu	2	8	18	18+14	8+1	2	
	72. Hafnium	Hf	2	8	18	32	8+2	2	
	73. Tantalum	Ta	2	8	18	32	8+3	2	
	74. Tungsten	W	2	8	18	32	8+4	2	
	75. Rhenium	Re	2	8	18	32	8+5	2	

Table 10 (continued)

Period	Atomic number and name of element	Chemical symbol	Number of electrons in layer						
			K	*L*	*M*	*N*	*O*	*P*	*Q*
VI	76. Osmium	Os	2	8	18	32	8+6	2	
	77. Iridium	Ir	2	8	18	32	8+7	2	
	78. Platinum	Pt	2	8	18	32	8+9	1	
	79. Gold	Au	2	8	18	32	18	1	
	80. Mercury	Hg	2	8	18	32	18	2	
	81. Thallium	Tl	2	8	18	32	18	3	
	82. Lead	Pb	2	8	18	32	18	4	
	83. Bismuth	Bi	2	8	18	32	18	5	
	84. Polonium	Po	2	8	18	32	18	6	
	85. Astatine	At	2	8	18	32	18	7	
	86. Radon	Rn	2	8	18	32	18	8	
VII	87. Francium	Fr	2	8	18	32	18	8	1
	88. Radium	Ra	2	8	18	32	18	8	2
	89. Actinium	Ac	2	8	18	32	18	8+1	2
	90. Thorium	Th	2	8	18	32	18	8+2	2
	91. Protactinium	Pa	2	8	18	32	18+2	8+1	2
	92. Uranium	U	2	8	18	32	18+3	8+1	2
	93. Neptunium	Np	2	8	18	32	18+5	8	2
	94. Plutonium	Pu	2	8	18	32	18+6	8	2
	95. Americium	Am	2	8	18	32	18+7	8	2
	96. Curium	Cm	2	8	18	32	18+7	8+1	2
	97. Berkelium	Bk	2	8	18	32	18+9	8	2
	98. Californium	Cf	2	8	18	32	18+10	8	2
	99. Einsteinium	En	2	8	18	32	18+11	8	2
	100. Fermium	Fm	2	8	18	32	18+12	8	2
	101 Mendelevium	Mv	2	8	18	32	18+13	8	2

The copper atom has eighteen electrons in its *M* layer and one electron in its *N* layer

$$\left\{\begin{array}{cccccc} & K & L & M & N & \\ \oplus & -2 & -8 & -18 & -1 & \end{array}\right\}$$

Only now, when the *M* layer is complete (the number of electron units having reached the limit value), do the electrons begin to gradually fill the *N* layer, until their number in this layer reaches eight in the inert gas krypton (No. 36):

$$\left\{\begin{array}{cccccc} & K & L & M & N & \\ \oplus & -2 & -8 & -18 & -8 & \end{array}\right\}$$

The electron layers in the atoms of the fifth period elements beginning with rubidium (No. 37) and ending with the inert gas xenon (No. 54) are filled in the same manner as in the atoms of the fourth period (see Table). Therefore the structure of the xenon atom is

$$\begin{matrix} & K & L & M & N & O \\ \oplus & -2 & -8 & -18 & -18 & -8 \end{matrix}$$

The sixth period contains thirty-two elements. Hence, between xenon (No. 54) and the next inert gas radon (No. 86), thirty-two electrons must be added. Their distribution among the layers takes place in the following order. A sixth electron layer *P* is started in caesium (No. 55), the next element after caesium, barium (No. 56), having two electrons in its *P* layer:

$$\begin{matrix} & K & L & M & N & O & P \\ \oplus & -2 & -8 & -18 & -18 & -8 & -2 \end{matrix}$$

Then, as in the two preceding periods, the building of the outer layer is temporarily discontinued and in the element lanthanum (No. 57) the new electron is added to the *O* layer:

$$\begin{matrix} & K & L & M & N & O & P \\ \oplus & -2 & -8 & -18 & -18 & -9 & -2 \end{matrix}$$

Lanthanum is followed by the rare-earth elements (lanthanides). In the atoms of these elements the number of electrons in the outer layer *P* remains the same as in barium, but the *N* layer is built up to 32 electrons, ending with element No. 70, ytterbium:

$$\begin{matrix} & K & L & M & N & O & P \\ \oplus & -2 & -8 & -18 & -32 & -8 & -2 \end{matrix}$$

After this, from lutetium (No. 71) to the end of the sixth period, the layers are filled with electrons in the same general order as in the two preceding long periods, the *O* layer being first built up to eighteen electrons (element No. 79), and then only the electrons being further added to the *P* layer, until their number in this layer reaches 8 in the inert gas radon (No. 86):

$$\begin{matrix} & K & L & M & N & O & P \\ \oplus & -2 & -8 & -18 & -32 & -18 & -8 \end{matrix}$$

In the seventh period a new electron layer, the *Q* layer, is started, and is built up as far as the second member of the period, radium (No. 88). In the atom of the next element, actinium, the new electron enters the *P* layer. After thorium the electrons begin to fill the lower lying *O* layer, analogously to the lanthanide atoms in the sixth period.

Thus, a new electron layer is built up in each period, and in the long periods the internal layers are completed besides. Therefore,

*the quantity of electron layers in an atom equals the number of the period in which the respective element is situated.**

The establishment of the structure of the atomic electron shells influenced the very structure of the Periodic Table, accounting for a number of changes in the earlier division of elements into periods. In earlier periodic tables the zero group used to be placed at the left of group one, so that each period began with an inert gas, hydrogen remaining outside of any period. But now it became obvious that each new period should begin with an element in which a new electron layer first appears in the form of a single valency electron (hydrogen and the alkali metals) and should end with the element in which that layer contains eight electrons, forming the highly stable electron octet characteristic of the inert gases. This natural division of elements into periods led to the arrangement given in the Table on pp. 88-89, in which the zero group is placed after group VII at the right-hand side of the Table.**

The theory of atomic structure also solved the problem of the position of the rare-earth elements (Nos. 58 to 71) in the Periodic Table. Owing to their great similarity these elements could not be distributed among the various groups. The data given in Table 10 show that the difference between the atoms of these elements lies in the structure of their internal electron layers, while the number of electrons in their outer layers, on which the chemical properties of the elements chiefly depend, is the same in all. For this reason the rare-earth elements (lanthanides) are now placed outside the general Table, their position in Mendeleyev's Table being indicated in the box of element No. 57 (La).

But the main significance of this theory was that it revealed the physical sense of the Periodic Law which had been rather vague in Mendeleyev's time. A glance at the table of electron arrangement in the atoms of the chemical elements will convince us that as the charges on the atomic nuclei increase the same combinations of electrons in the outer layer of the atom keep constantly repeating themselves. Thus, the periodic gradation in properties of the chemical elements is due to periodic returns to the same electron groupings.

56. Dependence of the Properties of the Elements on the Structure of Their Atoms. Now we can establish more precisely the dependence of the chemical properties of the atoms on the structure of their electron shells. Besides the number of electrons in each atom and

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* The palladium atom is an exception and has only four electron layers, there being no electrons in its *O* layer.

** Sometimes in present-day tables the zero group is combined with the eighth, in which case the zero group is regarded as the main subgroup of the eighth group while the elements of the eighth group proper are considered to form a secondary subgroup.

their arrangement in the layers, we must take into account the relative size of the atoms, an idea of which is given in Fig. 48.

First, let us consider the gradation in properties through each period. As was stated in § 32, within each period (except the first) the metallic properties, strongest in the first member of the period, gradually become less pronounced in the subsequent members, giving way to non-metallic properties: each period begins with a typical metal and ends with a typical non-metal, followed by an inert gas.

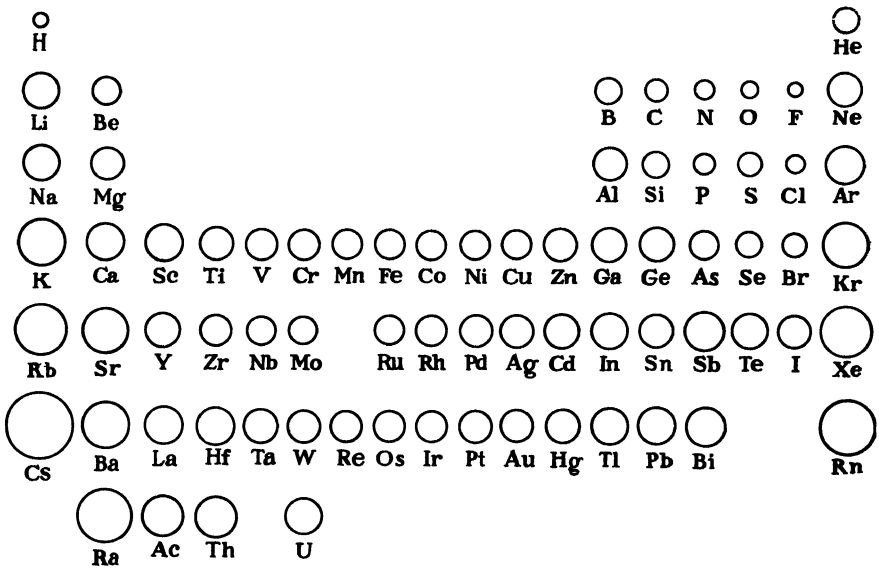


Fig. 48. Relative sizes of the atoms

The regular gradation of properties of the elements through the periods can be explained as follows. As was indicated above, the most characteristic feature of metals, from a chemical point of view, is the ability of their atoms to part readily with their outer electrons and become positively charged ions, while non-metals, on the contrary, are characterized by the ability to gain electrons, forming negative ions.

To split an electron off an atom, making the latter a positive ion, a certain amount of energy must be expended; this energy is called the *energy of ionization* and is usually expressed in large calories per gram-atom of the element.

The energy of ionization is determined by bombarding atoms in an electric field with fast electrons. The least field intensity under

which the velocity of the electrons becomes high enough to ionize the atoms is called the **ionization potential** of the atoms of the element in question and is expressed in volts.

A simple relation exists between the energy of ionization and the ionization potential, making it possible to express the readiness of atoms to yield electrons either in large calories per gram-atom or in volts.

The ionization potential is smallest in the elements at the beginning of each period, i.e., in hydrogen and the alkali metals, and largest in the elements ending the period, i.e., the inert gases. Its value can serve as a measure of the metallic properties of the element: the lower the ionization potential, the more easily the electron can be split off the atom and therefore the stronger the metallic properties of the element should be.

The value of the ionization potential depends on three factors: the charge on the nucleus, the atomic radius and a special kind of interaction between the electrons in the electric field of the nucleus due to their undulatory properties. Obviously, the higher the charge on the nucleus and the smaller the atomic radius, the stronger is the attraction of the electron to the nucleus and the higher the ionization potential.

The nuclear charge of the elements increases gradually from the alkali metal to the inert gas of each period, while their atomic radius decreases. In consequence, the ionization potential gradually grows, and the metallic properties weaken. The ionization potentials of the inert gases are higher than those of the halogens, in spite of the fact that the atomic radii of the former are larger than those of the latter in the same period. This is due to the strong influence of the third of the above-mentioned factors, electronic interaction, which makes the outer electron shell of the atom of an inert gas especially stable from an energetic point of view, removal of an electron from this shell requiring the expenditure of a considerably greater amount of energy.

The capture of an electron by the atom of a non-metal, converting its electron shell into the stable shell of an inert gas atom, is accompanied by the evolution of energy. The amount of energy evolved calculated for one gram-atom serves as a measure of the so-called, **electron affinity** of the elements. The higher the electron affinity, the more easily the atom can gain an electron. The electron affinity of metallic atoms is zero, as the atoms of metals are incapable of gaining electrons. On the other hand, the electron affinity of non-metallic atoms becomes higher as they approach the inert gas of their period in the Periodic Table. Therefore, non-metallic properties become more and more pronounced towards the end of each period.

In order to evaluate more exhaustively the metallic and non-metallic properties of the elements, a new concept, that of "electro-

negativity of an element," has been suggested. The electro-negativity of an element equals the sum of its ionization potential and electron affinity expressed in the same units. Obviously, the higher the electro-negativity, the more pronounced the non-metallic properties of the element.

Below are given the electro-negativities of the elements of the short periods (except the inert gases), the electro-negativity of lithium being accepted as unity:

H—2.1						
Li—1	Be—1.5	B—2.0	C—2.5	N—3.0	O—3.5	F—4.0
Na—0.9	Mg—1.2	Al—1.5	Si—1.8	P—2.1	S—2.5	Cl—3.0

Within each period the electro-negativity of the element increases with its atomic number.

The transition from metallic to non-metallic properties in the elements of the short periods is connected also with the change in the number of outer electrons in their atoms, which increases regularly from one in the first member of the period to eight in the last. At the same time, the ability of the atoms to yield electrons (manifestation of their metallic properties) decreases and they acquire a capacity for gaining electrons (non-metallic properties).

Experiment shows that beginning with lithium, atoms having small numbers of electrons (under four) in their outer layer are capable only of losing electrons, but never gain them. Such are the atoms of the elements we call metals. On the contrary, atoms with a larger number of outer electrons, though they can also lose electrons, gain them much more easily and the more so, the more electrons they already have in their outer layer. This property is possessed by the atoms of the non-metals.

In the long periods the gradation of properties is, on the whole, the same as in the short periods, only the metallic properties weaken much more slowly. This is due to the fact that the outer electron layer grows less regularly, since from the third member of the period to the end of its first half, the electrons build up the second last incomplete layer, while in the case of the rare-earth elements in the sixth period, it is not even the second last, but the third last layer, that is built up. Therefore the elements in the first half of the period have not more than two electrons in the outer layer of their atoms and are characterized by predominantly metallic properties (their electron affinity equalling zero). The atomic radii of these elements decrease very little and their ionization potentials hardly increase at all, as a result of which their metallic properties weaken very slowly. Only in the second half of the period does the number of outer electrons grow as consistently as in the short periods and the

metallic properties gradually give way to non-metallic. The period ends in an inert gas.

The above relation between the structure of the atoms and their chemical properties is of very great interest. We see that it is mainly the electrons of the outer layer that influence the chemical properties of the atom. The structure of the second last layer influences the chemical properties much less. Thus, for instance, elements of long periods, in whose atoms the second last electron layer is being built up, differ comparatively little in chemical nature (e.g. Cr, Mn, Fe, Co, Ni). Yet, as the second last layer is filled with electrons, the properties of the elements change in a definite direction. Finally, the almost complete identity of properties of the rare-earth elements shows that the change in the number of electrons in the third last layer of the atom influences its chemical properties insignificantly. However, even here the increase in the number of electrons causes a gradual, though minute, change in properties, manifested, for instance, in the decrease in strength of the bases from element No. 58 (cerium) to element No. 71 (lutetium).

Vertically the Table is divided into nine columns, each containing the elements of a definite group. The group number corresponds to the maximum positive valency (known as the oxygen valency) which the elements of the group can manifest. If we compare this value with the arrangement of electrons in the atoms we can easily see that in all the elements of the short periods (except oxygen and fluorine) that maximum valency is exactly equal to the number of electrons in the outer layer of the atom.

The long periods are somewhat different in this respect. In the atoms of the short period elements the number of electrons in the second last layer equals two or eight. Having lost their outer electrons, these atoms become ions with the stable octet structure of the inert gases and, naturally, cannot lose any more electrons. In the large periods, however, only the first two members have eight electrons in their second last layer. In the atoms of the subsequent elements the number of electrons in the second last layer gradually increases until it reaches eighteen (in the first member of the second half of the period). But a layer of eighteen electrons proves to be almost as stable as the octet layer. Therefore, atoms with eighteen electrons in their second last layer (e.g. Cu, Zn, Ga, etc.) also turn into ions with stable shells when they lose their outer electrons. Thus, the maximum valency of atoms of the second half of each long period, which have eighteen electrons in their second last layer (just like that of atoms with two or eight electrons in their second last layer) equals the number of electrons in the outer layer.*

* Exceptions are copper, silver and gold, whose maximum valency equals two and three, though their outer layer contains only one electron.

As to the rest of the elements of the long periods, which contain more than eight but less than eighteen electrons in their second last layer, they can lose part of the electrons of that layer besides their outer electrons, namely, the number necessary for the remaining electrons to form a stable octet shell. For instance, the element scandium (No. 21) can lose only three electrons, titanium four, vanadium five, etc. The total number of electrons which can be lost determines the maximum valency of these elements indicated by their group number.*

Long before the appearance of the theory of atomic structure a definite relationship was found to exist between the maximum oxygen valency of an element and its hydrogen valency, the sum of these valencies always equalling 8.

This relationship is easily explained from the standpoint of the electronic conception of valency. Since the atoms of all elements (with the exception of fluorine) are positively charged in oxygen compounds and negatively in their compounds with hydrogen, the oxygen valency is precisely the positive valency due to loss or displacement of valency electrons; on the other hand, the hydrogen valency is a negative valency manifested by the atom gaining the number of electrons needed to form an octet in its outer layer. It is clear that the sum of these two valencies must equal eight.

It should be noted, however, that this rule pertains only to non-metals forming gaseous compounds with hydrogen.

There are some metals which also form compounds with hydrogen, but these compounds are solids, not gases. In the latter the metal is charged positively owing to its lower electro-negativity, and the hydrogen is negatively charged. In this case the hydrogen valency is a positive valency, and, of course, equals the oxygen valency of the metal.

As was indicated in § 32, the elements of each group of the Periodic Table, beginning with the fourth horizontal series, are divided into two subgroups: an even subgroup, consisting of elements with predominantly metallic properties, and an odd subgroup, containing elements with weaker metallic properties or with predominantly non-metallic properties.

The difference in properties of the elements of the even and odd subgroups follows directly from the structure of their atoms. While there are never more than two electrons in the outer layer of the atoms of elements of the even subgroups, atoms of elements of the odd subgroups may contain as many as seven outer electrons. Therefore the *elements of the even subgroups do not gain electrons, which characterizes them as metals.*

* This does not hold for the elements of the eighth group.

The odd subgroups also contain metals, but consist mainly of elements that gain electrons readily, i.e., of non-metals.

The strengthening of the metallic properties of the elements of the main subgroups with increasing atomic numbers can also be easily explained by the structure of their atoms. Although their nuclear charge increases with their atomic number, the number of electron layers in their atoms increases simultaneously, as well as the repulsive action of those layers on the outer electrons. Their atomic radii also increase considerably, lowering their ionization potentials and, therefore, their non-metallic properties.

57. Radioactive Elements and Their Disintegration. Up till now in considering the periodic system we have left aside the radioactive elements and their position in the Table. To elucidate this question we shall have to consider radioactive phenomena in greater detail than we did in Chapter IV.

After the discovery of the radioactivity of uranium salts in 1896, it was found that the compounds of thorium, radium, polonium, actinium and a number of other elements are also radioactive. Many of the radioactive elements occur in nature in almost imponderable quantities. Obviously, under such conditions their investigation meets with tremendous difficulties. However, these difficulties have been successfully overcome and at present the chemical properties of almost all the radioactive elements have been determined experimentally.

Radioactive elements possess all the properties of ordinary elements: they have quite definite atomic weights, form chemical compounds in accordance with their position in the Periodic Table and give characteristic spectra. But besides these properties, which are common to all the elements, they possess a specific capacity for radiating energy over long periods of time.

The rays emitted by radioactive elements fall into three groups: alpha rays, beta rays and gamma rays.*

The atoms of the radioactive elements are unstable and gradually disintegrate, forming new atoms, new chemical elements differing in properties from the parent elements (for instance the atoms of the metal radium break up into the inert gases radon and helium). The disintegration of the atoms is accompanied by the emission of alpha and beta particles, in quantities depending on the number of atoms disintegrating. The emission of gamma rays is a secondary phenomenon usually caused by the beta rays, just like a cathode discharge striking the anticathode causes the emission of X-rays (§ 36).

* It will be remembered that alpha rays are streams of helium ions bearing two positive charges each, beta rays are beams of electrons and gamma rays carry no charge at all, but, like X-rays, are electromagnetic oscillations propagated at the velocity of light.

The long-term radiation of energy by radioactive substances at first sight seems to contradict the Law of Conservation of Energy. Actually there is no contradiction at all, inasmuch as the source of radiated energy is the internal energy of the atoms, which decreases as they change into other atoms.

The change of energy accompanying the disintegration of atoms of radioactive elements is much greater than the change of energy in ordinary chemical reactions. It has been calculated, for instance, that the complete decay of one gram of radium is accompanied by the liberation of 3.7×10^6 Cal., i.e., approximately 500,000 times as much as during the combustion of one gram of coal. For this reason radioactive disintegration is practically not affected by the temperature and remains the same at the lowest and at the highest temperatures.

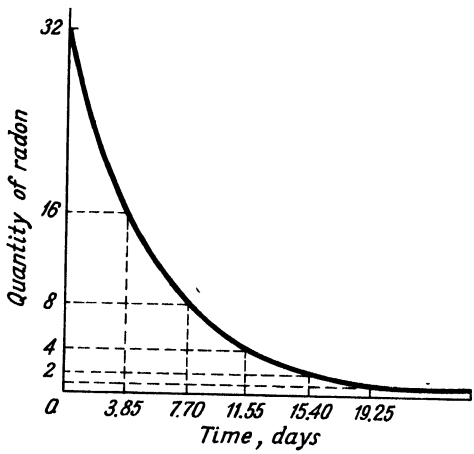


Fig. 49. Rate of disintegration of radon

The rate of decay of radioactive elements varies enormously. It is characterized by the so-called **radioactive constant**, indicating the fraction of the total number of atoms of the radioactive element actually present that disintegrates per second. The higher the radioactive constant, the faster the element disintegrates.

The rate of disintegration does not remain constant in time. A study of the process of radioactive decay shows that the *quantity of atoms of a radioactive element, breaking up at each given moment, is proportional to the quantity of atoms actually present.* It follows, therefore, that if half the radioactive element present breaks up in the course of a certain period of time, half the remainder, i.e., half as much, will disintegrate in the next equal period; the amount that disintegrates in the period after that will be again half as much as in the previous period, etc.

For instance, it has been established by observing the change in quantity of radon, that one half of the initial amount remains after 3.85 days, $^1/_4$ after another 3.85 days, then $^1/_8$, etc.

The rate of disintegration of radon is shown graphically in Fig. 49, where the time is plotted along the horizontal axis and the quantity of radon along the vertical axis. The time necessary for half the

initial quantity of a radioactive element to decay is called its *half-life period.* This value characterizes the lifetime of the element. For various radioactive elements it varies over an immense range, from fractions of a second to billions of years. In particular, the half-life period of radium equals 1,580 years, i. e., any definite quantity of radium, whatever that quantity may be, diminishes to one half in 1,580 years.

58. Radioactive Series. Elucidation of the nature of radioactivity led to the striking conclusion that elements can change into one another by disintegrating. If the resulting element is radioactive, it breaks down further into a third element, and so on until it turns into an element incapable of further decay. A series of such elements is called a radioactive series. By way of example we may consider the changes taking place in radium. As we know, radium disintegrates to form radon, a radioactive element which breaks up in its turn, forming radium A. The latter is also radioactive and upon decay forms a succession of other radioactive elements—radium B, radium C, etc. The end product of this series is radium G, which is quite a stable element, identical in chemical properties to ordinary lead.

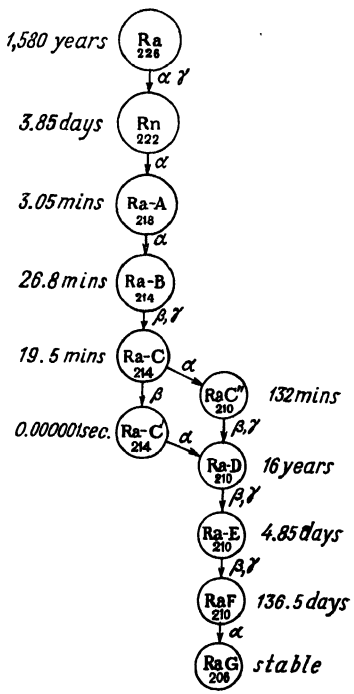


Fig. 50. Diagram of transformations of radium

The entire process of successive transformations of radium is shown schematically in Fig. 50, in which the atomic weights of the elements, their half-life periods and the rays emitted during each transformation are indicated.

Uranium, thorium, and actinium, which also possess radioactive properties, disintegrate in a way similar to radium. A study of these transformations has shown that radium is itself but an intermediate link in the long chain of transformation products of uranium, from which it originates according to the scheme in Fig. 51.

At present there are three series of natural radioactive elements known, the starting points of which are uranium, thorium and actinium (see Appendix, p. 691). The end product of all three series is lead. Besides, recently a fourth radioactive series has been discovered,

which begins with the artificially produced element neptunium and ends with bismuth.

The presence of lead in uranium ores leads to an interesting conclusion regarding the age of our planet. Knowing the half-life periods of the radioactive elements in the uranium series, we can easily calculate the time needed for a certain part of the uranium to change into lead. The lead content in uranium ores constitutes an average of 20 per cent. If we calculate therefrom the time of its formation

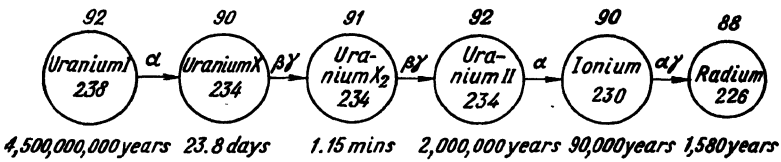


Fig. 51. Diagram of transformations of uranium into radium

from the ore we get 1,500 million years. But since the uranium ore cannot be older than the earth's crust, the same figure shows the minimum age of the earth.

59. Isotopes. The study of radioactivity enriched chemistry with the knowledge of a large number of new chemical elements. All these elements had to be arranged somehow in the Periodic Table. But there immediately arose a difficulty consisting primarily in the fact that the number of blank spaces in the Table was far smaller than the number of radioactive elements. This led investigators to study the chemical properties of the radioactive elements, whereas prior to this they had been interested almost exclusively in their radioactive properties. It was soon established that many of the radioactive elements, though of different atomic weights and radioactive properties, were practically identical in their chemical properties. For instance, ionium, one of the products of uranium decay, turned out to be chemically indistinguishable from thorium, radium B from radium D and radium G, etc.

But if several elements possess identical chemical properties it is quite logical to place them in the same box of the Periodic Table. It was on these grounds that all the radioactive elements were arranged in the Table, seven radioactive elements falling, for instance, into the same box as lead. Groups of elements occupying the same position became known as **pleiads** and the elements constituting the pleiads, and hence possessing identical chemical properties but different atomic weights, were called **isotopes.***

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

To comprehend the origin of isotopes we must turn to the transformations of radioactive elements and consider them from the standpoint of the theory of atomic structure.

We know already that the transformations of radioactive elements are accompanied by the emission of alpha particles, i. e., helium nuclei possessing two positive charges, and beta particles or electrons; at the same time, gamma rays are also sometimes emitted. Since the atom of any element consists of a nucleus and electrons it is evident that the alpha particles can originate only in the nucleus. The same must be assumed concerning the beta particles which cannot be the electrons surrounding the nucleus, because in losing the latter the atom is merely converted into a positive ion, but does not become an atom of another element. At the same time, there are some radioactive changes which are accompanied by the emission of only beta particles.

Hence arose the assumption that the nuclei of radioactive elements are complex formations consisting of helium nuclei and electrons. Of course, since the nucleus as a whole is charged positively, the number of positive charges on it is greater than the number of electrons.

60. Law of Shift. Now let us see how the properties of the elements change during radioactive transformations depending on the particles emitted. The relationship observed in this connection is very simple and is known as the **Law of Shift:**

> *An element formed from another element by the emission of alpha rays occupies a position in the Periodic Table in accordance with its chemical properties, two groups to the left of the parent element; an element formed by beta radiation is shifted one group to the right of the parent element.*

The Law of Shift follows directly from the theory of atomic decay, if we assume that not only alpha particles, but beta particles as well, are ejected from the nucleus. With the loss of an alpha particle the charge on the nucleus decreases by two units and therefore the atomic number also becomes two units smaller, as a result of which the element shifts two places to the left in the Periodic Table (for instance, radium is in the second group, whereas radon, derived from it, is in the zero group). On the other hand, the emission of a beta particle increases the charge on the nucleus by one, and the element shifts one position to the right.*

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* As new neutral atoms (and not ions) are formed during radioactive changes, it is evident that the emission of alpha particles by the nucleus of a radioactive element must be accompanied by a simultaneous loss of two electrons from the outer shell of the atom, and the emission of beta particles by a gain of one electron in the outer shell.

The table in Fig. 52 is a graphic illustration of the Law of Shift. The table shows the successive shifts of radioactive elements formed during the decay of uranium, thorium and actinium from group to group of the periodic system.

The theory of atomic decay not only determines the position of the disintegration products in the Periodic Table, but makes it possible also to calculate their atomic weights. Indeed, when an

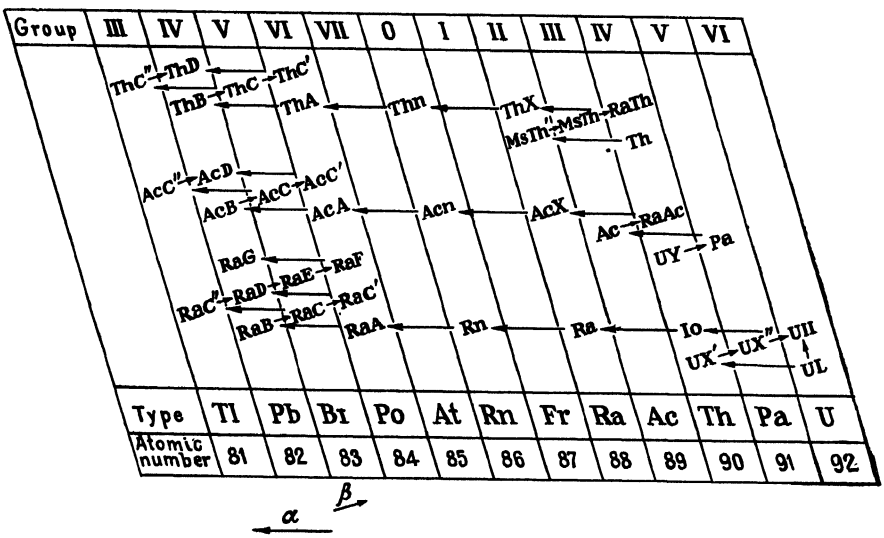


Fig. 52. Shift of radioactive elements through the Periodic Table

alpha particle is ejected from the nucleus, the mass of the nucleus, and therefore the atomic weight, decreases by four units, whereas the emission of beta particles practically does not change the mass of the atom as a whole, owing to the insignificant mass of these particles. Thus, the atomic weight of an element formed by alpha radiation is four units less than that of the parent element, while the atomic weight of an element produced by beta radiation remains practically the same as that of the parent element.

If the atom ejects first an alpha particle and then two beta particles, the charge on the nucleus (and therefore all the properties of the element) remains unchanged, but the atomic weight becomes four units less, and thus we get an isotope of the parent element. In this way, for instance, we get the isotope RaG, or lead (No. 82), from RaD (No. 82).

Establishment of the concept of isotopy made it possible, as stated above, to include all the radioactive elements in the Periodic Table. The radioactive isotopes constitute ten pleiads situated in the last

two rows of Mendeleyev's Table. The arrangement of the pleiads in the groups of the Periodic Table is shown in Fig. 52. Seven pleiads consist of radioactive elements only; the other three have one non-radioactive element each. The typical elements of each pleiad are those that have the longest lifetime, i. e., are the most stable; these elements are indicated at the bottom of the table. All the members of each pleiad have the same nuclear charge and identical chemical properties, and differ from one another only in atomic weight and radioactive properties. The pleiads of lead and polonium contain the greatest numbers of isotopic elements.

61. Isotopes of Non-Radioactive Elements. The possibility of existence of isotopes follows as a corollary from the theory of disintegration of radioactive elements. But since most radioactive elements have been obtained in very insignificant, "imponderable" quantities, the atomic weights of isotopes were calculated only on the basis of the law of radioactive decay and could not be verified by direct measurement.

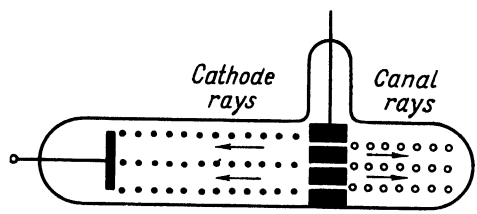


Fig. 53. Canal rays

In a short time, however, a real proof of the existence of isotopes was found. As has already been stated, the end product of disintegration of uranium and thorium is lead. But the lead derived from uranium must have an atomic weight of 206, and that from thorium, 208. Meanwhile, the atomic weight of ordinary lead is 207.2. This led scientists to investigate the lead which is always contained in uranium and thorium ores. After numerous, very exact determinations the atomic weight of uranium lead was finally established to be equal to 206.1; the atomic weight of thorium lead proved to be equal to 207.97. Thus, both lead isotopes were found in nature. They were found to be exactly identical in all chemical properties to ordinary lead and to each other, and to differ only in atomic weight. Ordinary lead is mainly a mixture of the above two isotopes.

After the discovery of the isotopes of lead there naturally arose the idea that other elements might also be pleiads of isotopes. This question was solved finally in 1922 when the English physicist Aston developed a new method of determining atomic weights, based on analysis of **canal** rays.

Canal rays are formed in a cathode-ray tube if the cathode is placed in the middle of the tube and provided with apertures ("canals"). If current is passed through such a tube, beams of invisible rays are emitted from these apertures and travel in a direction opposite to the cathode discharge (Fig. 53). The particles of the canal rays are atoms

or molecules of the substances the gas in the tube consists of, which have lost one or several electrons, and are therefore positively charged.

Taking advantage of the fact that canal rays are deflected in magnetic and electric fields, Aston constructed an apparatus which made it possible to determine the presence of isotopes in various simple substances. This apparatus was called the *mass spectrograph.*

The mass spectrograph is shown diagrammatically in Fig. 54. The canal rays pass through two narrow parallel slits A_1 and A_2 and enter the electric field between the two condenser plates B_1 and B_2 in the form of a narrow beam. Here the rays diverge, as the positively charged particles are deflected differently by

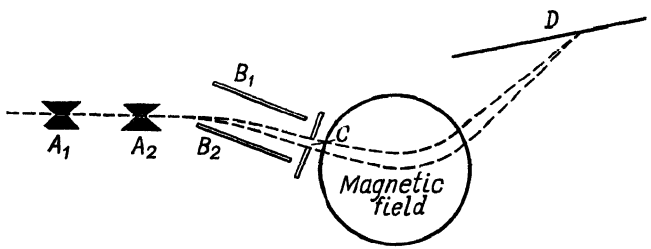


Fig. 54. Diagram of mass spectrograph

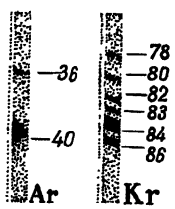


Fig. 55. Mass spectra of argon and krypton

the charged plates of the condenser, depending on their mass, charge and velocity. Part of the diverged beam is singled out by slit C and enters a magnetic field, the direction of which is such as to make the beam converge again. If all the particles are of equal mass and charge and differ only in their velocity, the convergent rays will form a distinct black line on the photographic plate D; but if the beam contains particles with different masses, a number of lines will appear on the plate, each corresponding to particles of a definite mass (Fig. 55).

Aston called this system of lines a **mass spectrum.** Knowing the position of the lines for any definite substance the masses corresponding to the other lines can be found by comparison.

Using his apparatus Aston undertook an investigation of various elements which showed that many simple substances are mixtures of isotopes. For instance, ordinary chlorine consists of two isotopes with the atomic weights 35 and 37, copper also of two isotopes of atomic weights 63 and 65; magnesium has three isotopes with the atomic weights 24, 25 and 26, etc.

Thus, the previous idea as to the absolute identity of all atoms of the same element proved to be erroneous. Many simple substances were found to consist of atoms of various weights, and what we call the atomic weight of an element is but a certain mean value, the average weight of the atoms of the simple substance. It is remarkable that the atomic weights of all known isotopes, determined with an accuracy of 0.001, were found to be whole numbers. On these grounds

Aston made the following generalization which he called the **rule of whole numbers**: *the true atomic weights of all elements are whole numbers.* All deviations of conventional atomic weights from whole numbers are due to the fact that many simple substances are mixtures of isotopes.

The isotopes of one and the same pleiad are denoted by the usual symbols used for the corresponding elements with the addition of a superscript index in their upper right-hand corner, indicating the atomic weight of the isotope. Thus the isotopes of chlorine are denoted by Cl^{35} and Cl^{37}, the isotopes of magnesium by Mg^{24}, Mg^{25} and Mg^{26}, etc.

At present all the chemical elements have been investigated for isotopes. It has been established that most elements are pleiads of isotopes and only very few of them have no isotopes at all. The number of isotopes in some pleiads is quite large; for instance, eight each have been detected for cadmium and tellurium, and ten for tin. The total number of known isotopes of only the non-radioactive elements has reached 250; if we add to this number the isotopes of the radioactive elements, both existing in nature and produced by artificial means (§ 266), the total number of discovered isotopes, i. e., types of atoms known to us, exceeds 400.

Since the chemical properties of isotopes are practically identical, their separation is a very difficult problem. Still, making use of phenomena depending mainly on atomic masses, and not on their chemical properties, it has been found possible to partially separate several simple substances into isotopes. For instance, in 1921 two fractions of mercury, differing in atomic weight by 0.189, were obtained by fractional distillation. In 1932 two almost pure fractions of Ne^{20} and Ne^{22} were isolated from ordinary neon, and in 1939 the isotopes of chlorine were separated completely by repeated diffusion. At present a large number of isotopes of various elements have been obtained in the pure form by this method.

It was stated above that the chemical properties of isotopes are practically identical. This means that even if there is any difference between the chemical properties of isotopes, it is so small that we have as yet been unable to detect it. An exception to this are the isotopes of hydrogen, H^1 and H^2, discovered in 1932. Owing to the great relative difference between their atomic weights (one isotope is twice as heavy as the other) the properties of these isotopes are perceptibly dissimilar. In consequence of this, they have been separated completely from one another by chemical means. The hydrogen isotope having an atomic weight of 2 is called **deuterium** and is denoted by a special symbol D. Deuterium is present in ordinary hydrogen in quantities of about 0.017 per cent. There is also a radioactive isotope of hydrogen H^3, called tritium (half-life around

twelve years) which can be produced only by artificial means. Tritium has not been discovered in nature.

Heavy Water. Upon the electrolysis of ordinary water, which together with the molecules of H_2O contains an insignificant quantity of D_2O molecules formed by the heavy isotope of hydrogen, the molecules decomposed are predominantly those of H_2O. Therefore, if water is electrolyzed for a long time, the residue is gradually enriched in D_2O molecules. By repeated electrolysis and distillation Lewis and MacDonald succeeded in 1933 in evolving from such a residue a small amount of water consisting almost entirely of D_2O molecules, which was called "heavy water".

The properties of heavy water differ essentially from those of ordinary (light) water.

Below are given some of the constants of ordinary and heavy water.

	H_2O	D_2O
Molecular weight	18	20
Freezing point, degrees C	0	3.82
Boiling point, degrees C	100	101.4
Density at 20°C	0.9982	1.1056
Maximum density temperature, degrees C	4	11.6

Heavy water dissolves salts less readily than ordinary water. The difference in properties of heavy and ordinary water becomes especially distinct in chemical reactions: reactions with heavy water are much slower than with light water. Investigation of the influence of heavy water on vital processes revealed its strong biological effect on certain organisms.

Heavy water has found practical application as a moderator in nuclear reactors (see § 267).

Besides heavy water, many other compounds have been obtained containing deuterium instead of ordinary hydrogen. Such are, for example, heavy ammonia ND_3, heavy hydrogen chloride DCl, etc.

The production of heavy water, as well as the separation of the isotopes of many elements, has founded a rapidly developing new field of chemistry, namely, the chemistry of isotopes.

Isotopic Indicators. In the course of the past decade wide use has been made of so-called isotopic indicators or "labeled atoms" in the study of the mechanism of chemical and biological processes. Their use is based on the fact that in chemical transformations the paths of transition of any element we may be interested in can be traced by changing the concentration of one of its isotopes in one of the reactants. Since the behaviour of all the isotopes of the same element in chemical reactions is practically identical, the change in the isotopic composition of the element in the various reaction products makes it possible to trace its path.

Two examples of successful solutions of disputable problems in organic chemistry by means of the new method are given below.

1) For a long time in organic chemistry the mechanism of the reaction of saponification (hydrolytic splitting of esters into alcohols and acids) was a point of controversy. Two schemes are possible for this reaction, differing in the point of rupture and formation of the bonds. For instance, in the case of ethyl acetate:

$$CH_3CO-\boxed{OC_2H_5+H}-\overset{*}{O}H \rightleftarrows CH_3CO-\overset{*}{O}H + C_2H_5O-H \qquad (I)$$

$$CH_3COO-\boxed{C_2H_5+H\overset{*}{O}}-H \rightleftarrows CH_3COO-H + C_2H_5-\overset{*}{O}H \qquad (II)$$

The question as to which of these schemes was the right one was solved simply and unambiguously by employing for the reaction water which contained an increased amount of the heavy oxygen isotope O^{18}. The heavy isotope of oxygen (denoted in the equations by an asterisk) should pass into the acid according to equation I and into the alcohol according to equation II. The latter equation was excluded as when the alcohol obtained was burnt the resulting water was of normal density, i. e., the alcohol did not contain any heavy oxygen isotopes.

2) The use of the heavy oxygen isotope O^{18} in studying the assimilation of carbon dioxide by plants (in the experiments carbon dioxide and water enriched in O^{18} were used) indicated that it proceedes according to the equations:

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

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

Thus it was established that the oxygen returned by plants to the atmosphere comes entirely from the water and not from the carbon dioxide.

The applications of this new method of investigation were greatly extended after the discovery and production of a number of isotopes of radioactive elements (§ 266).

Investigation of the elements by Aston's method soon revealed that besides atoms of different weights forming a single pleiad of isotopes there also existed atoms of equal weights belonging to different pleiads and therefore having different nuclear charges. Examples of these are: Ar^{40}, K^{40} and Ca^{40}, Cr^{54} and Fe^{54}, Cd^{112} and Sn^{112} and others. Atoms with equal weights but different chemical properties are called **isobars.** The existence of isobars is especially graphic evidence of the fact that the mass of the atom does not determine its chemical properties, and that *the main value on which the properties of the atom depend is the charge on its nucleus.*

The discovery of isotopy called for a revision of the chemical element concept. As has already been indicated, the concept "chemical element" had recently been almost identified with the concept "atom." It was thought that there were as many chemical elements as different kinds of atoms. But now, with the discovery of isotopes, the number of different types of atoms had increased to approximately 250 (not counting the isotopes of the radioactive elements) and may continue to increase. Naturally, there arises the question whether isotopes of the same pleiad should be considered separate elements or, as previously, the same element. Many considerations (identity of the chemical properties of isotopes, difficulty of their separation and others) favour the latter treatment. That is why the International Committee on Atomic Weights resolved, as far back as 1923, to consider that a chemical element is determined by its atomic number and may consist of atoms of either identical or different weights. Elements consisting of identical atoms are usually called "pure", and those consisting of atoms of different weights—"mixed" elements.

Thus, a chemical element is a species of atoms characterized by a definite positive nuclear charge.

CHAPTER VIII

Chemical Kinetics and Chemical Equilibrium

Chemical kinetics is the branch of chemistry that deals with the velocities of chemical processes. This chapter is a brief review of the fundamentals of chemical kinetics.

62. Rate of Chemical Reactions. A study of chemical reactions shows that they can take place at very different rates. Sometimes the reaction takes place so rapidly that it may practically be considered instantaneous; such, for instance, are many reactions between salts, acids and bases taking place in aqueous solution, or reactions which we call explosions. In other cases the rate of reaction is so small that it would take years or even centuries for a perceptible amount of the reaction products to form.

The rate of velocity of a reaction is measured by the change in concentration of the reactants per unit time.

Concentration is the quantity of substance per unit volume. In measuring reaction rates concentrations are usually expressed as the number of moles of a substance contained in one litre.

Suppose that at a certain moment of time the concentration of one of the reactants was two moles per litre and a minute later became 1.8 moles per litre, i. e., diminished by 0.2 mole. The decrease in concentration shows that of the quantity of the substance in question contained in one litre, 0.2 mole reacted in the course of one minute. Hence, the change in concentration can serve as a measure of the quantity of substance which underwent transformation per unit time, i. e., a measure of the velocity of the reaction. On these grounds, the reaction rate is expressed as the number of moles per litre transformed per unit time. In the above case the reaction rate equals 0.2 mole per minute. Since substances react in equivalent quantities, the rate of reaction can be determined by the change in concentration of any of the reactants.

The velocity of each reaction depends on the nature of the reactants, on their concentration and on the conditions of the reaction (temperature, pressure, presence of catalysts).

The dependence of the reaction rate on the concentration of the reactants can easily be understood if we proceed from molecular-kinetic conceptions. By way of example let us consider a reaction between

two gaseous substances mixed in a known volume at a definite temperature.

The gas molecules travelling in all directions at rather high velocities inevitably collide with one another. They can interact, obviously, only when they collide; hence, the more often the molecules collide, the sooner the initial substances will be converted into new ones, and the higher will be the rate of reaction. But the frequency of collision between the molecules depends primarily on their number per unit volume, i. e., on the concentrations of the reactants.

It must not be thought that each collision between molecules necessarily leads to the formation of new molecules. The kinetic theory makes it possible to calculate the number of collisions taking place per unit time at any given concentration and temperature of the reactants; experimental determination of reaction rates, on the other hand, shows how many molecules actually undergo change during the same time interval. The latter number is always less than the former. Evidently, there are certain more "active" molecules, which possess more energy than the rest at the moment of collision. Chemical interaction takes place only when such active molecules collide, other molecules flying apart unchanged after collision. But no matter what the relative quantity of active molecules in each separate case, their absolute number per unit volume, and hence the number of effective collisions, increases with the concentration, which means that the reaction rate also increases.

Now let us attempt to establish a quantitative relationship between the velocity of reaction and the concentrations of the reactants. For this purpose we shall consider a concrete reaction, for instance the formation of hydrogen iodide from iodine and hydrogen:

$$H_2 + I_2 = 2HI$$

Suppose we mixed equal volumes of hydrogen and iodine vapours in a vessel at a certain temperature and compressed the mixture until the concentration of each gas became equal to 0.1 mole per litre. The reaction sets in. Let 0.0001 mole each of H_2 and I_2 be converted per minute into HI, i. e., let the rate of reaction be 0.0001 mole per minute. If we increase the concentration of one of the gases, say hydrogen, two-, three- or fourfold (by introducing the corresponding quantity of the gas into the same vessel), the number of collisions between the H_2 and I_2 molecules per unit time will obviously also increase the same number of times and therefore the rate of the reaction between them will also increase that number of times. If the concentrations of both gases are increased simultaneously, say, one twofold and the other fourfold, the reaction rate will increase eightfold and will become equal to $0.0001 \times 2 \times 4 = 0.0008$ mole per minute. Thus, we come to the following conclusion:

The rate of a chemical reaction is proportional to the product of the concentrations of the reactants.

This very important principle was established in 1867 by two Norwegian scientists Guldberg and Waage and is known as the **Law of Mass Action** or the **Law of Acting Masses.**

Passing over to a mathematical expression of the Law of Mass Action, we shall begin with the simplest reactions in which, as is the case with the formation of HI, one molecule of one substance reacts with one molecule of another. Since we are now interested only in the substances entering into the reaction, we can express such reactions by the general equation:

$$A + B = C$$

Denoting the concentrations of the substances A and B respectively by [A] and [B], and the reaction velocity at those concentrations by v, we get:

$$v = K \times [A] \times [B]$$

where K is a proportionality factor, called the velocity constant which remains invariable for any given reaction at a given temperature and characterizes the influence of the nature of the reacting substances on he rate of the reaction between them.

If we put in the above equation [A] = 1 and [B] = 1, then

$$v = K$$

Hence, it can be seen that the velocity constant K numerically equals the reaction rate when the concentrations of the reactants (or their product) equal unity.

The expression for the reaction rate has a somewhat different form when the number of molecules of one of the substances taking part in the reaction is greater than one, for instance:

$$2A + B = D \text{ or } A + A + B = D$$

For this reaction to take place, two molecules of A must collide simultaneously with one molecule of B. Mathematical analysis shows that in such a case the concentration of A must appear twice in the rate-of-reaction equation:

$$v = K \times [A] \times [A] \times [B] = K \times [A]^2 \times [B]$$

In the general case, when m molecules of A react simultaneously with n molecules of B, the rate-of-reaction equation has the form:

$$= K \times [A]^m \times [B]^n$$

The above may be illustrated by the following concrete examples:

$$H_2 + I_2 = 2HI \qquad v = K\,[H_2]\cdot[I_2]$$
$$2NO + O_2 = 2NO_2 \qquad v = K\,[NO]^2\cdot[O_2]$$

The rate of any reaction diminishes continuously in time, since the reacting substances are gradually expended and their concentration becomes lower and lower. Therefore, when we speak of the velocity of a reaction we always mean the velocity at a given moment, i. e., the quantity of substance which would undergo change if the concentrations existing at that moment were sustained artificially in the course of a definite period of time.

The conclusions concerning the dependence of the reaction rate on the concentrations of the reactants do not pertain to solid substances participating in the reaction. Since solid substances react only at their surfaces, the rate of reaction in this case depends on the surface area of the solid and not on its bulk concentration; therefore, if there are solids taking part in the reaction together with gases and dissolved substances, the reaction rate (with a definite degree of subdivision of the solid) varies only in dependence on the concentrations of the gaseous or dissolved substances. For example, the velocity of the reaction of combustion of coal

$$C + O_2 = CO_2$$

is proportional only to the concentration of oxygen:

$$v = K\,[O_2]$$

In practice, when measuring reaction rates, apparent deviations from the Law of Mass Action are often observed. This is due to the fact that *many reactions take place in several steps*, i. e., may be divided up into several consecutive simpler processes. The Law of Mass Action in this case is true for each separate elementary process, but not for the reaction as a whole. For instance, the reaction between iodic acid HIO_3 and sulphurous acid H_2SO_3 is expressed by the summary equation

$$HIO_3 + 3H_2SO_3 = HI + 3H_2SO_4$$

but the measured rate of this reaction does not increase proportionally to the cube of the H_2SO_3 concentration but almost exactly in proportion to the first degree of its concentration, apparently contradicting the Law of Mass Action. Let us assume, however, that the reaction under consideration proceeds in two steps, so that first the HIO_3 changes *slowly* into iodous acid HIO_2 (as yet an unknown compound) according to the equation:

$$HIO_3 + H_2SO_3 = HIO_2 + H_2SO_4$$

and then HIO_2 reacts *very rapidly* with H_2SO_3 forming HI and H_2SO_4:

$$HIO_2 + 2H_2SO_3 = HI + 2H_2SO_4$$

In this case the *observed* reaction rate will obviously be determined by the rate of the former, slower process, i. e., according to the Law of Mass Action, it should increase proportionally to the first and not third power of the concen-

tration of H_2SO_3. (Actually, this reaction takes place in an even more complex manner.)

Investigations have established that most gaseous reactions take place in a very complex manner and do not obey the Law of Mass Action in its simple form. Therefore, the conventional chemical reaction cannot give a reliable idea of how the reaction rate will change depending on the concentration, unless supplemented by a study of the actual mechanism of the reaction.

The investigations of the Russian scientist N. Shilov were devoted to ascertainment of the mechanism of chemical reactions, the chief problem of chemical kinetics. Shilov studied the kinetics of chemical reactions in solution, particularly, the mechanism of what are known as "conjugate reactions".

If of two reactions with one common participant

$$\text{(I)}\quad A + B \rightarrow M \quad \text{and} \quad \text{(II)}\quad A + C \rightarrow N$$

the second will not proceed without the first, the reactions are called conjugate. The substance A, participating in both reactions, is called the **actor**. The substance B, reacting directly with the actor, is called the **inductor**, and the substance C, reacting with A only in the presence of an inductor, is called the **acceptor**.

One of the examples of conjugate reactions is the oxidation of arsenous acid H_3AsO_3 by bromic acid $HBrO_3$ in the presence of sulphurous acid. Bromic acid (in this case the actor) oxidizes sulphurous acid, but does not oxidize arsenous acid directly. However, if a mixture of sulphurous and arsenous acids is treated with bromic acid, both are oxidized.

Shilov's theory explains the mechanism of conjugate reactions by the fact that a chemical reaction usually does not take place directly, according to its summary equation, but passes through a series of intermediate steps. Thus, for instance, the reaction between bromic and sulphurous acids is expressed summarily by the equation

$$HBrO_3 + 3H_2SO_3 = 3H_2SO_4 + HBr$$

This equation reveals only the general results of the reaction, but gives no idea of its course. The $HBrO_3$ molecule can hardly be expected to react with three molecules of H_2SO_3 at once. It is much more probable that the reaction actually takes place by steps:

$$HBrO_3 + H_2SO_3 = H_2SO_4 + HBrO_2$$
$$HBrO_2 + H_2SO_3 = H_2SO_4 + HBrO$$
$$HBrO + H_2SO_3 = H_2SO_4 + HBr$$

Bromic acid itself cannot oxidize arsenous acid; however, one of the intermediate reaction products (for instance, $HBrO_2$ or HBrO) may be capable of doing so. This accounts for the fact that bromic acid oxidizes arsenous acid only in the presence of an inductor, namely H_2SO_3.

The above example shows that in conjugate reactions the inductor acts very much like a catalyst, causing a reaction which will not take place in its absence. However, a sharp line must be drawn between inductors and catalysts: the former are used up during the reaction whereas the latter are not.

A very important factor for the reaction rate, besides the concentration, is the temperature. It has been established by experiment that the reaction rate increases two- or threefold for every ten-degree rise of temperature. If the temperature is lowered the reaction rate decreases an equal number of times. The factor showing the num-

ber of times the rate of any definite reaction increases when the temperature is raised 10° is called the *temperature coefficient of the reaction.*

Assuming the temperature coefficient of a reaction to be two, it will readily be found that if, for instance, the reaction takes ten minutes at 0° C it will take only 0.6 seconds at 100° C. On the other hand, a reaction completed in ten minutes at 100° will take about seven days at 0° . Hence it is clear that many reactions which proceed rapidly at high temperature, take place so slowly at ordinary temperature that they do not seem to us to take place at all (for instance, the formation of water from hydrogen and oxygen).

The rapid growth of reaction rates with rising temperatures cannot be attributed only to the increase in the number of collisions between molecules. According to the kinetic theory the velocity of the molecules increases in proportion to the square root of the absolute temperature, while the rate of reaction increases much more rapidly. It must be considered that a rise in temperature not only causes more frequent collisions, but increases the number of effective collisions resulting in chemical interaction as well, i. e., increases the relative quantity of active molecules. This may be attributed to the fact that as the temperature rises the molecules become less stable and therefore more amenable to chemical reaction.

Finally, the third factor which greatly influences the reaction rate is the presence of catalysts, substances which alter the reaction rate, themselves remaining chemically unchanged and quantitatively undiminished after the reaction. Usually the influence of catalysts is manifested in acceleration of the reaction. Sometimes the catalyst may increase the reaction rate one thousandfold and more. Catalysts are, as a rule, finely ground metals.

In considering the influence of various conditions on the rate of reaction we considered mainly reactions which take place in uniform or **homogeneous** systems (gas mixtures, solutions). Reactions in **heterogeneous** systems are much more complex.

A system is called heterogeneous if it consists of two or more components having different physical and chemical properties and separated from one another by interfaces. The separate uniform parts of a heterogeneous system are called its **phases.** For instance, ice, water and the water vapour above them form a heterogeneous system consisting of three phases: solid (ice), liquid (water) and gas (water vapour). An acid and a piece of metal dropped into it form a system of two phases, etc.

In a heterogeneous system the reaction always takes place at the interface between two phases, since only there do the molecules of both phases collide. For this reason, besides the above three factors, the velocity of a heterogeneous reaction depends on the surface area

of contact between the reacting phases. Any increase in the surface area leads to an increase in the reaction rate. For instance, pulverized coal, having a large surface area, burns much more rapidly than lump coal; metals dissolve much more quickly in acids when finely divided, etc. Another important factor influencing the rate of a heterogeneous reaction is diffusion, by virtue of which fresh portions of the reacting substances are brought to the phase boundary. The velocity of a reaction can be increased considerably by artificially accelerating diffusion through shaking, mixing or stirring.

63. Chemical Equilibrium. Many chemical reactions proceed in such a way that the initial substances are transformed entirely into the reaction products, in which case we say that *the reaction is complete.* Thus, when potassium chlorate is heated it changes entirely into potassium chloride and oxygen:

$$2KClO_3 = 2KCl + 3O_2$$

The reverse reaction, namely, the production of potassium chlorate from potassium chloride and oxygen, has been found impossible to effect, at least, under any conditions known to us. Reactions of this kind are called practically **irreversible or one-way reactions.**

Of a different nature is the reaction between hydrogen and magnetic iron oxide. If we pass hydrogen over heated iron oxide the latter changes into iron, while the hydrogen combines with oxygen of the oxide to form water:

$$Fe_3O_4 + 4H_2 = 3Fe + 4H_2O$$

On the other hand, if powdered iron is subjected to the action of water vapour at the same temperature, magnetic iron oxide and hydrogen result. This reaction is expressed by the same equation as above, read from right to left:

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2$$

Thus, two directly opposite reactions take place at the same temperature: the iron oxide reacting with the hydrogen changes into iron and water vapour, and the latter react to form oxide and hydrogen again.

Processes which can take place in both directions under the same conditions are called **reversible.**

To show that a chemical process is reversible, the equality sign in the equation of the reaction is replaced by two arrows pointing in opposite directions:

$$Fe_3O_4 + 4H_2 \rightleftarrows 3Fe + 4H_2O$$

The reaction proceeding from left to right is conventionally called the **forward reaction** and the opposite reaction is called the **reverse, or back reaction.**

A characteristic feature of reversible reactions is that they are not complete unless the resultants are removed from the sphere of reaction (e. g., *reactions between gases in a closed vessel*). Even though the reactants may be taken in equivalent quantities, they are never used up completely to form the reaction products. The reaction proceeds only to a certain limit and then apparently stops.

To illustrate this let us consider a concrete example. At a high temperature carbon dioxide and hydrogen react to form carbon monoxide and water. This reaction is reversible and can be expressed by the equation

$$CO_2 + H_2 \rightleftarrows CO + H_2O$$

It has been established by experiment that if one gram-molecule of carbon dioxide is mixed with one gram-molecule of hydrogen and the mixture heated to 1,200° C the reaction limit will be reached as soon as 0.6 gram-molecule of carbon monoxide and an equal quantity of water vapour form. Hence, of the initial substances taken, 0.4 gram-molecule of carbon dioxide and 0.4 gram-molecule of hydrogen remain unchanged:

	CO_2	$+ H_2 \rightleftarrows$	CO	$+ H_2O$
Initial quantities of reactants (in gram-moles)	1	1	0	0
Quantity of substances after reaction limit is reached (in gram-moles) .	0.4	0.4	0.6	0.6

It will be readily understood that the "cessation" of the reaction in question is due to the functioning of a back reaction. Indeed, after the carbon dioxide is mixed with the hydrogen, a reaction sets in between the two resulting in the formation of carbon monoxide and water. As this reaction proceeds the concentration of the initial substances decreases, so that the reaction rate becomes slower and slower. At the same time the back reaction becomes possible. The molecules of carbon monoxide and water colliding with one another can recombine into molecules of carbon dioxide and hydrogen. At first, while the number of carbon monoxide and water molecules is small, they collide rather rarely. But as the molecules of these substances accumulate, the collisions become more and more frequent, gradually increasing the velocity of the back reaction. At length the velocity of the back reaction becomes equal to that of the forward reaction, i. e., the number of molecules of carbon dioxide and hydrogen disappearing in each unit of time becomes equal to the number of them reappearing as a result of the back reaction. From this moment on the concentrations of all four gases remain unchanged, despite the fact that the initial carbon dioxide and hydrogen have not reacted completely.

If we began with carbon monoxide and water instead of carbon dioxide and hydrogen we should have come to the same result.

A state of a system of reacting substances in which their concentrations do not change is called chemical equilibrium. Chemical equilibrium is attained when the rate of the forward reaction becomes equal to that of the back reaction.

The reaction appears to have ceased. But actually this is not the case; both reactions continue to proceed, but one of them cancels the results of the other.

Since chemical equilibrium is not due to cessation of the reaction but to equality of the rates of two opposite processes, it is essentially a dynamic equilibrium. It can be compared, for instance, with the equilibrium of water in a reservoir which is being simultaneously filled and discharged. If the amount of water entering the reservoir equals the amount flowing out of it, the quantity of water in the reservoir will stop changing, just as the quantity of each of the substances stops changing when chemical equilibrium is reached.

A chemical equilibrium, once established between any given substances, will last indefinitely if the conditions remain unaltered. But a change in concentration of even one of the participants will immediately disturb the equilibrium of the reaction and cause changes in the concentrations of all the other substances as well.

For instance, suppose some additional carbon dioxide is introduced into a vessel containing carbon dioxide, hydrogen, carbon monoxide and water vapour in equilibrium with each other. The increase in the concentration of the carbon dioxide will obviously accelerate the left-to-right reaction, making it predominate temporarily over the back reaction. As a result of this, the concentrations of carbon dioxide and hydrogen gradually begin to decrease, while those of carbon monoxide and water increase. This change in concentrations will continue until the accumulation of molecules of carbon monoxide and water on the one hand, and the disappearance of carbon dioxide and hydrogen on the other, equalize the velocities of both reactions. Then equilibrium is restored, but now with different concentrations of all four substances.

The change of concentration caused by a disturbance of equilibrium is called a displacement or shift of equilibrium. If the concentrations of the substances in the right half of the equation increase (of course, with a corresponding decrease in the concentrations of the substances in the left), we say that the equilibrium *has shifted to the right* or in the direction of the forward reaction; if the concentration undergoes the opposite change, we say that the equilibrium *has shifted to the left.* For instance, in the above case the equilibrium shifts to the right, as it is the concentrations of the carbon monoxide and the water that increase.

Now let us express the condition of equilibrium in mathematical form.

Suppose we have a reversible reaction expressed by the general equation:

$$A + B \rightleftarrows C + D$$

where A and B are two substances which react to form two new substances C and D. Let the concentrations of these substances be, respectively, [A], [B], [C], and [D]. Suppose the rate of the reaction proceeding in the direction of the upper arrow is v_1, and that of the reverse reaction v_2. Since the reaction rate is proportional to the product of the concentration of the reacting substances, then for the forward reaction

$$v_1 = K_1 \cdot [A] \cdot [B]$$

Similarly, for the back reaction

$$v_2 = K_2 \cdot [C] \cdot [D]$$

When equilibrium is established the velocities of both reactions become equal, i. e.,

$$K_1 \cdot [A] \cdot [B] = K_2 \cdot [C] \cdot [D]$$

Modifying this equation we get:

$$\frac{[C] \cdot [D]}{[A] \cdot [B]} = \frac{K_1}{K_2}$$

Since K_1 and K_2 are constants, their ratio is also a constant. Denoting it by K, we have:

$$\frac{[C] \cdot [D]}{[A] \cdot [B]} = K$$

where [C], [D], [A] and [B] denote the concentrations of the respective substances in equilibrium.

The constant K is called the **equilibrium constant.** It is a value characteristic for each reaction and does not depend on the concentration, but varies with the temperature. Its physical sense will easily be understood if we remember that it equals the ratio $K_1 : K_2$ and therefore shows by how many times the velocity of the forward reaction exceeds that of the back reaction at equal temperatures and with unit concentrations.

The above equation is the mathematical expression of the Law of Mass Action, applied to reversible reactions. Its sense may be formulated as follows:

In reversible reactions equilibrium is attained when the product of the concentrations of the resultants divided by the product of the concentrations of the reactants equals a certain constant value for the reaction in question at a given temperature.

If more than one molecule of each of the substances is involved in the reaction:

$$mA + nB = pC + qD$$

the equation of the equilibrium constant becomes

$$\frac{[C]^p \cdot [D]^q}{[A]^m \cdot [B]^n} = K$$

If there are solids participating in the reaction their concentrations are not included in the expression for the equilibrium constant for the same reason that they are not included in the expression for the rate of reaction (see p. 186). Thus, in the case of the reaction between carbon dioxide and heated coal

$$CO_2 + C \rightleftarrows 2CO$$

the equilibrium constant is expressed as the ratio:

$$K = \frac{[CO]^2}{[CO_2]}$$

The equilibrium of the above reaction can be disturbed only by changing the concentration of carbon dioxide or carbon monoxide; neither increase, nor decrease of the quantity of coal can influence the state of equilibrium.

Using the equation for the equilibrium constant, we can easily determine which way the equilibrium will shift if the concentration of any of the reacting substances is changed. This can be shown, by way of example, for the reaction between carbon dioxide and hydrogen considered above.

The equilibrium constant of this reaction is expressed by the equation

$$K = \frac{[CO] \cdot [H_2O]}{[CO_2] \cdot [H_2]}$$

Suppose that after equilibrium was established, we increased the concentration of hydrogen in the gaseous mixture. Since the ratio

$$\frac{[CO] \cdot [H_2O]}{[CO_2] \cdot [H_2]}$$

must remain constant, increasing the denominator of the fraction (the concentration of hydrogen) disturbs the equilibrium and will accelerate the reaction leading to a decrease of the denominator and a simultaneous increase of the numerator, i.e., the reaction of transformation of carbon dioxide and hydrogen molecules into molecules of carbon monoxide and water. When, as a result of this the previous ratio between the reacting substances is restored, equilibrium will again be established, but now the concentration of carbon dioxide

will be lower than it was before the hydrogen was added, while the concentration of water vapour and carbon monoxide will be higher. A similar result would obviously be obtained if we increased the concentration of carbon dioxide (as established above) or if we decreased the concentration of carbon monoxide of water vapour. In all these cases the equilibrium shifts towards the formation of carbon monoxide and water vapour. On the other hand, increase of the concentration of carbon monoxide and water vapour or decrease of the concentration of carbon dioxide and hydrogen will cause the opposite effect, i.e., an equilibrium shift towards the formation of new quantities of carbon dioxide and hydrogen.

Two very important conclusions can be drawn from all this.

1. In order to use up one of the reactants of a reversible reaction more completely, an excess of the other reactant must be used.

2. If one of the resultants is removed from the sphere of reaction as it forms, the equilibrium will shift towards the formation of that product, and thus the reversible reaction can practically be completed. For instance, if the water formed as a result of the reaction between carbon dioxide and hydrogen is continuously removed from the reaction mixture, these gases can be completely converted into carbon monoxide and water vapour.

Likewise, when hydrogen is passed over heated magnetic iron oxide (see p. 190), the latter is completely converted into metallic iron, as the water vapour formed during the reaction is continuously removed from the sphere of reaction together with the excess of hydrogen. In a closed vessel this reaction will not go to completion.

The constancy of the ratio between the concentrations of reacting substances at equilibrium makes it possible to carry out a number of very important calculations. Given below are several typical examples of such calculations for simple reactions.

Example 1. A reversible reaction is expressed by the equation: $A + B \rightleftarrows 2C$. When equilibrium was attained the concentrations of the three substances were [A] = [B] = 3 moles per litre; [C] = 4 moles per litre. Find the equilibrium constant and the initial concentrations of A and B.

The equilibrium constant of the above reaction is given by the equation

$$K = \frac{[C]^2}{[A] \cdot [B]}$$

Substituting the concentrations into this equation, we find:

$$K = \frac{4^2}{3 \cdot 3} = \frac{16}{9} = 1.78$$

To determine the initial concentrations of A and B it must be taken into account that according to the equation of the reaction one molecule of A and one molecule of B react to form two molecules of C. Hence it follows that the formation of four moles of C requires the expenditure of two moles of A and two

moles of B. Thus, the initial concentrations of A and B were five moles per litre each.

Example 2. The equilibrium constant for the reaction $A + B \rightleftarrows C + D$ equals two. Compute the concentrations of the four substances at equilibrium if the initial concentrations of A and B were:

$$[A]=5 \text{ moles per litre}; \quad [B]=1 \text{ mole per litre}$$

It can be seen from the equation of the reaction that one gram-molecule of C and one of D are formed from each gram-molecule of A and B. Let the number of moles of A and B that have reacted be x. Then the concentrations of all four substances at equilibrium will be as follows:

$$[C]=[D]=x; \quad [A]=5-x; \quad [B]=1-x$$

Substituting these values into the equilibrium constant equation we get:

$$2=\frac{x^2}{(5-x)\cdot(1-x)}; \quad x^2-12x+10=0; \quad x_1=11.1; \quad x_2=0.9$$

Discarding the first root as impossible, we find the concentration at equilibrium: [C] = [D] = 0.9 mole per litre; [A] = 4.1 moles per litre; [B] = = 0.1 mole per litre.

It is easy to see that under these conditions

$$\frac{[C]\cdot[D]}{[A]\cdot[B]}=2$$

64. Le Châtelier's Principle. Having examined the influence of changes in concentration of the reacting substances on the state of equilibrium, we can now consider the influence of changes in temperature and pressure on equilibrium.

Raising the temperature accelerates all chemical reactions in general, but the acceleration is different with different reactions. In most cases the velocities of the forward and back reactions do not change equally and one of them begins to proceed more rapidly. However, accumulation of the resultants of the predominating reaction on the one hand and disappearance of its reactants on the other gradually equalize the rates of both processes. Thus equilibrium is re-established, but now with other concentrations of each of the substances than before. Hence it follows that each temperature has a corresponding state of equilibrium, just as, for instance, each temperature has a corresponding solubility of substance.

The direction in which the equilibrium shifts due to temperature changes is determined by the **Law of Van't Hoff**, which applies to any system in equilibrium:

> *If the temperature of a system in equilibrium changes, an increase in the temperature will shift the equilibrium in the direction of the process during which heat is absorbed, and a decrease will shift it in the opposite direction.*

In relation to reversible chemical processes, this means that a rise in temperature causes a shift of equilibrium towards the endothermal

reaction, while a decrease in temperature will shift the equilibrium in the reverse direction.

Here are some examples:

Hydrogen iodide decomposes, when heated, into iodine and hydrogen. The reaction is reversible and at high temperatures proceeds from left to right with the absorption of heat:

$$2HI \rightleftarrows H_2 + I_2 - 12 \text{ Cal.}$$

If the temperature is raised, the equilibrium shifts to the right, the concentration of hydrogen and iodine in the mixture increasing and that of hydrogen iodide decreasing.

Any reversible decomposition of substance is called dissociation in chemistry. If the decomposition is due to heat it is called *thermal dissociation.*

Many other substances dissociate upon heating just like hydrogen iodide. In all such cases raising the temperature, in accordance with the Law of Van't Hoff, increases the degree of dissociation (i.e., the relative quantity of decomposed substance), shifting the equilibrium towards the formation of the dissociation products.

An example of a reaction proceeding with evolution of heat may be that of the formation of sulphur trioxide from sulphur dioxide and oxygen:

$$2SO_2 + O_2 \rightleftarrows 2SO_3 + 46.8 \text{ Cal.}$$

In this case raising the temperature would shift the equilibrium to the left, as the back reaction, obviously, proceeds with absorption of heat (see, for instance, p. 72). To shift the equilibrium to the right, i.e., to increase the content of SO_3 in the reaction mixture, the temperature should be lowered.

The Law of Van't Hoff is a particular case of a more general law determining the influence of various factors on an equilibrium system and known as **Le Châtelier's Principle.** In application to chemical equilibrium it may be formulated as follows:

> *A change in any of the conditions of the chemical equilibrium of a system, such as temperature, pressure or concentration, will shift the equilibrium in the direction of the reaction opposing the change.*

Applying this principle to a change of temperature, we see that a rise in temperature should shift the equilibrium in the direction of the reaction which will lower the temperature, i.e., which proceeds with the absorption of heat. Lowering the temperature causes a shift of equilibrium towards the reaction during which heat is evolved.

A change in pressure due to compression of the reaction mixture will result in a shift of equilibrium if gaseous substances are involved

in the reaction. In such a case, according to the Principle of Le Châtelier, the equilibrium should shift in the direction of the reaction which weakens the change made, i.e., decreases the pressure if it was increased, and increases it if it was decreased. But in a closed space at constant temperature the reaction can change the pressure only if it leads to a change in the total number of molecules of gaseous substances. For instance, the reaction of formation of nitrogen dioxide from nitric oxide and oxygen at a high temperature is reversible and is not complete:

$$2NO + O_2 \rightleftarrows 2NO_2$$

Since only two molecules of nitrogen dioxide result from two molecules of nitric oxide and one of oxygen, the transformation of nitric oxide and oxygen into nitrogen dioxide in a closed vessel will obviously cause the pressure to drop. The back reaction, namely, the decomposition of nitrogen dioxide into nitric oxide and oxygen, will lead to an increase in pressure. Therefore, if we compress the gas mixture after equilibrium has been established, thus increasing the pressure, then, according to Le Châtelier's Principle, *after* the compression the equilibrium will begin to shift to the right and the pressure will again decrease. On the contrary, if we allow the mixture to occupy a larger volume, thus lowering the pressure, the equilibrium will shift to the left, as a result of which the pressure will again rise. Thus we come to the following conclusion:

Increasing the pressure shifts the equilibrium towards the formation of a smaller number of gas molecules; decreasing the pressure shifts it towards the formation of a larger number of gas molecules.

Of course, if the number of molecules of gaseous substances does not change during the reaction as, for instance, in the reaction

$$CO_2 + H_2 \rightleftarrows CO + H_2O$$

neither increase nor decrease of the pressure will disturb the equilibrium.*

Finally, it will readily be seen that equilibrium shifts caused by changes in concentration of the reacting substances also obey Le Châtelier's Principle. Indeed, if we increase the concentration of one of the substances involved in an equilibrium, the latter always shifts in the direction of the reaction reducing the concentration of the same substance. For instance, in the reaction between carbon dioxide and hydrogen an increase in the concentration of carbon dioxide will shift the equilibrium towards the formation of carbon

* The same conclusion can be derived from the Law of Mass Action, as a change in pressure reduces essentially to a change in concentration of the reactants.

monoxide and water vapour, thus bringing the concentration of carbon dioxide down again. On the other hand, lowering the concentration of any of the substances causes a shift of equilibrium towards the formation of that substance.

Introduction of a catalyst into a system at equilibrium does not alter the state of equilibrium, as the catalyst accelerates the forward and back reactions equally. Nevertheless, the role of catalysts in reversible reactions is very great. At low temperatures owing to the low velocity of reactions, equilibrium between the reacting substances is usually attained very slowly. We would have to wait a long time for a considerable quantity of reaction products to form. Of course, equilibrium could be reached more quickly by raising the temperature, but if the formation of the product interesting us leads to the liberation of heat, the quantity we should obtain in this way would be very small, since at a high temperature the equilibrium would be greatly displaced in the direction of the back reaction. Catalysts make it possible to accelerate the attainment of equilibrium without raising the temperature, and thus to obtain the same quantity of substance in less time.

CHAPTER IX

Hydrogen

65. Hydrogen in Nature. Hydrogen (Hydrogenium; at. wt. 1.008) occurs in the free state in but negligible quantities, mainly in the upper layers of the atmosphere. Sometimes it escapes together with other gases during volcanic eruptions, as well as from drill holes during the extraction of mineral oil. But hydrogen is very abundant in the form of compounds. This is evident from the fact that it constitutes one-ninth of water by weight. Besides, hydrogen is found in all vegetable and animal substances, is a constituent part of mineral oils and many other minerals. Altogether, hydrogen constitutes approximately one per cent of the earth's crust, including water and air.

Hydrogen was discovered in the early XVI century by Paracelsus. In 1776 the English chemist Cavendish established its properties and pointed out the features distinguishing it from other gases. Lavoisier was the first to prepare hydrogen from water, and he proved that water is a chemical compound of hydrogen and oxygen (1783).

66. Preparation of Hydrogen. The hydrogen atom consists of a nucleus and one electron. Hydrogen atoms form more or less polarized covalent bonds with the atoms of non-metals. In some of these compounds (H_2O, HCl, etc.) the state of the hydrogen atom is close to that of the ion H^+.

The chief source for the preparation of hydrogen is water. Hydrogen can be prepared from it by making use of the ability of many metals to displace hydrogen from water, forming hydroxides or oxides. The alkali metals sodium and potassium, as well as calcium, barium and others, react with water very readily at ordinary temperatures.

If a piece of sodium is dropped into a dish of water a violent reaction ensues; the sodium darts, sputtering, to and fro over the surface of the water, liberating hydrogen. So much heat is given off during this reaction that the sodium melts into a ball which rapidly diminishes in size and soon disappears altogether (Fig. 56). Sometimes so much heat is given off that the hydrogen liberated bursts into flame.

The reaction between sodium and water can be expressed by the equation

$$2Na + 2H_2O = 2NaOH + H_2$$

This reaction consists essentially in a sodium atom losing an electron to a hydrogen ion of the water molecule and turning into a positively charged ion. The latter becomes part of NaOH, while the hydrogen ion turns into an atom which subsequently combines with another hydrogen atom to form an H_2 molecule. The reaction with potassium and calcium proceeds analogously.

Other metals besides those mentioned also react with water, but at higher temperatures. Thus, magnesium displaces hydrogen from

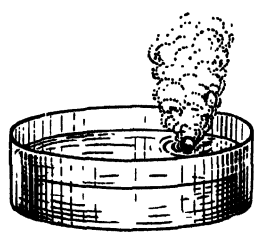


Fig. 56. Sodium ball on the surface of water

water at the boiling point of the latter, zinc and iron—only when heated in a stream of water vapour. In all these cases the hydrogen, which is in a state close to that of hydrogen-ion, gains electrons from the atoms of the metal and turns into neutral atoms.

The following are the chief methods of preparing hydrogen for industrial purposes:

1. The *steam-iron method*, based on the reaction between iron and water vapour when the latter is passed over heated iron turnings:

$$3Fe + 4H_2O \rightleftarrows Fe_3O_4 + 4H_2 + 35.6 \text{ Cal.}$$

The reaction is reversible and proceeds with evolution of heat from left to right. Therefore, according to Le Châtelier's Principle, the lower the temperature, the more the equilibrium will shift towards the formation of hydrogen. However, at low temperatures equilibrium is established too slowly, owing to the very low rate of the reaction. For this reason the reaction is accomplished in practice at temperatures not under 700°C. At 700°C the equilibrium mixture contains approximately equal volumes of hydrogen and water vapour, i.e., half the steam put through remains unused. Since the hydrogen formed is removed immediately from the sphere of reaction

together with the excess of water vapour, the process goes on continuously until all the iron is converted to magnetic iron oxide.

2. The *conversion method* consists in passing water vapour through a layer of heated coal:

$$C + H_2O = CO + H_2$$

The resulting mixture of carbon monoxide and hydrogen is known as **water gas** and can be used as gaseous fuel. If the process is carried out for the purpose of obtaining hydrogen, the carbon monoxide is removed from the mixture by passing it over heated ferric oxide together with steam, the ferric oxide acting as a catalyst. The carbon monoxide reacts with the water vapour forming hydrogen and carbon dioxide. This reaction, called **conversion** of carbon monoxide, can be represented by the equation

$$(H_2) + CO + H_2O \rightleftarrows CO_2 + H_2 + (H_2) + 10.2 \text{ Cal.}$$

At a low temperature the equilibrium favours the forward reaction, but as the temperature rises, it shifts towards the formation of the initial substances.

Since the rate of reaction is high enough only at temperatures not under 450°C, steam is added to the water gas in much greater amount than required by the equation of the reaction, as a result of which the equilibrium remains greatly displaced to the right in spite of the high temperature, thus raising the degree of conversion of carbon monoxide.

The carbon dioxide formed as a result of conversion is separated from the hydrogen by washing the gas mixture with water under a pressure of 20 atm. To finally purify the hydrogen it is passed through several more solutions which absorb all its impurities.

Large quantities of hydrogen used to produce synthetic ammonia are prepared in this way.

3. *Deep Freezing of Coke-Oven Gas.* When coal is heated without access of air to 900-1,200°C a gas is produced known as coke-oven gas, which is a mixture containing about 50-60 per cent hydrogen; the solid residue is coke. To extract the hydrogen from the coke gas the latter is cooled until all the gases except hydrogen separate out as liquids.

4. *Electrochemical Method.* If there is a source of cheap electric power at hand it is economically feasible to produce hydrogen from water by decomposing it with electricity. The advantage of this method is the high purity of the product. About 18 per cent of the world production of hydrogen is obtained by this method.

Another raw material for the production of hydrogen which has been used more and more extensively in the past fifteen years is the methane of the natural gases evolved in oil refining. In 1940, 5 per

cent of the hydrogen employed for ammonia synthesis in the U.S.A. was obtained from this new raw material; by 1945 this figure had risen to 45 per cent and by 1953 to 66 per cent.

Hydrogen can be prepared from methane by various methods:

1) by thermal decomposition of methane:

$$CH_4 = C + 2H_2 + 18 \text{ Cal.}$$

2) by the reaction between methane and water vapour:

$$CH_4 + H_2O = CO + 3H_2 - 49 \text{ Cal.}$$

3) by the reaction between methane and carbon dioxide or a mixture of carbon dioxide and water vapour:

$$CH_4 + CO_2 = 2CO + 2H_2 - 60.1 \text{ Cal.}$$
$$3CH_4 + CO_2 + 2H_2O = 4CO + 3H_2 - 158.6 \text{ Cal.}$$

4) by the oxidation of methane:

$$2CH_4 + O_2 = 2CO + 4H_2 + 16.1 \text{ Cal.}$$

In all these methods except the first the gaseous mixtures obtained contain a comparatively large amount of carbon monoxide. To increase the hydrogen yield these mixtures are subjected to conversion with water vapour.

If the hydrogen is not consumed on the spot it can be transported in a compressed state in steel cylinders in which it is kept under high pressure.

Hydrogen can be prepared in the laboratory by the action of dilute sulphuric or hydrochloric acid on zinc:

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

Iron may be used instead of zinc, but in this case the reaction is much slower.

Hydrogen produced by the action of acids on zinc and other metals always contains water vapour and certain other gaseous impurities. If dry hydrogen is required the gas is freed from water vapour by passing it through concentrated sulphuric acid, which absorbs moisture avidly. To remove other admixtures solutions of various salts are used.

67. Properties and Uses of Hydrogen. At ordinary temperatures hydrogen is a colourless, odourless gas. Below —240°C hydrogen can be converted under pressure into a colourless liquid. If this liquid is rapidly evaporated solid hydrogen results as colourless crystals melting at —259.4°C.

Hydrogen is the lightest of all gases; it is almost 14.5 times lighter than air. One litre of hydrogen at S.T.P. weighs only 0.09 gram. Hydrogen is very slightly soluble in water but dissolves in consider-

able quantities in certain metals, such as palladium, platinum and others. One volume of palladium is capable of dissolving up to 900 volumes of hydrogen.

The hydrogen molecule consists of two atoms linked together by a duplet of electrons rotating about the nuclei of both atoms. The structure of the hydrogen molecule (Fig. 57) is similar to that of the helium atom, for which reason hydrogen is inert at ordinary temperatures. At higher temperatures the bond between the atoms is weakened and hydrogen becomes active.

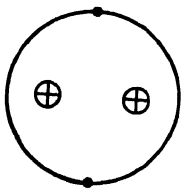


Fig. 57. Structure of hydrogen molecule

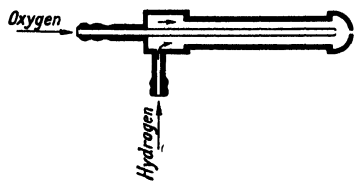


Fig. 58. Detonating gas torch

Especially interesting among the physical properties of hydrogen is its specific heat, which is considerably lower at low temperatures than might have been expected according to the kinetic theory of gases. This is due to the existence of two modifications of hydrogen known as *orthohydrogen* and *parahydrogen*. Both modifications consist of H_2 molecules and have identical chemical properties, but differ somewhat in specific heat, melting and boiling points and some other physical properties. This difference is due to the fact that the hydrogen nuclei (protons) of the H_2 molecule rotate around their axes in the same direction in *ortho*hydrogen and in opposite directions in *para*hydrogen.

At ordinary temperatures hydrogen consists of three parts of *ortho*hydrogen and one of *para*hydrogen in equilibrium with each other. Lowering the temperature shifts the equilibrium towards the formation of *para*hydrogen, and as its specific heat is lower than that of *ortho*hydrogen, the specific heat of the mixture decreases when the *para*hydrogen content in it rises.

The chemical properties of hydrogen are due to the ability of its atoms to lose their only electron and become positively charged ions. However, this change is not complete, as even in reactions with the most active non-metals, hydrogen forms polar covalent and not ionic bonds. Sometimes hydrogen atoms gain electrons to form negatively charged H′-ions having the shell of the inert gas helium. Hydrogen is present in the form of such ions in compounds with some of the most active metals (K, Na, Ca, etc.). These compounds are called metallic hydrides and, contrary to the gaseous compounds of hydrogen with the non-metals, are solid crystalline substances (hydrides will be dealt with in greater detail when describing the respective metals).

If a lighted match is applied to a jet of hydrogen issuing from a small aperture, the hydrogen ignites and burns with a pale flame, the combustion product being water:

$$2H_2 + O_2 = 2H_2O + 136.8 \text{ Cal.}$$

If a mixture of two volumes of hydrogen and one of oxygen is ignited the gases combine almost instantaneously throughout the volume of the mixture, causing a violent explosion. That is why this mixture is called **detonating gas.**

Owing to the liberation of a large amount of heat during the combustion of hydrogen, the hydrogen flame has a very high temperature ($\sim$ 1,000°C). But the temperature can be raised still higher (up to 2,500-3,000°C) by introducing an excess of oxygen into the hydrogen flame. To produce such a flame a special torch is used (Fig. 58) consisting of two tubes of different diameters, one inside the other. The hydrogen is let into the space between the tube walls and ignited at the exit. After this a jet of oxygen is carefully introduced into the hydrogen flame through the inner tube. The gases mix at the outlet aperture of the torch and give a very hot flame capable of melting almost all the metals, even the most refractory. Iron or steel wire burns in such a flame like in oxygen, throwing off brilliant sparks in all directions. If the flame is directed at a piece of lime the latter becomes white-hot and begins to emit a dazzling bright light. The oxy-hydrogen flame is used for fusing refractory metals, for **gas welding**, for cutting and drilling metals.

At ordinary temperatures hydrogen practically does not react with oxygen. If the gases are mixed and left standing in a glass vessel, no indications of water can be detected even after several years. But if a mixture of hydrogen and oxygen is placed in an airtight vessel and kept in it at 300°C a little water will form after a few days. At 500°C the hydrogen will combine completely with the oxygen in several hours, and if the mixture is heated to 700° C the temperature rises very rapidly, and the reaction is complete instantaneously. Therefore, to make the mixture explode, at least one point of it must be heated to 700°C.

The absence of any perceptible reaction between hydrogen and oxygen at ordinary temperatures is due to the fact that the rate of reaction under these conditions is very low. The reaction rate being assumed to decrease twofold with each ten-degree drop of temperature (see pp. 187-8), it can easily be calculated that if the formation of a perceptible quantity of water takes three days at 300°C, it would require over 2 million years at ordinary temperatures (20°C).

Catalysts can greatly increase the rate of reaction between hydrogen and oxygen. If, for instance, a piece of platinized asbestos (i.e.. a

piece of asbestos coated with finely divided platinum) is introduced into a mixture of hydrogen and oxygen, the reaction between the gases is so greatly accelerated that they soon explode.

At high temperatures hydrogen will abstract oxygen from many compounds, including most metallic oxides, from which it liberates the metals. For instance, if hydrogen is passed over heated cupric oxide the following reaction takes place:

$$CuO + H_2 = Cu + H_2O$$

The addition of oxygen to a metal is called **oxidation**, while the reverse process, by which oxygen is removed from the oxide and the metal thus re-liberated, is known as **reduction.**

The addition of hydrogen to any substance is also called reduction or **hydrogenation.**

Several other substances besides hydrogen, for instance coal, are capable of removing oxygen from various compounds. All such substances are called **reducing agents**, or **reductants.** Hydrogen is one of the most active reducing agents.

The applications of hydrogen are very diverse. Hydrogen is used to fill observation balloons. Owing to its very low boiling point (—252.7°C), liquid hydrogen is used to produce low temperatures. The fat industry uses hydrogen for the hydrogenation of fats, meaning the conversion of liquid vegetable oils into solids. In the fuel industry hydrogen is employed to produce liquid fuel from coal. Hydrogen is used to reduce some of the rare metals from their oxides.

The largest amount of hydrogen is used by the basic chemical industry to obtain synthetic ammonia for the production of nitric acid and artificial fertilizers.

68. Monatomic Hydrogen. If hydrochloric acid is added to a solution of ferric chloride $FeCl_3$ and a piece of zinc dropped into the solution, the hydrogen liberated rapidly converts the ferric chloride into ferrous chloride $FeCl_2$ which can be observed by the yellow colour of the solution changing to green, the characteristic colour of ferrous chloride:

$$FeCl_3 + H = FeCl_2 + HCl$$

If gaseous hydrogen is passed through a solution of $FeCl_3$, e.g., from a gas-holder, the above reaction will not take place. It may be assumed that the specific activity manifested by hydrogen in this case is due to the fact that the hydrogen reacts with ferric chloride "in statu nascendi" (at the moment of liberation) from the chemical compound before its atoms have a chance to combine into molecules.

This assumption, suggested last century, was indirectly confirmed when *monatomic hydrogen*, i.e., hydrogen consisting of separate

atoms and not of H_2 molecules, was produced in the free state and its reactivity studied.

At high temperatures the hydrogen molecule dissociates into atoms:

$$H_2 \rightleftarrows 2H$$

This reaction can be brought about, for instance, by heating tungsten wire electrically in an atmosphere of highly rarefied hydrogen. The reaction is reversible, and the higher the temperature, the more the equilibrium shifts to the right. At 2,000°C the amount of dissociated molecules is but 0.1 per cent, at 3,000°C it is 9 per cent, at 4,000°C 62.5 per cent and at 5,000°C 94.7 per cent, i.e., the dissociation is almost complete.

Monatomic hydrogen can be obtained also by the action of a silent electric discharge on ordinary hydrogen under a pressure of 0.5 mm Hg. The hydrogen atoms formed under such conditions do not reunite immediately into molecules, making it possible to study their chemical properties. Monatomic hydrogen reduces many metallic oxides even at ordinary temperatures, combines directly with sulphur, nitrogen and phosphorus; with oxygen it forms hydrogen peroxide.

When hydrogen is decomposed into its atoms a large quantity of heat is absorbed, amounting to 105 Cal. per gram-molecule:

$$H_2 \rightleftarrows 2H - 105 \text{ Cal.}$$

This shows that hydrogen atoms must be much more active than hydrogen molecules. For ordinary hydrogen to take part in any reaction its molecules must first be decomposed into atoms, which requires a large amount of energy. In reactions involving monatomic hydrogen this energy is not required.

The heat expended on the decomposition of the hydrogen molecules into atoms is liberated again when the atoms recombine into molecules.

This is the basic principle of monatomic hydrogen torches. A jet of hydrogen from a cylinder passes through an electric arc struck between two tungsten electrodes, whereupon the hydrogen molecules decompose into atoms. The latter re-unite into molecules at a short distance from the arc, producing a very hot flame. The high temperature of the flame is not due in this case to combustion of the hydrogen, but to the combination of its atoms into molecules. This process takes place especially rapidly on the surface of various metals which can be heated in such a way to temperatures over 4,000°C. All the metals melt easily in the monatomic hydrogen flame, even tungsten, the most refractory of them all (m.p. 3,370°C). Since monatomic hydrogen is a very active reducing agent, its flame is especially suitable for welding metals subject to oxidation.

69. Beketov's Metal Displacement Series. In considering the methods of preparation of hydrogen it was pointed out that some metals displace hydrogen from water more readily, others with greater difficulty and still others (iron, zinc) require a high temperature for this purpose; finally, there are some metals, such as copper and mercury, which do not displace hydrogen even at high temperatures.

In the vertical series given below the most active metals are at the top; these are the alkali metals potassium and sodium which react vigorously with water, liberating hydrogen. They are followed by the alkaline-earth metals, barium, strontium and calcium, of which only calcium, the most important among them, has been included in the series. The alkaline-earth metals are less active than the alkali metals; although they displace hydrogen from water, the reaction takes place much less violently. Magnesium, the next metal, acts on water very slowly at ordinary temperatures, while zinc and iron react only with superheated steam.

The list includes also hydrogen which, although it does not belong to the metals, is chemically similar to them.

All the metals above hydrogen in this series will displace it from dilute acids; the velocity of the reaction increases upwards from lead to potassium. Metals below hydrogen (beginning with copper) do not displace hydrogen from acids.

The metals were first arranged in the above sequence by the Russian scientist N. Beketov as a result of his investigations on the displacement of elements by one another from their compounds. Beketov called this series the "Metal Displacement Series".

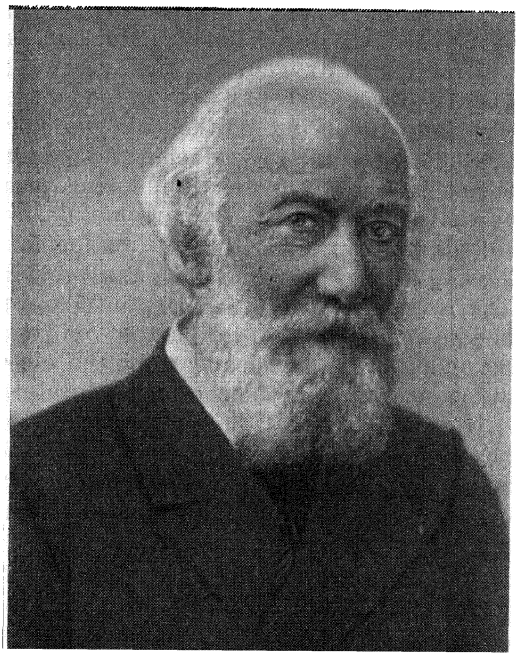
Metal Displacement Series

Potassium	Nickel
Sodium	Tin
Calcium	Lead
Magnesium	Hydrogen
Aluminium	Copper
Manganese	Mercury
Zinc	Silver
Iron	Gold

Nikolai Nikolayevich Beketov (1826-1911), Professor of the Kharkov University, afterwards Academician, was one of the most distinguished Russian scientists, the author of investigations on chemical bonds and the stability of chemical compounds.

Beketov's most famous work is his "Studies of the Phenomena of Displacement of Elements by One Another", published in 1865. Studying the action of hydrogen under pressure on mercury and silver salts, Beketov discovered the remarkable fact that under such conditions these metals are displaced by hydrogen, and came to the conclusion that the chemical action of the gas was proportional to its pressure or mass, thus anticipating the Law of Mass Action

Nikolai Nikolayevich
Beketov
(1826-1911)



formulated in more general form by Guldberg and Waage only two years later. On the basis of his investigations Beketov arranged all the metals in a sequence which afterwards became known as the electrochemical or e.m.f. series. He discovered the capacity of aluminium for displacing metals from their oxides at high temperatures. This discovery afterwards formed the basis of aluminothermy (see § 201) which has found wide application in metallurgy. Beketov's works in the thermal chemistry of the alkali metals are also widely known.

One of Beketov's great merits was the revival of physical chemistry as an indepedent science, the foundations of which had been laid by M. Lomonosov. Beketov continued the latter's initiative by introducing in 1865 a course of lectures and laboratory work in physical chemistry at the Kharkov University.

70. Oxidation-Reduction (Redox) Reactions. In examining the properties of hydrogen in § 67 it was pointed out that hydrogen is capable of reducing many oxides, abstracting oxygen from them, and this process was contrasted with oxidation, i.e., the addition of oxygen. At first the oxidation and reduction concepts expressed nothing but the addition and abstraction of oxygen. Very soon, however, they received a broader meaning. Oxidation began to include, besides the addition of oxygen, the abstraction of hydrogen from substances, on the grounds that abstraction of hydrgen takes

place mostly under the action of oxygen (for example $4NH_3+3O_2 = 2N_2 + 6H_2O$). Similarly, reduction began to include not only the abstraction of oxygen, but the addition of hydrogen as well. Subsequently these concepts were extended still further to include many reactions involving neither oxygen nor hydrogen, but essentially analogous to typical oxidation and reduction reactions. For instance, the combustion of metals in chlorine, bromine, and sulphur vapours. as well as any addition of non-metals, was termed oxidation:

$2Al + 3Br_2 = 2AlBr_3$ is analogous to $4Al + 3O_2 = 2Al_2O_3$

$2FeCl_2 + Cl_2 = 2FeCl_3$ is analogous to $4FeO + O_2 = 2Fe_2O_3$

The reverse change of $AlBr_3$ into Al or $FeCl_3$ into $FeCl_2$ came to be known as reduction. Thus the "oxidation" and "reduction" concepts became rather vague and only the electron theory of structure of substance defined them quite accurately.

If typical oxidation-reduction reactions are examined from an electronic point of view it will easily be seen that they are always accompanied by the transference of electrons from one set of atoms or ions to another, the oxidized substance losing electrons, and the reduced substance gaining them. Some examples are given below.

1. *Combustion of Magnesium in Oxygen*:

$$2\overset{\downarrow}{Mg} + \overset{\downarrow}{O_2} = 2Mg^{++} + O^{--} \quad (4e^-)$$

The magnesium atom has two electrons in its outer layer. When reacting with oxygen, two magnesium atoms lose four electrons to an oxygen molecule (two atoms) and become doubly positively charged Mg^{++}-ions. The latter unite with the resulting oxygen ions into crystals of magnesium oxide, MgO. Thus, the combustion (oxidation) of magnesium is accompanied by the transition of electrons from magnesium to oxygen.

2. *Reduction of Cupric Oxide by Hydrogen*:

$$\overset{\downarrow}{Cu}^{++}O^{--} + \overset{\downarrow}{H_2} = Cu + H_2O \quad (2e^-)$$

In cupric oxide the copper ion bears two positive charges. In the course of the reaction electrons pass from the hydrogen atoms (molecules) to the cupric-ion; the copper becomes neutral, while the hydrogen ions formed combine with the oxide ions into water molecules. Hence, it can be seen that the reduction of cupric oxide is accompanied by the addition of electrons to it (rather to Cu^{++}-ion).

3. *Reaction Between Ferric Chloride and Hydrogen Iodide in Solution.* If solutions of ferric chloride and hydrogen iodide are mixed, free

iodine is liberated and the ferric chloride is converted to ferrous chloride:

$$2Fe^{+++}Cl_3^- + 2H^+I^- = 2Fe^{++}Cl_2^- + I_2 + 2H^+Cl^-$$

($2e^-$)

In this reaction ferric chloride is usually said to be reduced to ferrous chloride and hydrogen iodide to be oxidized to free iodine. But it can be seen from the above equation that the electrons are transferred only from I^--ion to Fe^{+++}-ion, the latter turning into Fe^{++}-ion and I^--ion turning into neutral iodine atoms which then form I_2 molecules; Cl^--ion and H^+-ion undergo no change as a result of the reaction. Thus, actually, it is not ferric chloride that changes into ferrous chloride but Fe^{+++}-ion that changes into Fe^{++}-ion; likewise, it is not hydrogen iodide, but I^--ion that is oxidized into iodine atoms.

The following conclusions may be drawn from the above examples:

1. Oxidation consists essentially in the loss of electrons by the atoms or ions of the substance being oxidized, while reduction consists essentially in the gain of electrons by the atoms or ions of the substance being reduced. Therefore today any process in which a substance loses electrons is called oxidation; on the other hand, any gain of electrons is regarded as reduction.

2. No oxidation of any substance can take place without simultaneous reduction of some other substance, since the loss of electrons by one set of atoms or ions is connected with another set of atoms or ions gaining them.

For instance, in the combustion of magnesium in oxygen or air the magnesium is oxidized and simultaneously the oxygen is reduced; when hydrogen reacts with cupric oxide, the latter (or rather, Cu^{++}-ion) is reduced, while the hydrogen is oxidized, etc.

Thus, every reaction accompanied by a transference of electrons is a unity of two opposite processes, namely, oxidation and reduction.

That is why all such reactions are now called **oxidation-reduction**, or **redox** reactions.

The substances whose atoms or ions gain electrons during the reaction are called **oxidizing agents**, or **oxidants**, while the substances that lose the electrons are called **reducing agents** or **reductants**.

During the reaction the oxidizing agent abstracts electrons from the substance oxidized and is itself reduced. On the other hand, the reducing agent loses electrons and is thus oxidized. For instance, in the reaction between ferric chloride and hydrogen iodide (see above) the oxidizing agent is Fe^{+++}-ion, which accepts one electron and is reduced to Fe^{++}-ion, while the reducing agent, I^--ion, loses one electron and is oxidized to iodine atoms.

This can be represented graphically by expressing the oxidation and reduction processes by separate "electronic" equations (see p. 113):

$$\underset{\substack{\text{reduc-}\\\text{ing}\\\text{agent}}}{I^-} - e^- = I \quad \text{(oxidation)}$$

$$\underset{\substack{\text{oxidi-}\\\text{zing}\\\text{agent}}}{Fe^{+++}} + e^- = Fe^{++} \quad \text{(reduction)}$$

The above described (§ 66) reactions of preparation of hydrogen from water and acids by the action of certain metals on them are also oxidation-reduction reactions. In all these reactions the metal atoms lose electrons, and are therefore the reducing agents, while hydrogen-ion gains electrons, and is therefore the oxidizing agent. For instance, in the reaction

$$\overset{2e^-}{\overbrace{}}$$

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

Zn is the reducing agent, while H^+-ion is the oxidizing agent.

Consequently, hydrogen, regarded above (§ 67) as a reducing agent, acts as an oxidizing agent when it is in the form of positively charged ions.*

The transition of electrons from one set of atoms or ions to another in redox reactions is naturally accompanied by a change in valency of the elements participating in the reaction. The valency change is a characteristic feature, by which the reaction can immediately be classed as redox. Since oxidation consists in the loss of electrons by atoms or ions and reduction in their gain, *the algebraic valency value increases during oxidation* (i.e., positive valency increases and negative valency decreases), *and decreases during reduction.* This will readily be seen if we examine the valency changes in the oxidized and reduced atoms or ions in the above examples. For instance, in the reaction between ferric chloride and hydrogen iodide the valency of the iron (the charge on the Fe^{+++}-ions) decreases from + 3 to + 2, while the valency of the iodide (the charge on the I^--ions) increases from −1 to 0 in free iodine, etc.

The above theory of oxidation-reduction reactions was developed by the Russian Academician L. Pisarzhevsky (1874-1938)—the first scientist to make extensive use of the electron theory for explaining chemical processes.

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* In reactions with the active metals hydrogen atoms are also oxidants, gaining electrons and turning into negatively charged H^--ions (see p. 203).

CHAPTER X

Water. Solutions

WATER

71. Water in Nature. Water is the most abundant substance on earth. Almost $^3/_4$ of the surface of the globe is covered with water, which fills all natural basins, forming oceans, seas, rivers and lakes. There is a great deal of water in the gaseous state (water vapour) in the atmosphere; water lies in immense quantities as snow and ice on the peaks of high mountains and in the polar regions all year round. Water is present not only on the surface of the earth, but in its depths as well, impregnating the soil and various rocks, and forming the source of springs and fountains.

Natural water is never absolutely pure. The purest form is rain water, but even it contains various impurities entrapped from the air, such as dissolved gases, dust and microorganisms.

Falling on the earth, rain water drains partly into streams and rivers, and is partly absorbed by the soil and various rocks to form subsoil waters. Seeping through the upper layers of the earth, water dissolves various substances on its way. That is why the water of wells, springs, rivers and lakes always contains dissolved substances. The content of these substances in fresh waters varies greatly but is generally between 0.01 and 0.05 per cent.

Salt water contains up to 4 per cent of dissolved substances, mostly common salt. Ocean water contains 3.5 per cent of salts, sea water from 0.5 to 3.9 per cent, depending on the water abundance of the rivers falling into the particular sea (the Mediterranean Sea contains 3.9 per cent, the Black Sea 1.8 per cent, the Baltic Sea 0.5 per cent).

Water containing a large quantity of calcium and magnesium salts is called **hard**, in contradistinction to **soft** water, such as rain water, which contains very little dissolved matter. Hard water gives little suds with soap; meat and vegetables soften with great difficulty when boiled in it, and it forms a large amount of scale on the walls of boilers.

Besides soluble impurities, natural water always contains suspended solid particles of sand and clay, plant and animal residues, as well as all kinds of microorganisms. The latter may include morbific bacteria which cause various diseases when they penetrate into the organisms of men or animals.

To free natural water from suspended particles it is filtered through a layer of some porous substance, such as charcoal, burnt clay, etc. Large-scale filtering is done exclusively through sand and gravel. Most of the bacteria are also arrested by the filters. Drinking water is chlorinated besides, for disinfection. Complete sterilization of water requires not over 0.7 gram of chlorine per ton of water.

Only insoluble impurities can be removed from water by filtration. Absolutely pure water, not containing even soluble substances, is obtained by distillation.

72. Physical Properties of Water. Pure water is a colourless transparent liquid with no taste or odour. The weight of 1 ml. of pure water at 4°C is accepted as the metric unit of weight and is called the **gram.**

Unlike most other substances, the densities of which increase continuously upon cooling, the highest density of water is at 4°C. Above and below this temperature the density of water is lower. This anomaly of water is of very great importance, as it accounts for the fact that deep bodies of water do not freeze to the bottom in winter, so that life can be retained in them.

Of no smaller importance in the life of nature is another anomaly of water, namely, the fact that water has the highest specific heat of all solid and liquid substances. This makes it grow cold slowly in winter and warm up slowly in summer and thus act as a temperature regulator on the globe.

The freezing point of pure water is accepted as the starting point of the centigrade thermometer scale and is designated by 0; the boiling point of water at normal pressure is indicated on the scale by 100.

The composition of water by weight is 11.11 per cent hydrogen and 88.89 per cent oxygen. Hence, the simplest formula of water is H_2O. Determination of molecular weight of water by the density of its vapour at high temperatures shows it to be 18, which corresponds to its simplest formula. However, as the boiling point of water is approached, the vapour density increases somewhat and the molecular weight becomes a little higher than 18. The molecular weight of liquid water, determined by dissolving it in suitable solvents according to the method described in § 82, also proves to be higher than that corresponding to its simplest formula. All these facts led to the conclusion that along with simple H_2O molecules liquid water contains more complex molecules in equilibrium with the latter, the composition of these complex molecules being expressed by the general formula $(H_2O)_x$. Such a combination of simple molecules into more complex ones without the chemical nature of the substance changing is called molecular *association.*

Molecular association is generally due to the polarity of the molecules, as a result of which they attract each other by their unlike

poles, forming double, triple, etc., molecules (Fig. 59). But in the case of water the chief cause of association is the formation of "hydrogen" bonds, as they are called, between the molecules.

Investigations have established that when covalently linked with the atom of a highly electronegative element (especially fluorine or oxygen) the hydrogen atom is capable of combining with one more atom of the same element. This second bond is called a hydrogen bond.

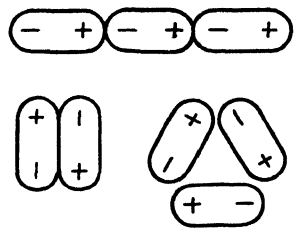
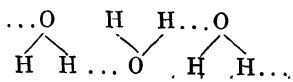


Fig. 59. Association of polar molecules

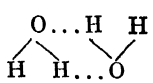
This peculiarity of the hydrogen atom is due to the fact that when it loses its only electron to form a bond with a strongly electronegative element a nucleus of very small size remains, almost devoid of any electron shell. It is, therefore, not repelled but attracted by the electron shell of any third atom and may interact with it.

In liquid water the hydrogen bond arises between the hydrogen atom of one water molecule and the oxygen atom of another according to the scheme



in which the hydrogen bonds are designated by dots. In the same way even more complex molecular aggregates may form in water.

The most stable are the double molecules $(H_2O)_2$, the formation of which is apparently accompanied by the appearance of two hydrogen bonds:



The association of water molecules accounts for the above-mentioned anomalies in its properties. It is supposed that at 0°C water consists to a considerable extent of $(H_2O)_3$ molecules. When heated from 0°C to 4°C the triple molecules dissociate into $(H_2O)_2$ molecules which give water its greater density, probably on account of the presence of the two hydrogen bonds in them. Further heating leads to the double molecules breaking up into simple ones, so that the density of water gradually decreases.

But even at 100°C water and water vapour still contain a certain amount of double molecules, as a result of which the density of water vapour at 100°C does not quite correspond to the simplest formula of water, H_2O.

The high specific heat of water is also due to the dissociation of complex molecules upon heating. Since dissociation is accompanied by absorption of heat, water when heated requires the expenditure of heat not only for raising its temperature but for decomposing its associated molecules as well.

Water Vapour. Like any liquid, water evaporates more or less rapidly when left in an open vessel. If, however, the liquid is placed in a closed container, empty or occupied by some gas, it will evaporate only until a dynamic equilibrium is established between the liquid and its vapour, whereupon the same number of molecules will evaporate per unit time as return to the liquid. A vapour in equilibrium with the liquid it originated from is called **saturated.** Its pressure at any given temperature is different for different liquids. For instance, at 20°C the pressure of saturated water vapour equals 17.4 mm. Hg, that of alcohol 43.9 mm. Hg, of ether 442 mm. Hg, etc.

Evaporation is an endothermal process. Therefore, according to Le Châtelier's Principle, raising the temperature will shift the equilibrium between the liquid and its vapour towards evaporation, and the vapour pressure will increase.

The pressure of water vapour at several different temperatures is as follows:

Temperature, degrees C . . .	0	20	40	60	80	100
Pressure, mm. Hg	4.6	17.4	55.0	149.2	355.5	760

When the vapour pressure of a liquid reaches the value of the external pressure the liquid begins to boil. The boiling point of water at normal atmospheric pressure is 100°C, because at this temperature the pressure of water vapour becomes equal to 760 mm. Hg.

The transformation of water into steam involves the absorption of a large amount of heat. To convert one mole of water at 100°C into steam at the same temperature 9.7 Cal. must be expended. During the reverse transformation of steam into water the same amount of heat is released.

Ice. If heat is removed from water at a temperature of 0°C and ordinary pressure, the water passes into its solid state—ice. On the contrary, if ice at 0°C is heated, it melts into water. A mixture of water and ice will remain unchanged at 0°C if it neither receives heat from, nor loses it to, the environment. On these grounds *the freezing point or, which is the same, the melting point, may be defined as the temperature at which a liquid is in equilibrium with the solid phase of the same substance.*

The amount of heat given off when water freezes (and that absorbed when ice melts) equals 1.42 Cal. per mole of water.

The transition of water into ice is accompanied by a considerable increase in volume, as a result of which the specific gravity of ice

equals only 0.92, i.e., ice is lighter than water. As the pressure is increased, the water-ice transition point is lowered at first (e.g., at a pressure of 615 atm. water freezes only at —5°C) but afterwards (above 2,000 atm.) it begins to rise again and at very high pressures is above 0°.

Investigations have shown that at pressures above 2,000 atm. five various forms of ice with specific gravities greater than unity can exist, besides ordinary ice; these varieties are denoted by the Roman numerals II,III,IV, V, and VI. The name "hot ice" has been suggested for ice VI, which forms under a pressure of 20,760 atm., as it melts at +76° C.

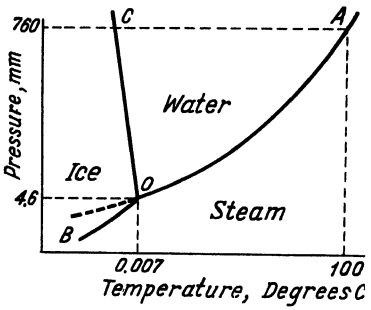


Fig. 60. Diagram of state of water

Ice, like water, can evaporate. In a closed space the evaporation of ice continues until the pressure of the vapour formed from it reaches a certain definite value for each given temperature. The vapour pressure of ice at 0°C is the same as that of water vapour at 0°C, i.e., equals 4.6 mm. Hg. As the temperature decreases, the vapour pressure of ice falls rapidly: at —20°C it equals only 0.8 mm. Hg and at —50°C it is only 0.3 mm. Hg. That is why ice evaporates much more slowly than water.

The above dependence of the vapour pressure of water on the temperature, as well as the conditions of simultaneous existence of water in the various phases, can be represented graphically by means of what is known as the *diagram of state of water* (Fig. 60).

On this diagram *OA* is the vapour pressure curve of water and *OB* that of ice. The points of the curve *OA* show at which temperatures and pressures water and steam can exist simultaneously; those of the curve *OB* show the conditions of equilibrium between ice and its vapour. The curves intersect at point *O*, which shows the temperature and pressure at which all three phases can exist together in equilibrium. Therefore point *O* is called the *triple point*; it stands for a pressure of 4.6 mm. Hg and a temperature of +0.007°C. The curve *OC* shows the influence of the pressure on the melting point of ice. Each point on this curve corresponds to a definite pressure and a definite temperature at which ice and water are in equilibrium with each other. The curves *OA*, *OB* and *OC* divide the entire area of the diagram into three fields, each of which corresponds to stability of only one of the three physical states of water. At temperatures and pressures corresponding to points in the area *AOC* water can

exist only in the liquid state. Similarly, the points of the areas marked "ice" and "steam" on the diagram indicate the temperatures and pressures at which only the solid or only the gaseous phases can exist.

73. Chemical Properties of Water. Of the chemical properties of water we must point out primarily the high stability of its molecules to heat. However, at temperatures above 1,000°C water vapour begins to dissociate perceptibly into hydrogen and oxygen:

$$2H_2O \rightleftarrows 2H_2 + O_2 - 136.8 \text{ Cal.}$$

Since this reaction goes on with absorption of heat, a rise in temperature should shift the equilibrium to the right, according to Le Châtelier's Principle. However, even at 2,000°C the degree of dissociation is only 1.8 per cent. If the temperature drops below 1,000°C the equilibrium is shifted practically almost completely towards the formation of water; at ordinary temperatures there is such an insignificant quantity of free hydrogen and oxygen molecules left that we have no means of detecting them.

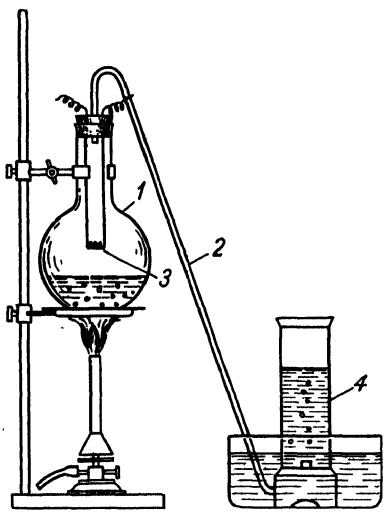


Fig. 61. Apparatus for demonstrating dissociation of water at high temperatures:
1—flask; *2*—gas delivery tube; *3*—platinum filament; *4*—cylinder for collecting products of dissociation of water

Various methods are used for determining the degree of dissociation of substances at high temperatures. One of them is based on what is known as "equilibrium blocking". If the dissociation products formed at a high temperature are quickly cooled, the equilibrium does not get a chance to shift immediately, and does not shift afterwards, due to the very slow rate of the reaction at low temperatures. Thus, the ratio that existed between the substances at the high temperature remains unchanged and can then be determined by analysis.

The dissociation of water at high temperatures can be demonstrated by the following experiment. A little water is placed in flask *1* (Fig. 61) fitted with a rubber stopper carrying gas delivery tube *2* and two large-diameter copper wires connected by thin platinum filament *3*. The water in the flask is heated to boiling, and after all the air has been expelled from the flask by the water vapour, the end of the delivery tube is brought under cylinder *4* filled with water. After this the platinum filament is heated to a high temperature by passing electric current through it. Gas bubbles thereupon immediately begin

to escape from the tube and gradually fill the cylinder. When the cylinder is full of gas it is taken out of the water and a flame applied to its mouth. The explosion indicates that the cylinder had been full of detonating gas.

In spite of its stability to heat water is a very reactive substance. The oxides of many metals and non-metals combine with water to form bases and acids; many salts form crystal hydrates with water; the most active metals react with water liberating hydrogen, etc. Later on we shall become acquainted with other reactions in which water participates.

SOLUTIONS

Solutions play a very important part in life and in the practical activities of man. Suffice it to mention that the processes of food assimilation by man and animals involve the dissolving of nutritious substances. All the most important physiological liquids (blood, lymph, etc.) are solutions. Finally, all industrial processes based on chemical processes are connected more or less with the use of various solutions.

Having daily to deal with solutions, men long since took an interest in their properties, but the fundamental relationships governing their behaviour were established only in the XVIII century.

Lomonosov gave a great deal of attention to the study of solutions. He investigated the influence of the temperature on the dissolving of various substances, thermal phenomena taking place when substances dissolve, the freezing of solutions, crystallization phenomena, etc. He established that the act of dissolving is always accompanied by an energy effect, and in this connection indicated the necessity of distinguishing strictly between two types: a) processes of dissolving during which heat is released, such as when metals are dissolved in acids, which is essentially a chemical reaction between the acid and the metal, since evaporation of the solution does not lead to deposition of the initial metal, but of its salt with the acid used; b) processes of dissolving during which heat is absorbed, such as the dissolving of a salt in water, whereupon the solute undergoes no chemical change, but is deposited as the same substance when the solution is evaporated.

74. Properties of Solutions. A solution is a solid or liquid homogeneous system consisting of two or more components, the relative quantities of which may vary over quite a wide range. The most important are liquid solutions, which will be dealt with in this paragraph.

Any solution consists of a dissolved substance called the **solute** and the medium through which the solute is uniformly distributed as molecules or as ions, this medium being commonly known as the

solvent. However, it is not always easy to determine which of the substances is the solvent and which the solute. Usually the component, which in the pure form has the same physical state as the solution itself, is considered the solvent (for instance, in the case of an aqueous solution of a salt the solvent is, of course, water). If both components possess the same physical state out of solution (e.g., alcohol and water), the component present in greater quantity is the solvent.

The homogeneity of solutions makes them very similar to chemical compounds. The evolution of heat observed when some substances are dissolved also indicates that a certain chemical reaction takes place between the solvent and the solute. The difference between solutions and chemical compounds is that the composition of the latter is constant, while the composition of a solution prepared from any given components may sometimes vary over quite a wide range. Besides, many properties of the separate components can be detected among the properties of the solution, which is not the case with chemical compounds. The inconstancy of the composition of solutions approaches them to mechanical mixtures, but they differ sharply from the latter by their homogeneity. Thus, solutions are intermediate between mechanical mixtures and chemical compounds.

75. The Act of Dissolving. To prepare a solution of any substance it is enough to leave the latter in contact with the solvent for some length of time. When this is done, most solid substances and all gases dissolve only to a certain limit. For instance, if more than 36 gr. of common salt is added to 100 gr. of water at room temperature the salt will not dissolve entirely no matter how long we shake the water with the salt. A solution in which the solute will not dissolve any longer even after prolonged shaking is called a **saturated solution** at any given temperature.

The solid substance evidently dissolves in the liquid as follows. As we know, the molecules of any substance are in constant motion, this motion being of an oscillatory nature in solid substances. When we place a solid in a liquid which can dissolve it, individual molecules are gradually torn away from its surface as a result of interaction with the molecules of the solvent. Due to diffusion these molecules are distributed evenly throughout the bulk of the solvent. The separation of the molecules from the surface of the solid is caused by their own oscillatory motion on the one hand, and by attraction on the part of the solvent molecules on the other. This process would continue until all the solute present dissolved, were it not for the reverse process, namely, crystallization, proceeding simultaneously. When the molecules which have passed into solution collide with the surface of the substance not yet dissolved, they are attracted back to it and form part of its crystals. Obviously, the higher the concentration of the solution, the faster the solute molecules will deposit from it. And

since the concentration keeps increasing as the substance dissolves, there comes a moment at length when the rate of solution becomes equal to the rate of crystallization and the following dynamic equilibrium is established:

$$undissolved\ solute \rightleftarrows solute\ in\ solution$$

in which the number of molecules dissolved per unit time equals that falling out of the solution again. Then, the concentration of the solution stops increasing, i.e., the solution becomes saturated.

Hence, *a saturated solution is one which can remain in equilibrium indefinitely with an excess of the solute.*

76. Concentration of Solutions. To obtain a saturated solution the solute is added to the solvent in a large enough quantity to leave part of it undissolved. Saturated solutions are used comparatively rarely. In most cases unsaturated solutions are used, i.e., solutions with lower solute concentrations than those of saturated solutions.

The concentration of a solution is the quantity of solute contained in a definite weight or in a definite volume of the solution. Solutions with high solute concentrations are called **concentrated** and with low concentrations—**dilute.**

The concepts "concentrated" and "saturated" should not be confused. A concentrated solution is by no means necessarily a saturated one. For instance, a solution containing 20 gr. KNO_3 in 100 gr. of water is quite concentrated, but if its temperature is 20°C it is far from saturated. To obtain a saturated solution at this temperature 31.5 gr. of potassium nitrate would have to be taken for every 100 gr. of water.

A saturated solution may be very dilute if the solute is only slightly soluble. By way of example it may be pointed out that a saturated solution of gypsum contains but 0.21 gr. of solute in 100 gr. of solution at 20°C.

The concentration of solutions can be expressed quantitatively in various ways. Three methods of expressing concentrations are the most current in chemical practice:

1. *By the percentage of solute with respect to the total quantity of solution.* For example, a 15 per cent solution of common salt contains 15 gr. of salt and 85 gr. of water in every 100 gr. of solution.

2. *By the number of moles of solute contained in one litre of solution.* Solutions with their concentrations expressed in this manner are called **molar.** They are denoted by the letter M preceded by a coefficient indicating the "molarity" of the solution, i.e., the number of moles per litre of solution. For example, a 2 M solution contains two moles of solute in one litre, a 0.3 M solution contains 0.3 mole per litre, etc.

A solution of a given molarity, for instance a 0.5 M solution of soda ash Na_2CO_3, is prepared as follows: 0.5 mole of soda ash, i.e., 53 gr. (the molecular weight of Na_2CO_3 being 106), is weighed out and placed in a one-litre measuring flask, which has a mark scratched on its neck indicating a volume of exactly one litre (Fig. 62). Then enough water is added to dissolve all the soda ash, after which the flask is filled up to the mark with water.

The use of molar solutions is convenient in the respect that equal volumes of solutions of equal molarity contain equal numbers of solute molecules.

Sometimes the concentration of a solution is expressed by the number of moles of solute in 1,000 gr. of solvent. In contradistinction to molar solutions such solutions are called **molal.**



Fig. 62. Measuring flask

3. *By the number of gram-equivalents* of solute contained in one litre of solution.* Such solutions are generally known as **normal solutions.**

A solution which contains one gram-equivalent of solute per litre is called a uninormal or just *normal* solution and is denoted by the letter "N". If the solution contains 0.5 gram-equivalent per litre it is called semi-normal (0.5 N), if it contains 0.1 gram-equivalent, deci-normal (0.1 N), etc.

When preparing normal solutions of complex substances—acids, bases and salts—it must be kept in mind that the equivalent weight of an acid equals its molecular weight divided by its basicity, i.e., by the number of atoms of replaceable hydrogen in the acid molecule.

The equivalent weight of a base equals its molecular weight divided by the valency of the metal atom in it.

As to salts, their equivalent weights are found by dividing the molecular weight of the salt by the number of atoms of the metal in its molecule and by the valency of the metal.

For instance:

The equivalent weight of HNO_3 (mol. wt. 63) equals $63 : 1 = 63$
The equivalent weight of H_2SO_4 (mol. wt. 98) equals $98 : 2 = 49$
The equivalent weight of $Ca(OH)_2$ (mol. wt. 74) equals $74 : 2 = 37$
The equivalent weight of $Al_2(SO_4)_3$ (mol. wt. 342) equals $342 : (2 \times 3) = 57$

Normal solutions are widely used in chemistry in reactions between dissolved substances. If normal solutions are used, it is easy to pre-calculate the volume ratios in which they should be mixed for the dissolved substances to react without residue. Since the weights of the reacting substances are proportional to their equivalent weights,

* A gram-equivalent is the number of grams of a substance equal to its equivalent weight.

the solutions should be taken for the reaction in volumes containing equal numbers of gram-equivalents of their solutes. If the normalities of the solutions are equal, the volumes taken will obviously also be equal; if they are different, the volumes will be inversely proportional to their normalities.

If the volumes of the solutions expended on the reaction are v_1 and v_2, and their normalities, i.e., concentrations expressed in gram-equivalents per litre, are, respectively c_1 and c_2, the relation between these values can be expressed by the proportion:

$$v_1 : v_2 = c_2 : c_1$$

or

$$v_1 \cdot c_1 = v_2 \cdot c_2$$

This relation can be used not only to calculate the volumes of solutions needed to carry out various reactions, but also for the reverse, namely, to find the concentrations of the solutions, and hence the weights of the reactants, by the volumes expended on the reaction.

Example 1. How many millilitres of 0.3 N NaCl solution must be added to 150 ml. of a 0.16 N $AgNO_3$ solution to precipitate all the silver in solution as AgCl?

We write the proportion:

$$0.3 : 0{,}16 = 150 : x$$

whence

$$x = \frac{0.16 \cdot 150}{0.3} = 80 \text{ ml.}$$

Example 2. 24 ml. of a 0.2 N solution of alkali had to be added to 40 ml. of a sulphuric acid solution to neutralize it. Find the number of grams of H_2SO_4 contained in the volume of solution taken.

Denoting the unknown normality of the sulphuric acid solution by x, we write the proportion:

$$40 : 24 = 0.2 : x$$

whence

$$x = \frac{24 \cdot 0.2}{40} = 0{,}12$$

Since a gram-equivalent of sulphuric acid (mol. wt. 98) equals 98 : 2= 49, one litre of 0.12 N solution obviously contains $49 \times 0.12 = 5.88$ gr. H_2SO_4. The quantity of sulphuric acid contained in 40 ml. of solution can be found from the proportion:

$$1{,}000 : 40 = 5.88 : x$$

$$x = \frac{40 \times 5.88}{1{,}000} = 0.2352 \text{ gr.}$$

Finding the volumes of solutions expended on reactions is the basis of a method of quantitative determination of substances known as *volumetric analysis.*

The volumes of solutions can be measured accurately by means of burettes (Fig. 63). A burette is a glass tube narrowed at the lower end and furnished with a cock for drawing the liquid, or with a glass tip connected to the burette by means of a piece of rubber tubing with a pinch cock. The tube is usually calibrated to tenths of a millilitre. When a definite volume of liquid has to be measured out at once, a pipette (Fig. 64) is commonly used.

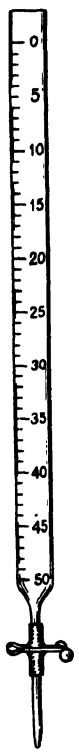


Fig. 63. Burette



Fig. 64. Pipette

For volumetric determinations it is necessary to bring out the end point of the reaction between the dissolved substances by some sufficiently clear-cut external indication, such as a change in the colour of the solution. For this purpose a small amount of indicator is added to the test solution; an indicator is a substance which does not influence the course of the reaction, but changes its colour abruptly as soon as an excess of one substance in the solution is replaced by a very slight excess of the other. For instance, in reactions between acids and alkalis the indicator may be a solution of litmus, which changes its colour with the transition of acid solution to alkaline and vice versa.

The determination is carried out as follows. A definite volume of the test solution is measured out into a small beaker by means of a pipette, and several drops of an indicator solution are added to it. The beaker is held under a burette, from which a second solution of exactly known concentration is added in small portions, until the colour of the indicator changes. Then the volume of solution added is read off by the calibrations on the burette. The concentration of the test solution is calculated from the ratio between the volumes of the solutions used up in the reaction (see Example 2).

In volumetric analysis the concentration of the solution is often expressed by the number of grams of solute in one ml. of solution. The concentration expressed in this manner is called the **titre** of the solution. Hence, the method of determining concentrations described above is called **titration.**

77. Solubility. Solubility is the ability of a substance to dissolve in any given solvent.

The measure of solubility of a substance at any given conditions is the concentration of its saturated solution. Therefore, numerically solubility can be expressed in the same way as concentration, for

instance, as the percentage content of the solute or in moles per litre of solution. Very often solubility is also expressed as the number of grams of substance which can dissolve in 100 gr. of solvent.

The solubility of various substances in water varies over a wide range. If over 10 gr. of substance can dissolve in 100 gr. of water at room temperature, the substance is considered soluble; if less

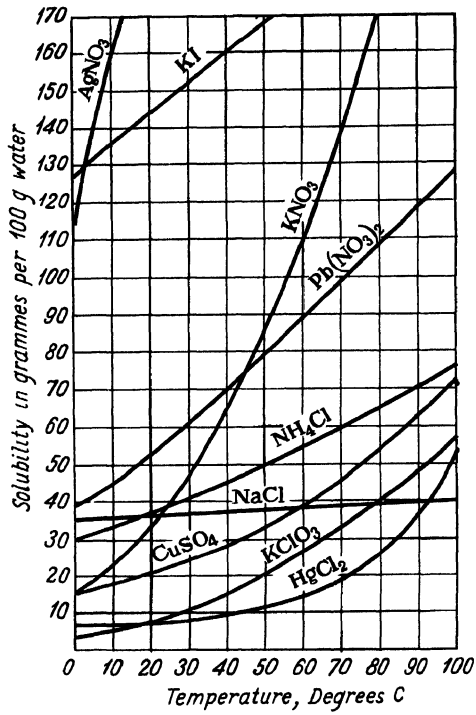


Fig. 65. Solubility curves of various salts

than 1 gr. of substance will dissolve, it is termed slightly soluble, and the substance is practically insoluble if less than 0.01 gr. of it passes into solution. Absolutely insoluble substances do not exist.

The solubility of almost all solids increases with rising temperature. For instance, the following amounts of potassium nitrate can dissolve in 100 gr. of water depending on the temperature.

Temperature, degrees C	0	20	40	60	80	100
Solubility, grams	13.5	31.5	64	110	169	247

The change in solubility with increasing temperature is usually non-uniform and different for various substances.

The dependence of the solubility on the temperature can be expressed very conveniently by graphs. Fig. 65 shows several characteristic solubility curves. The abruptly rising solubility curves of potassium nitrate KNO_3, lead nitrate $Pb(NO_3)_2$ and silver nitrate $AgNO_3$ show that the solubilities of these substances increase rapidly with the temperature. On the contrary, the solubility of sodium chloride NaCl changes little as the temperature rises, which is indicated by the all but horizontal solubility curve of this salt. Sodium sulphate Na_2SO_4 has a more complex solubility curve (Fig. 66). Up to 32°C

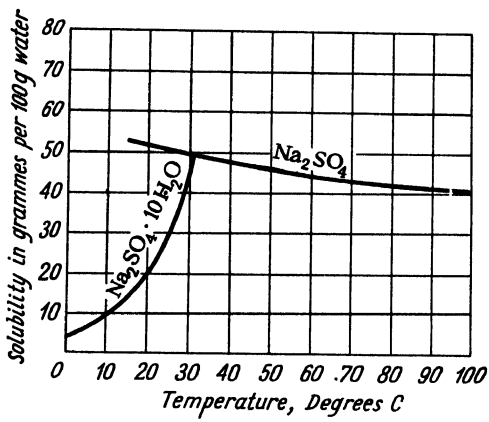


Fig. 66. Solubility curve of sodium sulphate

it rises steeply, showing that the solubility increases rapidly. At 32° C there is a sharp break in the curve, after which it slopes gently downwards. Hence, sodium sulphate has its highest solubility at 32° C.

Liquids can also dissolve in liquids. The solubility of some of them in each other is unlimited, in which case they are said to be miscible in all proportions, such as alcohol and water; others dissolve in one another only to a certain limit.

Thus, if ether is shaken with water, two layers appear, the upper layer being a saturated solution of water in ether, and the lower a saturated solution of ether in water. In most cases of this kind the mutual solubility of the liquids increases with the temperature until a point is reached where the liquids become miscible in all proportions.

Unlike solids and liquids, the solubility of gases decreases as the temperature rises. If a glass of cold water is left standing in a warm room, its inner walls presently become covered with bubbles of air which had been in solution in the water and was liberated as the

water grew warmer. The air dissolved in water can be removed entirely by boiling (that is why boiled water tastes different from unboiled).

Besides the temperature, the solubility of gases is influenced greatly by their pressure. The gas molecules above a liquid in a closed vessel bombard the surface of the liquid and dissolve in it at a rate proportional to the concentration of the gas. On the other hand, after passing into solution, the molecules strike the surface of the liquid from the inside from time to time and break through it. As the concentration of the molecules in solution increases, due to the dissolving of the gas, the rate of their emergence, i.e., the number of molecules leaving the solution per unit time, also increases, until it finally becomes equal to the rate at which they pass into solution. Then a state of equilibrium is established, i.e., the liquid becomes saturated with the gas:

$$\text{gas over liquid} \rightleftarrows \text{dissolved gas}$$

Now, if we increase the pressure of the gas, say, twofold, the concentration of its molecules above the liquid will increase the same number of times, and therefore, so will the rate at which the gas dissolves. The equilibrium is disturbed, and in order to re-establish it at the new pressure the concentration of dissolved molecules must also obviously be doubled.

We thus come to the conclusion known as **Henry's Law:**

> *The weight of a gas dissolved in a given volume of a liquid is directly proportional to the pressure of the gas.**

For example, at 0° C and normal pressure 0.335 gr. of carbon dioxide will dissolve in 100 ml. of water, but if the pressure is doubled, 0.670 gr. will dissolve in the same amount of water. However, since the density of the gas also increases in proportion to the pressure, these 0.670 gr. at doubled pressure will occupy the same volume as 0.335 gr., at normal pressure. Therefore: *the volume of gas dissoluble in a given volume of a liquid does not depend on the pressure.* For this reason the solubility of gases is usually expressed in millilitres instead of grams, indicating the volume of gas that will dissolve at a given temperature in 100 ml. of solvent.

The solubility of several gases in water at 0° C and 20° C is given in Table 11.

If there is a mixture of several gases above the liquid, the solubility of each of them does not depend on the total pressure of the mixture, but only on the partial pressure of the gas in question. This

* This law holds strictly only for gases of comparatively low solubility, and which do not react chemically with the solvent.

Table 11

Solubility of Gases in Water

Gas	Solubility of gas, ml. per 100 ml. water	
	at 0° C	at 20° C
Hydrogen	2.15	1.82
Oxygen	4.89	3.1
Nitrogen	2.35	1.54
Carbon dioxide	171	87.8
Chlorine	491	226
Methane	5.56	3.30

must be taken into account when calculating the solubility of gases in mixture with other gases.

Suppose, for instance, it is required to calculate the composition of air dissolved in water. If atmospheric air is assumed to consist, in round figures, of $^1/_5$ of oxygen and $^4/_5$ of nitrogen by volume, the partial pressure of the oxygen under a total pressure of one atmosphere will be 0.2 atm. and that of nitrogen 0.8 atm. At normal pressure and a temperature of 20° C 100 ml. of water will dissolve 3.1 ml. of oxygen and 1.54 ml. of nitrogen. Hence, at a pressure of 0.2 atm. the amount of oxygen dissolved should be $3.1 \times 0.2 = 0.62$ ml. (reduced to a pressure of 1 atm.); the amount of nitrogen dissolved at a pressure of 0.8 atm. should be $1.54 \times 0.8 = 1.232$ ml. Thus, the air dissolved in water will contain approximately 33 per cent oxygen, i.e., considerably more than atmospheric air.

Solutions of gases in liquids should be kept in airtight jars, since it is impossible otherwise to maintain above the liquid the pressure at which it was saturated with the gas: if the jar is open, the gas will diffuse into the air, its partial pressure will drop, and the dissolved gas molecules will gradually come out of solution.

78. Mendeleyev's Hydrate Theory. When solids are dissolved in liquids, the usual energy effect is absorption of heat, so that the temperature of a freshly prepared solution is lower than that of the liquid used for its preparation.

Some solids dissolve, liberating heat. For instance, when caustic soda, potash or anhydrous copper sulphate are dissolved in water, the temperature rises perceptibly.

Heat is liberated also sometimes when liquids, and always when gases are dissolved.

The quantity of heat absorbed (or liberated) when one mole of a substance is dissolved is called its heat of solution.

The heat of solution is negative in value if heat is absorbed during solution, and positive if heat is evolved. For instance, the heat of solution of ammonium nitrate equals —6.32 Cal., that of Glauber's salt —18.76 Cal. and of caustic potash +13.3 Cal., etc.*

When a solid dissolves, its crystal lattice is broken down and its molecules (or ions) distributed through the bulk of the solvent, all this requiring the expenditure of energy. Therefore, the act of dissolving proper should lead to absorption of heat. But if in some cases the reverse is observed, it shows that simultaneously some chemical reaction is taking place between the solvent and the solute, during which more heat is liberated than is required to break down the crystal lattice.

Indeed, by various methods of investigation it has been proved that when dissolved the molecules of many substances unite with the molecules of the solvent to form a special type of compounds called **solvates**. Particularly, when the solvent is water, these compounds are called **hydrates** and the process of their formation **hydration.**

The formation of solvates is due to the polarity of the solute molecules, owing to which the latter attract the polar molecules of the solvent. It is obvious that the more polar both types of molecules are, the more stable the solvates. And since water molecules have the highest polarity of all ordinary solvents, we have to deal mostly with hydrates in practice.

The idea of the existence of hydrates in aqueous solutions was suggested and grounded in the eighties of last century by Mendeleyev.

Mendeleyev held that solution is not only a physical process, as was thought at that time, but a chemical process as well; that the substances dissolving in water could form various compounds with it. This becomes evident primarily from a study of solution heats. "If the act of dissolving consisted only in a change of physical state," wrote Mendeleyev, "the amount of heat developed by gases or absorbed by solids upon dissolving would correspond to that change of state; actually, upon dissolving, a gas always gives off more and a solid absorbs less heat, owing to the fact that chemical union, accompanied by the evolution of heat, takes place during solution."

Another confirmation of the chemism of solution is that many substances crystallize out of their aqueous solutions in a form containing what is known as water of crystallization (see below), a definite number of water molecules combining with each molecule

* Solution heat values vary slightly depending on the quantity of solvent used and the temperature at which the solute is dissolved. The above figures are for room temperature and a large amount of water (one mole of solute per 200 or 400 moles of water).

of solute. "This," wrote Mendeleyev, "leads us to believe that there are such or similar compounds between the solute and the solvent in the solutions themselves, though in liquid (and partly decomposed) form."

Indeed, in studying the dependence of the specific gravities of sulphuric acid solutions on their concentration, Mendeleyev detected a number of bends on the dependence curves, indicating the existence of definite compounds between sulphuric acid and water in the solution. Similar data were obtained by him for solutions of calcium chloride and several other substances.

Mendeleyev's views on solutions and on the act of dissolving were expounded by him in the form of his hydrate theory in his major work "Investigation of Aqueous Solutions by Their Specific Gravity" and in his textbook "Principles of Chemistry." These views were challenged in their time by many scientists, especially after the appearance of the Theory of Electrolytic Dissociation (see Chapter XII). However, later investigations in this field fully confirmed Mendeleyev's assumption as to the existence of hydrates in solutions, and his hydrate or "chemical" theory of solution, extended and brought into conformity with Van't Hoff and Arrhenius's "physical" theory, has now become a composite part of the general theory of solutions.

Hydrates are rather unstable compounds, decomposing in many cases upon evaporation of their solutions. But often the hydrate water is so stably combined with the molecules of the solute that it remains a composite part of the crystals of the latter when they fall out of solution. Such crystalline formations containing water molecules as independent units, are known as **crystal hydrates**, and the water contained in them is called **water of crystallization** or hydration. Crystal hydrates are especially common with various salts.

The composition of crystal hydrates is usually expressed by formulas showing the amount of crystallization water contained in them. For example, the crystal hydrate of copper sulphate (blue vitriol) containing five gram-molecules of water per gram-molecule of $CuSO_4$ is expressed by the formula $CuSO_4 \cdot 5H_2O$, the crystal hydrate of sodium sulphate (Glauber's salt) by the formula $Na_2SO_4 \cdot 10H_2O$, etc.*

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* According to the old chemical nomenclature the products of the reaction between oxides and water were also called hydrates. However, those hydrates differ considerably from crystal hydrates. While water is contained in the latter as integral molecules, in hydrated oxides the oxide and water molecules are broken down and new molecules formed from their atoms. For instance, calcium hydroxide (formerly called hydrated calcium oxide) does not contain any water molecules and is regarded as consisting of calcium and hydroxyl radicals. Therefore its composition is represented by the formula $Ca(OH)_2$ and not $CaO \cdot H_2O$.

The strength of the bond between a substance and its water of crystallization is unequal in different crystal hydrates. Many of them can lose their water of crystallization even at room temperature. Thus, for instance, if transparent crystals of ordinary "washing" soda ($Na_2CO_3 \cdot 10H_2O$) are left standing in the air they "effloresce," i.e., lose water very readily, become dull and gradually turn into a powder. Other crystal hydrates have to be heated quite strongly before they will part with their water.

To see what the loss of water by crystal hydrates depends on, the following experiment may be performed: introduce a tiny crystal of blue vitriol into the Torricellian vacuum of a barometric tube. The crystal immediately begins to lose water, and the mercury in the tube will gradually be depressed until the pressure of water vapour reaches a certain value. If the temperature is increased the crystal loses more water, the pressure of its vapour increases and the mercury will drop still further. On the contrary, if the temperature is lowered, part of the water recombines with the salt, the vapour pressure falls and the mercury rises. Thus, the decomposition of blue vitriol into the anhydrous salt and water is a reversible process.

In a closed space the following equilibrium exists:

$$CuSO_4 \cdot 5H_2O \rightleftarrows CuSO_4 + 5H_2O$$

At each temperature the state of equilibrium corresponds to a definite pressure of the water vapour formed, called the *vapour pressure of the crystal hydrate.* When the temperature is raised the equilibrium shifts towards the formation of the anhydrous salt, as should be expected according to Le Châtelier's Principle, since decomposition of the crystal hydrate is accompanied by absorption of heat; when the temperature falls the reverse reaction takes the upper hand.

The vapour pressure of various crystal hydrates is far from identical. For instance, at 30° C the vapour pressure of Glauber's salt, $Na_2SO_4 \cdot 10H_2O$, equals 27 mm., that of blue vitriol, $CuSO_4 \cdot 5H_2O$, 12.5 mm. and of barium chloride, $BaCl_2 \cdot 2H_2O$, only 4 mm. Hg.

Atmospheric air always contains water vapour, usually about 60 per cent of the amount needed to saturate it. Those crystal hydrates whose vapour pressure is higher than the pressure of the water vapour contained in the air, gradually lose their water at ordinary temperatures, i.e., effloresce; such are Glauber's salt, washing soda and others. Crystal hydrates with smaller vapour pressures do not apparently decompose, while some of them even absorb water vapour from the air. For instance, granular calcium chloride $CaCl_2 \cdot 2H_2O$ is used to dry gases precisely because its vapour pressure is very low and it combines with water vapour to form a new hydrate containing more water, namely $CaCl_2 \cdot 6H_2O$.

The formation of hydrates is accompanied by a release of heat. When a substance subject to hydration is dissolved, the total thermal effect is the sum of the thermal effect of dissolving proper and that of hydration. Since the first of these processes is endothermal and the second exothermal, the total thermal effect of the act of dissolving must be equal to the algebraic sum of the effects of these two processes and may be either positive or negative. Consequently, if we determine separately the heat of solution and the total thermal effect of the act of dissolving, the heat of hydration can be calculated therefrom.

Example. When one mole of anhydrous calcium chloride is dissolved, 17.4 Cal. are liberated, and when one mole of the calcium chloride crystal hydrate $CaCl_2 \cdot 6H_2O$ is dissolved 4.3 Cal. are absorbed. The latter value is evidently the heat of solution, since hydration does not take place in this case, the solute being already hydrated. Denoting the heat of hydration by Q, we may write on the basis of the above:

$$Q - 4.3 \text{ Cal.} = 17.4 \text{ Cal.}$$

hence

$$Q = 21.7 \text{ Cal.}$$

Thus, the heat of hydration of $CaCl_2$ equals 21.7 Cal.

79. Supersaturated Solutions. The solubility of most substances decreases as the temperature falls and therefore if hot saturated solutions are cooled, the excess of solute usually crystallizes out. However, if these solutions are cooled carefully and slowly, care being taken not to let any solid particles of the solute drop into the solution, the crystals may not fall out. In this case the resulting solution contains considerably more solute than is required to saturate the solution at that temperature. This phenomenon was discovered and studied in detail by the Russian Academician T. Lovits (1794), who called such solutions **supersaturated**. If left undisturbed they may remain unchanged for years. But if only a tiny crystal of the solute is thrown into the solution, other crystals immediately begin to grow around it and in a short time the entire excess of solute will have crystallized out. Sometimes crystallization may be initiated by simply shaking the solution or by rubbing a glass rod against the walls of the vessel containing the solution. A considerable amount of heat is liberated during crystallization, so that the vessel and the solution become perceptibly warmer. Supersaturated solutions are obtained very readily with Glauber's salt, borax, hypo, etc.

From the above it follows that supersaturated solutions are unstable systems capable of existing only if there are no solid particles of the solute present in the solution. The possibility of these solutions existing for a long time is due to the difficulty of the initial formation

of minute "germ" crystals, called **crystallization centres**, from which crystallization spreads through the bulk of the solution.

Since the crystals of each substance are characterized by a quite definite arrangement of the particles forming them, the appearance of a crystallization centre evidently requires that the particles, which are in a state of continuous disorderly movement in the solution, be grouped at some point of the solution precisely in the order characteristic of the crystals of the substance in question. A considerable length of time may pass before such a group arises spontaneously.

CHAPTER XI

Properties of Solutions

80. Osmotic Pressure. Investigation of the properties of dilute solutions reveals a close analogy between the gaseous state of substance and its state in solution.

Just as the molecules of a gas, owing to their motion, occupy the greatest possible volume and exert pressure on the walls of their containers, so the molecules of a dissolved substance also tend to occupy a maximum volume. The volume of the gas is determined by the size of the vessel, while the volume through which the molecules of a solute can be distributed is determined by the volume of the solution. If a concentrated solution of some substance, say a solution of sugar, is placed in a cylinder and a layer of pure water carefully poured onto it, the sugar molecules will gradually become uniformly distributed throughout the entire volume of the liquid. This phenomenon is known as **diffusion**. Diffusion continues until the concentration of the sugar molecules becomes uniform in all the layers of the liquid.

Distribution of the sugar and water molecules evenly throughout the volume of liquid may take place in two ways: either the sugar molecules leave the lower layer and pass into the upper until their concentration in both layers becomes equal, or water molecules pass from the upper layer into the lower until they mix uniformly with the sugar molecules. The final result is obviously the same in both cases. Actually, the concentration is equalized in both ways, i.e., both by the sugar molecules passing into the water and by the water molecules passing into the sugar solution.

Now suppose the water and the sugar solutions are separated by a porous membrane through which the water molecules can pass freely, but which the sugar molecules cannot penetrate. Such a "semi-permeable" membrane can be obtained, for instance, by impregnating a porous clay cylinder with copper sulphate solution and then immersing the cylinder in a solution of potassium ferricyanide. As a result of this treatment copper ferricyanide will be deposited in the pores of the cylinder and the cylinder walls will become semi-permeable.

If a cylinder thus treated is filled with a solution of sugar and immersed in pure water the concentrations will be equalized (rather, the concentration of the sugar solution will decrease) only as a result of migration of the water molecules. A greater number of the latter will diffuse into the solution than out of it; for this reason the volume of the solution will gradually increase and the sugar concentration in it decrease. Such unidirectional diffusion through a semi-permeable partition is called **osmosis**. If there is enough water available its passage into the solution through the semi-permeable partition should, strictly speaking, continue indefinitely, unless it is stopped by some force acting in the opposite direction.

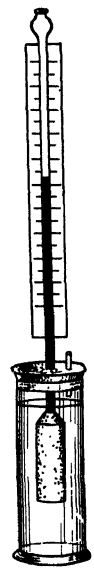


Fig. 67. Apparatus for demonstrating osmotic pressure of solution

Now take a vessel with semi-permeable walls and a long narrow vertical tube at the top (Fig. 67). Fill it with a solution of sugar and immerse it in a vessel containing the pure solvent. As a result of osmosis the volume of the solution gradually increases and the solution begins to fill the vertical tube. As the level of the solution in the tube rises, there appears an excess hydrostatic pressure equal to the difference between the levels of the solution and the solvent; this pressure counteracts the penetration of solvent molecules into the solution. When the hydrostatic pressure reaches a certain value, osmosis ceases. The force which causes osmosis is called the *osmotic pressure of the solution*. The magnitude of the osmotic pressure is determined by the external pressure on the solution under which osmosis ceases.*

Osmosis plays a very important part in the life of animals and expecially plant organisms. Cell walls are membranes which are easily penetrated by water but are almost impermeable to the substances dissolved in the cellular fluid. Passing into the cells water raises the pressure within them, slightly distending the cell walls and keeping them in a tense state. That is why the soft organs of a plant, such as grass stems, leaves, flower petals, possess a certain elasticity. If the plant is cut the volume of cellular fluid decreases due to the evaporation of water through the cell walls, the cell walls fall in and become flabby: the plant withers. But if the partly withered plant is placed in water osmosis again sets in, the cell walls again become tense and the plant resumes its previous appearance.

* In the experiment described the measure of osmotic pressure would be the pressure of the liquid column in the vertical tube.

Osmosis is also one of the factors causing the rise of water up the stem of a plant, the growth of its cells and many other phenomena.

The first exact measurements of osmotic pressure carried out by the German scientist Pfeffer led to the establishment of the following two rules:

1. *The osmotic pressure of a solution is directly proportional to the concentration of the solute.*
2. *The osmotic pressure is proportional to the absolute temperature of the solution.*

In 1866 the Dutch physico-chemist Van't Hoff first drew attention to the complete analogy between these rules and the gas laws of Boyle-Mariotte and Gay-Lussac. Using the numerical data obtained in measurements of the osmotic pressure he showed that the osmotic pressure of dilute solutions can be expressed by an equation quite similar to the equation of state of a gas

$$PV = RT$$

where P is the osmotic pressure and V the volume of solution containing one gram-molecule of solute. It was found that the constant R has the same numerical value as in the gaseous equation of state (0.082 l. atm./deg.). Hence it follows that Avogadro's Law is also applicable to dilute solutions. Indeed, experiment shows that *equimolecular solutions (i.e., solutions containing equal numbers of molecules per litre) of various substances have equal osmotic pressures at the same temperature.* In particular, solutions containing one gram-molecule of solute in 22.4 l. have an osmotic pressure equal to 1 atm. at 0° C.

Solutions of equal osmotic pressure are called **isotonic.**

Thus the *osmotic pressure*, like the pressure of a gas, *depends only on the number of molecules of the solute* at constant volume and temperature, and does not depend on the nature of the solute or the solvent.

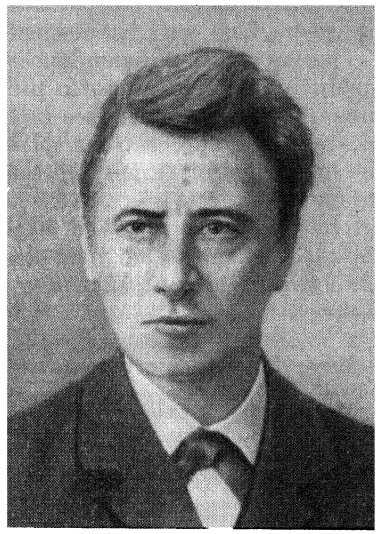
If in the above equation the molecular volume V is replaced by the concentration C expressed in moles per litre ($V = 1/C$) the resulting expression is more convenient for osmotic pressure calculations:

$$P = CRT$$

The profound analogy between gases and solutions is clearly expressed in the following principle known as the **Law of Van't Hoff:**

The osmotic pressure of a solution equals the pressure which would be exerted by the solute if it were in a gaseous state at the same temperature and occupied a volume equal to that of the solution.

Jacobus Hendricus Van't Hoff
(1852-1911)



This law expresses the essence of the Van't Hoff theory of solutions. It must, however, be stressed that despite the complete analogy of numerical relationships, the mechanisms of gaseous and osmotic pressure are absolutely different.

Jacobus Hendricus Van't Hoff, one of the founders of modern physical chemistry, was born in Rotterdam (Holland) in 1852. After graduating technical school at Delft, he studied chemistry at the Universities of Bonn, Paris and Utrecht. In 1874 he received a Doctor's degree in Mathematics and Natural Philosophy at the Utrecht University.

Between 1877 and 1896 Van't Hoff was a professor of chemistry at the Amsterdam University where, besides chemistry, he taught also geology and mineralogy. In 1896 he moved to Berlin and from then on devoted himself entirely to scientific research.

At the very beginning of his scientific activities Van't Hoff put forth and developed the idea of directional valency of the carbon atom and laid the foundations of stereochemistry, i. e., the science of the spatial arrangement of atoms in molecules. But Van't Hoff's main field of research was physical chemistry.

He studied the laws of chemical reactions, chemical equilibrium, dilute solutions, osmotic pressure. From 1896 to the end of his life Van't Hoff worked on salt equilibria in solutions.

Van't Hoff was a Corresponding Member of the Petersburg Academy of Sciences and from 1898, an Honorary Member of the Moscow Society of Researchers of Nature.

The Law of Van't Hoff holds only for dilute solutions. In the case of concentrated solutions considerable deviations from this law are observed. Even greater deviations are observed in aqueous

solutions of electrolytes, substances which conduct current in aqueous solution. This will be discussed in detail in the following chapter.

Thanks to the dependence between the molar concentration of a solution and its osmotic pressure, the molecular weights of many substances, not obtainable in the gaseous state but dissolving readily in some solvent, can be determined by the osmotic pressure. On the other hand, knowing the molar concentration of a solution, we can calculate its osmotic pressure. In such calculations it is useful to remember that the osmotic pressure of a solution containing one mole of solute per litre may be assumed to be equal to 22.4 atm. (though actually at such a concentration the pressure is somewhat higher).

Example. Calculate the osmotic pressure of a solution containing 9 gr. of glucose per litre.

The molecular weight of glucose is 180; hence, 9 gr. of glucose is 0.05 mole. Since the osmotic pressure is proportional to the quantity of solute, the osmotic pressure sought (x) can be found from the proportion:

$$22.4 : x = 1 : 0.05$$

hence

$$x = 22.4 \cdot 0.05 = 1.12 \text{ atm.}$$

Direct measurement of the osmotic pressure is rather difficult, but is not absolutely necessary. Van't Hoff showed that the osmotic pressure is closely related to certain other more easily measured properties of dilute solutions, namely: the lowering of the vapour pressure, the lowering of the freezing point and the elevation of the boiling point. Having determined any of these values, we can calculate the osmotic pressure of the solution. Since all the above values, like the osmotic pressure, vary in proportion to the number of particles of solute in solution, they can also be used to determine the molecular weight of dissolved substances.

81. Vapour Pressure of Solutions. In considering the physical properties of water (§ 72) it was indicated that the pressure of the saturated vapour of each liquid is a constant value at any given temperature. Experiment shows that when any solid is dissolved in a liquid, the vapour pressure of the liquid is lowered. Thus *the vapour pressure of a solution is always lower than the vapour pressure of the pure solvent at the same temperature.* The difference between the numerical vapour pressure values of the pure solvent and the solution is usually called the vapour pressure lowering of the solution.

In 1887 on the basis of numerous experiments with solutions of various solids and non-volatile liquids the French physicist Raoult established the following law:

The lowering of the vapour pressure in dilute solutions of non-electrolytes at constant temperature is proportional to the quantity of substance dissolved in a given weight of solvent.

This law can be explained by the molecular kinetic theory.

It has been pointed out that the saturated vapour pressure above a liquid depends on the number of molecules evaporating from the surface of the liquid per unit time. But in a solution part of the free surface is taken up by the molecules of the non-volatile solute. Therefore the number of molecules leaving the surface of the solution per unit time is smaller than in the case of the pure solvent at the same temperature, and the vapour pressure decreases. For instance, the vapour pressure of a solution in which the solute molecules constitute $^1/_{20}$ of the total number of molecules, is $^1/_{20}$ less than that of the pure solvent.

The dependence between the lowering of the vapour pressure and the amount of substance dissolved can be expressed mathematically. Let the vapour pressure of the pure solvent be p, the lowering of the vapour pressure Δp, the number of moles of solute n, and the number of moles of solvent N. Then Raoult's Law for dilute solutions can be expressed thus:

$$\Delta p = \frac{p \cdot n}{N}$$

Raoult's Law, establishing the dependence between the vapour pressure of a solution and the amount of solute in it, holds only for solutions of solids or non-volatile liquids. It cannot be extended to the immense field of homogeneous liquid mixtures, all the composite parts of which possess perceptible volatility. Meanwhile, such mixtures are of great practical importance. An investigation of the vapour pressures and boiling points of liquid mixtures was the subject of the classical works of the Russian scientist Konovalov. The relationships discovered by him and known as the "Laws of Konovalov" are included in all textbooks on physical chemistry. These laws are used to solve a great variety of problems connected with the distillation and separation of liquid mixtures.

Measurement of the lowering of the vapour pressure of a solution can be used directly for determining the molecular weight of dissolved substances. In practice, however, another, more convenient method is used, based on measurement of the lowering of the freezing point or the elevation of the boiling point of the solution.

82. Freezing and Boiling of Solutions. All pure substances are characterized by strictly definite freezing and boiling points. Thus, under normal atmospheric pressure pure water freezes at 0° C and boils at 100° C: benzene freezes at 5.5° C and boils at 80.1° C, etc.

These temperatures remain unchanged until the entire bulk of the liquid has frozen or turned into vapour.

It is different with solutions. The presence of the solute raises the boiling point and lowers the freezing point of the solvent, and the more concentrated the solution, the greater these effects. Therefore, solutions freeze at lower and boil at higher temperatures than the pure solvents.* It can easily be shown that this is a direct consequence of the lowering of the vapour pressure of the solution.

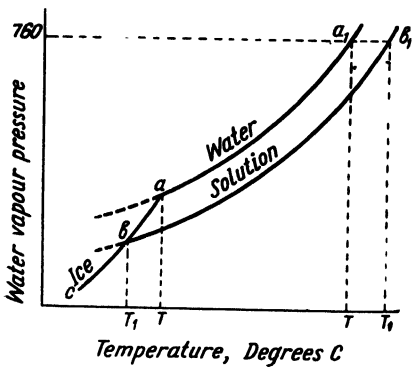


Fig. 68. Vapour pressure vs. temperature curves for water, ice and a solution

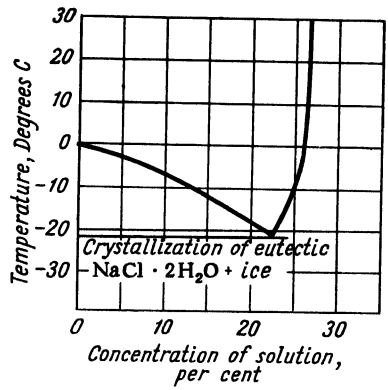


Fig. 69. Freezing curve of solutions of common salt

As we know, any liquid begins to boil at the temperature where the pressure of its saturated vapour becomes equal to the surrounding pressure. For instance, under a pressure of 760 mm. Hg water boils at 100° C because at that temperature the pressure of the water vapour becomes exactly equal to 760 mm. Hg. If, however, any substance is dissolved in the water, its vapour pressure decreases. Hence, to bring the vapour pressure of the resulting solution up to 760 mm. Hg, the solution must obviously be heated to above 100° C. Therefore, the boiling point of a solution is always higher than that of the pure solvent.

The lower freezing point of a solution compared to the pure solvent is due to the fact that the freezing point is the temperature at which the solid and liquid phases of the substance can exist simultaneously (p. 216). However, for this it is necessary that the vapour pressures of the solid and liquid phases be equal, otherwise the vapour will pass from one phase to the other until the phase over which the vapour pressure is higher disappears entirely. Ice and water can

* Here and in the following, solutions of solids or very slightly volatile liquids are meant.

exist together indefinitely at 0° C precisely for the reason that at 0° C the vapour pressure of ice (4.6 mm. Hg) equals that of water. This temperature is the freezing point of pure water.

If we take a solution instead of pure water, its vapour pressure at 0° C will be less than 4.6 mm. Hg; for this reason ice immersed in such a solution melts rapidly. Co-existence of the ice and the solution is possible only at a temperature below 0° C, namely, at the temperature where their vapour pressures are equal. In other words, the solution freezes at a temperature below the freezing point of the pure solvent.

All these relationships become especially clear if they are expressed as graphs showing the relation vapour pressure vs. temperature. In Fig. 68, aa_1 is the vapour pressure curve of pure water and bb_1 that of a solution. Since the vapour pressure of the solution at any temperature is lower than that of pure water, bb_1 lies below aa_1. To determine the boiling points of water and the solution by means of these curves at any desired pressure, say, at 760 mm. Hg, draw a straight line parallel to the abscissa axis from the corresponding point of the ordinate axis. From a_1 and b_1, the points of intersection of this line with the vapour pressure curves drop a perpendicular to the abscissa axis. The temperatures T and T_1 correspond to the boiling points of water and the solution, since their vapour pressures are equal at these temperatures. It will be seen that the boiling point of the solution is higher than that of pure water.

In Fig. 68, ac represents the vapour pressure curve of ice. It was stated above that at the freezing point the vapour pressures of the solid and liquid phases of the solvent or of the solid solvent and the solution must be equal. The points a and b of intersection of aa_1 and bb_1 with ac correspond to this condition. The freezing points of water and the solution are found as the projections of a and b on the abscissa axis. In this case, as can be seen in the figure, the temperatures T and T_1 are arranged in the reverse order, i.e., the freezing point of the solution is lower than the freezing point of water.

When dilute solutions freeze, a quantity of pure solvent crystallizes out first, e.g., pure ice in the case of an aqueous solution. Since the concentration of the solution increases as the ice crystallizes out, the freezing point does not remain constant but keeps falling.* However, crystallization of the ice and lowering of the freezing point continue only until the concentration of the solution reaches a certain definite value for each given substance, at which the entire solution freezes into a solid mass. Under the microscope it can be

* For this reason the freezing point of a solution is defined as the temperature at which the solid phase begins to crystallize out.

seen to consist of thin layers of ice and solute in the solid form. A mass of this kind is called a **eutectic**. The temperature at which the eutectic forms is called the **eutectic temperature** and the corresponding concentration of the solution, the **eutectic concentration.**

For instance, if we cool a 10 per cent solution of common salt, the first crystals of ice will begin to appear at about —7° C. As the ice falls out, the concentration of the remaining solution increases and the freezing point drops lower and lower. Finally, when the NaCl concentration reaches 24.42 per cent, the entire solution freezes into a solid white mass, a eutectic. This takes place at a temperature of —21.2° C, which is therefore the eutectic temperature for a solution of common salt.

An analogous picture is observed when saturated solutions, i.e., solutions containing a higher concentration of solute than the eutectic, are cooled. In this case it is the solute and not the ice that begins to crystallize out first when the solution is cooled. For example, if a saturated NaCl solution, containing 26.4 per cent of the solute at 20° C, is cooled, the salt will crystallize out first. As the salt falls out, the concentration of the solution decreases, and when it becomes equal to 24.42 per cent, a eutectic forms (at —21.2° C). Thus, when any saturated solution is cooled, a certain amount of crystals first falls out of the solution and then, finally, a eutectic forms.

Fig. 69 shows the freezing curve of solutions of common salt of various concentrations. It can be seen from the figure that as the concentration increases, the freezing point drops. The lowest point of the curve corresponds to the eutectic temperature —21.2° C and the eutectic concentration 24.42 per cent NaCl. If the concentration is further increased, the freezing point (i.e., the temperature at which the solid phase begins to drop out) again rises but it is salt this time, and not water, that falls out of the solution in the solid form.

The eutectic temperature is the lowest of all the possible freezing points of solutions of the given substance. It varies for different substances over a wide range. Thus, the eutectic temperature for potassium nitrate is only —2.9° C (with a eutectic concentration of 10.9 per cent KNO_3); for common salt it is —21.2° C, for calcium chloride, —55° C, for sulphuric acid, —75°C, etc.

The low eutectic temperature of common salt accounts for the melting of ice when sprinkled with salt. Ice and salt cannot exist together at temperatures above —21.2° C; therefore when mixed with salt, ice immediately begins to melt. The ability of ice to absorb great quantities of heat when melting is utilized for the preparation of cooling mixtures, discovered by Boyle in 1665 and studied very thoroughly by T. Lovits. In 1792 Lovits artificially achieved a temperature of —50° C for the first time, by mixing snow with cal-

cium chloride. Obviously, no temperature lower than the eutectic can be obtained in this way.

Just as the solid phase which crystallizes out of a dilute solution upon freezing consists of the pure solvent, so when solutions of solids in liquids are boiled, the vapour formed consists of the pure solvent. Therefore, as the liquid evaporates, the concentration of the solution increases and the boiling point keeps rising until the solution becomes saturated and crystallization sets in. As soon as crystallization begins the concentration of the solution stops changing and the boiling point becomes constant.

The quantitative aspect of the freezing and boiling of solutions was studied by Raoult who experimentally established the following principles known as the **Laws of Raoult**:

1. *The lowering of the freezing point is proportional to the quantity of substance dissolved in a given weight of the solvent.*

Thus, a solution containing 5 gr. of sugar in 100 gr. of water freezes at —0.27° C, while one containing 10 gr. freezes at —0.54° C, etc.

2. *Equimolecular quantities of various substances dissolved in the same weight of a given solvent lower its freezing point an equal number of degrees.*

For instance, if 0.1 gram-molecule of sugar (34.2 gr.) are dissolved in 1,000 gr. of water, the freezing point is lowered 0.186° C. An equal depression is caused by 0.1 gram-molecule of glucose (18 gr.), 0.1 gram-molecule of hydrogen peroxide (3.4 gr.), etc.

The freezing point lowering corresponding (by calculation) to one gram-molecule of substance dissolved in 1,000 gr. of solvent (*molecular lowering*) is a constant for each given solvent. It is called the **cryoscopic*** constant of the solvent. The cryoscopic constant differs for different solvents. Its values for a number of solvents are given below.

Cryoscopic Constants

Water	1.86° C	Benzene	5.0° C
Acetic acid	3.9°C	Naphthalene . . .	6.9° C

Quite analogous laws were established by Raoult with respect to the boiling point elevation. The molecular elevation of a boiling point, i.e., the elevation caused by 1 gram-molecule of substance dissolved in 1,000 gr. of a solvent, is called the **ebullioscopic**** constant of the solvent.

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* From the Greek *kryos*, cold, and *skopeo*, I see.
** From the Latin *ebullire*, to boil out.

Ebullioscopic Constants

Water	0.52°	Benzene	2.57°
Ether	2.12°	Chloroform . . .	3.88°

Raoult's Laws can be expressed mathematically by the following equation:

$$\Delta t = K \times C \tag{1}$$

where Δt is the lowering of the freezing point or the elevation of the boiling point of the solvent; C is the number of moles of solute per 1,000 grams of solvent; K is a proportionality coefficient equal respectively to the cryoscopic or ebullioscopic constant of the solvent (when $C = 1$, $\Delta t = K$).

As the number of moles of substance equals its weight in grams (m) divided by its molecular weight (M), $\frac{m}{M}$ can be substituted for C in the above equation, hence

$$\Delta t = K \frac{m}{M} \tag{2}$$

Raoult's Laws are applicable with the same limitations as the Law of Van't Hoff, concentrated solutions and solutions of electrolytes deviating considerably from these laws.

A theoretical grounding of Raoult's Laws was given by Van't Hoff, who pointed out their connection with the law of osmotic pressure and derived an equation for calculating the osmotic pressure from the freezing point lowering and the boiling point elevation of a solution.

Raoult's Laws form the basis of some very convenient methods of determining the molecular weights of dissolved substances. For such estimations a weighed portion of the substance in question is dissolved in a definite quantity of solvent and the lowering of the freezing point or elevation of the boiling point it causes is found. From these data the molecular weight of the dissolved substance can easily be calculated if the cryoscopic or ebullioscopic constant of the solvent is known. On the other hand, knowing the molecular weight of the solute, the cryoscopic or ebullioscopic constant can be found in the same way.

The method of determining molecular weights by the freezing point lowering of a solvent is called *cryoscopic*, and by the boiling point elevation, *ebullioscopic*.

Both methods are widely practised in chemistry, as by using different solvents the molecular weights of all kinds of substances can be determined. The molecular weights of a number of metals

have been found by the lowering of the solidification points of solutions of metals in one another.

Given below is an example of determination of the molecular weight by the freezing point lowering.

Example. When 2.76 grams of glycerine were dissolved in 200 grams of water, the freezing point was lowered 0.279° C. The cryoscopic constant of water equals 1.86° C. Find the molecular weight of glycerine.

First we find the number of grams of glycerine corresponding to 1,000 grams of water in our solution:

$$m = \frac{2.76 \cdot 1{,}000}{200} = 13.8 \text{ gr.}$$

Substituting the data given in the problem into equation (2), we find the molecular weight of glycerine:

$$0.279 = \frac{1.86 \cdot 13.8}{M}$$

$$M = \frac{1.86 \cdot 13.8}{0.279} = 92$$

CHAPTER XII

Theory of Electrolytic Dissociation

83. Deviation of Solutions of Acids, Bases and Salts from Laws Derived for Dilute Solutions. In the previous chapter we considered Van't Hoff's theory of solutions which explains the most important properties of dilute solutions on the basis of the analogy existing between solutions and gases. All the conclusions of this theory were brilliantly confirmed by the results of experimental studies carried out with solutions of very many substances. For solutions of one kind, however, these relationships did not hold. These were solutions of ordinary salts, as well as those of most acids and soluble bases. The osmotic pressure of these solutions, calculated from the lowering of their vapour pressures or freezing points and the elevation of their boiling points, proved invariably to be considerably greater than required by theory. On the contrary, molecular weights determined by measuring these values were always found to be smaller than the true values.

For example, if one gram of common salt is dissolved in 100 grams of water, the freezing point lowering is 0.617° C. As the cryoscopic constant of water equals 1.86°, we get the following value for the molecular weight of common salt:

$$M = \frac{1.86 \cdot 10}{0.617} = 30{,}1$$

Actually, the molecular weight of common salt is 58.5, i.e., almost twice as high.

Calculating the freezing point lowering to be expected according to the true molecular weight in this case, we find:

$$\Delta t = \frac{1.86 \cdot 10}{58.5} = 0{,}318°$$

Thus, the lowering observed is almost twice the theoretical. And since the freezing point lowering is proportional to the osmotic pressure, the latter will consequently also be higher than the "normal" according to Van't Hoff's theory.

A similar deviation from theory was observed also for solutions of other salts, as well as for solutions of most acids and bases.

As was stated in § 80, the osmotic pressure is expressed by the equation:

$$P = CRT$$

To extend this equation to solutions with "abnormal" osmotic pressure Van't Hoff introduced into it a correction factor i (called the **isotonic coefficient**) showing the number of times the osmotic pressure of the solution exceeds the normal:

$$P = iCRT$$

The coefficient i was determined for each solution experimentally either by the vapour pressure lowering or by the freezing point lowering and boiling point elevation. Since all these values are proportional to the osmotic pressure, the number of times the osmotic pressure of the solution is higher than the normal could be found by establishing the number of times either of the above values was greater than those calculated theoretically.

Let P' be the osmotic pressure of the solution, $\Delta t'_{b.p.}$ the elevation of the boiling point and $\Delta t'_{f.p.}$ the lowering of the freezing point of a solution, which does not obey the laws of Van't Hoff and Raoult, and P, $\Delta t_{b.p.}$ and $\Delta t_{f.p.}$ the magnitudes of the same values calculated theoretically according to the molar concentration of the solution. Then the coefficient i is expressed by the following ratios:

$$i = \frac{P'}{P} = \frac{\Delta t'_{b.p.}}{\Delta t_{b.p.}} = \frac{\Delta t'_{f.p.}}{\Delta t_{f.p.}}$$

The values of the coefficient i found by Van't Hoff for a number of salts in 0.2 N. solution according to the freezing point lowering are given in Table 12.

Table 12

Value of Coefficient i for 0.2 N Solutions of Some Salts

Salt	Formula	Freezing point lowering		
		calculated according to Raoult's formulas, $\Delta t_{f.p.}$	observed $\Delta t'_{f.p.}$	$i = \frac{\Delta t'_{f.p.}}{\Delta t_{f.p.}}$
Potassium chloride . . .	KCl	0.372	0.673	1.81
Potassium nitrate . . .	KNO_3	0.372	0.664	1.78
Magnesium chloride . .	$MgCl_2$	0.186	0.519	2.79
Calcium nitrate	$Ca(NO_3)_2$	0.186	0.461	2.48

The data in Table 12 show that the coefficient i differs for various salts. Besides, it was found to grow as the dilution of the solution was increased, gradually approaching the whole numbers 2, 3, 4. For salts of analogous composition these numbers are identical. For instance, in the case of all salts of univalent metals and unibasic acids the coefficient i becomes equal to 2 if their solutions are dilute enough; with salts of bivalent metals and the same acids it becomes equal to 3, etc.

Thus, when acids, bases and salts are dissolved in water they cause a much higher osmotic pressure than equimolecular quantities of any other substances.

How can this phenomenon be accounted for without contradicting Van't Hoff's theory?

It should be indicated, first of all, that an analogous phenomenon is observed in certain gases or substances in the gaseous state.

For instance, if the vapours of ammonium chloride NH_4Cl, phosphorus pentachloride PCl_5, iodine and other substances are heated in a closed vessel, they are found to have a higher pressure than that which follows from the Law of Gay-Lussac. On the other hand, their molecular weights, calculated from determinations of their vapour densities, turn out to be lower than the theoretical.

In the case of gaseous substances this phenomenon can easily be attributed to dissociation. If, say, ammonium chloride NH_4Cl breaks up into NH_3 and HCl molecules, the pressure depending on the number of particles should obviously increase twofold with constant volume.

On the other hand, under constant pressure the volume of the gas should increase twofold, and hence the density should be twice as low. If the dissociation is incomplete, only part of the molecules having decomposed, the pressure will have some intermediate value.

It is natural to assume that in solutions with abnormally high osmotic pressures the solute molecules also break up into particles of smaller size. Since the osmotic pressure does not depend on the weight of the solute, but only on the number of particles per unit volume of solution, it should also increase if their number becomes larger.

This assumption was first put forth in 1887 by the Swedish scientist Arrhenius and formed the basis of his theory explaining the behaviour of acids, bases and salts in aqueous solution.

Arrhenius arrived at this theory by studying the electrical conductivity of solutions.

Svante Arrhenius, a Swedish scientist, physical chemist, was born in 1859. He was a professor at the University of Stockholm and Director of the Nobel Institute. As a result of an investigation of the electrical conductivity of solutions, in 1887 he suggested a theory to explain the conduction of electric cur-

Svante Arrhenius
(1859-1927)



rent by solutions of acids, alkalis and salts, known as the Theory of Electrolytic Dissociation.

Arrhenius also carried out a number of studies in astronomy, cosmic physics and in the field of the application of physico-chemical laws to biological processes.

84. Electrical Conductivity of Solutions. As was indicated above (see § 46), electric current is readily conducted by molten salts and bases, as well as metals. Aqueous solutions of bases and salts are also good conductors of current. Anhydrous acids are very poor conductors, but aqueous solutions of acids conduct current well. Solutions of acids, bases and salts in most other liquids do not conduct current, but in such solutions the osmotic pressure is also normal. Aqueous solutions of sugar, alcohol, glycerine and other solutions with normal osmotic pressure do not conduct current either.

The different attitude of substances to electric current can easily be demonstrated by the following experiment.

Two graphite or metal electrodes are connected by means of wires to the lighting mains (Fig. 70). An electric lamp is cut into one of the wires as a rough indicator of the presence of current in the circuit. The free ends of the electrodes are dipped into dry common salt or anhydrous sulphuric acid. The light does not go on, because these

substances do not conduct current and the circuit remains open. The same will be observed if the electrodes are dipped into a beaker containing pure distilled water. But if only a small amount of salt is dissolved in the water or any acid or base added to it, the lamp immediately begins to burn brightly. The light will not burn if the electrodes are lowered into a solution of sugar, glycerine, etc.

Thus, among solutions, current is conducted predominantly by aqueous solutions of acids, bases and salts. The dry salts, anhydrous acids and bases (in the solid form) do not conduct current; pure water hardly conducts current either. Obviously, profound changes of some kind take place in the acids, bases and salts when dissolved in water, as a result of which the resultant solutions begin to conduct current.

When electric current passes through solutions it causes chemical changes in them, just as when it passes through fusions; these changes consist in the evolution of decomposition products of the solute or solvent from the solution. Substances which conduct electric current in solution are called **electrolytes**. Acids, bases and salts are electrolytes.

The chemical process which takes place when a current is passed through an electrolyte solution is called **electrolysis**. An investigation of the products liberated at the electrodes when acids, bases and salts are electrolyzed, showed that metals or hydrogen are always liberated at the cathode and acid or hydroxyl radicals at the anode, the radicals then undergoing further change. Thus, the primary products of electrolysis are the same composite parts of acids, bases and salts which pass without changing from substance to substance during exchange reactions.

85. Theory of Electrolytic Dissociation or Ionization. In 1877 one of the scientific periodicals carried an article by Arrhenius entitled "Dissociation of Substances Dissolved in Water." In this article Arrhenius presented the results of his investigations on the electrical conductivity of solutions and pointed out the close relation between the ability of solutions to conduct electricity and their failure to obey the laws of Raoult and Van't Hoff.

Arrhenius showed that the osmotic pressure and hence the coefficient i of any solution could be found by measuring its electrical conductivity. The values of i derived by him from conductivities coincided very closely with those found by Van't Hoff for the same solutions by other methods.

According to Arrhenius, the excessively high osmotic pressure of electrolytes was due to dissociation of their molecules into electrically charged particles which he called ions.* This increases the total

* This term was first used by Faraday in a slightly different sense.

number of particles in solution, and therefore also the osmotic pressure on the one hand, and makes the solution capable of conducting current due to the formation of ions, on the other.

The assumptions put forth by Arrhenius in the above-mentioned article were subsequently developed into an integral theory known as the **Theory of Electrolytic Dissociation** or the **Ionization Theory.**

The main theses of this theory are as follows:

1. When electrolytes are dissolved in water their molecules break up to a greater or lesser degree into ions, i.e., electrically charged particles. Each substance forms two kinds of ions, carrying positive and negative charges respectively. The positively charged ions of acids, bases and salts are those of hydrogen and metals, while the

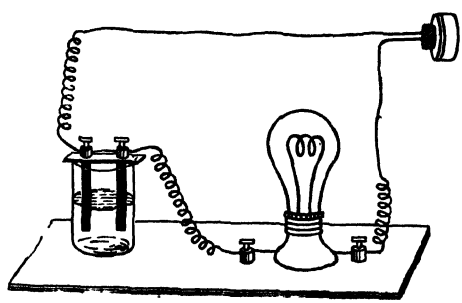


Fig. 70. Set-up for comparing conductivity of solutions

negatively charged ions are acid and hydroxyl radicals. For instance, crystals of common salt NaCl break up into positively charged sodium ions Na^+ and negatively charged chloride ions Cl^-; molecules of nitric acid HNO_3, into positively charged hydrogen ions H^+ and negatively charged NO_3^- ions, etc. Thus, ions may be "simple" or "elementary," i.e., formed by a single atom (Na^+, Cl^-) and "complex," made up of several atoms, such as NO_3^-.

The total number of positive charges acquired by one kind of ions equals the total number of negative charges on the ions of the other kind, so that the solution as a whole remains electrically neutral.

2. The difference between ions on the one hand and neutral atoms and molecules on the other, is that the former possess electrical charges, but this makes their properties absolutely different. For instance, hydrogen-ion* bears no resemblance at all to ordinary

* Hydrogen-ion (spelled with a hyphen) denotes hydrogen ions collectively, regarded as a separate substance, in contradistinction to hydrogen ion, which denotes a single ion. The same refers to all other ions. —*Tr.*

gaseous hydrogen: the latter is almost insoluble in water, whereas hydrogen-ion can be contained in solution in very large quantities; sodium-ion does not act on water whilst metallic sodium reacts vigorously with water to form sodium hydroxide; chloride-ion has neither the odour, the colour, nor any of the other properties of gaseous chlorine; SO_4^{--}-ion can exist only in solution, and only while it is negatively charged; no neutral molecules of such a composition are known; the same can be said of hydroxyl-ion and many others.

When an electric current is passed through the solution, the ions begin to travel in two opposite directions: the positively charged ions move towards the negatively charged electrode, the cathode, while the negative ions move in the opposite direction, towards the positive electrode, the anode. Ions which are attracted to the cathode are called **cations**, and those attracted to the anode, **anions**. When the ions reach the electrodes they are discharged and simultaneously lose the characteristic properties due to the charges they bear, turning into neutral atoms or groups of atoms. The latter are either evolved from the solution, or undergo further change to form new substances.

A very important point in the Arrhenius theory is the statement that decomposition into ions is not effected by the electric current, as previously thought, but occurs as soon as the electrolyte is dissolved in water. Any solution contains free ions, independent of whether it is undergoing electrolysis or not. The only effect of the current on the solution is that it makes the ions travel towards the electrodes, where they are discharged.

The break-up of electrolytes into ions under the action of the solvent is known as **electrolytic dissociation** or **ionization**, and is expressed by conventional chemical equations, in which the formulas of the substances that are breaking up are written on the left side, and the ions formed from them on the right side. We shall denote the charges on free ions in solution by the signs $\cdot$ and $'$, leaving the designations $^+$ and $^-$ for ions combined in crystals of salts and other ionic compounds. Thus, the dissociation of HCl into ions is expressed by the equation

$$HCl = H^{\cdot} + Cl'$$

The presence of positively and negatively charged ions in the solutions of electrolytes can be proved by the following experiment.

A sealed tube containing a solution of potassium iodide KI is clamped to a revolving disc (Fig. 71). The tube has platinum wires fused into it with platinum electrodes fastened to them. The ends of the wires are connected by means of a special device to a sensitive volt-

meter. If the disc is rotated at a high speed, the indicator of the voltmeter will be deflected perceptibly showing that unlike charges have appeared at the electrodes *a* and *b*. It will be found that the end of the tube nearer the edge of the disc is charged negatively while that nearer the centre is charged positively.

Obviously, the negatively charged iodide ions, being the heavier, are thrown outwards with a greater force, and therefore, to a greater distance from the axis of rotation than the lighter potassium ions,

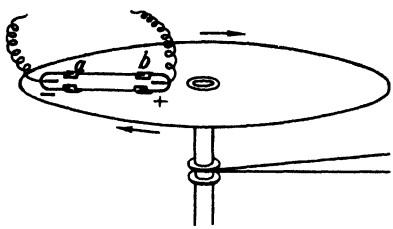


Fig. 71. Revolving disc with tube containing electrolyte solution

which bear positive charges. Therefore, there will be more iodide than potassium ions at the end of the tube at the edge of the disc, and that electrode will be charged negatively. On the other hand, the end of the tube at the centre of the disc will contain a greater number of potassium ions, and therefore a positive charge will appear.

If the same experiment is performed with a solution of silver nitrate, $AgNO_3$, the edge end of the tube, where the heavier silver ions accumulate, will be charged positively, and the centre end, negatively.

These experiments are a good proof of the actual existence of oppositely charged ions in solutions of electrolytes.

The presence of ions in electrolyte solutions affords a simple explanation of the abnormal osmotic phenomena mentioned at the beginning of this chapter. By way of example we considered the osmotic pressure of a dilute solution of common salt, which was found to be almost twice as high as that calculated according to the Law of Van't Hoff. Now we shall have no difficulty in understanding why this is so. The "molecule" of common salt (in Arrhenius's time it was not yet known that there are no separate molecules in crystals of common salt) breaks up in solution into two ions, $Na^{\cdot}$ and Cl'. If all the "molecules" which passed into solution dissociated into ions, the number of ions formed would be twice the original number of molecules. A gram-molecule of common salt would yield not

6.02×10^{23} particles but twice as many. And since the osmotic pressure does not depend on the nature of the particles in solution, but only on their number, it should also increase twofold.

In exactly the same way the osmotic pressure of a very dilute solution of barium chloride, which dissociates according to the equation

$$BaCl_2 = Ba^{\cdot\cdot} + 2Cl'$$

is three times as high as that calculated according to the Law of Van't Hoff, since the number of particles in solution is three times as high as if the barium chloride were in the form of $BaCl_2$ molecules.

Thus, the peculiar behaviour of aqueous solutions of electrolytes, which at first sight contradicts the Law of Van't Hoff, was explained on the basis of this very law.

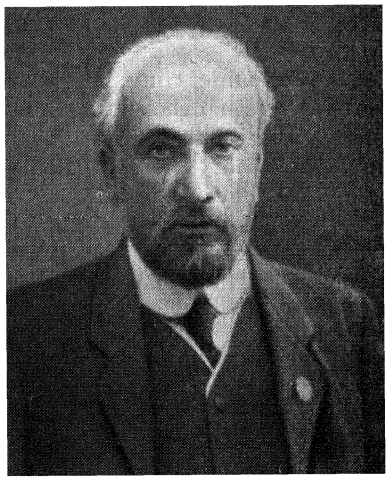
However, the theory of Arrhenius made no allowance for all the complexity of the phenomena taking place in solutions. Mechanistic by nature, it regarded ions as absolutely free particles, independent of the molecules of the solvent. Arrhenius's theory was opposed by Mendeleyev's hydrate theory, based on the idea of interaction between the solute and the solvent (combination of the solute particles with those of the solvent). The credit for overcoming the apparent contradiction between the two theories belongs to Kablukov, who was the first to put forth the very important assumption that ions hydrate, i. e., form unstable compounds with water molecules. This assumption, which is now an undeniable fact, led subsequently to a combination of the theories of Arrhenius and Mendeleyev. The entire subsequent progress of the chemistry of solutions has shown that the Theory of Electrolytic Dissociation not only does not contradict the hydrate theory, but cannot develop further without basing itself on the conceptions introduced by Mendeleyev.

Ivan Alexeyevich Kablukov was born in 1857, in the village of Prussy, Moscow Gubernia. After graduating the Moscow University in 1880 he worked first in the field of organic chemistry. In 1889 Kablukov went to Leipzig, where he worked in the laboratory of Ostwald for some time, together with Arrhenius, on the electro-conductivity of solutions. After his return to Russia Kablukov continued his investigations in the field of the conductivity of solutions. The result of these investigations was his Doctor's thesis entitled "The Present-Day Theory of Solutions (of Van't Hoff and Arrhenius) in Relation to the Science of Chemical Equilibrium," which greatly influenced the development of physical chemistry in Russia and promoted the further development of the Theory of Electrolytic Dissociation.

Especially important among Kablukov's numerous works were his investigations in the field of salt equilibria.

Kablukov devoted his whole life to extensive pedagogical and educational work. He delivered lectures at the Moscow University and at the Institute of Agriculture, wrote the textbooks "Fundamentals of Inorganic Chemistry" and "Fundamentals of Physical Chemistry" by which more than one generation of chemists studied, and was a member of many scientific societies.

Ivan Alexeyevich Kablukov
(1857-1942)



86. The Act of Dissociation. At the time the Theory of Electrolytic Dissociation originated, atoms were still considered the simplest indivisible particles of matter. The conception of the complex structure of atoms came much later. For that reason it was difficult then to comprehend the origin of the electrical charges on the particles formed when electrically neutral molecules dissociate, and why only the molecules of acids, bases and salts are subject to such dissociation. But with the development of the science of atomic and molecular structure, all these phenomena became clear.

We know now that many electrolytes consist of ions even in the solid form. When considering the constitution of crystals in Chapter VI, it was indicated that salt crystals were built up not of molecules, but of separate positively and negatively charged ions arranged in a definite order in the crystal lattice and held in position by forces of electrostatic attraction. Many solid bases, apparently, have a similar structure. Naturally, when such electrolytes are dissolved in water, the ions would be expected to pass into solution as independent units and not in the form of neutral molecules, which do not exist in the solid electrolyte.

The break-up of crystals into separate ions evidently takes place in the following manner. Water molecules possess a certain polarity, i.e., are what we call dipoles. When a crystal of any salt, say potassium chloride, comes into contact with water, the ions at its surface begin to attract the polar water molecules (Fig. 72). The water molecules are attracted to the potassium ions by their negative

poles and to the chloride ions by their positive poles. But if the ions attract the water molecules, the latter attract the ions with the same force.

At the same time, the attracted water molecules are subject to impacts from other molecules in motion. These impacts are strong enough to separate the ions from the crystals and make them pass into solution. The first layer of ions is followed by a second, and thus the crystal gradually dissolves.

After passing into solution the ions may remain linked to the water molecules, in which case they form what are known as **ionic hydrates.** The existence of such hydrated ions has been confirmed

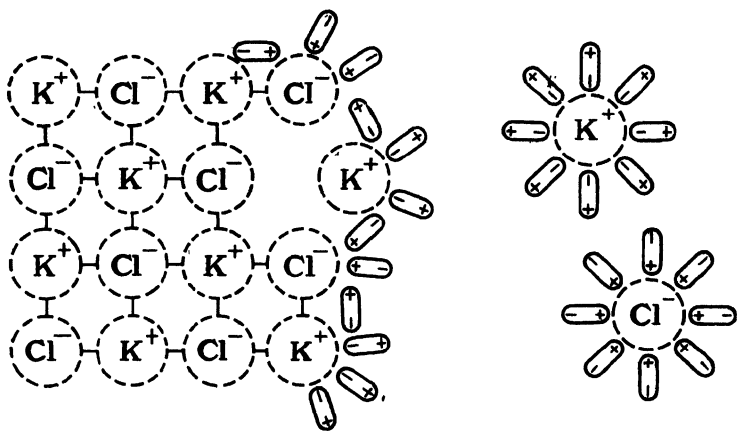


Fig. 72. Mechanism of dissolving salt

in many cases. For instance, hydrogen ions in solution are always combined with one molecule of water each forming a *hydronium* or *oxonium ion* H_3O^+. The ions of many metals are also hydrated in solution. Cations are usually smaller in size than anions; therefore cations attract water molecules more strongly. The smaller the radius of the cation, the smaller the number of water molecules contained in the hydrated ion. The small beryllium cation Be^{++} forms a tetrahydrate $[Be(H_2O)_4]^{++}$; the larger cations Mg^{++} and Al^{+++} form hexahydrates $[Mg(H_2O)_6]^{++}$ and $[Al(H_2O)_6]^{+++}$; while such large cations as K^+ and others are still more hydrated.

Thus, dissociation results, strictly speaking, not in the formation of ions, but of compounds between ions and solvent molecules (ionic hydrates). For the sake of simplicity, however, in ionization equations the formulas of the ions are usually used instead of those of their hydrates (or solvates), the more so, since the degree of hydration of the ions, i. e., the number of water molecules combined with

them, is very often unknown and may vary depending on the concentration of the solution and other conditions.

In solution the ions or their hydrates are in a state of incessant disorderly motion. Upon colliding they may combine into hydrated molecules which may again decompose into ions. The higher the concentration of the solution, the more often the ions collide, therefore solutions, especially concentrated ones, may contain unionized molecules together with the ions.

Not only substances with ionic crystal lattices decompose into ions in aqueous solutions, but also many other substances, consisting of molecules, provided the latter are polar. A scheme of the dissocia-

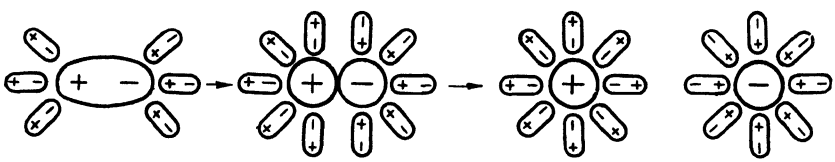


Fig. 73. Dissociation of polar molecules in solution

tion of polar molecules is shown in Fig. 73. The molecules of water attracted to the ends of the polar molecule stretch the latter, moving its poles apart, as a result of which it breaks up into separate ions. If the positive ion is a proton (i. e., a hydrogen nucleus) it will be stably linked to a water molecule as an oxonium ion $H_3O^{\cdot}$. For instance, when hydrogen chloride is dissolved in water, the chemical reaction that takes place can be expressed by the equation

$$H_2O + HCl = H_3O^{\cdot} + Cl'$$

In this reaction the polar covalent bond between the atoms of hydrogen and chlorine is so split, that the electron pair remains entirely in the possession of the chlorine atom which becomes a Cl' ion, while the proton embeds itself in the electron shell of the oxygen atom of a water molecule to form an oxonium ion $H_3O^{\cdot}$.

A similar chemical reaction takes place when other acids are dissolved in water; for instance, in the case of nitric acid:

$$H_2O + HNO_3 = H_3O^{\cdot} + NO_3'$$

87. Ionizing Influence of Various Solvents. Up till now we have considered dissociation only in aqueous solutions. There are, however, other solvents besides water, such as formic acid, ethyl alcohol, acetone, in which electrolytes are also dissociated, though in much smaller degree. Such solvents are known as *ionizing solvents*. Their molecules, like the molecules of water, are distinctly polar. On the contrary, in non-polar or slightly polar solvents, such as benzene, ether, carbon disulphide, ionization does not occur.

The ionizing capacity of various solvents can be judged best of all by their dielectric constants.

The dielectric constant is a value showing by how many times the force of interaction between two charges in a given medium is smaller than in a void. The dielectric constant of a solvent is closely related to the polarity of its molecules. The high value of the dielectric constants of some liquids is due to the high dipole moments of their molecules.

The dielectric constants of some solvents at 18° C are given below.

Dielectric Constants of Some Solvents

Water	81	Chloroform	5.1
Formic acid	58	Ether	4.3
Ethyl alcohol	27	Carbon disulphide	2.6
Acetone	21	Benzene	2.3

The highest dielectric constant among ordinary solvents is that of water, which is at the same time the best ionizing solvent. The dielectric constant of water equals 81. This means that in aqueous solutions the force of interaction between charged ions is 81 times smaller than that acting in the corresponding crystals. The dielectric constants of such solvents as ether, benzene and carbon disulphide, in which ionization does not occur, are very small. The dielectric constants of alcohol, acetone and other slightly ionizing solvents are intermediate values.

Investigation of the ionizing action of non-aqueous solvents was initiated by Kablukov, who in 1889 first measured the conductivity of hydrogen chloride dissolved in diethyl ether and in amyl alcohol. After this, many chemists began to study non-aqueous solutions. As a result of their works, the theory of electrolytic dissociation was extended to a new field, and the ionizing influence of the medium on the molecules of the solute became clear.

88. Mechanism of Passage of Current Through Solutions. According to present-day views, electric current in metallic conductors is a stream of electrons moving from the negative pole of the current source to its positive pole.

A current source, say a galvanic cell, is an apparatus in which more electrons accumulate on the negative pole than on the positive pole, which gives rise to a sort of electron pressure on the former. If the poles of the cell are connected by means of a metal wire, the electrons begin to move along the wire under the influence of the pressure, from the negative pole to the positive, just like a gas passing from higher pressure to lower. The electrons leaving the negative pole are immediately replenished at the expense of the current source, as a result of which the electrons circulate continuously through

the conductor connecting the poles. The current source acts like a pump, drawing the electrons in through the positive pole and discharging them back into the conductor through the negative pole.

If the wire is cut, one end of it will become negatively charged, as an excess of electrons accumulates on it, whilst the other will become charged positively, due to a deficiency of electrons, and the motion of the electrons along the conductor will cease.

Now suppose two electrodes connected to the poles of a current source and hence charged, one positively and the other negatively, are dipped into a solution of an electrolyte, say hydrochloric acid. Water itself is not a conductor and electrons cannot move through it as they do through a wire, but the ions in solution are attracted

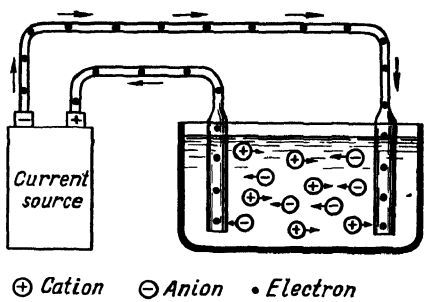


Fig. 74. Mechanism of passage of current through solution

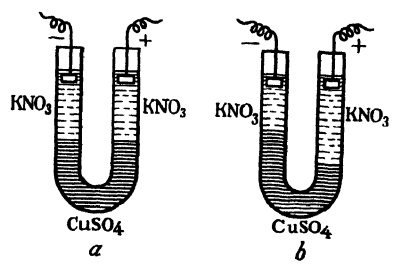


Fig. 75. U-tubes with copper sulphate solution:
a—before switching on current;
b—with current switched on

to the electrodes and immediately begin to move in two opposite directions, the positive ions towards the cathode and the negative towards the anode (Fig. 74). When they reach the cathode, the positive ions gain from it the electrons they lack and become neutral atoms. At the same time, the negative ions give their "surplus" electrons away to the anode and also become neutral ions or radicals. Due to continuous passage of electrons from the cathode to the ions and from the ions to the anode, the travel of the electrons through the wires connecting the poles of the current source with the electrodes is sustained. But within the solution the motion is not that of electrons, but of positively and negatively charged ions. The latter apparently carry the electrons through the solution from the cathode to the anode, although actually the electrons yielded by the anions to anode are not those which passed into the solution from the cathode, but those belonging to the anions themselves.

It is clear from the above that solutions which do not contain ions cannot conduct current.

The movement of ions caused by the passage of current through a solution can be demonstrated by an experiment. For this purpose it is especially convenient to use salts with coloured ions. Take, for instance, a blue solution of copper sulphate. The colour of this solution cannot be attributed to the presence of SO_4'' -ion in it, as many solutions containing this ion are colourless (for instance, solutions of H_2SO_4, Na_2SO_4, $ZnSO_4$, etc.). Dilute solutions of cupric salts, on the other hand, are blue in colour; hence, we must conclude that the blue colour is due to the presence of cupric-ion (or rather its hydrate).

To observe the movement of these ions, a solution of blue vitriol in warm water containing a little agar-agar (an organic substance obtained from seaweeds) is placed in a U-tube (Fig. 75). The solution cools into a jelly which will not hinder the motion of the ions perceptibly. The space above the jelly in both arms of the U-tube is filled with a colourless solution of some salt, say KNO_3, to which agar-agar is also added. If current is passed through, the blue cupric ions travel towards the negative electrode and gradually turn the colourless layer of agar-agar in the left arm of the tube blue from bottom to top. At the same time the boundary between the blue and colourless solutions in the right arm of the tube shifts downwards.

Ions migrate at various velocities, depending on the temperature and the voltage, as well as on the nature of the ions. The higher the temperature and the greater the voltage, the faster the ions move. Hydrogen ions are the fastest, but even they move very slowly, only about 0.2 cm. per minute at a temperature of 18°C and a voltage drop of one volt per cm. The velocities of some other ions under the same conditions are: OH'—0.11 cm. per min., Na'—0.027 cm. per min., Cl'—0.0415 cm. per min., NO_3'—0.039 cm. per min.

89. Degree of Ionization. As stated in § 85, the anomalously high osmotic pressure in solutions of electrolytes is due to dissociation of their molecules into ions. If all the dissolved molecules broke down into ions, it might be expected that the osmotic pressure in solutions of electrolytes would always be a whole number of times greater than the normal pressure observed in equimolecular solutions of non-electrolytes. Meanwhile, in determining the coefficient i for solutions of various salts, Van't Hoff found that this coefficient is represented by fractions which, however, approach the whole numbers 2, 3, 4... as the solution is diluted. To explain these facts, Arrhenius suggested that in ordinary solutions only part of the molecules may be ionized; moreover, the higher the concentration of the solution, the smaller the proportion of ionized molecules.

The reason for incomplete dissociation, in Arrhenius's opinion, was that the decomposition of molecules into ions in solution was

accompanied by the reverse process, that of recombination into molecules. While the rate of dissociation decreases as the molecules break up, the rate of the reverse process increases. This results in a state of equilibrium where the relative quantities of unionized molecules and ions remain constant, i. e., dissociation is not complete.

Thus electrolytic dissociation, like any other dissociation, is a reversible process, expressed in dissociation equations by two arrows instead of the equal sign, for example:

$$NaCl \rightleftarrows Na^{\cdot} + Cl'$$
$$KOH \rightleftarrows K^{\cdot} + OH'$$

The ionization of acids, for instance of HCl, should be written as follows:

$$HCl + H_2O \rightleftarrows H_3O^{\cdot} + Cl'$$

Whilst the direct reaction consists in the splitting away of a proton from a hydrogen chloride molecule and its combination with a molecule of water, the reverse reaction consists in the splitting away of the proton from an oxonium ion $H_3O^{\cdot}$ and its combination with a Cl′ ion to form a HCl molecule. The chloride ion plays the same part with respect to the oxonium ion as the water molecule with respect to the hydrogen chloride molecule.

In simplified form the equation of ionization of hydrogen chloride is written as follows:

$$HCl \rightleftarrows H^{\cdot} + Cl'$$

However, when using such a mode of recording (which we shall employ often in the future), it must be remembered that the dissociation of acids is not a simple decomposition of their molecules into ions, but a more complex chemical reaction involving water molecules.

The ratio of the number of ionized molecules to the total number of molecules dissolved is called the degree of ionization of an electrolyte. For example, if 78 out of every 100 HCl molecules dissolved in water dissociated into ions, the degree of ionization would be 0.78 or 78 per cent. Hence, the degree of ionization shows the proportion of dissolved molecules that has broken down into ions.

The degree of ionization depends both on the nature of the dissolved electrolyte and on the concentration of the solution: *when the solution of any electrolyte is diluted, its degree of ionization increases.* This means that the equilibrium existing in solution between the unionized molecules and the ions shifts towards the formation of ions. It is not difficult to prove that such a shift of equilibrium is in full agreement with Le Châtelier's Principle. Indeed, in diluting the solution with water, we decrease the concentration of particles, both molecules and ions, in it and therefore lower its osmotic pressure. But lowering the pressure should shift the equilibrium in the

direction of the reaction which will increase the pressure again, i. e., towards the formation of a larger number of ions.

As the degree of ionization depends on the concentration of the solution, we must always indicate the concentration when referring to the degree of ionization for any electrolyte.

The numerical values of the degree of ionization of electrolytes can be determined by various methods. We shall examine a method based on determination of the isotonic coefficient of the solution.

The isotonic coefficient i, as indicated above (see p. 247), shows how many times the osmotic pressure, the boiling point elevation and the freezing point lowering, actually observed in the solution of an electrolyte, are greater than the same values calculated theoretically under the assumption that the solute has not dissociated:

$$i = \frac{P'}{P} = \frac{\Delta t'_{b.p.}}{\Delta t_{b.p.}} = \frac{\Delta t'_{f.p.}}{\Delta t_{f.p.}}$$

Since all these values are proportional to the number of solute particles in solution, the isotonic coefficient should obviously be equal to the ratio between the total number of molecules and ions in the solution to the initial number of molecules dissolved.

On this basis, the relation between the isotonic coefficient and the degree of ionization can easily be expressed in mathematical form.

Suppose N molecules of electrolyte were dissolved in water, and that each of them can break down into n ions.

If the degree of ionization is α, the number of molecules broken down into ions will equal $N\alpha$, the number of ions formed will be $N\alpha n$, and the number of molecules left unionized will be $N(1-\alpha)$. Hence, the total number of particles (molecules plus ions) in solution will be:

$$N(1-\alpha)+N\alpha n \text{ or } N[(n-1)\alpha+1]$$

but since the number of molecules dissolved is N, we get the following expression for the isotonic coefficient:

$$i = \frac{N[(n-1)\alpha+1]}{N} = (n-1)\alpha+1$$

hence the degree of ionization

$$\alpha = \frac{i-1}{n-1}$$

Thus, to determine the degree of ionization of an electrolyte we need only find the value of the coefficient i for the given solution, which can be done most easily by measuring the lowering of the freezing point (cryoscopic method). On the other hand, knowing the concentration of the solution and the degree of ionization of a dissolved

electrolyte, the isotonic coefficient, and consequently, the osmotic pressure, as well as the freezing and boiling points of the solution, can easily be calculated (by the same formula).

Example 1. A solution containing 8 gr. NaOH in 1,000 gr. of water freezes at —0.677° C. Find the degree of ionization of NaOH in this solution.

We find the theoretical lowering of the freezing point by the formula $\Delta t = \frac{K \times m}{M}$. Since the molecular weight of NaOH equals 40, $m = 8$ and $K = 1.86$,

$$\Delta t = \frac{1.86 \times 8}{40} = 0.372°$$

The freezing point lowering actually observed is $\Delta t' = 0.677°$, hence

$$i = \frac{0.677}{0.372} = 1.82$$

Substituting the value of i in the formula for determining α and taking into account that NaOH dissociates into two ions, we get:

$$\alpha = \frac{1.82 - 1}{2 - 1} = 0.82 \text{ or } 82 \text{ per cent}$$

Example 2. In decinormal solution potassium sulphate is ionized to a degree of 71 per cent. What is the osmotic pressure of the solution at 0° C?

We first calculate the theoretical osmotic pressure. A decinormal solution of K_2SO_4 contains $^1/_{20}$ mole per litre. Its osmotic pressure, if not ionized, should be 20 times lower than the osmotic pressure of a solution containing one mole per litre. Therefore,

$$P = \frac{22.4}{20} = 1.12 \text{ atm.}$$

According to the problem $\alpha = 0.71$. The K_2SO_4 "molecule" breaks down into three ions, hence

$$0.71 = \frac{i - 1}{3 - 1}; \quad i = 2.42$$

Having found i, we determine P':

$$2.42 = \frac{P'}{1.12}; \quad P' = 2.71 \text{ atm.}$$

In practice, the degree of ionization of electrolytes is usually determined not by the cryoscopic method, but by a simpler one, involving measurement of the electrical conductivity of solutions.

As we know, the conductivity of a solution is its capacity for conducting current. There is a close relation between the electrical conductivity and ionization. As only the dissociated part of the electrolyte is active in conducting current, it is clear that, other conditions being equal, the more molecules ionized, the better the solution will conduct current. Therefore, by measuring the conductivity of the solution, we can calculate the degree of ionization of

the molecules in it. A detailed description of the procedure being beyond the scope of this textbook, we shall note only that the degrees of ionization of various electrolytes calculated by the conductivity of their solutions coincide quite well with the respective values obtained by the cryoscopic method. This was in its time one of the important factors which led to universal recognition of Arrhenius's theory.

Making use of the relation between the conductivity and the degree of ionization, it can easily be shown by experiment that the latter value increases as the solution is diluted.

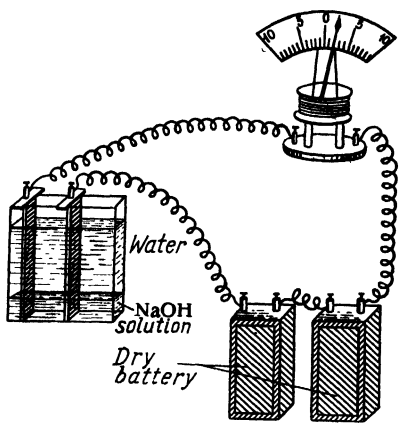


Fig. 76. Set-up for demonstrating rise in electrical conductivity of a solution with dilution

Two long copper plates several centimetres apart are lowered to the bottom of a rectangular vessel (Fig. 76) and connected to the poles of a battery of two dry cells, a galvanometer being cut into the circuit. The vessel is first filled with distilled water. The indicator of the galvanometer will remain at rest, since water does not conduct current. Then, a concentrated solution of caustic soda (sodium hydroxide) is added carefully through a funnel with a long stem reaching down to the bottom of the vessel, so that the solution forms a thin layer at the bottom. The small number of Na^+ and OH^- ions in the concentrated solution fills the non-conducting interval which formerly existed in the circuit, and the indicator of the galvanometer is deflected a little, due to the presence of a slight current. Now stir the liquid in the vessel carefully. The deflection of the indicator gradually increases, showing that the conductivity is rising; the indicator will stop moving only after the liquid becomes homogeneous. Since the amount of caustic soda between the electrodes remains unchanged when the liquid is stirred, the rise in the conductivity, from the standpoint of Arrhenius's theory, is due to an increase in the number of ions in the solution. Thus the degree of ionization of caustic soda increases as the solution is diluted.

90. Strong and Weak Electrolytes. Measurement of the degree of ionization of various electrolytes has shown that different electrolytes dissociate into ions in solutions of equinormal concentration very differently.

An especially great difference in degrees of ionization is observed in the case of acids. For instance, nitric and hydrochloric acids break down almost completely into ions in 0.1 N solution; but carbonic, hydrocyanic and other acids ionize under the same conditions to a very insignificant degree.

Of the water-soluble bases (alkalis), ammonium hydroxide is slightly ionized, whilst the other alkalis are greatly ionized. All salts, with very few exceptions, dissociate readily into ions.

The variety of degrees of ionization among different acids is due to the nature of the valency bond between the atoms forming their molecules. The more polar the bond between hydrogen and the rest of the molecule, the more easily the hydrogen can split off, and the more the acid will be ionized. Besides, the degree of ionization of electrolytes depends also on the charges of the ions formed. For instance, with salts which already exist as ions in the solid form, the attraction between singly charged ions in the solution will obviously be weaker than between multicharged ions. Therefore, solutions of salts of the type X^+Y^- (such as NaCl, KNO_3, etc.) should contain less unionized molecules than solutions of salts of the type $X^{++}Y^{--}$ ($CuSO_4$, $ZnSO_4$, etc.), i. e., the degree of ionization of the former should be higher than that of the latter, which is actually the case. Salts of the types $X_2^+Y^{--}$ or $X^{++}Y_2^-$ (Na_2SO_4, $CaCl_2$) obviously occupy an intermediate position.

Electrolytes which dissociate readily into ions are known as **strong** electrolytes in contradistinction to **weak** electrolytes, which yield but insignificant quantities of ions in aqueous solution. Solutions of strong electrolytes retain a high conductivity even at very high concentrations. On the contrary, the conductivity of solutions of weak electrolytes drops rapidly as the concentration increases. Strong electrolytes include such acids as hydrochloric, nitric, sulphuric and several others, the alkalis (except NH_4OH) and almost all salts.

Polybasic acids and polyacidic bases ionize by steps. Thus, for instance, sulphuric acid molecules ionize first according to the equation

$$H_2SO_4 \rightleftarrows H^+ + HSO_4^-$$

or, to be more precise:

$$H_2SO_4 + H_2O \rightleftarrows H_3O^+ + HSO_4^-$$

The second hydrogen ion splits off according to the equation

$$HSO_4^- \rightleftarrows H^+ + SO_4^{--}$$

or

$$HSO_4^- + H_2O \rightleftarrows H_3O^+ + SO_4^{--}$$

with much greater difficulty, as it has to overcome the attraction of the doubly charged SO_4'' ion, which, of course, attracts the hydrogen ion more strongly than the singly charged HSO_4' ion. Therefore, the second step of ionization, or secondary ionization, as we say, takes place much less intensively than the first step, so that ordinary solutions of sulphuric acid contain but a small quantity of SO_4''-ion.

Phosphoric acid H_3PO_4 ionizes in three steps:

$$H_3PO_4 \rightleftarrows H^{\cdot} + H_2PO_4'$$
$$H_2PO_4' \rightleftarrows H^{\cdot} + HPO_4''$$
$$HPO_4'' \rightleftarrows H^{\cdot} + PO_4'''$$

H_3PO_4 molecules dissociate actively into $H^{\cdot}$- and H_2PO_4'-ion. H_2PO_4'-ion behaves like a weaker acid, ionizing into $H^{\cdot}$ and HPO_4'' to a smaller degree. HPO_4''-ion ionizes like a very weak acid, yielding hardly any $H^{\cdot}$- and PO_4'''-ion at all.

Bases containing more than one hydroxyl radical in their molecules also dissociate by steps. For instance:

$$Ba(OH)_2 \rightleftarrows BaOH^{\cdot} + OH'$$
$$BaOH^{\cdot} \rightleftarrows Ba^{\cdot\cdot} + OH'$$

As to salts, *normal salts* always break up into ions of metals and acid radicals. For example:

$$CaCl_2 \rightleftarrows Ca^{\cdot\cdot} + 2Cl'$$
$$Na_2SO_4 \rightleftarrows 2Na^{\cdot} + SO_4''$$

Acid salts, like polybasic acids, ionize by steps. For instance:

$$NaHCO_3 \rightleftarrows Na^{\cdot} + HCO_3'$$
$$HCO_3' \rightleftarrows H^{\cdot} + CO_3''$$

However, the degree of ionization in the second step is very small, so that a solution of an acid salt contains but an insignificant quantity of hydrogen-ion.

Basic salts ionize into basic and acid radicals. For example:

$$Fe(OH)Cl_2 \rightleftarrows FeOH^{\cdot\cdot} + 2Cl'$$

Secondary dissociation of the ions of basic radicals into metallic and hydroxyl ions hardly takes place at all.

Table 13 gives the numerical values of the degrees of ionization of some acids, bases and salts in 0.1 N solution.

Table 13

Degree of Ionization of Acids*, Bases and Salts in 0.1 N Solution at 18° C

Electrolyte	Formula	Degree of ionization, per cent
Acids		
Hydrochloric	HCl	92
Hydrobromic	HBr	92
Hydroiodic	HI	92
Nitric	HNO_3	92
Sulphuric	H_2SO_4	58
Sulphurous	H_2SO_3	34
Phosphoric	H_3PO_4	27
Hydrofluoric	HF	8.5
Acetic	CH_3COOH	1.3
Carbonic	H_2CO_3	0.17
Hydrogen sulphide	H_2S	0.07
Hydrocyanic	HCN	0.01
Boric	H_3BO_3	0.01
Bases		
Barium hydroxide	$Ba(OH)_2$	92
Potassium hydroxide	KOH	89
Sodium hydroxide	NaOH	84
Ammonium hydroxide	NH_4OH	1.3
Salts		
Potassium chloride	KCl	86
Ammonium chloride	NH_4Cl	85
Sodium chloride	NaCl	84
Potassium nitrate	KNO_3	83
Silver nitrate	$AgNO_3$	81
Sodium acetate	$NaCH_3COO$	79
Zinc chloride	$ZnCl_2$	73
Sodium sulphate	Na_2SO_4	69
Zinc sulphate	$ZnSO_4$	40
Copper sulphate	$CuSO_4$	40

As the concentration is increased, the degree of ionization diminishes. Therefore, in very concentrated solutions, even strong acids are ionized comparatively little. By way of example, the degrees of

* In the case of polibasic acids the degree of primary ionization is given.

ionization of the concentrated acids usually used in the laboratory are as follows:

	Degree of ionization, per cent
Hydrochloric acid (35 p. c. HCl)	13.6
Nitric acid (62 p. c. HNO_3)	9.6
Sulphuric acid (95 p. c. H_2SO_4)	1

91. Ionization Constant. Since according to the theory of Arrhenius electrolytic dissociation is a reversible reaction, leading to a state of equilibrium between the unionized molecules and the ions, it obeys the Law of Mass Action. Hence, the equilibrium constant of this reaction can be derived in exactly the same way as for other reversible reactions. Take, for instance, an electrolyte, the molecule of which XY breaks down into X' and Y' ions:

$$XY \rightleftarrows X' + Y'$$

Denoting the concentration of unionized molecules by $[XY]$, and the concentrations of the ions by $[X']$ and $[Y']$, we have at equilibrium:

$$\frac{[X'] \cdot [Y']}{[XY]} = K$$

The equilibrium constant K is in this case called the **constant of ionization** or **dissociation**. Its value characterizes the ability of the electrolyte to ionize. Indeed, from the previous equation it can be seen that the higher the value of K, the greater must be the concentration of the ions at equilibrium, i.e., the more the electrolyte is ionized.

A definite relation exists between the ionization constant and the degree of ionization of an electrolyte, making it possible to express either of these values in terms of the other. If C is the molar concentration of an electrolyte which breaks down into two ions, and its degree of ionization in a given solution is α, the concentration of each of the ions will be $C\alpha$, and the concentration of unionized molecules $C(1-\alpha)$. Then the equation of the ionization constant becomes

$$\frac{(C\alpha)^2}{C(1-\alpha)} = K \text{ or } K = \frac{\alpha^2}{1-\alpha} \times C$$

This equation is the expression of Ostwald's **Dilution Law.** It enables computation of the degree of ionization for various concentrations if the ionization constant of the electrolyte is known. On the other hand, if the degree of ionization is determined at any definite concentration, the ionization constant can easily be computed

therefrom. In these calculations the concentration of unionized molecules is expressed in gram-molecules (moles) per litre. Accordingly, the concentration of the ions is expressed in gram-ions per litre.

A **gram-ion** is a quantity of an ion the weight of which in grams is numerically equal to its weight in oxygen units. For instance, a gram-ion of Cl' equals 35.5 gr., a gram-ion of OH' equals 17 gr., etc.

The equilibrium constant does not depend on the concentration of the initial substances of the reaction. Therefore, if equilibrium actually exists in a solution of an electrolyte, the value of the ionization constant should be the same no matter what concentration of the solution it is calculated for. Let us attempt to carry out a calculation of this sort and thus verify Arrhenius's theory.

We shall calculate the ionization constant for some weak electrolyte, acetic acid, for instance, which ionizes according to the equation

$$CH_3COOH \rightleftarrows H^+ + CH_3COO'$$

proceeding, say, from a 0.1 N solution. The degree of ionization of acetic acid in 0.1 N solution equals 0.0132. Substituting these figures into the equation of the equilibrium constant

$$K = \frac{\alpha^2}{1-\alpha} \times C$$

we get:

$$K = \frac{(0.0132)^2}{1-0.0132} \times 0.1 = 0.0000176 \text{ or } 1.76 \cdot 10^{-5}$$

Now we carry out a similar calculation for a 0.01 N solution in which the degree of ionization equals 0.041:

$$K = \frac{(0.041)^2}{1-0.041} \cdot 0.01 = 0.0000175 \text{ or } 1.75 \cdot 10^{-5}$$

These two values found for the ionization constant of acetic acid are in very good agreement. They agree also with the values calculated for other concentrations of acetic acid. Hence, the ionization of acetic acid, a typical weak electrolyte, obeys the Law of Mass Action.

The picture is entirely different in solutions of strong electrolytes. By way of illustration, the results of calculations of the ionization constant of potassium chloride in solutions of various concentrations are given in Table 14.

Here K is no longer a constant, as it does not remain invariable but increases with the concentration of the solution. Variability of K is characteristic not only of potassium chloride but of any

Table 14

Ionization of Potassium Chloride at 18° C

KCl concentration	α	*K*
2 N	0.712	3.52
1 N	0.756	2.34
0.5 N	0.788	1.46
0.1 N	0.862	0.536
0.01 N	0.942	0,152

strong electrolyte. Hence, the Law of Mass Action is obviously inapplicable to strong electrolytes.

Thus, in the case of weak electrolytes, the theory of Arrhenius quite agrees with experimental data; but for strong electrolytes it requires essential corrections.

92. State of Strong Electrolytes in Solution. The theory of Arrhenius derives all its conclusions on the assumption that no perceptible forces act between the ions in solution and that the mobility of the ions does not depend on their concentration. But ions are electrically *charged particles.* If in solutions of weak electrolytes where the ionic concentration is insignificant, the forces of electrical interaction between ions may be neglected, in solutions of strong electrolytes this is not quite the case. Owing to the considerable concentration of the ions, the mean distance between them is comparatively small. For instance, in a saturated solution of sodium chloride the mean distance between the ions is only twice as large as in NaCl crystals. Under such conditions the forces of interionic attraction and repulsion are quite high. These forces cause strong electrolytes to deviate from the Law of Mass Action.

We now have at our disposal a well-developed theory explaining the peculiar behaviour of strong electrolytes in solution by making allowance for the action of interionic forces. Owing to the mathematical complexity of this theory, only a general idea of it can be given in this book.

From investigations of crystal structure we know that salts, which are the most typical strong electrolytes, consist of separate ions, and not molecules, even in the solid form. But if there are no molecules as such in the bulk of the solid, it is natural to assume there are none in the solution of the substance either. Therefore it must be considered that all strong electrolytes are *completely ionized* in aqueous solutions, independent of their concentration. However, in such solutions the ions are not quite free, their motion being

impeded by mutual attraction. Owing to this attraction, each ion is surrounded by a sphere-shaped swarm of ions of the opposite charge, a so-called "ionic atmosphere." While the solution is in equilibrium, i.e., no chemical reactions, diffusion, etc., are taking place in it, the ionic atmosphere is symmetrical and the forces acting on the central ion cancel each other.

If electrodes connected with a source of electric current are dipped into the solution, the oppositely charged ions begin to move in opposite directions, each ion tending to leave its ionic atmosphere. But the atmosphere the ion attempts to leave keeps drawing it back, as a result of which the motion of the ion is retarded, and therefore the number of ions passing through the solution per unit time, i.e., the current, decreases. The higher the concentration of the solution, the stronger the retarding action of the ionic atmosphere and the lower the conductivity of the solution. Hence the impression that the number of ions in solution decreases with growing concentration. Actually, however, ionization is complete at all concentrations; therefore, by measuring the conductivity, we can determine only the *apparent degree of ionization.*

The forces of interionic attraction and repulsion affect the measured osmotic pressure in a similar manner, so that despite complete ionization, the latter is lower than might be expected for a doubled, trebled, etc., number of particles. For the same reason, the ability of the ions to enter into chemical reaction is weakened. In brief, all the properties of a solution of electrolyte which depend on the concentration of its ions manifest themselves as if the number of ions in solution were smaller than that corresponding to their concentration (in gram-ions per litre), calculated on the assumption of complete ionization of the molecules.

To evaluate this inhibited ability of ions to enter into reaction, a value is now employed known as the **activity.** *The activity of an ion is its effective conventional concentration, according to which it acts during chemical reactions.* The activity of an ion equals its concentration multiplied by a certain fraction, called its **activity coefficient.** An activity coefficient less than 1 means that the actions of the ion are limited; if the activity coefficient equals 1, the actions of the ion are not hindered. The latter is true only of very dilute solutions, in which the ions are so far apart that the interionic forces may be practically neglected.

If the activities of ions are used instead of their concentrations, the Law of Mass Action becomes applicable to strong electrolytes.

Thus, in contradistinction to the conceptions of Arrhenius, the present-day theory of ionization assumes that strong electrolytes are practically completely ionized. Therefore, if we sometimes speak of the degree of ionization of strong electrolytes, we really mean the apparent degree of ionization found by the conductivity or cryoscopic method.

93. Properties of Acids, Bases and Salts from the Point of View of the Ionization Theory. In the foregoing paragraphs we have become acquainted with the Theory of Ionization. Now we shall examine the properties of substances—acids, bases and salts—which are electrolytes in aqueous solution, on the basis of this theory.

1. *Acids.* As we know, acids have the following generic properties:

a) sour taste;

b) ability to change the colour of many indicators, particularly to turn litmus red;

c) ability to dissolve certain metals with the evolution of hydrogen;

d) ability to react with bases to form salts.

All these properties of acids are manifested only in solution, moreover, almost exclusively in aqueous solution. For instance, dry hydrogen chloride and its solution in benzene possess no acidic properties at all, do not even turn litmus paper red, but its solution in water, hydrochloric acid, is one of the most typical acids; similarly anhydrous sulphuric acid does not act at all on zinc at ordinary temperatures, while its aqueous solution reacts vigorously with zinc, liberating hydrogen.

As we know now, aqueous solutions of acids do not contain molecules, but mainly free ions. It is clear, therefore, that the properties of such solutions must also depend on the properties of the separate ions and not on integral molecules.

Since the formation of hydrogen-ion is a *sine qua non* in the ionization of any acid, all the properties common to aqueous solutions of acids must be attributed to hydrogen-ion or, more precisely, to oxonium-ion. It is they that turn litmus red, react with metals, account for the sour taste of acids, etc. When the hydrogen-ion is removed, as by neutralization, the acid properties disappear. Therefore the Theory of Ionization defines *acids as electrolytes which ionize in aqueous solution to form hydrogen-ion and yield no other positively charged ions.* The last phrase is necessary because certain acid salts, such as KH_2PO_4 or $NaHSO_4$, also split off hydrogen ions in aqueous solution, at the same time yielding positively charged metal ions.*

Acids in which the above properties are well pronounced, are called **strong** acids. Since the bearer of the acid properties is hydrogen-ion, the higher the concentration of the latter in the acid solution at any definite dilution, i.e., the better the acid ionizes, the stronger it will be. Examples of strong acids are hydrochloric and nitric acids, which are probably completely ionized, but in 0.1 N

* Hydrogen-ion may form also when salts of heavy metals are dissolved in water, due to interaction between the metal cations and water (see § 102).

solution have an apparent degree of ionization of approximately 92 per cent, due to the electrical interaction between their ions. On the other hand, acids with low degrees of ionization, such as acetic, carbonic and others, are considered weak.

Thus the measure of the strength of acids is their degree of ionization.

The strength of acids can be judged by various reactions. By way of example we may indicate the rate of liberation of hydrogen from various acids during their reaction with metals.

Perform the following experiment. Pour normal solutions of hydrochloric, phosphoric and acetic acids into separate small flasks. Throw an identical piece of zinc or magnesium into each flask and close them quickly with stoppers carrying gas delivery tubes the outlets of which are immersed in a water bath under inverted burettes (Fig. 77).

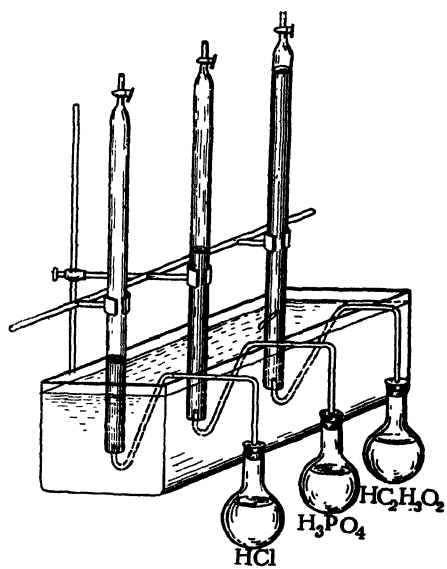


Fig. 77. Apparatus for comparing various acids with respect to rate of hydrogen liberation

Hydrogen will be liberated the most rapidly by the hydrochloric acid, much more slowly by the phosphoric acid and very slowly by the acetic acid. Thus, if we judge the strength of the acids by the rate of liberation of hydrogen, the strongest of these three acids is hydrochloric and the weakest, acetic, this being in full agreement with their respective degrees of ionization.

The difference in strength of acids is gradually smoothed over as they are diluted, since with increasing dilution the degree of ionization of all electrolytes grows, approaching 100 per cent. With very high dilution all acids and bases are ionized almost completely, i.e., are equally strong. However, we must not conclude from this that the more dilute an acid, the more vigorous its action. Actually, the action of an acid depends on the concentration of hydrogen-ion in its solution, which in its turn depends both on the degree of ionization and on the total concentration of the acid. Although the degree of ionization increases as the solution is diluted, the total concentration of the acid decreases, and, moreover, usually more rapidly

than the former grows. Therefore, in dilute solutions the concentration of hydrogen-ion is always lower than in concentrated. This is easy to see in the case of hydrochloric acid (Table 15).

Table 15

Degree of Ionization and Hydrogen-Ion Concentration in HCl Solutions

HCl concentration	Degree of ionization, per cent	Hydrogen-ion concentration, gr.-ions per litre
10 N	12	1.2
1 N	78	0.78
0.1 N	92	0.092

2. *Bases.* Aqueous solutions of bases possess the following generic properties:

a) a peculiar "soapy" taste;

b) ability to change the colour of indicators inversely to acids, for instance, to turn litmus blue;

c) ability to react with acids to form salts.

Since the presence of hydroxyl-ion is common to all solutions of bases, it is obvious that the bearer of their basic properties is hydroxyl-ion. Therefore, from the standpoint of the ionization theory *bases are electrolytes which ionize in aqueous solution, splitting off hydroxyl-ions.**

The strength of bases, like that of acids, depends on the degree of their ionization. The strongest bases are sodium hydroxide and potassium hydroxide which are probably completely ionized in aqueous solution, although their apparent degree of ionization in 0.1 N solution is about 90 per cent. Most bases are weak electrolytes.

3. *Salts.* Salts may be defined as electrolytes which ionize upon being dissolved in water to form positive ions other than hydrogen-ion and negative ions other than hydroxyl-ion. There are no ions common to aqueous solutions of all salts; therefore salts possess no common properties. Salts, as a rule, are highly ionized, their ionization being the higher, the lower the valency of their ions.

94. Hydroxides and Their Ionization. All oxygen acids and all bases may be regarded as products of combination of the corresponding oxides with water and they may be united under the common name of **hydrated oxides** or **hydroxides.** For instance, sulphuric

* Some salts, when dissolved in water, also give rise to hydroxyl-ion, but the latter originates from the water molecules and not from the salts (see § 102).

acid may be regarded as the hydrated oxide of hexavalent sulphur, nitric acid, as the hydrated oxide of pentavalent nitrogen, etc.

Classification of hydrated oxides as acids or bases depends on the ions they yield in aqueous solution. If hydrogen-ion is formed upon ionization, the hydrated oxide is called an acid; if it ionizes, yielding hydroxyl-ion, it is classed as a base.

In this connection, two types of ionization of hydrated oxides may be distinguished:

the acid type of ionization:

$$R{-}O{-}H \rightleftarrows RO' + H^{\cdot}$$

and the base type of ionization:

$$R{-}O{-}H \rightleftarrows R^{\cdot} + OH'$$

Thus, when hydrated oxides ionize, the rupture may occur either at the bond between the oxygen and the hydrogen (acid type of ionization) or in that between the element R and the oxygen (base type of ionization). The type of ionization depends on the position of the element R in the Periodic Table, determining the relative strength of the bonds between the element and oxygen, on the one hand, and between oxygen and hydrogen, on the other.

Knowing the properties of the hydrated oxide, i.e., whether it is acidic or basic, we write its formula accordingly, putting the hydrogen in front of it if it is an acid, or the metal, if it is a base. For instance, boric acid is represented by the formula H_3BO_3 and not $B(OH)_3$; ferric hydroxide by the formula $Fe(OH)_3$ and not H_3FeO_3.

Besides acidic and basic, there exist also amphoteric hydroxides which, depending on the medium, may behave either as acids or as bases. Examples are $Zn(OH)_2$, $Al(OH)_3$, etc., with which we shall become acquainted when we come to the metals.

Amphoteric hydroxides react both with acids and with alkalis to form salts. For instance, zinc hydroxide dissolves in acids, forming zinc salts:

$$Zn(OH)_2 + H_2SO_4 = ZnSO_4 + 2H_2O$$

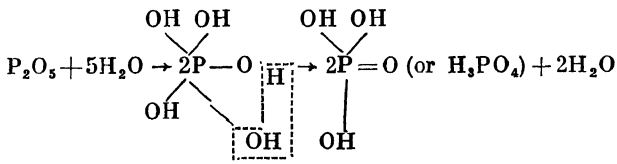
but zinc hydroxide dissolves also in alkalis, acting in this case as zincic acid H_2ZnO_2 and forming salts of this acid:

$$H_2ZnO_2 + 2NaOH = Na_2ZnO_2 + 2H_2O$$

In practice, the nature of hydrated oxides and the class they belong to are established either by means of indicators, if they are soluble in water (soluble acids, alkalis), or by their attitude towards acids and alkalis, if they are not. Acid hydroxides dissolve in alkalis but are insoluble in other acids; basic hydroxides dissolve in acids but

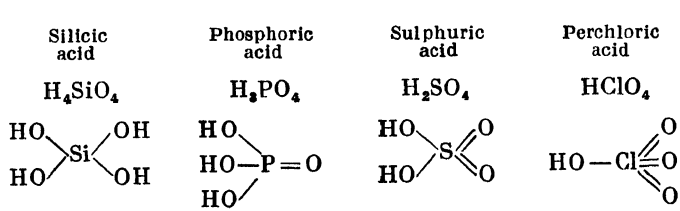
are insoluble in alkalis, and amphoteric hydroxides dissolve both in acids and in alkalis.

The composition of any hydroxide ought to be expressed by the general formula $R(OH)_x$, where x is the valency of the element R. However, hydroxides in which the valency of R is greater than two, often split off part of their water to form compounds with lower water contents. For instance, the hydroxide of trivalent chromium can exist in the form of $Cr(OH)_3$, but also in the form of $Cr{<}^{O}_{OH}$. Elements having a valency of more than four seldom form hydroxides with a complete number of hydroxyl groups. Thus, pentavalent phosphorus should have had a hydrated oxide of the formula $P(OH)_5$, but orthophosphoric acid, the highest hydroxide of phosphorus in hydrogen, contains only three hydroxyl radicals. Its formation from phosphoric anhydride P_2O_5 and water may be represented as follows:

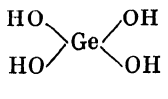


Experimental data show that the atoms of the elements in the second period can be chemically linked with not more than three oxygen atoms. Therefore, the formula of nitric acid is HNO_3 or $HO-N{<}^{O}_{O}$ but not $(HO)_5N$; the formula of carbonic acid is H_2CO_3 or $(HO)_2C=O$ and not $(HO)_4C$.

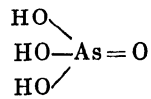
Atoms of the elements of the third and fourth periods are usually chemically linked directly with as many as four oxygen atoms, as can be seen from an examination of the formulas of their hydroxides:



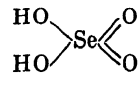
Germanic acid H_4GeO_4



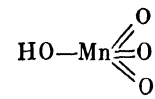
Arsenic acid H_3AsO_4



Selenic acid H_2SeO_4



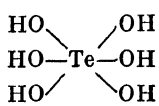
Permanganic acid $HMnO_4$



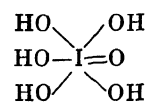
Acids like metasilicic H_2SiO_3 and metaphosphoric HPO_3 seem at first sight to be exceptions to this rule. However, the formulas given above for these acids are their empirical formulas, and do not reflect the true composition of their molecules, which, according to present-day data, corresponds to the formulas $(H_2SiO_3)_x$ and $(HPO_3)_x$, where x equals three or more.

The largest number of oxygen atoms which can be grouped around the atom of an element of the fifth period (in its corresponding valency state) equals six. Examples are telluric and periodic acids:

Telluric acid H_6TeO_6



Periodic acid H_5IO_6



Thus, the composition of hydroxide molecules is determined not only by the valency of the elements (which in its turn depends on the group of the element in the Periodic Table), but also by the period in which the element is located.

95. Shift of Ionic Equilibria. Like any other chemical equilibrium, the equilibrium existing in solutions of electrolytes between their ions and unionized molecules remains unaltered as long as the external conditions are the same; any change in these conditions causes a shift of equilibrium in one direction or the other. We have already seen that increasing the volume of the solution by adding water to it shifts the equilibrium towards the formation of new quantities of ions (the degree of ionization rises); decreasing the volume by evaporation causes the reverse effect.

The equilibrium is disturbed also if the concentration of one of the ions in the solution is altered: an increase in the concentration will shift the equilibrium towards the formation of unionized molecules, simultaneously decreasing the concentration of the other ion. For instance, if a solution of an acetate salt containing a large amount of CH_3COO'-ion is added to a solution of acetic acid, CH_3COOH, which ionizes according to the equation

$$CH_3COOH \rightleftarrows H^+ + CH_3COO'$$

the ionization equilibrium shifts to the left, i. e., the degree of ionization of acetic acid falls. Hence, we come to the conclusion that *the introduction into the solution of a weak electrolyte of like ions* (i. e., ions identical to one of the electrolyte ions) *decreases its degree of ionization.* On the other hand, reducing the concentration of one of the ions causes new portions of the molecules to ionize. For instance, if hydroxyl-ion is introduced into a solution of the above acid the ionization of the acid increases due to binding of the hydrogen-ion.

Let us examine one more important case of equilibrium shift, namely, in a saturated solution of electrolyte. It was stated on page 225, that when a solid is dissolved in water it stops dissolving as soon as the solution becomes saturated, i. e., as soon as a state of equilibrium is reached between the solute molecules still in the solid and those already in solution. When strong electrolytes, such as salts with ionic crystals, are dissolved, separate ions and not molecules, pass into solution and consequently equilibrium in saturated solutions is set up between the ions which have passed into solution and the solid phase of the solute or, more precisely, between the free ions in solution and the bound ions in the salt crystals. For instance, in a saturated solution of calcium sulphate, $CaSO_4$, the following equilibrium should exist:

$$\underset{\text{bound ions in the solid salt}}{Ca^{++}(SO_4)^{--}} \rightleftarrows \underset{\text{free ions in solution}}{Ca^{\cdot\cdot} + SO_4''}$$

Applying the Law of Mass Action to this heterogeneous equilibrium and keeping in mind that the concentration of the solid phase is not included in the expression for the equilibrium constant (see p. 193) we may write:

$$[Ca^{\cdot\cdot}] \cdot [SO_4''] = K$$

Thus, *in a saturated solution of a slightly soluble electrolyte the product of the concentrations of its ions is constant at any definite temperature.* As this value characterizes the ability of the electrolyte to dissolve, it is called the **solubility product** of the electrolyte and is designated by SP.

Replacing K in the above equation by SP_{CaSO_4}, we get:

$$SP_{CaSO_4} = [Ca^{\cdot\cdot}] \cdot [SO_4'']$$

The numerical value of the solubility product can easily be found if we know the solubility of the electrolyte. For instance, the solubility of calcium sulphate $CaSO_4$ at 20°C is 1.5×10^{-2} moles per litre, meaning that one litre of saturated $CaSO_4$ solution at 20°C contains 1.5×10^{-2} moles of $CaSO_4$. Since each $CaSO_4$ "molecule" upon ioniza-

tion yields one $Ca^{\cdot\cdot}$ ion and one SO_4'' ion, the concentration of each of them evidently equals 1.5×10^{-2} gram-ions per litre. Therefore, the solubility product of calcium sulphate is

$$SP_{CaSO_4}=[Ca^{\cdot\cdot}]\cdot[SO_4'']=1.5\cdot10^{-2}\cdot1.5\cdot10^{-2}=2.25\cdot10^{-4}$$

The above calculation, carried out on the basis of the classical theory of ionization, is not quite exact, as it makes no allowance for the influence of the electrostatic forces acting between the ions on the solubility of the electrolyte. If this influence is taken into account, the value obtained for $CaSO_4$ is a little smaller. In the case of very slightly soluble electrolytes the influence of these forces may be neglected.

It is clear that when the electrolyte molecule contains two or more identical ions, the concentrations of these ions should be raised to the corresponding power when calculating the solubility product. For example:

$$SP_{PbI_2}=[Pb^{\cdot\cdot}]\cdot[I']^2$$

Now what will happen if to a saturated solution of calcium sulphate we add another, more soluble electrolyte containing a common ion with calcium sulphate, say, potassium sulphate? Owing to the increase in the concentration of SO_4''-ion, the equilibrium existing in the solution will evidently begin to shift towards the formation of solid $CaSO_4$. In other words, $Ca^{\cdot\cdot}$- and SO_4'' -ions will be removed from the solution, forming a precipitate of $CaSO_4$, until the product of their concentrations again becomes equal to the solubility product of $CaSO_4$. As a result, the amount of calcium sulphate in solution will decrease.

The truth of the above can easily be demonstrated experimentally by adding a little concentrated K_2SO_4 solution to saturated solution of calcium sulphate. A white crystalline precipitate of $CaSO_4$ is immediately thrown down.

Thus, we come to the conclusion that the *solubility of an electrolyte decreases when like ions are introduced into its solution.* Exceptions to this rule are those cases when one of the ions in solution is bound by the ions introduced leading to the formation of larger (complex) ions.

It follows from this that a precipitate of any slightly soluble electrolyte will form during a reaction whenever the product of the concentrations of its ions in solution exceeds its solubility product.

The solubility product rule makes it possible to solve numerous problems involving the formation or dissolving of precipitates during chemical reactions, this being especially important for analytical chemistry. It must, however, be kept in mind that the *solubility product is a constant only for slightly soluble substances* and under the condition that the concentrations of the like ions introduced into the

solution are not too high. In the case of soluble electrolytes, the product of the concentrations of its ions in saturated solution may vary greatly, depending on the presence of greater or smaller quantities of other substances.* Therefore, calculations involving the solubility product rule lead to incorrect results in these cases. Nevertheless, the solubility product rule can be used successfully for qualitative explanations of various reactions in analytical chemistry.

96. Reactions in Solutions of Electrolytes as Reactions Between Their Ions. The chief value of the Theory of Ionization was that it threw an entirely new light on reactions taking place between electrolytes in aqueous solutions. When we dissolve a strong electrolyte in water we get a solution containing, according to present-day views, only ions, and not molecules, of the electrolyte. Each ion has its characteristic properties, which it retains in any solution regardless of the presence of other ions. For instance, hydroxyl-ion always turns litmus blue, gives the solution a soapy taste, etc., no matter what alkali we take. Thus, a solution of an electrolyte is essentially a mixture of ions (or their hydrates) and water molecules. Hence it is clear that when solutions of two strong electrolytes are mixed, only their ions, and not their molecules, which do not exist in solution, can enter into reaction. Therefore, the result of the reaction must depend exclusively on the kinds of ions contained in the initial solutions. Let us examine, for instance, the reactions which take place when solutions containing silver salts are mixed with solutions of various chloride salts:

$$AgNO_3 + NaCl = \downarrow AgCl + NaNO_3$$
$$Ag_2SO_4 + CuCl_2 = \downarrow 2AgCl + CuSO_4$$
$$AgCH_3COO + KCl = \downarrow AgCl + KCH_3COO$$

In all cases a characteristic white curd-like precipitate of insoluble silver chloride is formed.

The appearance of the same precipitate when three pairs of absolutely different substances react is difficult to explain on the basis of the molecular theory. If the formation of the precipitate is attributed to the fact that the reactants contain the elements chlorine and silver in all cases, a whole series of examples can be cited where under similar conditions no silver chloride results. For instance, if a solution of potassium chlorate $KClO_3$ is treated with a solution of silver nitrate $AgNO_3$, no precipitate will form in spite of the presence of chlorine in potassium chlorate. No precipitate appears either when various organic compounds containing chlorine, such as chloroform $CHCl_3$, chlorpicrin CCl_3NO_2 or others are acted on by silver salts.

* These changes take place due to changes in the activity coefficients of the ions.

But these difficulties immediately disappear if we take the standpoint of the ionization theory. Not the initial substances as such, but the ions they form in solution, enter into the reaction. All solutions of silver salts always contain $Ag^{\cdot}$-ion together with other ions, and all the solutions of chloride salts contain Cl'-ion. In mixing these solutions by pairs we make possible a reaction between the same ions, namely chloride and silver ions, and therefore we get the same precipitate, silver chloride, in all three cases. Evidently, silver chloride will result each time silver-ion encounters chloride-ion in solution.

Thus, with the aid of silver-ion we can easily detect the presence of chloride-ion in solution and vice versa, with the aid of chloride-ion we can detect the presence of silver-ion. Hence Cl'-ion can serve as a test for $Ag^{\cdot}$-ion, and $Ag^{\cdot}$-ion, as a test for Cl'-ion. But if chlorine is present in solution in any other form than free Cl'-ion, i. e., as a constituent of other ions or unionized molecules, silver-ion will be of no help in discovering the presence of chlorine.

It was stated above that potassium chlorate and organic compounds containing chlorine give no AgCl precipitate when acted upon by silver salts. This is due to the fact that potassium chlorate ionizes according to the equation

$$KClO_3 \rightleftarrows K^{\cdot} + ClO_3'$$

so that its solution contains no Cl'-ion, while the above organic chlorine compounds do not ionize at all.

All the above leads to the conclusion that *reactions between electrolytes in solution are reactions between their ions.*

97. Ionic Equations. Ordinary chemical equations make no allowance for the ionization of molecules and therefore to express the nature of reactions which take place between electrolytes in solution *ionic equations* are used. Let us derive such an equation for one of the reactions considered in the previous paragraph, say, for the reaction

$$AgNO_3 + NaCl = NaNO_3 + \downarrow AgCl \qquad (1)$$

To bring about this reaction we mix solutions of $AgNO_3$ and NaCl. The result is a precipitate of AgCl, while $NaNO_3$ remains in solution.

Taking into account that the salts $AgNO_3$, NaCl and $NaNO_3$ are completely ionized in solution and that only the precipitate AgCl consists of linked ions, equation (1) can be rewritten as follows:

$$Ag^{\cdot} + NO_3 + Na^{\cdot} + Cl' = Na^{\cdot} + NO_3' + \downarrow AgCl \qquad (2)$$

Now, what change took place when the solutions were mixed? NO_3'-ion and $Na^{\cdot}$-ion were free before mixing and remained so after

mixing. The reaction took place only between $Ag^{\cdot}$-ion and Cl'-ion, which combined to form insoluble silver chloride. Hence, NO_3'-ion and $Na^{\cdot}$-ion did not take part in the reaction. But then there is no need to indicate their presence in the reaction at all, just as the presence of water or air has not been indicated in any of the foregoing reactions. Cancelling the symbols of these ions in both sides of the equation we get:

$$Ag^{\cdot} + Cl' = \downarrow AgCl \qquad (3)$$

This is the ionic equation of the reaction in question. It is much simpler than the molecular equation, and at the same time expresses the entire essence of the reaction which has taken place. Obviously, whatever soluble salts of silver and hydrochloric acid we take, the reaction between them will be expressed by the same ionic equation, since in all these cases the same chemical process takes place, namely, the union of silver-ion with chloride-ion to form silver chloride.

Hence ionic equations, in contradistinction to ordinary molecular equations, do not pertain to any one reaction between definite substances, but embrace a whole group of analogous reactions. This is their main value and importance.

98. Mechanism of Exchange Reactions in Solutions of Electrolytes. An enormous number of the reactions taking place between electrolytes in aqueous solution are of the exchange type. We shall now examine the mechanism of these reactions in somewhat greater detail, proceeding from the assumption that strong electrolytes are completely ionized.

In the general form an exchange reaction can be expressed by the equation

$$AB + CD = AD + CB$$

Suppose AB and CD are strong electrolytes, so that their solutions contain only the free ions $A^{\cdot}$, B', $C^{\cdot}$ and D'. Then the result of the reaction will depend entirely on the solubility and ionizability of the resultants AD and CB. Two principal cases are possible: 1) the resultants are also strong electrolytes readily soluble in water and 2) one or both of the resultants are insoluble or are weak electrolytes.

Let us examine some concrete examples to see what happens in both cases.

If we mix solutions of two strong electrolytes, say, sodium chloride NaCl and potassium nitrate KNO_3, the reaction between them can be represented in the molecular form by the equation

$$NaCl + KNO_3 = NaNO_3 + KCl$$

Since the salts $NaNO_3$ and KCl are readily soluble in water it was formerly thought that this reaction is not complete and results in

a state of equilibrium between the reactant and resultant salts. Now we know that all four salts, being strong electrolytes, are completely ionized. Therefore, passing over to the ionic equation of the reaction we may write:

$$Na^{\cdot} + Cl' + K^{\cdot} + NO_3' = Na^{\cdot} + NO_3' + K^{\cdot} + Cl'$$

Hence, it is obvious that whether mixed or not, the solutions contain only the free ions:

$$Na^{\cdot},\ K^{\cdot},\ Cl' \text{ and } NO_3'$$

Thus, from the standpoint of the ionization theory *no reaction takes place at all in this case.* This conclusion is confirmed by the fact that when sodium chloride and potassium nitrate solutions are mixed heat is neither evolved nor absorbed, showing that no chemical change takes place.

It is a different thing if one of the resultants is a weak electrolyte. Take, for instance, the reaction which ensues when a solution of sodium acetate $NaCH_3COO$ is mixed with a solution of hydrochloric acid:

$$NaCH_3COO + HCl = CH_3COOH + NaCl$$

Before mixing, the solutions contained the ions $Na^{\cdot}$, CH_3COO', $H^{\cdot}$ and Cl'. After mixing the CH_3COO'-ion and $H^{\cdot}$-ion in the solution unite to form unionized molecules of a weak electrolyte, namely, acetic acid CH_3COOH. This continues until the quantity of $H^{\cdot}$-ion and CH_3COO'-ion left in solution corresponds to the low degree of ionization of acetic acid. As a result, the solution will contain $Na^{\cdot}$- and Cl'-ion, CH_3COOH molecules and an insignificant quantity of $H^{\cdot}$-ion and CH_3COO'-ion. Neglecting the latter, the reaction may be represented by the following ionic equation:

$$H^{\cdot} + C\ ^{\cdot} + Na^{\cdot} + CH_3COO' = Na^{\cdot} + Cl' + CH_3COOH$$

or, cancelling the ions not taking part in the reaction:

$$\mathbf{H^{\cdot} + CH_3COO' = CH_3COOH}$$

Hence, the entire reaction reduces to the formation of unionized acetic acid molecules from $H^{\cdot}$-ion and CH_3COO'-ion. Such a reaction is called displacement of a weak acid from its salt by a strong acid, because during the reaction the strong acid (hydrochloric) is replaced in the solution by the weak acid (acetic).

Another example of a reaction, during which a slightly ionized substance forms, is the reaction of neutralization of strong acids by strong bases, such as:

$$HCl + NaOH = NaCl + H_2O$$

Since one of the substances formed during this reaction, namely, water, is practically hardly ionized, we get, passing over to the ionic equation:

$$H^{\cdot} + Cl' + Na^{\cdot} + OH' = Na^{\cdot} + Cl' + H_2O$$
$$\mathbf{H^{\cdot} + OH' = H_2O}$$

The latter equation expresses the process of neutralization of any strong acid by any strong base in terms of the ionization theory. Therefore, neutralization reduces to the formation of water molecules from hydrogen- (or oxonium-) ion and hydroxyl-ion.

As any reaction consisting in the neutralization of a strong acid by a strong base involves only the union of hydrogen- and hydroxyl-ion, the quantity of heat liberated during such reactions should always be the same, independent of the nature of the acid or base. This conclusion is actually confirmed by experiment: when any strong acid is neutralized by any strong base about 13.8 Cal. of heat are evolved for each gram-molecule of water formed:

$$HCl + NaOH = NaCl + H_2O + 13.75 \text{ Cal.}$$
$$HNO_3 + KOH = KNO_3 + H_2O + 13.77 \text{ Cal.}$$
$$HCl + KOH = KCl + H_2O + 13.75 \text{ Cal.}$$

Reactions similar to those of the formation of weak electrolytes take place also when one of the resultants is insoluble and is evolved as a precipitate or a gas. The above-mentioned reactions between silver salts and chloride salts may be cited as examples, these reactions reducing to the formation of insoluble silver chloride from silver-ion and chloride-ion:

$$\mathbf{Ag^{\cdot} + Cl' = \downarrow AgCl}$$

Of course, there are no absolutely insoluble substances and therefore, when silver chloride forms, a certain amount of silver-ion and chloride-ion, corresponding to the solubility product of AgCl, remains in solution. Since this quantity is insignificant, it is neglected when the reaction is represented by an ionic equation. In exactly the same way we derive the ionic equations of other reactions accompanied by the formation of very slightly soluble substances.

Now let us see how the reaction proceeds when one of the reactants is a weak electrolyte. Of course, if the substances formed as a result of the reaction are strong electrolytes, no reaction will occur, as is the case, for instance, when solutions of CH_3COOH and KCl are mixed. But if one or both of the resultants are still weaker electrolytes than the reactants the latter may undergo almost complete change. Consider, for instance, the neutralization of acetic acid by sodium hydroxide:

$$CH_3COOH + NaOH = NaCH_3COO + H_2O$$

If we mix solutions of acetic acid and sodium hydroxide, we get a solution which will at first contain $Na^{\cdot}$-ion and OH'-ion, as well as a small quantity of $H^{\cdot}$-ion and CH_3COO'-ion in equilibrium with unionized acetic acid molecules

$$CH_3COOH \rightleftarrows H^{\cdot} + CH_3COO'$$

$H^{\cdot}$-ion and OH'-ion combine to form molecules of practically unionized water. As more and more hydrogen-ion is bound, the equilibrium between the molecules of acetic acid and its ions is disturbed and new molecules begin to ionize. This process will continue until all the molecules of acetic acid become ionized.

Thus, two processes take place simultaneously in the solution, namely, ionization of acetic acid molecules and formation of water molecules from hydrogen-ion and hydroxyl-ion. All this can be represented by the following scheme:

$$\begin{array}{c} CH_3COOH \rightleftarrows H^{\cdot} + CH_3COO' \\ \\ NaOH \rightarrow \overset{+}{O}H' + Na^{\cdot} \\ \downarrow \\ H_2O \end{array}$$

It would be incorrect in this case to represent the neutralization reaction by the same ionic equation as the neutralization of strong acids by strong bases, i. e.,

$$H^{\cdot} + OH' = H_2O$$

as there had been almost no free hydrogen-ion in the initial solution. The hydrogen-ion formed gradually in the course of the reaction from the acetic acid molecules; hence, the acetic acid molecules also participated indirectly in the reaction, supplying more and more hydrogen-ion as the latter was bound by hydroxyl-ion.

To reflect this in the ionic equation, acetic acid is represented in its molecular form, in which it mainly existed in the initial solution.

$$CH_3COOH + Na^{\cdot} + OH' = H_2O + Na^{\cdot} + CH_3COO'$$

Cancelling like terms we get:

$$\mathbf{CH_3COOH + OH' = H_2O + CH_3COO'}$$

This equation not only indicates the indirect participation of the acetic acid molecules in the reaction, but also shows that besides water molecules, a large amount of CH_3COO'-ion was formed as a result of the reaction, there having been hardly any of in the initial solution.

Since the neutralization of acetic acid (contrary to that of strong acids by strong bases) consists of two processes, namely, the ionization of acetic acid molecules and the formation of water molecules, the heat of neutralization equals 13.3 Cal. instead of 13.8 Cal. Obviously, 0.5 Cal. of heat is absorbed during the ionization of one mole of acetic acid. In other cases the absorption of heat during the ionization of a weak electrolyte may be even more considerable. For instance, during the neutralization of one mole of hypochlorous acid HClO by sodium hydroxide only 9.84 Cal. are evolved.

The following general conclusion may be drawn from the above examples of ionic reactions:

An obligatory condition for exchange reactions between electrolytes is the removal of ions of one kind or another from the solution as a result of the formation of slightly ionized substances, or practically insoluble substances which come out of solution as precipitates or gases. In other words, *reactions in solutions of electrolytes always proceed in the direction of the formation of the least ionized or least soluble substances. If no substances of this kind can form during the reaction, it will not take place.*

Special note should be made of reactions during which no insoluble substances are formed but, on the contrary, an insoluble substance dissolves under the action of a reagent of some kind.

Consider, for example, the dissolving of cupric hydroxide by acids:

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

At first sight it may appear that this reaction contradicts the above generalization. However, there is no contradiction at all, as one of the conditions determining the direction of the reaction, namely, the formation of a slightly ionized compound (water) is fulfilled, this fact being the reason why the cupric hydroxide dissolves.

To understand this process from the point of view of the ionization theory, it must first of all be taken into account that no substance is absolutely insoluble. Therefore, any liquid over a precipitate of an "insoluble" substance is a saturated solution of that substance. In the above case it is difficult to say whether the solution contains only Cu^{++}- and OH^{-}-ion or unionized $Cu(OH)_2$ molecules as well, as the conditions of ionization of the hydroxides of heavy metals are not known well enough. The chances are that such hydroxides form molecular lattices, and therefore, when dissolved, go into solution first as molecules, which then ionize to a greater or smaller degree. If this is the case, two interrelated equilibria should exist in saturated solutions of cupric hydroxide $Cu(OH)_2$: one equilibrium between the precipitate and the $Cu(OH)_2$ molecules which have passed into solution, and another between these molecules and the

ions they form:

$$\underset{\text{in precipitate}}{Cu(OH)_2} \overset{(1)}{\rightleftarrows} \underset{\text{in solution}}{Cu(OH)_2} \overset{(2)}{\rightleftarrows} \underset{\text{in solution}}{Cu^{\cdot\cdot} + 2OH'}$$

When cupric hydroxide is subjected to the action of an acid the hydroxyl ions combine with the hydrogen ions of the acid to form unionized water molecules. Their disappearance immediately disturbs equilibrium (2), causing the ionization of new $Cu(OH)_2$ molecules, which in its turn disturbs equilibrium (1), making part of the precipitate pass into solution. The hydroxyl-ion formed as a result of ionization again combines with hydrogen-ion and so on, until the entire precipitate passes into solution, provided there is enough acid to dissolve it completely. All this can be represented as follows:

$$\underset{\text{in precipitate}}{Cu(OH)_2} \rightleftarrows \underset{\text{in solution}}{Cu(OH)_2} \rightleftarrows Cu^{\cdot\cdot} + 2OH'$$

$$2HCl \rightarrow 2Cl' + \overset{+}{2H^{\cdot}}$$
$$\downarrow$$
$$2H_2O$$

The dissolving of precipitates of other insoluble electrolytes in water can be accounted for in a similar manner.

In writing these reactions as ionic equations the electrolytes in precipitate should be represented as unionized substances on the same grounds as acetic acid was represented in the form of molecules, when considering its neutralization by sodium hydroxide. Therefore, the dissolving of cupric hydroxide in hydrochloric acid is expressed by the following ionic equation:

$$Cu(OH)_2 + 2H^{\cdot} = Cu^{\cdot\cdot} + 2H_2O$$

Thus *to dissolve a slightly soluble electrolyte, one of the ions sent into solution by that electrolyte must be bound.** This is achieved mostly by introducing into the solution ions which form a slightly ionized substance with the ions of the electrolyte.

99. Deriving Ionic Equations. The great majority of reactions we shall come across in studying the properties of the individual elements and their compounds, take place in solutions of electrolytes between their ions. Therefore, it is very important to master the technique of deriving ionic equations.

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* The same conclusion can be deduced in another way by making use of the solubility product concept (see § 95). Indeed, in a saturated solution of a slightly soluble electrolyte the product of its ionic concentrations is a constant. In binding one of the ions of the electrolyte by adding other ions to the solution to form unionized molecules with it, we lower the product of ionic concentrations of the electrolyte; the solution becomes unsaturated and has to dissolve the precipitate in contact with it.

In the previous paragraph we considered in detail typical examples of ionic reactions. On the basis of all that was said there about ionic equations, the following order of deriving them may be recommended:

1. Write out the equation of the reaction in its molecular form.
2. Rewrite the equation leaving the insoluble or slightly ionized substances in the molecular form, and writing all the rest of them as the ions into which they break up.
3. Cancel the ions that do not take part in the reaction, i. e., that are found in equal numbers in the left and right sides of the equation.

To help remember these methods we shall consider two examples of deriving ionic equations.

Example 1. Derive the ionic equation of the reaction between hydrogen sulphide (a weak acid) and copper sulphate:

1) $CuSO_4 + H_2S = \downarrow CuS + H_2SO_4$
2) $Cu^{\cdot\cdot} + SO_4'' + H_2S = \downarrow CuS + 2H^{\cdot} + SO_4''$
3) $Cu^{\cdot\cdot} + H_2S = \downarrow CuS + 2H^{\cdot}$

Example 2. Derive the ionic equation of the reaction between lead hydroxide and hydrochloric acid:

1) $\downarrow Pb(OH)_2 + 2HCl = \downarrow PbCl_2 + 2H_2O$
2) $\downarrow Pb(OH)_2 + 2H^{\cdot} + 2Cl' = \downarrow PbCl_2 + 2H_2O$

Nothing can be cancelled from the latter equation, as both $H^{\cdot}$-ion and Cl'-ion participate in the reaction.

With a little practice, ionic equations can be written out directly without going through the first and second stages. For this purpose we must have a clear idea of: a) the formation of which substance causes the reaction to proceed; b) whether the ions needed for its formation are already in solution or result in the course of the reaction from molecules of slightly ionized or slightly soluble substances. In this case it is more convenient to write the equation beginning with its second half, i. e., first of all to put down the formula of the resulting substance, then the ions or ions and molecules needed for its formation, and finally, the ions obtained as a result of the reaction. After this, the proper coefficients must be selected.

To derive ionic equations, we must know which salts are soluble in water and which practically insoluble. Some general information on the solubility in water of the most important salts of the most common metals are given in Table 16.

Table 16

Solubility of the Most Important Salts in Water

	Solubility of salts
Acids	
HNO_3	All salts soluble
HCl	All salts soluble except AgCl, CuCl, $PbCl_2$ and Hg_2Cl_2
H_2SO_4	All salts soluble except $BaSO_4$, $SrSO_4$ and $PbSO_4$
H_2CO_3	Of normal salts only sodium, potassium and ammonium salts soluble
H_3PO_4	Ditto
H_2S	Ditto
Metals	
Na and K	Almost all salts soluble

100. Ionization of Water. One of the least ionized substances formed in reactions between ions is water. Pure water is a very poor conductor of electricity but still has a certain measurable conductivity due to the slight ionization of water into hydrogen- and hydroxyl-ion:

$$H_2O \rightleftarrows H^{\cdot} + OH'$$

The ionization of water will be readily understood, if it is taken into account that the bond between the hydrogen and oxygen atoms in water molecules is polar and similar in this respect to the bond between the hydrogen and halogen atoms in hydrogen halides.

The mechanism of ionization is the same in both cases: ionization of hydrogen chloride:

$$H_2O + H\overset{\cdot\cdot}{\underset{\cdot\cdot}{-}}Cl \rightleftarrows H_3O^{\cdot} + Cl'$$

ionization of water:

$$H_2O + H\overset{\cdot\cdot}{\underset{\cdot\cdot}{-}}O-H \rightleftarrows H_3O^{\cdot} + OH'$$

The concentration of hydrogen-ion and hydroxyl-ion in water can be calculated from the electrical conductivity of pure water. It has been found to equal 10^{-7} gram-ions per litre.

Applying the Law of Mass Action to the ionization of water, we may write:

$$\frac{[H^{\cdot}] \times [OH']}{[H_2O]} = K$$

This equation may be rewritten as follows:

$$[H^{\cdot}] \cdot [OH'] = [H_2O] \cdot K$$

Since the degree of ionization of water is very low, the concentration of unionized H_2O molecules may be considered a constant value not only in water but in any dilute aqueous solution as well. Therefore, substituting the new constant K_{H_2O} for $[H_2O]\cdot K$, we get:

$$[H^{\cdot}]\cdot[OH'] = K_{H_2O}$$

This equation shows that in the case of water and aqueous solutions the product of the hydrogen-ion and hydroxyl-ion concentrations is a constant value as long as the temperature remains unaltered. This constant is called the *ion-product for water*. Its numerical value can easily be obtained by substituting the concentrations of hydrogen-ion and hydroxyl-ion into the above equation

$$K_{H_2O} = 10^{-7}\cdot 10^{-7} = 10^{-14}$$

Solutions in which the concentration of hydrogen- and hydroxyl-ion is the same and equals 10^{-7} *gram-ions per litre each are called neutral solutions.* In acid solutions the concentration of hydrogen-ion is higher, and in alkaline solutions the concentration of hydroxyl-ion is higher. But whatever the reaction of a solution, the product of the $H^{\cdot}$-ion and OH'-ion concentrations must remain constant.

If, for instance, we add enough acid to pure water to raise the concentration of hydrogen-ion to 10^{-3}, the concentration of hydroxyl-ion will have to decrease so that the product $[H^{\cdot}]\cdot[OH']$ remains equal to 10^{-14}. Hence, in this solution the concentration of hydroxyl-ion will be:

$$[OH'] = \frac{10^{-14}}{10^{-3}} = 10^{-11}$$

On the other hand, if an alkali is added to water, raising the concentration of hydroxyl-ion, say, to 10^{-5}, the concentration of hydrogen-ion will become:

$$[H^{\cdot}] = \frac{10^{-14}}{10^{-5}} = 10^{-9}$$

101. The Hydrogen-Ion Index. It can be seen from the examples given in the previous paragraph that if we indicate the concentration of hydrogen-ion in any solution, the concentration of hydroxyl-ion can be calculated. Therefore, both the degree of acidity and the degree of alkalinity of a solution can be characterized quantitatively by the concentration of hydrogen-ion:

neutral solution $[H^{\cdot}] = 10^{-7}$
acid solution $[H^{\cdot}] > 10^{-7}$ (for example 10^{-6}, 10^{-4})
alkaline solution $[H^{\cdot}] < 10^{-7}$ (for example 10^{-8}, 10^{-11})

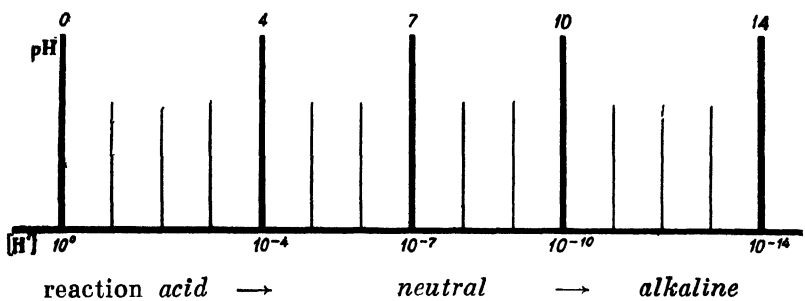
At present this method of expressing the acidity or alkalinity of a solution has given place to another still more simple and convenient

method: instead of indicating the true hydrogen-ion concentration, we indicate the logarithm of the latter with its sign reversed. This value is called the *hydrogen-ion index* and is designated pH:

$$pH = -\log [H^+]$$

For instance, if $[H^+]=10^{-5}$, then pH=5; if $[H^+]=10^{-9}$, then pH=9, etc. Hence, obviously, in neutral solution pH=7. In acid solutions pH<7, and the more acid the solution, the smaller it is. On the other hand, in alkaline solutions, pH>7 and the higher the alkalinity, the larger it is.

These relationships are shown graphically by the following diagram:



There are various methods of measuring pH values. Qualitatively the reaction of a solution can be determined by means of special reagents called **indicators**, which change colour depending on the concentration of hydrogen-ion.

The most widely used indicators are litmus, phenolphthalein and methyl orange. Their colours in acid, alkaline and neutral solution are as follows:

Indicator	Reaction of solution		
	acid	neutral	alkaline
Litmus	Red	Violet	Blue
Phenolphthalein	Colourless	Colourless	Red
Methyl orange	Red	Orange	Yellow

The hydrogen-ion concentration is of great importance in very many cases. It has to be taken into account not only in chemical investigations, but also in a great variety of industrial processes, as well as in the study of phenomena taking place in live organisms.

102. Hydrolysis of Salts. The ionization of water into hydrogen- and hydroxyl-ion accounts for a very important phenomenon, called hydrolysis of salts.

Hydrolysis* is, in general, any interaction between a substance and water, in which the constituent parts of the substance combine with the composite parts of water. For example, phosphorus trichloride PCl_3 reacts with water to form phosphorous acid H_3PO_3 and hydrochloric acid:

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl$$

In practice we especially often have to do with the hydrolysis of salts.

Salts, as we know, can be obtained by the neutralization of acids by bases. It is natural to assume, therefore, that solutions, at least of normal salts, i. e., those which are products of complete displacement of hydrogen in acids by metals, must react neutral. However, this assumption holds only with respect to salts formed from strong acids and strong bases. Salts obtained from weak acids and strong bases, or, vice versa, from strong acids and weak bases, do not react neutral when dissolved in water. For instance, a solution of ferric chloride $FeCl_3$ reacts acid, indicating, as we know, the presence of hydrogen-ion (oxonium-ion); a solution of sodium hypochlorite NaClO reacts alkaline, which is characteristic of hydroxyl-ion; a solution of potassium cyanide KCN (a salt of weak cyanic acid, HCN) also has an alkaline reaction, etc.

The ionization theory attributes these phenomena to the interaction of water ions with the ions of the dissolved salts, resulting in the formation of an excess of hydrogen- or hydroxyl-ion. Although the concentration of hydrogen-ion and hydroxyl-ion in water is very low, these ions are in equilibrium with an immense number of unionized water molecules. When one of them is bound by the ions of the salt, the equilibrium is disturbed, causing new water molecules to ionize, which may lead to an accumulation of considerable quantities of the other ion in solution, making the solution react acid or alkaline.

Any reaction between the ions of a salt and the ions of water, usually accompanied by a change in the concentration of the latter is called hydrolysis of the salt.

The chief cause of hydrolysis is the formation of slightly ionized substances (molecules or ions).

Hydrolysis may proceed differently, depending on the strength of the acid and base which went to form the salt.

Some of the most typical cases of hydrolysis are considered below.

* The word "hydrolysis" means literally "decomposition by water".

First case. *Salt of weak acid and strong base.* Example—sodium acetate $NaCH_3COO$. When dissolved in water, sodium acetate, like all typical salts, ionizes completely into $Na^{\cdot}$-ion and CH_3COO'-ion. Theoretically these ions could combine with the ions of water to form equivalent quantities of sodium hydroxide and acetic acid; but since sodium hydroxide is a strong base, sodium-ion does not combine with the hydroxyl-ion of water.

On the other hand, acetic acid is a very weak acid and therefore, when CH_3COO'-ion encounters the hydrogen-ion of water in solution, it immediately begins to combine with it to form CH_3COOH molecules. The decrease in the quantity of hydrogen-ion in solution disturbs the equilibrium between the molecules of water and its ions, causing further ionization of the water; fresh quantities of hydrogen-ion form, which in their turn, combine with CH_3COO'-ion into CH_3COOH molecules, etc.; at the same time, the amount of hydroxyl-ion in solution increases.

However, the reaction does not go very far in this direction. Since the ion-product for water $[H^{\cdot}]\cdot[OH']=10^{-14}$ is a constant, the concentration of hydrogen-ion decreases as hydroxyl-ion accumulates, and is soon so low that it can no longer be bound. Then new equilibria are established between the water molecules and their ions, on the one hand, and between the CH_3COOH molecules and the $H^{\cdot}$- and CH_3COO'-ions, on the other, after which the accumulation of hydroxyl-ion ceases.

Thus, when sodium acetate interacts with water, the following reaction takes place:

$$CH_3COO' + H_2O \rightleftarrows CH_3COOH + OH'$$

or in the molecular form

$$NaCH_3COO + H_2O \rightleftarrows CH_3COOH + NaOH$$

Although the equilibrium of this reaction is greatly displaced to the left, the ionic equation shows that the reaction gives rise to a certain excess of hydroxyl-ion in the solution, so that a *solution of* $NaCH_3COO$ *reacts alkaline.*

The reaction described involves hydrolysis of the salt of a weak unibasic acid. When salts formed by weak polybasic acids hydrolyze, the result is usually not the free acids, but acid salts or, more precisely, acid salt anions. For instance, if soda Na_2CO_3 is dissolved in water the CO_3'' -ion, like the CH_3COO'-ion, combines with the hydrogen-ion of the water; however, the result is not molecules of weak carbonic acid H_2CO_3, but HCO_3'-ion. The formation of predominantly HCO_3'-ion is due to the fact that it ionizes much less readily than H_2CO_3 molecules (see p. 265).

The hydrolysis takes place according to the equation

$$CO_3'' + H_2O \rightleftarrows HCO_3' + OH'$$

or, in the molecular form

$$Na_2CO_3 + H_2O \rightleftarrows NaHCO_3 + NaOH$$

As a result of this reaction, as in the hydrolysis of sodium acetate, an excess of hydroxyl-ion appears in the solution; therefore a solution of soda also reacts alkaline.

Second case. *Salt of strong acid and weak base.* This case is analogous to the previous one, with the sole difference that here the cations of the salt combine with the hydroxyl-ion of water, while the anions remain free. The hydrolysis product is usually a *basic salt* or basic salt cations. For instance, when cupric chloride $CuCl_2$, a salt of the weak base $Cu(OH)_2$ and hydrochloric acid, dissolves in water, the $Cu^{\cdot\cdot}$-ion, combining with hydroxyl-ion, may form either $Cu(OH)_2$ molecules or $CuOH^{\cdot}$-ion. Since the latter ionizes less readily than $Cu(OH)_2$ molecules, it predominates among the hydrolysis products of $CuCl_2$.

The reaction that takes place is represented by the equation

$$CuCl_2 + H_2O \rightleftarrows \underset{\text{basic salt}}{CuOHCl} + HCl$$

or, in the ionic form

$$Cu^{\cdot\cdot} + H_2O \rightleftarrows CuOH^{\cdot} + H^{\cdot}$$

Since this reaction gives rise to an excess of hydrogen-ion, solutions of salts of strong acids and weak bases react acid.

Third case. *Salt of weak acid and weak base.* In this case both the anion and the cation of the salt react with the water. The hydrolysis products are a weak acid and a basic salt or basic salt cations. For instance, when aluminium acetate $Al(CH_3COO)_3$ is dissolved in water, the following reactions ensue:

$$CH_3COO' + H_2O \rightleftarrows CH_3COOH + OH'$$
$$Al^{\cdot\cdot\cdot} + H_2O \rightleftarrows AlOH^{\cdot\cdot} + H^{\cdot}$$
$$AlOH^{\cdot\cdot} + H_2O \rightleftarrows Al(OH)_2^{\cdot} + H^{\cdot}$$

Thus, the hydrolysis of $Al(CH_3COO)_3$ results in CH_3COOH molecules, $AlOH^{\cdot\cdot}$-ion and $Al(OH)_2^{\cdot}$-ion or, in other words, acetic acid and the basic salts $AlOH(CH_3COO)_2$ and $Al(OH)_2CH_3COO$.

As to the reaction of solutions of such salts, it depends on the relative strength of the acids and bases the salts result from and may be neutral, slightly acid or slightly basic.

If the acid and base formed are very weak, and volatile or very slightly soluble besides, hydrolysis may be complete, i. e., the salt

may decompose entirely. This happens, for instance, when aluminium sulphide Al_2S_3 reacts with water:

$$Al_2S_3 + 6H_2O \rightleftarrows 2Al(OH)_3 + 3H_2S\uparrow$$

Now let us see whether hydrolysis will occur if the salt is of a strong acid and a strong base. By way of example, let us take sodium chloride as a typical salt of this kind. When it dissolves in water, this salt ionizes into sodium-ion and chloride-ion. Sodium-ion, as indicated above, will not combine with the hydroxyl-ion of water. Nor will chloride-ion combine with hydrogen-ion, because HCl is completely ionized; therefore, the concentrations of hydrogen-ion and hydroxyl-ion in the solution will remain the same as in pure water, and the NaCl solution will be neutral.

Thus, *salts of strong acids and strong bases do not hydrolyze.* In all other cases hydrolysis occurs.

It can be seen from the above equations that hydrolysis is the reverse of neutralization. This means that when solutions containing equivalent amounts of acids and bases are mixed, the reaction is complete only if both interacting substances are strong electrolytes. If the acid or the base is weak, there will always be a certain amount of unionized acid or basic molecules left in the solution after mixing, so that the solution will not react neutral.

The degree of hydrolysis, i. e., the ratio between the quantity of salt hydrolyzed and the total quantity of salt dissolved is different for different salts, and depends on the chemical nature of the acid and salt formed by hydrolysis, viz., the weaker the acid or the base, the higher the degree of hydrolysis.

For instance, the degrees of hydrolysis for the following salts in 0.1 N solution are:

Sodium acetate $NaCH_3COO$	0.008 p. c.
Borax $Na_2B_4O_7$	0.5 p. c.
Potassium cyanide KCN	1.2 p. c.
Soda Na_2CO_3	2.9 p. c.

The degree of hydrolysis of most salts of strong acids and weak bases is very low. Therefore, the basic salts produced when they hydrolyze, though practically insoluble in water, nevertheless, usually remain in solution due to their insignificant concentration.

Like any other reversible reaction, hydrolysis obeys the Law of Mass Action. Therefore, addition of water to the salt solution or removal of one of the hydrolysis products causes a shift of equilibrium towards the formation of an acid and a base. Heating acts in the same direction, because the degree of ionization of water, i. e., the concentration of $H^{\cdot}$- and OH'-ion increases greatly upon heating. On the contrary, addition of an acid or a base to the solution shifts the

equilibrium in the reverse direction. For instance, at ordinary temperatures ferric chloride $FeCl_3$ hydrolyzes according to the equation

$$Fe^{\cdots} + H_2O \rightleftarrows FeOH^{\cdot\cdot} + H^{\cdot}$$

If the solution is heated, hydrolysis is enhanced, resulting in more $Fe^{\cdots}$-ion reacting with the water and, at the same time, in the formation of $Fe(OH)_2^{\cdot}$-ion or even $Fe(OH)_3$ molecules alongside of $FeOH^{\cdot\cdot}$-ion, according to the equations:

$$Fe^{\cdots} + 2H_2O \rightleftarrows Fe(OH)_2^{\cdot} + 2H^{\cdot}$$
$$Fe^{\cdots} + 3H_2O \rightleftarrows \downarrow Fe(OH)_3 + 3H^{\cdot}$$

Addition of an acid dissolves the precipitate or decreases the content of $Fe(OH)_2^{\cdot}$-ion in the solution.

CHAPTER XIII

Air. The Inert Gases

103. Composition of the Atmosphere. The atmosphere is a mixture of many gaseous substances. Besides oxygen and nitrogen, which constitute its bulk, air contains carbon dioxide, water vapour, and small quantities of the noble or inert gases, discovered in the late XIX century. In addition to the gases enumerated, air contains more or less dust and certain chance admixtures. Oxygen, nitrogen and the inert gases are considered the constant constituent parts of air, as their content in air is practically the same everywhere. On the contrary, the content of carbon dioxide, water vapour and dust may vary depending on various conditions.

Carbon dioxide forms in nature as a result of the combustion of wood and coal, the respiration of animals, decay, etc. Especially large quantities of this gas are discharged into the atmosphere at large industrial centres by factories and plants, which burn immense quantities of fuel. In some parts of the globe carbon dioxide is discharged into the air as a result of volcanic action and from underground springs.

Despite the continuous addition of carbon dioxide to the atmosphere, its content in air is quite constant, constituting an average of about 0.03 per cent (by volume). This is due to the absorption of carbon dioxide by plants, as well as its relatively high solubility in water.

The *water vapour* content in the air may vary over a wide range, from several per cent to fractions of one per cent, and depends both on local conditions and on the temperature. The higher the temperature, the more vapour can be contained in the air; that is why the moisture content in the air is lower in winter than in summer.

The *dust in the air* consists mainly of minute particles of the mineral substances constituting the earth's crust, coal particles, plant pollen, as well as various bacteria. The amount of dust in the air varies greatly: it is lower in winter and higher in summer. After a rain shower the air becomes purer because the rain-drops carry the dust and bacteria down with them.

Finally, other chance impurities in air are such substances as hydrogen sulphide and ammonia, given off during the decay of

organic remains; sulphur dioxide, produced when sulphide ores are roasted or by the combustion of coal containing sulphur; nitrogen oxides, formed by electrical discharges in the atmosphere, etc. These impurities are usually present in insignificant quantities and are continually removed from the air by rain water, which dissolves them.

If only the constant component parts of air are taken into account, its composition can be expressed by the following figures:

	Percentage content by volume	by weight
Nitrogen	78.16	75.5
Oxygen	20.9	23.2
Inert gases	0.94	1.3

104. Physical Properties of Air. Pure air, free from dust, carbon dioxide and water vapour, is absolutely colourless and has neither taste nor odour. One litre of pure air weighs 1.293 gr. at 0°C and 760 mm. Hg. At temperatures below —140° and a pressure of about 40 atm. air condenses into a colourless liquid boiling at about —190°C.

The production of liquid air presents no extraordinary difficulties at present. There are many machines of various types for this purpose. The operating principle of most of them depends on the considerable temperature drop caused by the expansion of air under pressure (about 0.25° for each atmosphere of pressure lost). Thus, if air is compressed to 200 atm. and then expanded rapidly to 1 atm., its temperature will go down 50°. This temperature drop is used to preliminarily cool a second batch of compressed air. When the cooled compressed air is expanded it gets still colder. By repeating this operation several times, a temperature can be reached at which the air begins to condense into a liquid.

A diagram of one of the machines used for the liquefaction of air is shown in Fig. 78. The compressor *1*, by means of a piston, compresses the air entering the machine through valve *2*, to 200 atm. The heat liberated during compression is removed in cooler *3*, by running water. From the cooler the compressed air enters a coil *4* enclosed in an insulated chamber *5* and consisting of two very long spiral tubes, one inside the other. The air passes through the inner tube of the coil, down to valve *6* which opens for an instant, letting the air into chamber *7*, where it expands and is thus greatly cooled.

After cooling in this way, the air is returned to the compressor through the outer tube *8* of the coil, cooling the incoming compressed air as it runs counter-current to it. When valve *6* is opened a second time, the air that enters chamber *7* has already been preliminarily cooled by the previous portion of air. As a result, its temperature after expansion will be lower than the temperature of the previous portion, and it, in its turn, will cool the next batch still more. When the air gets cold enough, it begins to liquefy in the inner tube and drips into chamber *7*.

The liquid air obtained directly from the machine is usually turbid, due to the presence of suspended particles of carbonic anhydride, ice and other impurities, which can easily be removed by filtering through a paper filter.

In spite of its very low boiling point (about —190°C at ordinary pressure) liquid air can be kept for a considerable length of time in glass vessels with double walls, between which the air has been pumped out (Fig. 79). The "void" between the walls effectively prevents the liquid in the vessel from getting warmer, so that it evaporates very slowly. To further reduce the influx of heat from the outside, the walls of such vessels are silvered on the inside.

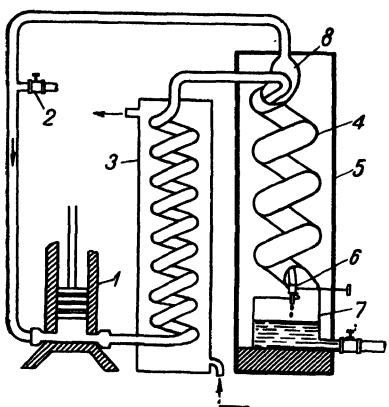


Fig. 78. Diagram of machine for production of liquid air:
1—compressor; *2*—air valve; *3*—cooler; *4*—coil; *5*—chamber; *6*—air valve; *7*—expansion chamber; *8*—outer tube of coil

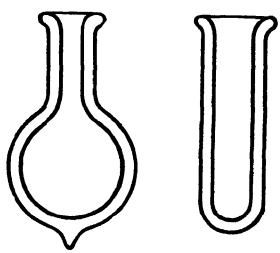


Fig. 79. Liquid air receivers

Alcohol, ether and many gases are readily solidified in liquid air. If, for instance, carbon dioxide is passed through liquid air, it forms white flakes resembling snow. Mercury immersed in liquid air turns into a solid malleable metal.

When cooled in liquid air, many substances acquire entirely new properties. Zinc and tin become so brittle that they can easily be pulverized, a lead bell begins to emit a pure ringing sound, while a frozen rubber ball breaks into small fragments if dropped on the floor.

As the boiling point of oxygen (—183° C) is higher than that of nitrogen (—196° C), oxygen liquefies more readily than nitrogen. Therefore, liquid air is much richer in oxygen than atmospheric.*

* The approximate composition of liquid air is: oxygen 54 per cent, nitrogen 44 per cent and inert gases 2 per cent.

Upon standing liquid air becomes even richer in oxygen due to the evaporation of nitrogen.

A glowing splint immersed in liquid air flashes out brightly, like in pure oxygen; a red-hot steel pen nib burns in it, emitting a blinding light.

In our days liquid air is produced in large quantities to obtain oxygen and nitrogen from it by fractional evaporation.

105. The Inert Gases. Up to the end of last century it was thought that air consisted only of oxygen and nitrogen. But in 1894 the English physicist Rayleigh noticed that the specific gravity of nitrogen produced from air is always a little higher than that of pure nitrogen produced from its compounds. Whereas a litre of the former weighs 1.2572 gr., a litre of the latter weighs 1.2505 gr. Rayleigh's discovery drew the interest of Ramsay, a professor of chemistry, who suggested that the difference in weight might be due to the presence of some heavier gas in the nitrogen. Both scientists undertook a study of atmospheric nitrogen. In order to isolate the hypothetical gas from it, Ramsay made use of the ability of nitrogen to combine with magnesium, when heated, to form magnesium nitride Mg_3N_2. After passing atmospheric nitrogen repeatedly through a tube containing red-hot magnesium, Ramsay obtained a small residue of a heavy gas that would not combine with this metal. Rayleigh used a different method: he passed electric sparks through a mixture of nitrogen and oxygen, whereupon the nitrogen combined with the oxygen to form nitric oxide NO, which then changed further into nitrogen dioxide NO_2; the latter was absorbed by a solution of alkali. As a result, Rayleigh also isolated from atmospheric nitrogen a small quantity of gas which would not combine with oxygen under the action of electric sparks. In this way, a new, hitherto unknown, gas was discovered in air, and it was named argon.

Argon Ar is a colourless gas almost one and a half times as heavy as air: one litre of it weighs 1.7809 gr. at S.T.P. Argon is a chemical element having an atomic weight of 39.944. From a chemical standpoint, argon is absolutely passive, whence its name (argon is the Greek for inactive). It does not combine with a single element under any conditions.

After argon, four more gaseous elements contained in air in insignificant quantities were discovered: *helium* He, *neon* Ne, *krypton* Kr and *xenon* Xe. Together with argon they are known as the **inert gases**, since, like argon, they are distinguished by their inability to react with other elements. Another peculiarity of the inert gases, related to this, is the fact that *their molecules consist of only one atom each*; in other words, their atoms are not combined into molecules.

Besides the above elements, the inert gases include the element *radon* Rn, discovered in the study of radioactive transformations and sometimes called also *emanation* or *niton*. Its content in atmospheric air is evidently insignificant.

The inert gases are the elements ending each period in the Mendeleyev Table; all together, they form the **zero group** of the Periodic System. With the exception of helium, they all have eight electrons in their outer electron layer, forming a very stable system. The outer layer of helium is just as stable, though it consists of only two electrons. For this reason the atoms of the inert gases tend neither to lose nor to gain electrons.

Inert Gases

Element	Symbol	Atomic weight	Atomic number	Arrangement of electrons in layers					
Helium	He	4.003	2	2					
Neon	Ne	20.183	10	2	8				
Argon	Ar	39.944	18	2	8	8			
Krypton . . .	Kr	83.80	36	2	8	18	8		
Xenon	Xe	131.3	54	2	8	18	18	8	
Radon	Rn	222	86	2	8	18	32	18	8

The inert gases do not combine with any of the elements and for that reason their atomic weights could not be determined by the usual methods described in § 22. To find their atomic weights a purely physical method was employed, based on determining the ratio between the specific heat of the gas at constant pressure to its specific heat at constant volume. The value of this ratio gives an idea of the number of atoms in the molecule of a gas. In this way it was established that the molecules of the inert gases consist of one atom each, and hence their molecular weights equal their atomic weights.

The physical properties of the inert gases and their content in air are characterized by the information in Table 17. These data show that the lower the atomic weight or atomic number of the inert gas, the lower its melting and boiling points: helium has the lowest boiling point and radon the highest.

Separation of the inert gases from one another is based on the difference of their boiling points.

Table 17

Physical Properties of the Inert Gases

Properties	Helium He	Neon Ne	Argon Ar	Krypton Kr	Xenon Xe	Radon Rn
Weight of one litre of gas, gr	0.18	0.90	1.78	3.74	5.89	9.73
Melting point, degrees C	—272.2	—248.6	—189.4	—157	—111.5	—71
Boiling point, degrees C	—268.9	—245.9	—185.8	—152.9	—108	—61.8
Approximate content in 1,000 volumes of air	0.0046	0.016	9.323	0.001	0.00008	—

Although the inert gases do not react with the other elements, the molecules of some of the inert gases may unite with water molecules at low temperatures to form unstable compounds of the hydrate type containing six molecules of water each. The formation of these hydrates is due to the fact that the non-polar molecules of the inert gases are polarized in the electric field of the highly polar water molecules; this gives rise to induced dipoles in the inert gas molecules, as a result of which they are attracted by the water molecules.

The higher the atomic weight of an inert gas, the more stable its hydrate. The most stable hydrate is that of xenon, but even it can exist at 0° C only under pressure (1.45 atm.). No hydrates of helium or neon have been obtained at all.

Comparatively stable molecular compounds of the heavy inert gases have also been obtained with certain organic substances such as phenol, toluene, etc.

The most interesting of the inert gases is helium. The history of its discovery is a striking example of the might of science. Helium was first discovered in 1868 by the French astronomer J. Janssen and the English astronomer N. Lockyer when studying the spectra of the atmosphere and solar prominences. A bright yellow line was detected in these spectra which had not been observed before in the spectra of the elements known at that time on the earth. The presence of this line was attributed to the existence of a new element on the sun, unknown on the earth, and called *helium** after the sun. About thirty years later, upon heating a rare mineral, cleveite, W. Ramsay, the English chemist, obtained a gas which he found to be identical with the helium discovered on the sun. Thus, helium had been discovered on the sun long before it was found on the earth.

Helium is the lightest of all gases except hydrogen. It is more than seven times as light as air.

* From the Greek "helios" (the sun).

For a long time helium was the only gas which could not be liquefied. Finally, in 1908, helium was compressed into a liquid which was found to boil at —268.9°C. By evaporating liquid helium, the lowest temperature (known on the earth) was obtained, only a few tenths of a degree above absolute zero. In 1926 helium was solidified for the first time. Solid helium is a transparent substance with a melting point of —272.2°C under a pressure of 26 atm.

On the earth helium is found not only in the atmosphere. Considerable quantities are evolved at certain points of the earth from its depths, together with the so-called "natural gases" (a mixture of various combustible gases). The waters of many mineral springs also evolve helium.

Owing to its lightness and inertness helium is used instead of hydrogen to inflate observation balloons. Although it is twice as heavy as hydrogen, its buoyant effect is only eight per cent less than that of hydrogen. The great advantage of helium over hydrogen is its non-flammability. Therefore, substitution of helium for hydrogen eliminates all danger of fire or explosion. The only obstacle to the wide use of helium in aeronautics is the difficulty of its production.

Another very important use of helium is in deep-sea work. Divers supplied with artificial air in which the nitrogen has been replaced by helium, can stay under water much longer and suffer much less from the morbid phenomena due to the change in pressure when rising to the surface.

Liquid helium is used to obtain very low temperatures.

The inert gases have found wide application in electrical engineering. Owing to its inactivity and insignificant thermal conductivity, argon is used in mixture with nitrogen to fill electric light bulbs. Argon is also used to fill tubes for illumination signs; such tubes emit a blue light. Neon is used to fill tubes for signs when a bright orange-red light is required. Neon tubes are used, besides, in electrical engineering as rectifiers and for other purposes. Krypton and xenon have a still lower thermal conductivity than argon, and therefore electric light bulbs filled with these gases have a longer life and are more economical than bulbs filled with nitrogen or argon.

CHAPTER XIV

The Halogens

Element	Symbol	Atomic weight	Atomic number	Arrangement of electrons in layers				
Fluorine . . .	F	19.00	9	2	7			
Chlorine . . .	Cl	35.457	17	2	8	7		
Bromine . . .	Br	79.916	35	2	8	18	7	
Iodine	I	126.91	53	2	8	18	18	7

106. General Features of the Halogens. Halogens is the name given to the elements *fluorine*, *chlorine*, *bromine* and *iodine* located in the seventh group of the Periodic Table and forming its main subgroup.* These elements received their name, which means literally "salt-forming," due to their ability to combine directly with the metals, forming typical salts, such as NaCl.

The atoms of the halogens have seven electrons in their outer layer. Therefore, they gain one electron very readily, passing into negative univalent ions, which characterizes them as typical non-metals (see § 56). Thus, the negative valency of the halogens is 1. The halogens may manifest positive valency as well, their maximum possible positive valency, evidently, being seven. However, the only halogens known at present to form compounds with such a valency are chlorine and iodine. The highest valency of bromine is 5, while fluorine possesses only negative valency.

Compounds in which the halogens are positively valent (their oxygen compounds) are generally less stable than those in which they are negatively valent and are almost unknown in nature.

The identical structure of the outermost electron layers of the halogens accounts for their great similarity, manifested both in their chemical behaviour and in the types and properties of the compounds they form. But, for all this similarity, there are also qualitative differences between them. To bring out these differences more

* This subgroup includes also the element astatine, No. 85, produced artificially.

vividly, we shall discuss the halogens all together, rather than separately.

107. The Halogens in Nature. Owing to their very high chemical activity, the halogens are found in nature only as compounds, mainly as salts of the hydrohalic acids.

Fluorine occurs in nature mostly as the mineral fluorspar* CaF_2, so named because it is added sometimes to iron ores to form fusible slags when smelting pig iron. Considerable quantities of fluorine are contained also in the rather widespread phosphorus minerals, phosphorite and especially apatite.

The most important natural compound of chlorine is common salt, table salt or sodium chloride, which is the chief raw material for the production of other chlorine compounds. Most of the salt on the earth is dissolved in the waters of the seas and oceans, where its content fluctuates around 3.5 per cent. The waters of many lakes and springs also contain considerable quantities of common salt in solution. In some lakes which have no outlets, the quantity of salt approaches the saturation limit (about 26 per cent), and the salt precipitates out of the water of these lakes and deposits at the bottom. Such, for instance, are the lakes Elton and Baskunchak in the lower reaches of the Volga, where the salt deposited at the bottom is extracted as "lake-salt".

Salt occurs also in the solid form, as thick seams of what is known as rock salt at certain points of the earth's crust. Very pure rock salt is mined in the U.S.S.R. in the Donets Basin and in the South Urals near Orenburg where the seams are sometimes over 100 metres thick. There are also deposits of rock salt in Transcaucasia, in Kazakhstan, Siberia and other places.

Other chlorine compounds besides common salt also occur in large quantities in nature; such are potassium chloride, as the minerals *sylvite* KCl and *carnallite* $KCl \cdot MgCl_2 \cdot 6H_2O$, magnesium chloride, contained in sea water and accounting for its bitter taste, etc.

Like chlorine, bromine occurs in nature mainly in the form of compounds with potassium, sodium and magnesium. Bromine compounds usually occur together with those of chlorine, but in much smaller quantities. Metal bromides are contained in sea water and in the water of certain lakes. In the U.S.S.R. especially large quantities of bromine are contained in the salt lakes of the Crimea and in the waters of the Kara-Bogaz-Gol Bay in the Caspian Sea.

Sea water contains iodine compounds also, but in such minute quantities that it is impossible to separate them out directly from the water. However, there are certain seaweeds which are capable of extracting iodine from sea water and accumulating it in their

* From the Latin *fluere*—to flow.—*Tr.*

tissues. Especially large quantities of such seaweeds are found on the coasts of Normandy, Bretagne and Scotland; they grow also in the Black Sea and along the Far Eastern coast of the U.S.S.R. The ashes of these seaweeds are found to contain iodine as salts of hydroiodic acid HI and are the principal source of iodine in Europe.

Considerable quantities of iodine (from 10 to 100 mgr. of I_2 per litre) are found in the waters of wells drilled in oil-bearing regions.

The total content of halogens in the earth's crust is very small. For chlorine it is 0.188, for fluorine 0.027, for bromine 0.0006 and for iodine 0.000006 per cent by weight.

108. Physical Properties of the Halogens. *Fluorine* is a gas at ordinary conditions with a pale greenish-yellow colour in thick layers. When greatly cooled, fluorine turns into a liquid which solidifies at −218° C.

Chlorine is a yellowish-green gas about two and a half times as heavy as air: one litre of chlorine at S.T.P. weighs 3.21 gr. Under a pressure of about 6 atm. chlorine turns into a liquid at ordinary temperatures. Liquid chlorine is usually stored and transported in steel cylinders or in special cisterns.

Bromine is a heavy, dark-brown liquid with a specific gravity of 3.12. It evaporates very readily forming reddish-brown vapours. Bromine may cause serious burns if it comes into contact with the skin.

Iodine is a solid, forming dark grey crystals with a slightly metallic lustre. The specific gravity of iodine is 4.93. When heated slowly at ordinary pressure iodine sublimates, i. e., turns into vapour without melting. Its vapours are of a violet colour; when cooled, the iodine vapours pass back into the solid state without going through the liquid phase. But if iodine is heated rapidly, especially under high pressure, it melts at 113° C.

All the halogens possess a very pungent odour. Inhalation of even very small quantities of the halogens causes serious irritation of the respiratory ducts and inflammation of the mucous membranes of the throat and nose. More considerable quantities of the halogens may cause a grave poisoning of the organism.

The most important physical constants of the halogens are given in Table 18. The data in this table show that the physical properties of the halogens gradate in a definite order from fluorine to iodine: their specific gravities grow, their melting and boiling points rise and their atomic radii increase.

The halogens are rather poorly soluble in water. One volume of water will dissolve about $2^1/_2$ volumes of chlorine at ordinary temperature, such a solution being known as *chlorine water*. If chlorine is

passed into water cooled to 0°C, greenish-yellow crystals of crystalline *chlorine hydrate* $Cl_2 \cdot 8H_2O$ precipitate out.

Table 18

Most Important Physical Constants of the Halogens

Constants	Fluorine F	Chlorine Cl	Bromine Br	Iodine I
Specific gravity . . .	1.11 (liq.)	1.57 (liq.)	3.12	4.93
Melting point, degrees C	—218	—101	—5.7	113
Boiling point, degrees C	—188.2	—34	59	183
Atomic radius, Å . . .	0.67	1.07	1.19	1.36

The solubility of bromine at 20°C is about 3.5 gr. while that of iodine is only 0.02 gr. per 100 gr. of water. Fluorine cannot be dissolved in water, as it decomposes the latter vigorously, liberating oxygen and forming HF:

$$2F_2 + 2H_2O = 4HF + O_2$$

(simultaneously some ozone is formed as well).

The halogens dissolve in many organic solvents, such as carbon disulphide, alcohol, ether, chloroform, etc., much better than in water. Solutions of bromine in all these solvents are of a yellowish-brown colour. A solution of iodine in alcohol and ether is dark brown, while in carbon disulphide and chloroform it is violet; the difference in the colouring of the solutions is due to the formation of iodine solvates, i. e., compounds of I_2 molecules with molecules of the solvent.

The high solubility of the halogens in organic solvents can be utilized to extract them from aqueous solution. If, for instance, an aqueous solution of iodine is shaken with a small quantity of carbon disulphide (which does not mix with water), almost all the iodine passes from the water into the carbon disulphide, colouring it violet.

109. Chemical Properties of the Halogens. The halogens are exceedingly active elements. They react with almost all simple substances. The reactions between the halogens and metals are especially rapid and involve the liberation of a large amount of heat. Thus, for instance, if molten metallic sodium is placed in a vessel containing chlorine, it will burn with a blinding flame, depositing white table salt on the vessel walls:

$$2Na + \overset{\overset{2e^-}{\frown}}{Cl_2} = 2Na^+ + Cl^-$$

Copper, iron, tin and many other metals also burn in chlorine, forming the corresponding salts. Iodine and bromine act in a similar way. In all these cases the metal loses electrons and the halogen gains them.

It was indicated in § 70 that substances which acquire electrons in the course of a reaction, abstracting them from other substances, are called oxidizing agents. This capacity for gaining electrons, especially pronounced in halogen atoms, is their most characteristic chemical property. *The halogens are very active oxidants.* The most active of them is fluorine and the least active iodine. The oxidizing properties of the halogens are manifested also in their reactions with various complex substances.

Several examples are given below.

1. If chlorine is passed through a pale green solution of ferrous chloride $FeCl_2$ the liquid turns yellow, owing to oxidation of the ferrous chloride $FeCl_2$ into ferric chloride $FeCl_3$:

$$2FeCl_2 + Cl_2 = 2FeCl_3$$

or in the ionic form

$$2Fe^{\cdot\cdot} + Cl_2 = 2Fe^{\cdots} + 2Cl'$$

(with $2e^-$ indicated over the arrow)

2. If hydrogen sulphide water (a solution of H_2S) is added to a solution of bromine, the yellowish-brown colour of bromine disappears and the liquid becomes milky due to the liberation of sulphur:

$$H_2S + Br_2 = S + 2HBr$$

or

$$H_2S + Br_2 = S + 2H^{\cdot} + 2Br'$$

(with $2e^-$ indicated over the arrow)

3. If an aqueous solution of iodine is treated with a solution of sodium sulphite Na_2SO_3, the solution becomes decolourized due to reduction of the iodine into hydrogen iodide as it oxidizes the sodium sulphite into sodium sulphate. The reaction involves the participation of water and is expressed by the equation

$$\overset{+IV}{Na_2}\overset{}{S}\overset{}{O_3} + \overset{0}{I_2} + H_2O = \overset{+VI}{Na_2}\overset{}{S}\overset{}{O_4} + 2\overset{-1}{H}\overset{}{I}$$

or in the ionic form

$$SO_3'' + I_2 + H_2O = SO_4'' + 2H^{\cdot} + 2I' \qquad (1)$$

In contradistinction to the previous reactions, where the atoms of simple substances or elementary ions were oxidized, in this case a complex SO_3'' ion is oxidized into an SO_4'' ion.

To understand this reaction better let us examine the oxidation and reduction processes separately.

The oxidation reaction can be represented by the following equation:

$$SO_3'' + H_2O - 2e^- = SO_4'' + 2H^+ \quad (2)$$

The oxidation of the SO_3'' ion consists in its losing two electrons; at the same time an oxygen ion breaks away from a water molecule (liberating two hydrogen ions) and unites with it. The result is an SO_4'' ion which has the same negative charge (—2) as the SO_3'' ion, though the valency of the sulphur has increased from +4 to+6.

The reduction process is represented by the equation

$$I_2 + 2e^- = 2I' \quad (3)$$

The iodine is reduced as a result of two electrons being added to its molecule, so that its valency drops from 0 to —1.

Adding up equations (2) and (3), we get equation (1).

A comparison of the chemical properties of the halogens shows that their activity decreases gradually from fluorine to iodine. As the atomic number of the halogens rises, the total number of electrons surrounding their nucleus increases, their atomic radius becomes larger and their outer electrons move farther and farther away from the nucleus, so that the attraction of the electrons by the latter becomes weaker. At the same time, the electron affinity of the atom decreases, as does the strength of the bond between the electron and the nucleus in the negative ion of the halogen.

The table below gives a comparison of the radii of the negatively charged halogen ions and the quantity of energy in calories evolved during the formation of one gram-ion of the corresponding element.

	Fluorine	Chlorine	Bromine	Iodine
Radius of negative ion, Å	1.33	1.81	1.96	2.20
Electron affinity, Cal.	98	88	83	76

These data show that as the radius of the ion increases, its electron affinity diminishes, which is in full agreement with the decrease in activity from fluorine to iodine.

Different electron affinity accounts readily for the order of displacement of the halogens from their compounds. Since the electron affinity of fluorine is the highest, it can take electrons away from the ions of any of the other halogens; chlorine can abstract electrons only from bromide and iodide ions, while bromine can remove them only from iodide ions. The reactions involved are typical oxidation-reduction reactions, during which the atom of one halogen oxidizes the ion of another, itself being reduced to the ionic state.

For example:

$$Cl_2 + 2KI = I_2 + 2KCl$$

$$\overset{\overset{2e^-}{\downarrow}}{Cl_2} + 2I' = I_2 + 2Cl'$$

In this reaction I′-ion acts as the reducing agent. The chemical activity of the negative ions of the halogens as reducing agents changes inversely to the chemical activity of their molecules or free atoms. The most active reducing agent is I′-ion and the least active, F′-ion. This is due to the fact that considerably less energy is required to split an electron away from I′-ion than from F′-ion.

Thus the chemical activity of the halogen molecules as oxidizing agents gradates in the following order:

$$F_2 > Cl_2 > Br_2 > I_2$$

On the other hand, the chemical activity of the halogen ions as reducing agents gradates in the reverse order:

$$I' > Br' > Cl' > F'$$

The difference in activity of the halogen molecules is especially pronounced in their reaction with hydrogen. Fluorine reacts with hydrogen explosively even at very low temperatures. Chlorine combines with hydrogen slowly at ordinary temperatures, but when heated a mixture of chlorine and hydrogen will react almost instantaneously, causing an explosion. Bromine will combine with hydrogen at a perceptible rate only at elevated temperatures, while iodine combines with hydrogen only when heated strongly, and the reaction is not complete owing to its reversibility.

It is noteworthy that light has a great influence on the reaction of combination between chlorine and hydrogen. In the dark there is no perceptible interaction at all; in dispersed light the reaction proceeds rather slowly, while in bright sunlight it takes place as rapidly as when the mixture is heated, and is accompanied by an explosion.

Investigation of this reaction led to the conclusion that it consists of a succession of steps. Absorbing the energy of the solar rays, some individual chlorine molecules decompose into atoms:

$$Cl_2 = 2Cl$$

Chlorine atoms are more active than the molecules, and immediately begin to react with the hydrogen molecules according to the equation

$$Cl + H_2 = HCl + H$$

The hydrogen atoms thus formed react in their turn with chlorine molecules, giving rise to new chlorine atoms:

$$H + Cl_2 = HCl + Cl$$

The latter again react with hydrogen molecules, etc.

Reactions of this kind, consisting of a sort of chain of consecutive reactions, are known as **chain reactions.**

Chain reactions play an important part in many chemical processes, particularly in those of combustion. Extensive investigations in the field of chain reactions were carried out by the Soviet Academician N. Semyonov who was the first to prove their abundance and great importance. Semyonov suggested a theory of chain reactions on the basis of which he also developed a theory of flammation and explosions which is of great practical importance. The services rendered by Semyonov are held in high esteem by the scientific world. He was awarded the Nobel Prize for 1956 by the Swedish Academy of Sciences for developing the theory of chain reactions and chemical processes.

Thus, both the physical and the chemical properties of the halogens gradate consecutively as the charges on their atomic nuclei and the number of electrons in their atoms increase. The non-metallic properties, most pronounced in fluorine, gradually weaken, and iodine begins to manifest even some metallic properties. This regularity in gradation of properties is a striking manifestation of the Law of Transition of Quantity into Quality.

110. Preparation and Uses of the Halogens. In natural compounds the halogens are contained (with very few exceptions) as negatively charged ions and therefore almost all the methods of obtaining the halogens in the free state consist essentially in oxidation of their ions. This is done by means of various oxidizing agents or by the action of electric current.

As we know, during electrolysis electrons pass from the cathode to the positively charged ions and from the negatively charged ions to the anode (see § 88). Therefore, reduction takes place at the cathode and oxidation at the anode. Thus, oxidation or reduction may be brought about by electric current as well as by the action of one substance on another.

Electric current is the most powerful means of oxidation and reduction.

Owing to its great electron affinity *fluorine* can be isolated from its compounds only by electrolysis. It was obtained for the first time in 1886 by the electrolytic decomposition of anhydrous liquid hydrogen fluoride HF with about 20 per cent of potassium fluoride KF added. The decomposition was carried out in an apparatus made of copper which resists fluorine (after it has become coated

with a layer of copper fluoride). The electrodes were made of platinum.

The method by which elementary fluorine was isolated is employed at present also for its commercial production. A fusion of the composition $KF \cdot 2\,HF$ (m. p. 70° C) is decomposed by electricity. Electrolysis is carried out in steel baths using graphite electrodes.

Chlorine is prepared at present in large quantities by the electrolysis of solutions of common salt. Chlorine is evolved at the anode, while sodium hydroxide forms at the cathode. Sometimes this reaction is employed to prepare the alkali, in which case chlorine is produced as a by-product (see § 208).

Chlorine is prepared in the laboratory by the action of various oxidants on hydrochloric acid. The reader will recall, for instance, the laboratory method of preparation of chlorine described in the secondary school course, by the action of manganese dioxide on hydrochloric acid:

$$\overset{+IV}{Mn}O_2 + 4H\overset{-I}{Cl} = \overset{+II}{Mn}Cl_2 + \overset{0}{Cl_2} + 2H_2O$$

In the ionic form this reaction can be expressed by the following equation:

$$\overset{2e^-}{\downarrow}\quad MnO_2 + 2Cl' + 4H^{\cdot} = Mn^{\cdot\cdot} + Cl_2 + 2H_2O$$

from which it can be seen that Cl'-ion is oxidized into atomic chlorine (which combines subsequently into Cl_2 molecules) and the tetravalent manganese in MnO_2 is reduced to bivalent $Mn^{\cdot\cdot}$-ion. Chlorine was obtained by this reaction for the first time by the Swedish chemist Scheele in 1774.

Chlorine can be obtained from hydrochloric acid in a similar way by using other oxidants instead of MnO_2 (such as PbO_2, $KClO_3$, $KMnO_4$).

Oxygen does not react perceptibly with HCl under ordinary conditions. But if a mixture of HCl and O_2 is passed through a tube heated to 400° and containing cupric chloride $CuCl_2$ as a catalyst, distributed over pieces of pumice, the hydrogen chloride (rather Cl'-ion) is oxidized by the oxygen:

$$4HCl + O_2 \rightleftarrows 2Cl_2 + 2H_2O$$

the chlorine yield being as high as 80 per cent. Formerly this reaction was often used for the preparation of chlorine.

Bromine and *iodine* can be prepared in a manner similar to chlorine by oxidizing HBr and HI with various oxidizing agents. They are usually produced on a commercial scale from the metal bromides or iodides by the action of chlorine on their solutions. Thus, the preparation of bromine and iodine is also based on oxidation of their

ions, with the difference that the oxidant used is chlorine. For example:

$$2Br' + Cl_2 = 2Cl' + Br_2^{++} \quad 2I' + Cl_2 = 2Cl' + I_2$$

In the U.S.S.R. bromine is extracted from the waters of Lake Sak (in the Crimea) which contain a considerable quantity of bromide salts, and from the "brine" (saturated solution) of the Kara-Bogaz Gol Bay. Bromine is now obtained also from drill hole waters.

The chief source for the preparation of iodine in the U.S.S.R. are the waters of drill holes. By the end of the First Five-Year Plan two large-scale plants had been built for the extraction of iodine from such waters at Surakhany and Nefte-Chala (the Azerbaijan S.S.R.); the capacity of these plants is quite sufficient to cover the requirements of the country in iodine.

The halogens are widely used in the chemical industry. Free fluorine is employed at present for the production of certain very valuable fluorine derivatives of hydrocarbons, possessing unique properties, such as lubricants capable of withstanding high temperatures, a reagent-proof plastic (teflon), refrigerants (freons), etc. Chlorine is used to prepare numerous inorganic and organic compounds. It is employed in the production of hydrochloric acid, calcium hypochlorite and other hypochlorites, chlorates, sulphur chloride, carbon tetrachloride, various chlorine derivatives of hydrocarbons, etc. Chlorine plays a very important part in the production of intermediate products for the synthesis of dyes and many medicinals and pharmaceuticals. A great quantity of chlorine, both in the free state and in the form of bleaching salts, is used for bleaching fabrics and paper pulp. Chlorine is used also to sterilize drinking water.

Bromine is necessary for the manufacture of various medicinals, certain dyes and silver bromide, which is used in large quantities in the photography industry.

Iodine is widely used in medicine in the form of tincture of iodine (a 10 per cent solution of iodine in alcohol) which is an excellent antiseptic and styptic. Besides, iodine is a constituent part of a number of pharmaceuticals.

111. Hydrogen Compounds of the Halogens. Of all the halogen compounds, the most important practically are the hydrogen halides and the salts of the hydrohalic acids.

All the hydrogen halides are colourless gases possessing a pungent odour, and condensing readily into liquids. Hydrogen fluoride liquefies at 19.5° C, and the other hydrogen halides, at lower temperatures. The hydrogen halides are very soluble in water. For instance, one volume of water will dissolve about 500 volumes of hydrogen chloride at 0° C; the solubility of hydrogen bromide and hydrogen iodide is about the same. Hydrogen fluoride is soluble in water in all proportions.

The aqueous solutions of the hydrogen halides are typical acids, only hydrofluoric acid being comparatively little ionized. The rest of them are among the most active acids.

All the hydrogen halides fume in the air, due to the formation of minute droplets of the corresponding acids with the water vapours in the air.

The stability of the hydrogen halides to heat falls abruptly from HF to HI due to the decrease in the electron affinity of the halogen atoms. While HF does not ionize into atoms to any perceptible degree even at very high temperatures, hydrogen iodide decomposes considerably into iodine and hydrogen at as low a temperature as 300° C.

The most important constants of the hydrogen halides are given in Table 19.

Table 19

Most Important Constants of Hydrogen Halides

Constants	Hydrogen halide			
	HF	HCl	HBr	HI
Specific gravity (liq.)	0.987	1.19	2.16	2.80
Melting point, degrees C	—83	—112	—88	—50.9
Boiling point, degrees C	19.5	—84	—67.0	—35.7
Heat of formation, Cal.	64	22.1	8.65	—6

The general method of preparing the hydrogen halides is by the action of concentrated sulphuric acid on the salts of the hydrohalic acids. Thus, for instance, hydrogen chloride is usually obtained by heating sodium chloride with concentrated sulphuric acid:

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$$

Since glass vessels must not be heated too strongly, only one of the hydrogen atoms of sulphuric acid takes part in the reaction when it is carried out in the laboratory, resulting in the acid salt:

$$NaCl + H_2SO_4 = NaHSO_4 + HCl$$

Even though two molecules of NaCl be taken for each molecule of sulphuric acid, the reaction will go no further than the formation of the acid salt. Only when this method is used for the industrial production of HCl, allowing very intense heating, does the acid salt interact further with a second molecule of NaCl to form the normal salt:

$$NaCl + NaHSO_4 = Na_2SO_4 + HCl$$

Hydrogen fluoride is prepared in a similar way. It is obtained from calcium fluoride, a natural compound of fluorine:

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF$$

As hydrogen fluoride attacks glass vigorously, the reaction is usually carried out in lead vessels, a protective layer of PbF_2 forming on their walls, and keeping the metal from further corrosion.

Hydrogen bromide and hydrogen iodide can also be obtained by the action of sulphuric acid on metal bromides and iodides. But during these reactions part of the hydrogen halides is oxidized by the sulphuric acid, liberating free bromine and iodine. For example:

$$2HBr + H_2SO_4 = Br_2 + SO_2 + 2H_2O \quad (2e^-)$$

Therefore these hydrogen halides are usually prepared by the action of water on the phosphorus compounds of bromine and iodine PBr_3 and PI_3. The latter undergo complete hydrolysis, forming phosphorous acid and the corresponding hydrogen halides:

$$PBr_3 + 3H_2O = H_3PO_3 + 3HBr$$
$$PI_3 + 3H_2O = H_3PO_3 + 3HI$$

Contrary to the preparation of the free halogens, the preparation of the hydrogen halides is not an oxidation-reduction reaction. As can be seen from the above examples, no change in valency, characteristic of oxidation-reduction processes, takes place during these reactions.

In practice we have to do mainly with aqueous solutions of the hydrogen halides, which are acids, the most important being hydrochloric acid.

Hydrochloric or *muriatic acid* is prepared by dissolving hydrogen chloride in water.

At present the principal industrial method for the preparation of hydrogen chloride is by synthesis from hydrogen and chlorine according to the equation

$$H_2 + Cl_2 = 2HCl + 43.8 \text{ Cal.}$$

This reaction is carried out by burning hydrogen in a stream of chlorine. "Synthetic" hydrochloric acid is obtained by absorbing the resulting hydrogen chloride in water.

Fig. 80 shows a diagram of a synthetic hydrochloric acid plant. The furnace *1* for burning hydrogen in chlorine is a vertical steel pipe with a special burner at its bottom consisting of two concentric steel tubes. Dry chlorine enters at the bottom through the inner tube *2* while dry hydrogen is introduced through the outer tube *3*. After

ignition the mixture continues to burn tranquilly with a large flame, forming hydrogen chloride. The latter is then passed through absorption columns *4* (only one column is shown in the figure), in which it is absorbed by water trickling downwards. Thus, by using pure hydrogen and pure chlorine for the synthesis, chemically pure hydrochloric acid can be produced directly.

The earlier "sulphate" method of preparation of hydrogen chloride still used at present is based on the reaction between concentrated sulphuric acid and common salt. At a high temperature this reaction takes place according to the following summary equation

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$$

Sodium sulphate Na_2SO_4 is obtained as a by-product.

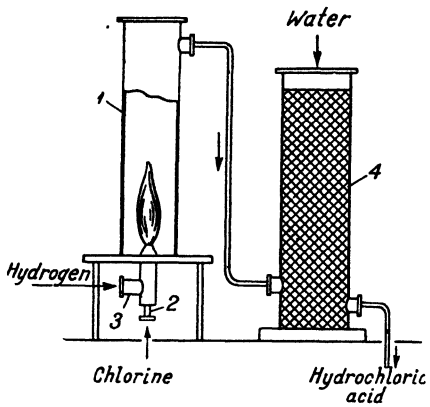


Fig. 80. Diagram of synthetic hydrochloric acid plant:
1—hydrogen combustion furnace; *2*—chlorine inlet; *3*—hydrogen inlet; *4*—absorption column

Of the two methods mentioned, the more perfect is the synthetic method. With this method the hydrogen liberated simultaneously with chlorine during the electrolytic preparation of the latter can be used, saving considerable quantities of sulphuric acid, which is indispensable for the production of mineral fertilizers, dyes and other products.

Pure hydrochloric acid is a colourless liquid with the pungent odour characteristic of hydrogen chloride. A saturated solution of hydrogen chloride at 18° C contains 42 per cent HCl. Ordinary concentrated hydrochloric acid contains about 37 per cent HCl and has a specific gravity of 1.19. This acid fumes in the air due to the liberation of hydrogen chloride and for this reason is called *fuming* hydrochloric acid. The technical acid is yellow due to the presence of impurities (mainly $FeCl_3$) and contains around 27.5 per cent HCl. Synthetic hydrochloric acid contains 31 per cent HCl.

If concentrated hydrochloric acid is heated, hydrogen chloride escapes first, together with a small quantity of water. This continues until the residue becomes a 20.2 per cent solution; the latter distills further without altering its composition, at a constant temperature of 110°. On the other hand, if dilute hydrochloric acid is heated, water escapes first. When the concentration of the residue reaches 20.2 per cent, the liquid begins to distill without altering its composition, as in the previous case. Thus, hydrogen chloride cannot be removed entirely from water by boiling.

The composition of the constant-boiling solution changes depending on the pressure, and therefore it cannot be regarded as a definite chemical compound between HCl and water, although at low temperatures various hydrates (such as $HCl \cdot H_2O$, $HCl \cdot 2H_2O$, etc.) can be isolated from hydrochloric acid.

Hydrochloric acid is one of the most important acids in chemical practice. It reacts readily with many metals, liberating hydrogen and forming salts, known as **metal chlorides** or just **chlorides**. Hydrochloric acid is used for the preparation of metal chlorides, for the production of ammonia, glue, carbonic acid, a number of organic preparations, in the leather industry (to treat leather before chrome tanning), in the food industry, in tinning and soldering and in many other branches of industry. A small quantity of hydrochloric acid is contained in the gastric juices of man and animals and plays an important part in digestion.

The chlorides of most metals are readily soluble in water and therefore are widely used in laboratory practice when it is necessary to introduce any definite metal ion into a reaction. Of the most important metals, only the chlorides of silver, univalent mercury and copper (AgCl, Hg_2Cl_2, CuCl) are insoluble. Lead chloride $PbCl_2$ is very slightly soluble.

The most important chlorides are considered below.

Sodium chloride NaCl or common salt is of very great importance in everyday life. First of all, salt is a necessary seasoning for our food. Then salt plays an important part as a means of preventing many food products from spoiling. Common salt serves as raw material for the production of chlorine, hydrochloric acid, caustic soda and soda ash; it is used in the dye, soap and many other industries.

Potassium chloride KCl is used in immense quantities in agriculture as a fertilizer.

Calcium chloride $CaCl_2 \cdot 6\ H_2O$ is employed for the preparation of cooling mixtures. Anhydrous calcium chloride is widely used in laboratory practice for drying gases, dehydrating ether and many other liquid organic substances.

Mercuric chloride $HgCl_2$, or corrosive sublimate, is a very strong poison. It is used to preserve wood and anatomical preparations as well as for the preparation of other mercury compounds. Very dilute solutions of corrosive sublimate (1 : 1,000) are used in medicine as an excellent disinfectant.

Silver chloride AgCl is the least soluble salt of hydrochloric acid. The formation of a precipitate of AgCl due to the reaction between Cl'-ion and $Ag^{\cdot}$-ion is a characteristic test for chloride-ion. Silver chloride is used in photography for the preparation of certain types of sensitized plates and papers.

It should be noted that when a metal of variable valency forms two different salts with hydrochloric or any other hydrohalic acid,

the ending "*ous*" (added to the name of the metal or its root) is used for the salt of lower valency, while the ending "*ic*" denotes the salt with the higher valency. For instance, $FeCl_2$ is called ferrous chloride, while $FeCl_3$ is ferric chloride; Hg_2Cl_2 is mercurous chloride, and $HgCl_2$—mercuric chloride, etc.

Hydrobromic and *hydroiodic* acids are very similar in properties to hydrochloric acid but are less stable. Since the electron affinity of bromine and iodine atoms is lower than that of chlorine atoms, Br'- and I'-ions are oxidized more readily than Cl'-ion, as we have already seen in the reaction between sulphuric acid and the metal bromides and iodides. Iodide-ion gives away its electron especially readily, and can be oxidized even by atmospheric oxygen. For this reason a solution of hydrogen iodide very soon turns red if left standing in the air, due to the liberation of free iodine:

$$4HI + O_2 = 2I_2 + 2H_2O \quad (4e^-)$$

Light greatly accelerates this reaction. Due to the readiness of iodide-ion to part with its electrons, *hydrogen iodide is an active reducing agent.* The salts of hydrobromic and hydroiodic acids are called **bromides** and **iodides**, respectively. Most of them are quite soluble in water. The insoluble salts are those of the same metals which form insoluble chlorides.

Solutions of sodium and potassium bromides are used in medicine under the name of "bromide" as sedatives in treating disorders of the nervous system. Silver bromide is used in large quantities for the preparation of photographic plates, films and papers. Potassium iodide is used in medicine for the treatment of certain diseases.

Hydrofluoric acid is a solution of hydrogen fluoride in water. The names hydrofluoric acid and fluorine originated from fluorspar, from which hydrogen fluoride is usually obtained (see footnote, p. 215).

Both hydrogen fluoride and hydrofluoric acid differ in properties from the rest of the hydrogen halides and hydrohalic acids. This difference, manifested even in the physical properties of hydrogen fluoride, namely in its melting and boiling points, which do not correspond to its low molecular weight, is due to the strong association of its molecules owing to the formation of hydrogen bonds between them (see p. 215):

$$\ldots H-F\ldots H-F\ldots H-F\ldots$$

The vapour density of hydrogen fluoride at 32° C shows that its formula at this temperature is $(HF)_2$, while at 90° C it consists of simple HF molecules. Likewise, HF molecules are strongly associated in solution.

Compared to HCl, HBr and HI, hydrofluoric acid ionizes very little and, along with F'-ion, contains a large quantity of HF_2'-ion formed by the union of F' ions with HF molecules. For this reason hydrofluoric acid forms a number of acid salts, such as KHF_2, thus behaving , in a sense, like a dibasic acid.

One of the remarkable properties of hydrofluoric acid is its capacity for reacting with silicon dioxide or silicic anhydride SiO_2, a constituent part of glass, to form gaseous silicon fluoride SiF_4 and water:

$$SiO_2 + 4HF = SiF_4 + 2H_2O$$

The use of hydrofluoric acid for etching drawings and inscriptions on glass, as well as for frosting glass articles (such as electric light bulbs), is based on this reaction.

To etch a drawing on glass, the latter is first coated with wax or paraffin, which are indifferent to HF; then the wax is cut or scratched off the parts where the drawing is to be inscribed, and the denuded surfaces are treated for some time with hydrofluoric acid or hydrogen fluoride vapours.

Large amounts of hydrogen fluoride are employed for the preparation of cryolite, used in the production of aluminium (§ 229). Besides, hydrogen fluoride is used as a catalyst in certain chemical processes such as the manufacture of high-quality motor fuel.

Hydrofluoric acid is employed also for the preparation of organic fluorides to be used in refrigerators, in the synthesis of certain types of dyes, lubricants and plastics. In analytical laboratories hydrofluoric acid is used for dissolving various silicates (salts of silicic acid).

The vapours of hydrofluoric acid are very poisonous. If concentrated hydrofluoric acid comes in contact with the skin it causes very serious burns which turn into ulcers that heal with great difficulty. Therefore, this acid should be handled very carefully. In the laboratory hydrofluoric acid is kept in vessels made of paraffin which it does not attack.

The salts of hydrofluoric acid—**fluorides**—are mostly insoluble in water, which distinguishes them from the salts of the other hydrohalic acids. But silver fluoride AgF dissolves readily in water, although AgCl, AgBr and AgI are practically insoluble.

Sodium fluoride NaF is used to destroy agricultural pests and as a preservant for impregnating wood.

112. Oxygen Compounds of the Halogens. The halogens do not combine directly with oxygen; hence their oxygen compounds can be obtained only indirectly and are not very stable. The most stable are the salts of their oxygen acids and the least stable, their oxides. In all their oxygen compounds the halogens are positively valent,

their valency being as high as seven in the highest oxygen compounds of chlorine and iodine.

The most numerous and practically important are the oxygen compounds of chlorine, which we shall examine in greater detail.

To give a more general idea, the formulas of the oxides and acids formed by chlorine are shown in Table 20 together with the names of the acids and the corresponding salts. Compounds which have not yet been obtained, but are assumed to exist, are enclosed in parentheses.

Table 20

Oxygen Compounds of Chlorine

Oxides	Acids		Name of salts
	formula	name	
Cl_2O	$HClO$	Hypochlorous	Hypochlorites
(Cl_2O_3)	$HClO_2$	Chlorous	Chlorites
ClO_2	—	—	—
(Cl_2O_5)	$HClO_3$	Chloric	Chlorates
Cl_2O_7	$HClO_4$	Perchloric	Perchlorates

All the oxygen compounds of chlorine are strong oxidants. When oxidizing, the positively valent chlorine atoms are usually reduced either to neutral chlorine or to negatively charged Cl′-ion. Of great practical importance are the hypochlorites and chlorates, salts of hypochlorous and chloric acids, respectively.

Hypochlorites. Their preparation is based on the reaction between chlorine and water, leading to the formation of hypochlorous acid:

$$Cl_2 + H_2O \rightleftarrows HClO + HCl$$

This is the *hydrolysis* of chlorine. It may be assumed that hydrolysis is preceded by polarization of the covalent bond between the chlorine atoms in the Cl_2 molecule, i. e., a shift of the common electron pair towards one of the atoms under the influence of the polar water molecules. After this the positively charged chlorine atom combines with the hydroxyl of water, displacing a proton, while the other chlorine atom is converted into a $[:\ddot{\underset{\cdot\cdot}{Cl}}:]^-$ ion, as shown by the following scheme:

$$:\bar{\underset{\cdot\cdot}{Cl}}: \Big| \overset{+}{\underset{\cdot\cdot}{Cl}}: + \ :\underset{\cdot\cdot}{O}: \Big| H \rightarrow H:\underset{\cdot\cdot}{O}:Cl + [:\underset{\cdot\cdot}{Cl}:]^- + H^+$$

It can be seen from the scheme that the hydrolysis of chlorine is an oxidation-reduction reaction, during which one of the chlorine

atoms, gaining an electron from the other, is reduced, while the other chlorine atom is oxidized.

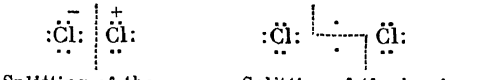
$$Cl - e^- = \overset{+1}{Cl}$$

$$Cl + e^- = \overset{-1}{Cl}$$

A reaction of this kind, in which one atom of an element is the oxidant and the other atom of the same element the reductant, is called a self-oxidation-self-reduction reaction.

The HCl and HClO produced during the hydrolysis of chlorine may react with each other to give chlorine and water again; hence, the reaction is not complete, equilibrium being established after approximately $^1/_3$ of the dissolved chlorine has reacted. Thus, chlorine water always contains a considerable amount of hydrochloric and hypochlorous acids alongside its Cl_2 molecules.

The splitting of the covalent bond between the chlorine atoms during its hydrolysis is of a different nature than the splitting of that between the same atoms under the action of light on chlorine, accompanied by the formation of free chlorine atoms

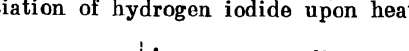


Splitting of the bond during hydrolysis

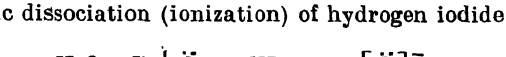
Splitting of the bond under the action of light

The first type of splitting of the covalent bond is called **heterogeneous** and the second **homogeneous.**

Other examples of homogeneous and heterogeneous splitting of bonds are the thermal dissociation of hydrogen iodide upon heating:



and the electrolytic dissociation (ionization) of hydrogen iodide when dissolved in water:



Hypochlorous acid HClO is very unstable and gradually decomposes in solution into hydrogen chloride and oxygen:

$$2HClO = 2HCl + O_2$$

As the hypochlorous acid decomposes, the equilibrium of the reaction between chlorine and water (shown on p. 320) shifts to the right, until all the chlorine has reacted with the water and only HCl remains in solution. This reaction is greatly accelerated by light and that is why chlorine water should always be kept in the dark.

Hypochlorous acid is a very active oxidizing agent; its formation during the reaction of chlorine with water accounts for the bleaching

properties of chlorine. Perfectly dry chlorine will not bleach, but in the presence of moisture dyes are rapidly broken down by the hypochlorous acid formed during the hydrolysis of chlorine.

If an alkali is added in small portions to chlorine water, neutralization of the hypochlorous and hydrochloric acids will also shift the equilibrium of the hydrolysis of chlorine to the right; the result is a solution containing salts of hypochlorous and hydrochloric acids:

$$HCl + HClO + 2KOH = KCl + KClO + 2H_2O$$

The result will obviously be the same if chlorine is passed directly through a *cold* solution of alkali:

$$2KOH + Cl_2 = KCl + KClO + H_2O$$

or in the ionic form:

$$2OH' + Cl_2 = Cl' + ClO' + H_2O$$

The liquid thus obtained, containing a mixture of hypochlorites and chlorides in solution, is called *eau de Javelle* (Javelle is a small town near Paris where this water was first prepared) and is used for bleaching; its bleaching properties are due to the fact that potassium hypochlorite decomposes readily under the influence of the carbon dioxide of the air, forming hypochlorous acid:

$$KClO + CO_2 + H_2O = KHCO_3 + HClO$$

The latter is the active bleaching agent.

A similar solution containing sodium hypochlorite can be obtained by passing chlorine through a solution of sodium hydroxide. Both solutions can be obtained also by the electrolysis of KCl and NaCl, if the chlorine liberated is allowed to react with the alkalis formed during the electrolysis (see p. 551).

The action of chlorine on dry slaked lime gives what is known as *bleaching powder* or *calcium hypochlorite*. Its chief constituent part is $Ca(ClO)_2$, which forms according to the reaction

$$2Ca(OH)_2 + 2Cl_2 = Ca(ClO)_2 + CaCl_2 + 2H_2O$$

but besides this, bleaching powder contains various basic calcium salts.

Bleaching powder is a white powder with a pungent odour and strong oxidizing properties. In moist air it decomposes gradually under the action of carbon dioxide, liberating hypochlorous acid, which accounts for its characteristic odour:

$$Ca(ClO)_2 + CO_2 + H_2O = CaCO_3 + 2HClO$$

The action of hydrochloric acid on bleaching powder results in the liberation of chlorine:

$$Ca(ClO)_2 + 4HCl = CaCl_2 + 2Cl_2 + 2H_2O$$

$$\begin{vmatrix} ^{+1} & & ^{0} \\ 2Cl + 2e^- = Cl_2 \\ ^{-1} & & ^{0} \\ 2Cl - 2e^- = Cl_2 \end{vmatrix}$$

Bleaching powder is widely used for bleaching vegetable fibres (fabrics, paper), for disinfecting cesspools, lavatories, drainage ditches, etc. In gas defence bleaching powder plays an important part as a means of degasing terrains contaminated with poison gases.

The quality of bleaching powder is evaluated by its "active chlorine" content, i. e., by the amount of chlorine liberated under the action of hydrochloric acid, expressed in per cent of the total weight of the product. Standard bleaching powder contains about 35 per cent of active chlorine.

Recently a new industrial method has been developed for preparing bleaching powder with a very high active chlorine content. This bleaching powder consists of almost pure calcium hypochlorite $Ca(ClO)_2$. It is prepared by the action of chlorine on milk of lime—a mixture of slaked lime with a small quantity of water. Calcium hypochlorite is formed as tiny crystals of the composition $Ca(ClO)_2 \cdot 3H_2O$. When the reaction is over, the precipitate is filtered and dried. The resulting technical product contains up to 70 per cent active chlorine.

Chlorates are salts of chloric acid $HClO_3$, which is a rather unstable compound. The best known and most important of these salts is *potassium chlorate* $KClO_3$, known also as Berthollet's salt.

If a solution of potassium hypochlorite is heated it loses its bleaching properties. This is due to the decomposition of KClO into potassium chlorate and potassium chloride according to the following equation:

$$3KClO = KClO_3 + 2KCl$$

or in the ionic form

$$3ClO' = ClO'_3 + 2Cl'$$

In this reaction $^2/_3$ of the chlorine atoms contained in the ClO′ ions, and having a valency of +1, are converted into Cl′ ions, i. e., are reduced, while the remaining atoms pass from the +1 into the +5 valency state, i. e., are oxidized.

If chlorine is passed through a *hot* solution of potassium hydroxide, $KClO_3$ results directly instead of KClO:

$$6KOH + 3Cl_2 = 5KCl + KClO_3 + 3H_2O$$

$$6OH' + 3Cl_2 = 5Cl' + ClO'_3 + 3H_2O$$

During this reaction $^1/_6$ of the chlorine atoms are oxidized to ClO'_3 ions and $^5/_6$ are reduced to Cl′ ions.

Since potassium chlorate is only slightly soluble in cold water, it crystallizes out of solution when the latter is cooled, and can thus be separated from the potassium chloride, which remains in solution.

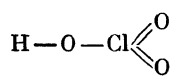
Potassium chlorate decomposes readily when heated, liberating oxygen:

$$2KClO_3 = 2KCl + 3O_2$$

Mixtures of potassium chlorate with various combustible substances (sulphur, charcoal, phosphorus) explode violently when struck. This is the basis of its use in artillery for the production of fuses. Potassium chlorate is employed in pyrotechnics for the preparation of Bengal lights and other highly flammable mixtures. But the chief consumer of potassium chlorate is the match industry. The head of an ordinary match contains about 50 per cent potassium chlorate.

Chloric acid $HClO_3$, corresponding to potassium chlorate, is known only in aqueous solution, condensable by evaporation to a concentration of 50 per cent. Chloric acid is an active oxidizing agent.

The structural formula of chloric acid is:



No anhydride of chloric acid is known. Instead, upon the decomposition of chloric acid, for instance, by the action of concentrated sulphuric acid on potassium chlorate, a yellowish-brown gas with a characteristic odour is liberated. This gas is *chlorine dioxide* ClO_2. Chlorine dioxide is very unstable and decomposes eruptively into chlorine and oxygen if heated or brought into contact with organic substances, etc. A mixture of potassium chlorate and sugar can be ignited by moistening it with a drop of sulphuric acid, as the chlorine dioxide liberated is a potent oxidant.

If potassium chlorate is heated carefully in the absence of a catalyst, it partly decomposes, liberating oxygen, and partly passes into *potassium perchlorate* $KClO_4$, a salt of perchloric acid:

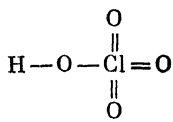
$$\overset{+V}{4KClO_3} = \overset{+VII}{3KClO_4} + \overset{-I}{KCl}$$

Perchlorates are more stable compounds than chlorates. If potassium perchlorate is acted on by sulphuric acid, free perchloric acid $HClO_4$ results, which, when pure, is a colourless liquid freezing at −112° C.

Perchloric acid $HClO_4$ is the most stable oxyacid of chlorine. At the same time, it is the strongest of all known acids: its apparent degree of ionization in 0.5 N solution is 88 per cent, which is higher than the apparent degree of ionization of hydrochloric acid under

the same conditions. Perchloric acid is not so active an oxidant as chloric acid.

The structure of perchloric acid may be expressed by the formula



If perchloric acid is heated with phosphorus pentoxide, the latter abstracts water from it, leaving *perchloric anhydride*:

$$2HClO_4 + P_2O_5 = 2HPO_3 + Cl_2O_7$$

Perchloric anhydride is an oily liquid with a boiling point of 83° C; it explodes violently when struck.

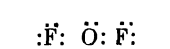
A comparison of the properties of the most important oxygen compounds of chlorine allows the following general conclusion to be drawn: *As the valency of chlorine increases, its oxyacids become more stable and their oxidizing properties become weaker. The most powerful oxidizing agent is hypochlorous acid and the weakest is perchloric acid.* On the contrary, *the strength of the chlorine oxyacid increases with the valency of the chlorine.* The weakest is hypochlorous acid (its ionization constant being about 10^{-8}), and the strongest is perchloric acid.

Oxygen Compounds of Fluorine. The only investigated compound of fluorine and oxygen is fluorine oxide or *oxygen fluoride* OF_2, first obtained only in 1927. It is a colourless gas which liquefies at —145° C, very poisonous and only slightly soluble in water.

Oxygen fluoride is prepared by the action of fluorine on a 2 per cent solution of alkali:

$$2NaOH + 2F_2 = 2NaF + OF_2 + H_2O$$

Its properties (low boiling point, slight solubility in water) indicate that the bonds between the fluorine and oxygen in oxygen fluoride are covalent. Its structure may be represented as follows:



Since the electronegativity of fluorine is higher than that of oxygen, the fluorine in oxygen fluoride should be regarded as negatively univalent and the oxygen as positively bivalent.

Oxygen Compounds of Bromine and Iodine. The only oxygen compounds of bromine known at present are *hypobromous acid* HBrO, *bromic acid* $HBrO_3$ and their salts. These compounds are prepared in the same way as the corresponding compounds of chlorine, but are less stable. Neither perbromic acid nor any of its salts have ever been discovered. The oxides of bromine are very unstable and exist only at low temperatures.

Iodine also forms only one oxide I_2O_5, called *iodic anhydride* and corresponding to *iodic acid* HIO_3. The sodium salt of this acid occurs as an impurity in

Chile saltpetre. The potassium salt can be prepared in the same way as potassium chlorate, by the action of iodine on a hot solution of the alkali.

Free iodic acid is prepared by oxidizing iodine in the presence of water. If chlorine is used as the oxidant, the reaction takes place according to the following equation:

$$I_2 + 5\overset{10e^-}{\underset{\downarrow}{Cl_2}} + 6H_2O = 2HIO_3 + 10HCl$$

Iodic acid is a crystalline substance, quite stable at ordinary temperatures. If heated to 200° C, iodic acid loses the elements of water and is converted into solid iodic anhydride:

$$2HIO_3 = I_2O_5 + H_2O$$

Above 300°C iodic anhydride decomposes, in its turn, into iodine and oxygen.

Another oxyacid of iodine is *periodic acid* HIO_4, which is prepared by the action of iodine on $HClO_4$:

$$2HClO_4 + I_2 = 2HIO_4 + Cl_2$$

If a solution of HIO_4 is evaporated, colourless crystals are deposited, having the composition $HIO_4 \cdot 2H_2O$ and a melting point of 130° C. However, this crystal hydrate should be regarded as a different, pentabasic acid H_5IO_6 (*para*periodic acid), as all five hydrogen atoms in it can be displaced by metals to form salts (e.g., Ag_5IO_6).

Periodic anhydride I_2O_7 has not been obtained.

113. Balancing Equations of Oxidation-Reduction Reactions. In the course of our acquaintance with the properties of the halogens we have frequently had to deal with oxidation-reduction reactions. These reactions are often represented by rather complex equations with large coefficients before the formulas of the reacting and resulting substances. The chief difficulty in deriving such equations is to balance them correctly. There are several methods of finding the coefficients; the simplest method is based on counting up the electrons gained and lost by the substances taking part in the reaction.

In oxidation-reduction reactions electrons are not acquired from the environment but just pass from one set of atoms or ions to another, and therefore the number of electrons gained by the oxidant must obviously be equal to the number of electrons lost by the reductant. Hence, to balance the equation of an oxidation-reduction reaction, we select the coefficients for the oxidizing and reducing substances so that the number of reacting atoms or molecules of the oxidant multiplied by the number of electrons it gains is equal to the product of the number of reductant atoms or molecules and the number of electrons each of them loses.

There is no difficulty in counting up the number of electrons yielded by the reducing agent and gained by the oxidizing agent if the change in valency of these agents due to the reaction is known.

When writing the equations of oxidation-reduction reactions it is necessary, of course, to know what becomes of the oxidizing and

reducing agents as a result of the reaction. In many cases this can be predicted beforehand, if the properties of the reacting substances are known. Allowance must also be made for the participation of water in the reaction, if it proceeds in aqueous solution; whether water participates in the reaction or not becomes evident when balancing the equation.

Now let us attempt to balance several equations of oxidation-reduction reactions and see how the coefficients are determined in concrete examples.

1. *Oxidation of Hydrogen Iodide by Concentrated Sulphuric Acid.* Under the action of concentrated sulphuric acid hydrogen iodide evolves free iodine and the sulphuric acid is reduced to hydrogen sulphide.

The unbalanced equation of this reaction is:

$$HI + H_2SO_4 \rightarrow I_2 + H_2S$$

First we determine the valencies of the elements involved in oxidation and reduction before and after the reaction, indicating them in Roman numerals above the symbols of the elements:

$$\overset{-I}{H}\overset{}{I} + H_2\overset{+VI}{S}O_4 \rightarrow \overset{0}{I_2} + H_2\overset{-II}{S}$$

It can be seen that the valency of the iodine has increased from -1 to 0; hence, iodine was oxidized, each of its ions losing one electron during the reaction. On the other hand, the valency of the sulphur decreased from $+6$ to -2, i. e., sulphur was reduced. The valency of the sulphur decreased as a result of electrons passing from hydrogen iodide to sulphuric acid. Each sulphur atom, covalently linked to oxygen atoms in sulphuric acid, gains eight electrons and is converted into an S^{--} ion. Denoting this atom by $\overset{+VI}{S}$, we record the passage of electrons during the reaction by the following electronic equations:*

$$\begin{array}{c|l} 8 & I' - e^- = \overset{0}{I} \\ 1 & \overset{+VI}{S} + 8e^- = S^{--} \end{array}$$

As the number of electrons yielded by the iodide ions must equal the number of electrons acquired by the sulphur atoms $\overset{+VI}{S}$ in the sulphuric acid molecules, eight iodide ions must obviously be taken for each sulphur atom, i. e., eight HI molecules for each H_2SO_4 molecule. This is indicated by the figures at the left of the above equations.

* In the following, atoms linked by a covalent bond in molecules of complex substances or in complex ions will be denoted by the symbols of the respective elements with a Roman numeral above them showing the valency of the element (atom).

Thus we find the coefficients for the oxidant and reductant, and at the same time the coefficients of the substances formed as a result of oxidation and reduction, as eight HI molecules will, quite obviously, form four I_2 molecules, and one H_2SO_4 molecule will give only one H_2S molecule. Filling in the coefficients now known we get:

$$8HI + H_2SO_4 \rightarrow 4I_2 + H_2S$$

Now, if we compare the number of hydrogen atoms on both sides of the equation we find that there are eight hydrogen atoms missing on the right side. Evidently, water is also formed during the reaction, besides the direct products of oxidation and reduction indicated. The number of molecules of water is determined by the number of missing hydrogen atoms. Adding four molecules of water to the right side, we get the balanced equation of the reaction:

$$8HI + H_2SO_4 = 4I_2 + H_2S + 4H_2O$$

Finally, we check the number of oxygen atoms on both sides of the equation to make sure that it has been balanced correctly.

2. *Oxidation of Copper by Dilute Nitric Acid.* The oxidation-reduction products of the reaction between copper and dilute nitric acid are cupric nitrate $Cu(NO_3)_2$ and nitric oxide:

$$\overset{0}{Cu} + H\overset{+V}{N}O_3 \rightarrow \overset{+II}{Cu}(NO_3)_2 + \overset{+II}{NO} \text{ (unbalanced)}$$

It can be seen that as a result of the reaction the copper atom is oxidized, losing two electrons, while the pentavalent nitrogen atom is reduced, acquiring three electrons:

$$\begin{array}{c|l} 3 & Cu - 2e^- = Cu^{\cdot\cdot} \\ 2 & \overset{+V}{N} + 3e^- = \overset{+II}{N} \end{array}$$

Hence, the oxidation of three copper atoms requires two nitric acid molecules, and as a result of oxidation and reduction, three cupric ions contained in $Cu(NO_3)_2$ and two NO molecules should be formed:

$$3Cu + 2HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO$$

However, comparing the number of atoms of copper and nitrogen on both sides, we find that there are six nitrogen atoms more at the right than at the left. To balance the number of nitrogen atoms, the coefficient of nitric acid on the left side must be increased to eight. Thus, a total of eight molecules of nitric acid participate in the reaction, but only two of them take part in the oxidation of the copper, since only two nitrogen atoms lower their valency from +5 to +2:

$$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO$$

Now we check the number of hydrogen atoms. On the left side there are eight hydrogen atoms, whereas the right side does not contain hydrogen at all. Obviously, four molecules of water are also formed during the reaction. Putting them down on the right side, we get the balanced equation of the reaction:

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O$$

Reactions in which the oxidant or reductant, besides its main function, is used to bind the ions formed during the reaction, are encountered quite often. In all such cases the coefficients are selected as shown above.

In the ionic form the reaction in question is expressed by the equation:

$$3Cu + 8H^{\cdot} + 2NO_3^{\prime} = 3Cu^{\cdot\cdot} + 2NO + 4H_2O$$

from which it is quite obvious that only two $NO_3^{\prime}$ ions, i. e., two molecules of nitric acid, and not eight, as shown in the molecular equation, are expended on the oxidation of the three copper atoms.

When verifying ionic equations it must be kept in mind that not only must the total number of atoms of each element be the same on both sides of the equation, but the algebraic sum of all the charges on the left side must equal the algebraic sum of the charges on the right side as well. For instance, in the above case the right side of the equation contains six positive charges $(+2 \times 3)$, and the algebraic sum of the charges on the left side also equals six $(+8-2)$.

On the basis of the above examples, the following order of balancing equations of oxidation-reduction reactions may be recommended:

1. Write out the unbalanced equation of the reaction, showing the reactants and resultants of the oxidation and reduction process.
2. Determine the valency of the elements taking part in the reaction before and after the reaction and decide which atoms or ions are oxidized and which reduced.
3. Write out the electronic equations for the oxidation process and for the reduction process and find the least factors by which these equations must be multiplied to make the number of electrons in both equations equal.

The figures thus found are the coefficients of the oxidant and reductant. This also determines the coefficients of the substances produced as a result of oxidation and reduction. The coefficients of any other substances that may be taking part in the reaction are selected afterwards by counting up the number of atoms (ions) in both parts of the equation.

In concluding, it should be noted that very many substances manifest oxidizing or reducing properties only in acid or alkaline solution. For instance, nitric acid, or rather $NO_3^{\prime}$-ion, is an active

oxidant in acid solution but has no oxidizing properties in neutral solution, when in the form of some salt of nitric acid; the halogens (chlorine, bromine) manifest their oxidizing properties most actively in alkaline solution, etc.

In practice a solution is usually made acid by adding sulphuric acid, and alkaline by means of sodium or potassium hydroxide.

The most important oxidants are: potassium permanganate and potassium bichromate in sulphuric acid solution, nitric acid, the halogens, potassium chlorate, sodium hypochlorite, hydrogen peroxide.

The most important reductants are: the base metals and hydrogen, carbon, silicon, carbon monoxide, compounds of bivalent tin, hydrogen sulphide, sulphurous acid, hydrogen iodide and others.

CHAPTER XV

The Oxygen Group

Element	Symbol	Atomic weight	Atomic number	Arrangement of electrons in layers					
Oxygen	O	16	8	2	6				
Sulphur	S	32.066	16	2	8	6			
Selenium	Se	78.96	34	2	8	18	6		
Tellurium	Te	127.61	52	2	8	18	18	6	
Polonium	Po	210	84	2	8	18	32	18	6

114. General Features of the Oxygen Group. The oxygen group includes the typical elements of the sixth group of the Periodic Table, viz., oxygen and sulphur, as well as selenium, tellurium and polonium of the odd series, which are similar to them in structure. The last named is a radioactive element and its chemical properties are almost unknown as yet.

Owing to the presence of six electrons in the outer layer of their atoms, the elements in question should be classed as non-metals, though less active than the halogens. Gaining two electrons, the atoms of the elements of this group become negatively doubly-charged ions in which form they are contained in their compounds with metals. They are negatively bivalent in their compounds with hydrogen as well. But they may be positively valent as well, e. g., in compounds with oxygen, where their valency equals $+4$ or $+6$. The only exception is oxygen itself, whose six outer electrons are so strongly linked with the nucleus that there is apparently not a single element except fluorine, whose atoms are capable of drawing them away from the oxygen atom. For this reason, oxygen is only negatively bivalent in all its compounds (except OF_2).

As in the case of the halogen group, the physical and chemical properties of the elements in the oxygen group gradate regularly, as their atomic numbers grow. The appearance of new electron layers increases the radii of the atoms, as a result of which their electron affinity decreases, the oxidizing properties of the neutral atoms grow weaker and the reducing properties of the negatively charged ions,

stronger. The generally non-metallic properties, well defined in oxygen, are much less pronounced in tellurium.

The most important constants of the oxygen group elements are given in Table 21.

Table 21

Most Important Physical Constants of the Oxygen Group Elements

Constants	Oxygen O	Sulphur S	Selenium Se	Tellurium Te
Specific gravity	1.20 (liq.)	2.07(rhomb.)	4.81	6.24
Melting point, degr. C .	—218.8	112.8	220	450
Boiling point, degr. C .	—183	444.6	685	1,390
Atomic radius, Å . . .	0.60	1.04	1.16	1.43
R″ ion radius, Å	1.32	1.74	1.91	2.11

OXYGEN (Oxygenium); at. wt. 16

115. Oxygen in Nature. Preparation and Properties of Oxygen. Of all the elements found on the earth, oxygen is the most abundant. It occurs in the free state in atmospheric air, which contains 23.2 per cent of oxygen by weight or 20.9 per cent by volume. In the combined form oxygen is found in water (88.9 per cent), various minerals and rocks, as well as in all plants and animals. The total amount of oxygen in the outer shell of the globe (air, water and the earth's crust) equals approximately half its weight.

Oxygen was first prepared in the pure form by Scheele in 1772 and then by the English chemist Priestley in 1774; the latter obtained it from mercuric oxide. However, Priestley did not know that the gas he had obtained was contained in air. Only several years later, having made a thorough study of the properties of this gas, Lavoisier established that it was a component part of air, and gave it the name oxygen.

Oxygen is a colourless odourless gas. It is a little heavier than air, one litre of oxygen at S. T. P. weighing 1.43 gr., while one litre of air under the same conditions weighs 1.29 gr. At —183° C and ordinary pressure oxygen condenses into a mobile bluish liquid and at —218.8° C solidifies into a snow-like mass. Oxygen is but sparingly soluble in water: 100 volumes of water will dissolve 4.9 volumes of oxygen at 0° C and 3.1 volumes at 20° C.

Oxygen is usually prepared in the laboratory from potassium chlorate, which decomposes when heated in the presence of manganese

dioxide (as catalyst) into oxygen and potassium chloride:

$$2KClO_3 = 2KCl + 3O_2$$

For industrial purposes oxygen is produced in large quantities from liquid air, which is chiefly a mixture of liquid oxygen (54 per cent), liquid nitrogen (44 per cent) and liquid argon (2 per cent). When liquid air is evaporated in special apparatuses, permitting the nitrogen given off to be collected (for technical purposes), the residue is almost pure oxygen, containing not over 3 per cent impurities (mainly argon, the boiling point of which is very close to that of oxygen).

Very pure oxygen can be prepared by the electrolysis of water. This method has received the widest application wherever cheap electric power is available.

Oxygen is marketed in steel cylinders, in which it is kept under a pressure of 150 atm.

One of the most characteristic features of oxygen is its property of combining with many elements with the evolution of heat and light. Such reactions are commonly called combustion. In 1746 Lavoisier proved that combustion consists in the union of the combusting substance with the oxygen of the air.

Combustion takes place in pure oxygen much more vigorously than in air. Although the same amount of heat is evolved during this process as during combustion in air, the reaction takes place more rapidly and none of the energy evolved is wasted on heating the nitrogen of the air; therefore, the temperature of combustion in oxygen is much higher than in air.

Oxygen plays an exceedingly important part in nature. It is usually indispensable for respiration, one of the most important vital processes. Of no less importance is another process in which oxygen takes part, that of the rotting and putrefaction of dead animals and plants; during these processes complex organic substances are transformed into more simple substances (in the long run into carbon dioxide, water and nitrogen), the latter being returned to the general cycle of substances in nature.

The applications of oxygen are very diverse. Oxygen is employed to obtain high temperatures, for which purpose various combustible gases (hydrogen, acetylene, illuminating gas) are burnt in special torches (see, for instance, § 67).

Oxygen is used to intensify chemical processes in many branches of industry (for instance, in the production of sulphuric and nitric acids, in the blast furnace process, etc.). Oxygen is used also in medicine (for inhalation in cases of carbon monoxide poisoning, respiration difficulties, etc.).

Mixtures of liquid oxygen with powdered charcoal, wood meal, oils, or other fuels are known as oxyliquids. They are very explosive and are used for blasting.

116. Ozone. If electric sparks are passed through oxygen or air, there appears a characteristic odour familiar to everyone who has had to do with electrostatic machines or induction coils. This odour is due to the formation of a new gaseous substance—*ozone*. Since ozone can be obtained from absolutely pure dry oxygen by the action of electric sparks, it follows that ozone consists of oxygen only, being a special modification of this element.

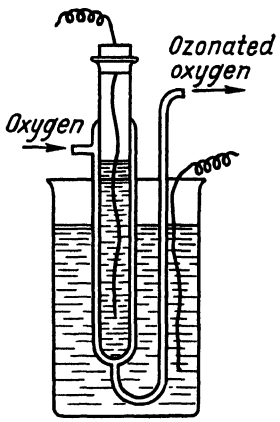


Fig. 81. Ozonator

The molecular weight of ozone is 48, while that of oxygen is 32. The atomic weight of oxygen equals 16; hence, the ozone molecule consists of three oxygen atoms, while the oxygen atom consists of only two. Thus, oxygen can exist in the free state in the form of two allotropic modifications, namely, oxygen proper O_2 and ozone O_3.

Ozone is prepared by the action of a silent electric discharge on oxygen. The apparatus used for this purpose is called an *ozonator*, shown in Fig. 81. It consists essentially of two glass tubes, one inside the other. Oxygen is drawn slowly between the tubes. A dilute solution of sulphuric acid is poured into the inner tube and the entire apparatus is immersed in a beaker containing the same solution. Leads from an induction coil are dipped into the solution. Thus, the solutions are electrodes and at the same time serve to cool the gas. When the coil is set to work a silent electric discharge occurs in the space between the tube walls. The oxygen coming out of the apparatus contains several per cent of ozone. The lower the temperature, the more ozone is produced.

The ozone can be separated from the oxygen by freezing, upon which the ozone condenses into a blue liquid with a boiling point of —112° C. Liquid ozone is very explosive.

The solubility of ozone in water considerably exceeds that of oxygen: 100 volumes of water at 0° C will dissolve 49 volumes of ozone.

At ordinary temperatures ozone is quite stable but decomposes readily when heated, turning back into oxygen. The decomposition of ozone is accompanied by evolution of heat and an increase in volume of one and a half times since every two ozone molecules turn into three molecules of oxygen:

$$2O_3 = 3O_2 + 68 \text{ Cal.}$$

Ozone differs from oxygen chemically in its stronger oxidizing properties: under the action of ozone a shining silver plate blackens rapidly, being covered with a layer of silver peroxide Ag_2O_2; metal sulphides are oxidized to the sulphates; a piece of paper moistened with turpentine will burst into flame; many dyes are discoloured. During these reactions the ozone molecule loses one oxygen atom, turning into ordinary oxygen.

Ozone will displace iodine from a solution of potassium iodide:

$$2KI + H_2O + O_3 = I_2 + 2KOH + O_2$$

If a piece of paper moistened with a solution of potassium iodide and starch solution is brought into contact with air containing ozone the paper immediately turns blue. This reaction is used for the detection of ozone.

A potent oxidizing agent, ozone kills bacteria and is therefore used to disinfect water and air.

Ozone is constantly forming in small quantities in the atmosphere as a result of electrical discharges. Ozone may form also during various oxidation processes, for instance, during the oxidation of moist phosphorus, turpentine, resinous substances, etc. The latter accounts for the presence of ozone in the air of coniferous forests; this air is especially beneficial, since it contains no bacteria.

117. Oxides and Hydroxides. Compounds of oxygen with other elements are called **oxides.**

Very many oxides (SO_2, P_2O_5, MgO, etc.) are obtained by direct union of the elements with oxygen.

The combustion of complex substances also usually leads to the formation of oxides of the elements constituting the substances burnt. For instance, the combustion of methane CH_4 results in the oxides of carbon and hydrogen:

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

Oxides may form also in other reactions involving substances which contain oxygen. Thus, when sulphuric acid is heated with charcoal, sulphur dioxide, carbon dioxide and water are formed.

$$2H_2SO_4 + C = 2SO_2 + CO_2 + 2H_2O$$

Almost all the elements form oxides in one way or another. The only exceptions are the inert gases contained in air, which do not combine with any elements.

The physical properties of oxides are exceedingly diverse. At ordinary temperatures most oxides are solids, comparatively few gases and some, liquids. The specific gravities, melting points and boiling points of oxides also vary over a very wide range.

Of the chemical properties of oxides attention must be drawn first of all to their attitude towards water. The majority of oxides combine directly or indirectly with water, forming compounds known by the generic name of **hydroxides** or **hydrated oxides**. When heated, almost all the hydroxides decompose into the oxide and water. Hydrated oxides belong to various classes of inorganic compounds; some of them are acidic in nature and belong to the acid class, others are bases and still others are amphoteric.

The classification of oxides is based on their attitude towards water and on the differences in the properties of the hydroxides they form. They can all be divided into the following five groups:

1. *Acid Oxides.* Acid oxides are those whose hydrates are acids. This group includes the oxides of non-metals and some of the highest oxides of metals (such as CrO_3, Mn_2O_7, etc.). Many acid oxides combine directly with water to form acids. For instance, the reaction between the oxide of hexavalent sulphur and water results in the hydrated oxide, known as sulphuric acid; the oxide N_2O_5 combined with water gives nitric acid HNO_3, etc. Hydrates of acid oxides which do not combine directly with water can be obtained indirectly.

The chief distinguishing feature of acid oxides is their capacity for interacting with alkalis to form salts. For example:

$$CO_2 + 2NaOH = Na_2CO_3 + H_2O$$

Acids, as a rule, do not act on acid oxides, and in the few cases where such a reaction takes place, it does not lead to the formation of a salt (cf. reaction between HF and SiO_2, p. 318).

2. *Basic Oxides.* This group includes oxides whose hydrates are bases.

Only the oxides of the most active metals, namely, potassium, sodium, calcium and several others, can combine directly with water to form soluble bases, known as **alkalis**. The majority of basic oxides, on the other hand, do not react with water. The hydroxides (bases) corresponding to these oxides are insoluble in water and are prepared by the action of alkalis on the salts of the corresponding metals. For example:

$$CuSO_4 + 2NaOH = \downarrow Cu(OH)_2 + Na_2SO_4$$

or

$$Cu^{\cdot\cdot} + 2OH' = \downarrow Cu(OH)_2$$

Basic oxides are formed by metals.

All basic oxides react with acids to form salts. For example:

$$MgO + H_2SO_4 = MgSO_4 + H_2O$$

or

$$MgO + 2H^{\cdot} = Mg^{\cdot\cdot} + H_2O$$

Basic oxides do not react with alkalis.

3. *Amphoteric Oxides.* Amphoteric oxides are those possessing the properties of both acid and basic oxides. They behave like basic oxides with respect to acids, dissolving in them to form salts; at the same time, they dissolve also in alkalis, again forming salts. An example of an amphoteric oxide is zinc oxide. With acids it gives salts of these acids:

$$ZnO + 2HCl = ZnCl_2 + H_2O$$

The reaction between zinc oxide and alkalis is usually represented by the equation:

$$ZnO + 2NaOH = Na_2ZnO_2 + H_2O$$

However, the salt produced by this reaction, called sodium zincate, actually has a somewhat different structure (see § 233).

The hydroxides of amphoteric oxides are also of a dual nature, possessing the properties of acids and bases (see § 94).

The most important property of the three groups of oxides discussed above is their ability to form salts: acid oxides form salts with alkalis; basic, with acids; amphoteric, with either of them. Therefore, all oxides belonging to the first three groups are united under the general name of **salt-forming oxides.**

4. *Indifferent Oxides.* Besides salt-forming oxides, there is another small group of oxides which form hydroxides neither directly nor indirectly and do not react with acids or alkalis. Such oxides are termed indifferent. An example of such an oxide is nitric oxide NO.

5. *Peroxides.* The so-called peroxides form a separate group of oxides. While the oxygen in ordinary oxides is chemically linked directly to the other elements, in peroxides the oxygen atoms are tied not only to the atoms of other elements but between themselves as well. Peroxides may be regarded as belonging to the oxide class only formally; essentially, they are salts of a very weak acid, namely, hydrogen peroxide.

118. Hydrogen Peroxide H_2O_2. Pure hydrogen peroxide is an almost colourless syrup-like liquid with a specific gravity of 1.46, solidifying at −1.7° C into needle-like crystals. It is a very unstable substance capable of decomposing eruptively into water and oxygen with the evolution of a great amount of heat:

$$2H_2O_2 = 2H_2O + O_2 + 46 \text{ Cal.}$$

Aqueous solutions of hydrogen peroxide are more stable and can be kept for quite a long time in a cool place. Heat and light greatly accelerate their decomposition: bubbles of oxygen begin to separate out of the solution and at length only pure water remains.

The decomposition of hydrogen peroxide is accelerated also by various catalysts. If, for instance, a little manganese dioxide MnO_2

is added to a test tube containing hydrogen peroxide solution, a violent reaction ensues with oxygen escaping. At the same time there are a few substances which can retard the decomposition of hydrogen peroxide. Such are, for instance, certain salts of phosphoric acid.

Hydrogen peroxide is formed as an intermediate product during the combustion of hydrogen, but owing to the high temperature of the hydrogen flame it decomposes immediately into water and oxygen. However, if a hydrogen flame is allowed to play on a piece of ice, traces of hydrogen peroxide can be detected in the water formed.

Hydrogen peroxide can be prepared also by the action of monatomic hydrogen on ordinary (molecular) oxygen.

During the formation of hydrogen peroxide from monatomic hydrogen and oxygen, the hydrogen atoms form covalent bonds with the oxygen atoms constituting the oxygen molecules, whereupon the double bond between the oxygen atoms turns into a single bond, as can be seen from the following scheme:

$$:\dot{\underset{\cdot}{\overset{\cdot}{O}}}::\dot{\underset{\cdot}{\overset{\cdot}{O}}}: + 2\dot{H} = H:\ddot{\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}}:\ddot{\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}}:H$$

Therefore, the ordinary structural formula of hydrogen peroxide, in which the bonds are designated by lines, is represented as follows:

$$H—O—O—H$$

However, this formula gives no idea of the spacial structure of the H_2O_2 molecules, in which the bonds between the hydrogen and the oxygen atoms are at an angle of about 100° to the bond between the oxygen atoms, as a result of which hydrogen peroxide molecules possess considerable polarity.

In H_2O_2 molecules the oxygen atoms are linked to one another by a non-polar covalent bond, while the bonds between the hydrogen and oxygen atoms are polar (owing to displacement of the common electrons towards the oxygen). Therefore, in aqueous solution hydrogen peroxide may split off hydrogen-ion under the influence of the polar water molecules.

Hydrogen peroxide can be prepared by a number of methods. For a long time the chief method was by the action of dilute sulphuric acid on barium peroxide BaO_2 or sodium peroxide Na_2O_2:

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2$$

At present, owing to the development of methods of preparing hydrogen peroxide by electrochemical means, this method has lost its significance.

The electrochemical methods of preparation of H_2O_2 make it possible to obtain pure and highly concentrated (85 to 90 per cent) solutions of hydrogen peroxide of high stability.

Hydrogen peroxide possesses the properties of a very weak dibasic acid ($K = 1.5 \times 10^{-12}$). It ionizes, albeit insignificantly, in aqueous solution:

$$H_2O_2 \rightleftarrows H^+ + HO_2^-$$
$$HO_2^- \rightleftarrows H^+ + O_2^{--}$$

Hydrogen peroxide can enter into an exchange reaction with some bases to form salts. For instance, when hydrogen peroxide reacts with barium hydroxide solution, a precipitate of the barium salt of hydrogen peroxide results:

$$Ba(OH)_2 + H_2O_2 = \downarrow BaO_2 + 2H_2O$$

The salts of hydrogen peroxide are called **peroxides.** Like other salts, they consist of positively and negatively charged ions, the negatively charged ions in this case being O_2^{--} ions of a structure expressed by the formula

$$\left[:\ddot{O}::\ddot{O}: \right]^{--}$$

Under the action of acids peroxides again form hydrogen peroxide and salts of the corresponding acid. Thus, the above reaction of formation of hydrogen peroxide from BaO_2 is that of the displacement of a weak acid from its salt by a strong acid.

The most characteristic chemical property of hydrogen peroxide is its highly pronounced oxidizing capacity, owing to which hydrogen peroxide can oxidize very many substances. By way of example, consider the oxidation of potassium iodide, leading to the liberation of iodine:

$$2KI + H_2O_2 = I_2 + 2KOH$$

or in the ionic form

$$2I' + H_2O_2 = I_2 + 2OH'$$

Since H_2O_2 molecules are capable of splitting off O_2'' ions in aqueous solution, the above reaction may be regarded as oxidation of iodine-ion I' by O_2''-ion:

$$\left| \begin{array}{l} 2I' - 2e^- = I_2 \\ O_2'' + 2e^- = 2O^{--} \end{array} \right.$$

Yielding two electrons to O_2'' ions, the iodine ions turn into neutral iodine atoms which combine subsequently into I_2 molecule, while each O_2''-ion accepts two electrons and becomes two O^{--} ions, which unite with hydrogen ions to form two hydroxyl ions. Thus,

O_2''-ion is the oxidant and I'-ion the reductant. Much less often, only during reactions with very strong oxidants, hydrogen peroxide may manifest reducing properties. For instance, the reaction between hydrogen peroxide and chlorine takes place as follows:

$$\overset{\overset{2e^-}{\downarrow\text{———}\mid}}{Cl_2 + H_2O_2 = 2HCl + O_2}$$

In this case O_2''-ion is the reducing agent. Losing two electrons to the chlorine atoms, it is converted into electrically neutral O_2 molecules.

The rather wide practical application of hydrogen peroxide is based on its oxidizing properties. Acting as an oxidant on various dyes, it is an excellent means of bleaching fabrics, straw and other materials; though decomposing the dyes, hydrogen peroxide hardly acts at all on the material being bleached.

Hydrogen peroxide is used also to refresh old pictures painted with oil colours and darkened with age due to transformation of the white lead into black lead sulphide under the action of traces of hydrogen sulphide contained in the air.

When the pictures are washed with hydrogen peroxide the black lead sulphide is oxidized into white lead sulphate:

$$PbS + 4H_2O_2 = PbSO_4 + 4H_2O$$

$$1 \mid \overset{-II}{S} - 8e^- = \overset{+VI}{S}$$

$$4 \mid O_2'' + 2e^- = 2O^{--}$$

Highly concentrated (85 to 90 per cent) hydrogen peroxide is used in mixture with certain combustible materials to produce explosives. A dilute (usually 3 per cent) solution of hydrogen peroxide is used in medicine as a disinfectant for washing wounds, as a gargle, etc.

SULPHUR (Sulfur); at. wt. 32.066

119. Sulphur in Nature. Preparation of Sulphur. Sulphur occurs in nature both in the free state, as "native" sulphur, and in the form of various compounds.

Deposits of native sulphur have been found in the Soviet Union in the Kara-Kum Desert of Turkmenia. Sulphur deposits occur also in the Uzbek S.S.R., in the Caucasus, on the Kerch Peninsula and at several points on the Volga. The largest sulphur deposits in other countries are those of the U.S.A., Italy and Japan.

Compounds of sulphur with various metals are very abundant. Many of them are valuable ores, used for the extraction of non-

ferrous metals (for example, lead glance PbS, zinc blende ZnS, copper glance Cu_2S, etc.).

Certain salts of sulphuric acid are also widely dispersed. Thus the calcium salt, $CaSO_4$, is found in nature as the minerals gypsum and anhydrite, which in some places form whole mountains. The magnesium salt, $MgSO_4$, is contained in sea water and together with $MgCl_2$ accounts for its characteristic bitterish taste. Finally, sulphur goes to make up many of the substances found in plants and animals.

The total sulphur content in the earth's crust is around 0.10 per cent.

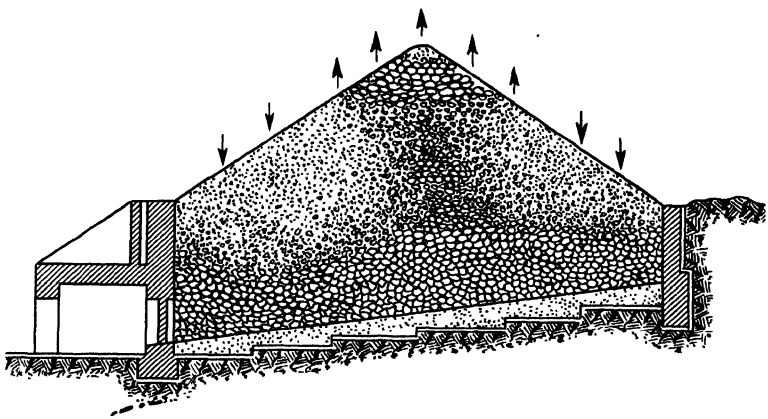


Fig. 82. Sulphur kiln

Native sulphur usually has a higher or lower content of foreign substances. To separate sulphur from its impurities, use is made of its ability to fuse readily. Sulphur is melted out of its ores by various methods. The choice of the method to be used in each case depends largely on the sulphur content in the ore, as well as on the composition and properties of the gangue.

The oldest method of melting out sulphur is heating it to its melting point at the expense of the heat evolved due to combustion of the sulphur itself or of some other fuel. This method is used to a certain extent in countries possessing large reserves of sulphur ores, for instance, in Italy.

Figure 82 is a diagram of one of the simplest (single-cell) sulphur kilns. It is a roofless chamber built of stone with its floor sloping down toward the front wall. At the bottom of the front wall is an outlet for the molten sulphur, plugged up with a thin partition of plaster of Paris. The kiln is charged with ore by hand, leaving air channels between the lumps of ore in all directions. The kiln is filled with ore, forming a cone at the top, which is covered with a

layer of burnt-out ore from the previous batch and coated with plaster of Paris or clay. The kiln is fired with bunches of straw, brushwood, etc.

When the sulphur starts burning, beginning from the upper layers of the ore, part of the sulphur melts and seeps down through the mass of ore to the bottom layers, and part of it sublimates. In the course of a melt the combustion zone keeps gradually descending.

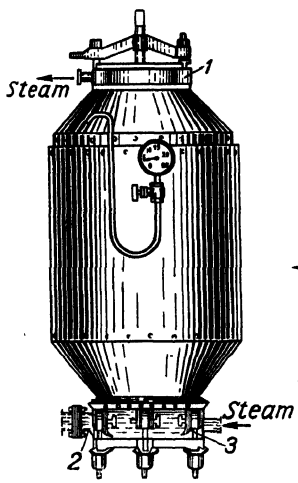


Fig. 83. Autoclave for melting sulphur:
1—upper hatch; *2*—outlet; *3*—lower hatch

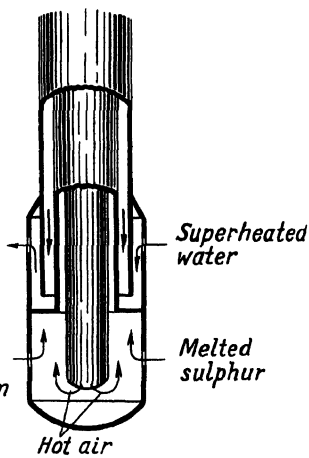


Fig. 84. Extractor used in sulphur wells

One melt takes 6 to 8 days to complete, after which the partition closing the sulphur outlet is pierced and the molten sulphur flows out of the kiln.

Four- and six-cell kilns, based on the same principle as the single-cell, are better than the latter, as they utilize the heat produced by the burning sulphur more fully.

Another method of melting sulphur, employed mainly in the U.S.S.R., consists in heating the concentrated ore in autoclaves with superheated steam. The autoclaves used for this purpose (Fig. 83) are steel cylinders calculated to resist a pressure of up to six atm. Three to four tons of ground ore mixed with a small quantity of water are loaded into the autoclave through upper hatch *1*; then superheated steam is passed into it, heating the ore to 140°-150° C.

Each melt takes about three hours. The molten sulphur is then forced out under pressure through outlet *2* at the bottom, laundered

to box trucks, and thence into moulds; the steam is let out through a hatch at the top and the residual gangue is discharged through hatch *3* in the bottom.

Of great interest is the Frasch process, widely used for sulphur mining in the U.S.A.

By this process the sulphur is melted underground, right in the deposit, by means of superheated water, delivered under a pressure

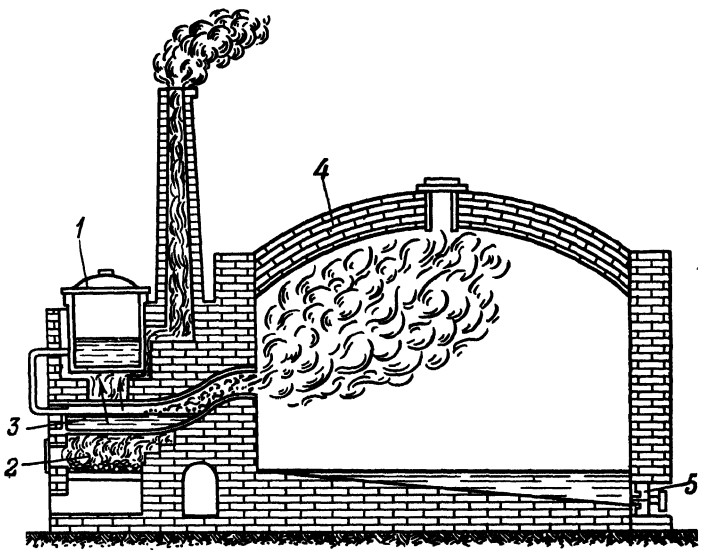


Fig. 85. Sulphur distillation furnace:
1—boiler for melting sulphur; *2*—stoker; *3*—retort; *4*—chamber; *5*—aperture for tapping molten sulphur

of 10 to 18 atm. through a system of three concentric pipes (see Fig. 84). Water at a temperature of about 170° C is pumped into the space between the outer and middle pipes, while hot compressed air is forced down through the inner pipe, to raise the molten sulphur to the surface. Excess water is removed through wells located some distance away from the sulphur wells.

Sulphur melted out of ores usually contains many impurities and is called *brimstone*. It is refined by distillation.

Fig. 85 shows a diagram of an arrangement for distilling sulphur. The sulphur is melted in an iron boiler *1* by hot gases coming out of stoker *2*; the heavy admixtures deposit at the bottom of the boiler, while the molten sulphur drains into a cast-iron retort *3* where it is heated to boiling. The sulphur vapour passes into a large masonry chamber *4*. At first, while the chamber is still cold, the sulphur

vapours condense directly into the solid state and deposit on the chamber walls in the form of a light-yellow powder termed *flowers of sulphur*. After the temperature of the chamber has risen above 120° C, the sulphur begins to condense into a liquid which is drawn off through opening *5* into wooden moulds where it solidifies into rods. Sulphur obtained in this way is known as *lump* or *rod sulphur*.

Considerable quantities of sulphur are obtained also by reducing sulphur dioxide with coal when smelting copper from sulphide ores.

The world production of sulphur (without the U.S.S.R.) is at present about 4 million tons per year.

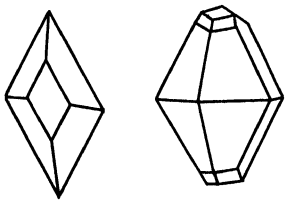


Fig. 86. Rhombic sulphur crystals

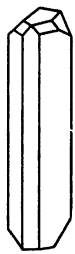


Fig. 87. Monoclinic sulphur crystal

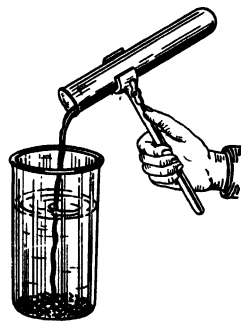


Fig. 88. Preparation of plastic sulphur

120. Properties and Uses of Sulphur. Sulphur is one of the elements capable of existing in the free state in several allotropic modifications.

Pure native sulphur is a solid yellow crystalline substance, having a specific gravity of 2.07 and a melting point of 112. 8°C. It is insoluble in water but dissolves readily in carbon disulphide, benzene and some other liquids. If such solutions are evaporated, sulphur is deposited as transparent yellow crystals of the orthorhombic system having the form of octahedra usually with bevelled corners or edges (Fig. 86). This sulphur is called *rhombic*. The rod sulphur usually found on the market consists of the same crystals but they are very minute and poorly formed.

An entirely different crystal form is obtained when melted sulphur is cooled slowly in a vessel until partly solidified and then the portion still in the liquid form is poured off. The sides of the vessel will then be found to be covered on the inside with a mass of long, dark-yellow, needle-like crystals of the monoclinic system (Fig. 87). This *monoclinic* sulphur has a specific gravity of 1.96 and melts at 119° C. However, it will remain unaltered only at temperatures above 96° C.

At ordinary temperatures crystals of monoclinic sulphur soon become lighter in colour and acquire all the properties of rhombic sulphur. Though externally these crystals continue to retain their prismatic form they now consist of minute octahedric crystals into which they fall apart if shaken. Their melting point and specific gravity become equal to those characteristic of rhombic sulphur.

Sulphur undergoes some very interesting changes if heated slowly to the boiling point. At 112.8° C it melts, turning into a yellow mobile liquid. Upon further heating the liquid darkens, acquiring a reddish-brown colour, and at about 250° C becomes so thick that for some time the vessel can be inverted without the sulphur pouring out. Above 300° C the liquid sulphur again becomes mobile but its colour remains dark. At length, at 444.6° C sulphur begins to boil giving off an orange-yellow vapour. When cooled, the same phenomena are repeated in the reverse order.

If molten sulphur heated to boiling is poured in a thin stream into cold water it turns into a soft rubbery brown mass which can be drawn out into threads (Fig. 88). This modification is called *plastic* sulphur. Plastic sulphur becomes brittle after a few hours, acquires a yellow colour and turns gradually into rhombic sulphur.

Besides the three modifications of sulphur described above, some others are known, which we, however, shall not discuss. They are all unstable and change quite rapidly into rhombic sulphur. That is why sulphur occurs in nature only in the rhombic form.

Determinations of the molecular weight of sulphur by the lowering of the freezing point of its benzene solutions lead to the conclusion that in these solutions the sulphur molecules consist of eight atoms each (S_8). Sulphur crystals are evidently made up of similar molecules. Thus, the difference in properties of the crystalline modifications of sulphur is due to dissimilar structure of the crystals (polymorphism) and not to their molecules containing different numbers of atoms (as in oxygen and ozone molecules).

At low temperatures sulphur vapours consist mainly of S_6 molecules and above 800° C, of S_2 molecules.

Molten sulphur probably consists of S_8 and S_6 molecules in equilibrium with each other. The higher the temperature, the more S_6 molecules are formed. This accounts for the changes in properties of molten sulphur when heated. If sulphur, heated almost to the boiling point, is cooled rapidly, the S_6 molecules do not have time to change into S_8 molecules and plastic sulphur results, gradually passing into crystalline sulphur.

In chemical properties sulphur is a typical non-metal. It will combine directly with many metals, such as copper, iron, zinc, etc., evolving considerable quantities of heat. Sulphur combines also with almost all the non-metals but far less readily and vigorously

than with metals. With oxygen sulphur gives several oxides, the two most important being SO_2 and SO_3, the anhydrides of sulphurous and sulphuric acids, H_2SO_3 and H_2SO_4, respectively. The compound between sulphur and hydrogen—hydrogen sulphide gas, H_2S—also possesses acidic properties in aqueous solution.

Sulphur is widely used in the national economy. Flowers of sulphur is employed in great quantities to destroy certain orchard pests.

Sulphur is used in the rubber industry to toughen and harden rubber; rubber acquires its valuable properties, namely resilience, elasticity, etc., only after being mixed with sulphur and heated to a definite temperature. This process is known as **vulcanization.**

Rubber containing a large quantity of sulphur is called *ebonite.* It is a solid and a very good electrical insulator. Then sulphur is used to prepare black gunpowder, matches, Bengal lights, ultramarine (a blue dye), carbon disulphide and many other products. In countries with large resources of sulphur it is also employed as a raw material for the production of sulphuric acid. Sulphur is used in medicine for treating certain skin diseases.

121. Hydrogen Sulphide H_2S. At a high temperature sulphur combines directly with hydrogen, forming hydrogen sulphide gas.

In practice hydrogen sulphide is usually prepared by the action of dilute acids on the metal sulphides, e.g., on iron sulphide:

$$FeS + 2HCl = FeCl_2 + H_2S$$

Hydrogen sulphide is a colourless gas with a characteristic odour resembling that of rotten eggs. It is a little heavier than air, liquefies at −60.7° C and solidifies at −85.6° C. In the air hydrogen sulphide burns with a bluish flame to form sulphur dioxide and water, i.e., the oxides of the elements constituting it:

$$\overset{-II}{2H_2S} + 3O_2 = 2H_2O + \overset{+IV}{2SO_2}$$

$$2 \mid \overset{-II}{S} - 6e^- = \overset{+IV}{S}$$

$$3 \mid O_2 + 4e^- = \overset{-II}{2O}$$

If a cold object of some kind, say, a porcelain dish, is introduced into a hydrogen sulphide flame, the temperature of the flame decreases considerably and the hydrogen sulphide is oxidized only to free sulphur which forms a yellow deposit on the dish:

$$2H_2S + O_2 = 2H_2O + 2S$$

Hydrogen sulphide is very inflammable; mixed with air, it is explosive. Hydrogen sulphide is very poisonous. Prolonged inhalation of air containing the gas even in small quantities causes serious poisoning.

Hydrogen sulphide is soluble in water. At 20° C one volume of water will dissolve two and a half volumes of hydrogen sulphide. A solution of hydrogen sulphide in water is called *hydrogen sulphide water*. If left standing in the air, especially in the light, hydrogen sulphide water soon becomes turbid due to the precipitation of sulphur. This takes place as a result of oxidation of the hydrogen sulphide by the oxygen of the air (see previous reaction). A solution of hydrogen sulphide in water turns blue litmus red and in general possesses acidic properties. This acid, often called hydrosulphuric acid, is dibasic, as both hydrogen atoms in the H_2S molecule can be displaced by metallic atoms to form sulphide salts. For instance, if hydrogen sulphide is passed through a solution of sodium hydroxide, the result is sodium sulphide, a soluble salt of hydrosulphuric acid:

$$2NaOH + H_2S = Na_2S + 2H_2O$$

If hydrogen sulphide is present in excess, for instance, if it is passed through the solution to saturation, the acid salt—*sodium hydrogen sulphide*—results:

$$NaOH + H_2S = NaHS + H_2O$$

Hydrosulphuric acid is a very weak acid. Its degree of ionization in 0.1 N solution is only 0.07 per cent. It ionizes mainly according to the equation

$$H_2S \rightleftarrows H^{\cdot} + HS'$$

but at the same time a very small amount of S″-ion forms as well:

$$HS' \rightleftarrows H^{\cdot} + S''$$

Hydrogen sulphide is characterized by a highly pronounced reducing ability. The reducing properties of hydrogen sulphide are due to the fact that S″-ion loses its electrons readily to form neutral sulphur atoms. The hydrogen sulphide which is continually forming in nature due to the decay of organic substances, does not accumulate in the air in any perceptible amounts, as the oxygen of the air soon oxidizes it to free sulphur.

Hydrogen sulphide is oxidized even more readily by the halogens, reducing them to hydrohalic acids. For instance:

$$\overset{\overset{2e^-}{\longrightarrow}}{H_2S + Br_2} = 2HBr + S$$

In general, all oxidants, including even comparatively weak ones, oxidize hydrogen sulphide rapidly to form sulphur; thus *hydrogen sulphide is one of the most active reducing agents.*

Hydrogen sulphide occurs in nature in volcanic gases and in the waters of mineral springs; for instance, in the U.S.S.R. it is found in the Caucasus (Pyatigorsk and Matsesta), at Staraya Russa and

in other places. Besides, it forms continually due to the decay of the proteins in animal carcases and dead plants, as well as the rotting of all kinds of wastes; for this reason cesspools, drainage waters, garbage piles, etc., often spread the odour of hydrogen sulphide. Especially large quantities of hydrogen sulphide are formed during the rotting of egg albumen, which accounts for the characteristic odour of rotten eggs.

122. Metal Sulphides. The salts of hydrosulphuric acid are called **sulphides**. They can be obtained by the direct union of metals with sulphur. For instance, if heat is applied to one point of a mixture of iron filings and sulphur, the reaction of combination thus initiated between the iron and the sulphur will progress of its own accord, accompanied by the evolution of a large amount of heat and the formation of iron sulphide:

$$Fe + S = FeS + 22.8 \text{ Cal.}$$

Many sulphides can be obtained by the action of hydrogen sulphide on aqueous solutions of the salts of the corresponding metals. For instance, if hydrogen sulphide is passed through a solution of any copper salt, a black precipitate of cupric sulphide immediately appears:

$$CuSO_4 + H_2S = \downarrow CuS + H_2SO_4$$

or in the ionic form

$$Cu^{\cdot\cdot} + H_2S = \downarrow CuS + 2H^{\cdot}$$

The precipitate is insoluble not only in water but in dilute acids as well. If the precipitate were soluble in dilute acids it would not form at all, as can be seen from the equation, since the reaction leads to the formation of hydrogen-ion. The attitude of silver, lead, mercury and some other metal salts to the action of hydrogen sulphide is similar to that of copper salts.

But if hydrogen sulphide water is added to a solution of an iron salt, no precipitate will appear. Iron sulphide dissolves in dilute acids liberating hydrogen sulphide, and as hydrogen-ion is formed together with the iron sulphide during the reactions, the former reacts with FeS to form hydrogen sulphide and ferrous-ion again. Thus, the reaction between hydrogen sulphide and iron salts is reversible and leads to a state of equilibrium:

$$Fe^{\cdot\cdot} + H_2S \rightleftarrows FeS + 2H^{\cdot}$$

which is shifted practically completely towards the formation of hydrogen sulphide and ferrous-ion.

To make the reaction go from left to right, the hydrogen-ion formed must be continuously removed. This can be achieved by adding an

alkali to the solution. The hydroxyl-ion will then bind the hydrogen-ion and the reaction will go to completion towards the right.

An even simpler method is to treat the ferric salt with a soluble sulphide instead of hydrogen sulphide, say, Na_2S; then no hydrogen-ion will form at all during the reaction, and the iron sulphide will be thrown down directly as a black precipitate:

$$FeSO_4 + Na_2S = \downarrow FeS + Na_2SO_4$$

or

$$Fe^{\cdot\cdot} + S'' = \downarrow FeS$$

Manganese and zinc sulphides, which are insoluble in water but soluble in dilute acids, can be obtained in a similar manner.

Finally, there are sulphides such as Na_2S, K_2S, which are soluble in water. They cannot, obviously, be obtained from the corresponding salts by the action of hydrogen sulphide or any other sulphides.

The difference in solubility of sulphides is utilized in analytical chemistry for successive precipitation of metals from the solutions of their salts.

Being salts of a very weak acid, sulphides hydrolyze readily. For instance, sodium sulphide hydrolyzes almost completely when dissolved in water, forming the acid salt:

$$Na_2S + H_2O \rightleftarrows NaHS + NaOH$$
$$S'' + H_2O \rightleftarrows HS' + OH'$$

Hydrogen sulphide can also react directly with some of the metals to form sulphides.

For instance, if a silver coin is immersed in hydrogen sulphide water it immediately turns black, due to the formation of silver sulphide on its surface. The oxygen of the air participates in this reaction, which takes place according to the following equation:

$$4Ag + 2H_2S + O_2 = 2Ag_2S + 2H_2O$$

For this reason silver and copper objects very soon become coated with a dark film if left in air containing hydrogen sulphide.

Metal Polysulphides. If a solution of any suphide, say, Na_2S, is shaken with sulphur, the latter dissolves, and if the solution is then evaporated, the residue will be found to contain, besides Na_2S, compounds of variable composition from Na_2S_2 to Na_2S_5. Such compounds are known as *polysulphides*.

When sulphur is fused with soda ash or potash, the result is also a mixture of polysulphides. This product was known to the alchemists as *liver of sulphur*.

Polysulphides decompose under the action of acids, liberating hydrogen sulphide and free sulphur, for instance:

$$Na_2S_4 + 2HCl = 2NaCl + H_2S + 3S$$

If, on the other hand, sodium or potassium polysulphides are added gradually to concentrated hydrochloric acid, hydrogen sulphide is not evolved, but a yellow oily liquid accumulates at the bottom of the vessel. This liquid contains

various *hydrogen polysulphides* and from it H_2S_2, H_2S_3 and others can be isolated. Hydrogen polysulphides are unstable, and gradually decompose in the air into hydrogen sulphide and sulphur.

The structure of the hydrogen polysulphides is probably analogous to that of hydrogen peroxide. For instance, the structure of hydrogen trisulphide H_2S_3 may be represented as:



The ordinary structural formula of this compound is:

$$H—S—S—S—H$$

Sulphides find wide application in the dye industry, as well as in the leather industry, where a mixture of potassium and sodium sulphides with lime is used to remove the hair from skins. Polysulphides are used for the manufacture of certain kinds of synthetic rubber.

123. Sulphur Dioxide SO_2 and Sulphurous Acid H_2SO_3. *Sulphur dioxide*, called also sulphurous anhydride or sulphurous acid gas, forms directly from sulphur and oxygen during the combustion of sulphur in air or oxygen. It can be obtained also by calcining ("roasting") various metallic sulphides in air: for instance, in the case of pyrite:

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2$$

This is the reaction usually employed for the production of sulphur dioxide in industry.

Sulphur dioxide is a colourless gas with the commonly known pungent odour of burning sulphur. It condenses quite readily into a colourless liquid with a boiling point of —10° C. Evaporation of liquid sulphur dioxide causes a sharp drop in temperature (down to —50° C).

Sulphur dioxide is very soluble in water. At 20° C one volume of water will dissolve 40 volumes of sulphur dioxide which partly reacts with the water to form sulphurous acid:

$$SO_2 + H_2O \rightleftarrows H_2SO_3$$

Under the action of heat the equilibrium of this reaction shifts to the left owing to the decrease in solubility of the sulphur dioxide, and the sulphur dioxide escapes gradually from the solution.

Sulphur dioxide is used for bleaching straw, wool, silk, and as a disinfectant for killing the germs of many microorganisms; sulphur dioxide is used for fumigation to destroy mould fungi in damp cellars and basements, wine barrels, fermentation tanks, etc.

Sulphurous acid H_2SO_3 is a very unstable compound. It is known only in aqueous solution. Any attempt to isolate sulphurous acid from water or obtain it in the pure form in any other way results

in its decomposing into sulphur dioxide and water. For instance, when concentrated sulphuric acid acts on sodium sulphite, sulphur dioxide is liberated instead of sulphurous acid:

$$Na_2SO_3 + H_2SO_4 = Na_2SO_4 + SO_2 + H_2O$$

Solutions of sulphurous acid must be kept in airtight vessels, otherwise they absorb oxygen from the air and are oxidized quite rapidly into sulphuric acid:

$$2H_2SO_3 + O_2 = 2H_2SO_4$$

Being readily oxidized, *sulphurous acid is a good reductant.* For instance, the free halogens are reduced by it into hydrohalic acids:

$$\overset{+IV}{H_2SO_3} + \overset{0}{Cl_2} + H_2O = \overset{+VI}{H_2SO_4} + 2\overset{-I}{HCl}$$

or in the ionic form

$$SO_3'' + Cl_2 + H_2O = SO_4'' + 2Cl' + 2H^{\cdot}$$

However, sometimes sulphurous acid may play the part of an oxidant, for instance, when it reacts with such an active reducing agent as hydrogen sulphide:

$$\overset{\overset{4e^-}{\downarrow\!\!\!

Some of the salts of sulphurous acid are of great industrial importance and are prepared in large quantities. Sodium hydrogen sulphite $NaHSO_3$ is used under the name of *antichlor* to destroy traces of chlorine in bleached fabrics, as it reduces chlorine to hydrogen chloride:

$$NaHSO_3 + Cl_2 + H_2O = NaHSO_4 + 2HCl$$

Calcium acid sulphite (or calcium bisulphite) $Ca(HSO_3)_2$ is used for treating wood to convert it into what is known as sulphite pulp, from which paper is produced.

124. Thiosulphuric Acid $H_2S_2O_3$. If an aqueous solution of Na_2SO_3 is boiled with sulphur and cooled after filtering off the excess sulphur, colourless crystals of a new substance separate from the solution. This substance is the sodium salt of *thiosulphuric acid* $H_2S_2O_3$ and has the formula $Na_2S_2O_3 \cdot 5H_2O$. Thiosulphuric acid may be regarded as sulphuric acid in which one oxygen atom has been substituted by a sulphur atom.

Substances obtained from ordinary acids by substituting sulphur for all or part of the oxygen in them are classed as **thioacids** and the corresponding salts are called thiosalts. That is why $H_2S_2O_3$ is now known as "thiosulphuric acid" instead of "hyposulphurous acid" as it was called formerly.

Thiosulphuric acid has not been obtained in the free state, but many of its salts are known, these salts being called thiosulphates. The most widely used of them is *sodium thiosulphate* $Na_2S_2O_3 \cdot 5H_2O$, more commonly known under the incorrect name of "hyposulphite" or just "hipo".

In industry sodium thiosulphate is usually prepared by oxidizing polysulphides with atmospheric oxygen. For instance:

$$2Na_2S_2 + 3O_2 = 2Na_2S_2O_3$$

If an acid, say, hydrochloric, is added to a solution of sodium thiosulphate, the odour of sulphur dioxide appears, and after some time the liquid becomes turbid, due to the liberation of sulphur.

Apparently, the first step consists in the formation of thiosulphuric acid:

$$Na_2S_2O_3 + 2HCl = H_2S_2O_3 + 2NaCl$$

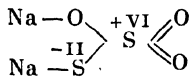
which, however, very soon decomposes according to the equation

$$H_2S_2O_3 = H_2O + SO_2 + S$$

The entire reaction may be represented in the ionic form by the following equation:

$$S_2O_3'' + 2H^+ = SO_2 + S + H_2O$$

A study of the properties of sodium thiosulphate shows that its sulphur atoms have different valencies: one of them should be regarded as having a valency of +6 while the valency of the other is —2. Therefore, the structural formula of sodium thiosulphate is as follows:



Hence, the formation of sodium thiosulphate by boiling a Na_2SO_3 solution with sulphur takes place according to the equation:

$$Na_2SO_3 + S = Na_2S_2O_3$$

or

$$SO_3'' + S = S_2O_3''$$

which is an oxidation-reduction reaction. The oxidant is free sulphur and the reductant SO_3''-ion. In oxidizing the S atoms of the latter from a valency of +4 to +6, the electrically neutral sulphur atoms are themselves reduced, their valency falling from 0 to —2

$$\left|\begin{array}{l} \overset{0}{S} + 2e^- = \overset{-II}{S} \\ \overset{+IV}{S} - 2e^- = \overset{+VI}{S} \end{array}\right.$$

The presence of bivalent sulphur $\overset{-II}{S}$ in the sodium thiosulphate molecule accounts for the reducing properties of the latter. Chlorine, for instance, is reduced by sodium thiosulphate to hydrogen chloride according to the equation:

$$Cl_2 + Na_2S_2O_3 + H_2O = 2HCl + S + Na_2SO_4$$

$$\left|\begin{array}{l} Cl_2 + 2e^- = 2Cl^- \\ \overset{-II}{S} - 2e^- = \overset{0}{S} \end{array}\right.$$

If chlorine is present in excess, the sulphur liberated at first may be oxidized to sulphuric acid:

$$S + 3Cl_2 + 4H_2O = H_2SO_4 + 6HCl$$

The use of sodium thiosulphate in the earlier types of gas masks for the absorption of chlorine was based on this reaction.

Sodium thiosulphate is used in large quantities in photography for fixing developed plates and paper, as it dissolves silver chloride and bromide.

125. Sulphur Trioxide SO_3. Sulphur dioxide unites with oxygen to form sulphur trioxide. Under ordinary conditions the direct combination of sulphur dioxide with oxygen takes place very slowly. The

reaction goes on much more rapidly and readily at a high temperature and in the presence of certain catalysts, such as finely divided platinum, oxides of vanadium, iron, chromium and others.

Small quantities of sulphur trioxide can be prepared in the laboratory with the arrangement shown in Fig. 89. Oxygen and sulphur dioxide are dried by being pressed through a three-necked jar *1* containing concentrated sulphuric acid. From here the gas mixture enters tube *2* containing platinized asbestos (asbestos coated with

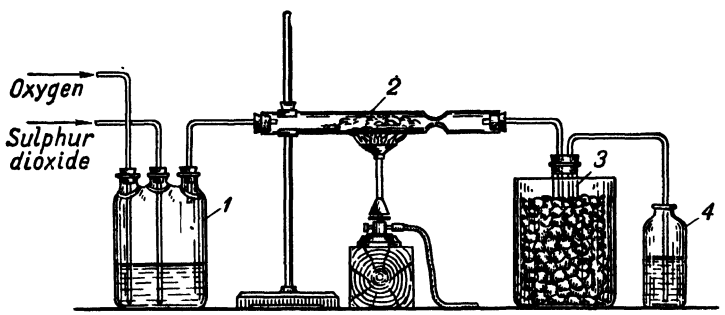


Fig. 89. Arrangement for preparation of sulphur trioxide:
1—three-necked jar; *2*—reaction tube; *3*—flask; *4*—absorption jar

very finely divided platinum) and heated by a gas burner. The oxygen combines with the sulphur dioxide:

$$2SO_2 + O_2 \rightleftarrows 2SO_3$$

The sulphur trioxide gas formed passes together with the excess gases into flask *3* cooled with ice. Part of the sulphur trioxide condenses here, and the rest passes into jar *4*, where it combines with water to form sulphuric acid.

Pure sulphur trioxide is a colourless, very mobile liquid with a specific gravity of 1.92, boiling at 44.8° C and freezing at 16.8° C into a transparent crystalline mass. Upon standing, especially in the presence of traces of moisture, the latter changes into long silky crystals which sublimate at 50° C without melting. This second modification of sulphur trioxide has a molecular weight corresponding to the formula $(SO_3)_x$.

Sulphur trioxide combines avidly with water evolving a large amount of heat and forming sulphuric acid:

$$SO_3 + H_2O = H_2SO_4 + 21 \text{ Cal.}$$

126. Sulphuric Acid H_2SO_4. Pure sulphuric acid is a colourless oily liquid which freezes at 10.5° C into a solid crystalline mass. When heated, anhydrous sulphuric acid (the so-called "monohydrate")

splits off SO_3. This reaction continues until a solution containing 98.3 per cent H_2SO_4 results, this solution boiling at 338° C with no further change in composition.

The concentrated acid on the market usually contains 96.5 per cent H_2SO_4 and has a specific gravity of 1.84. Due to its oily appearance sulphuric acid is sometimes called *oil of vitriol*. This name dates back to the time when sulphuric acid was prepared by calcining green vitriol.

Sulphuric acid is capable of dissolving considerable quantities of sulphur trioxide. Such solutions are known as oleums. From them a solid compound of sulphuric acid and sulphuric trioxide can be isolated, called *pyrosulphuric acid*, $H_2S_2O_7$.

When dissolved in water, sulphuric acid liberates a large amount of heat (19 Cal. per mole of acid) due to the formation of hydrates. The latter can be isolated in the solid form from the solution at low temperatures. The hydrate $H_2SO_4 \cdot 2H_2O$ melts at —38° C and $H_2SO_4 \cdot 4H_2O$, at —27° C.

Sulphuric acid absorbs water vapour avidly, and is therefore often used for drying gases. Its capacity for absorbing water also accounts for the charring of many organic substances, especially carbohydrates (cellulose, sugar, etc.), by concentrated sulphuric acid. Hydrogen and oxygen are contained in carbohydrates in the same weight ratio as in water. Sulphuric acid abstracts the elements of water from the carbohydrates, leaving the carbon as charcoal. Due to the low volatility of sulphuric acid, it is often used to displace other more volatile acids from their salts.

Sulphuric acid is a rather active oxidant; its oxidizing properties manifest themselves in reactions with many substances.

Strictly speaking, any acid may manifest oxidizing properties, as it always contains hydrogen-ion, which is capable of abstracting electrons from other substances. For instance, when zinc is treated with hydrochloric acid, the hydrogen-ion abstracts electrons from the neutral zinc atoms, changing them into positively charged ions, i. e., oxidizing them:

$$Zn + 2HCl = ZnCl_2 + H_2$$

or in the ionic form

$$\overset{\overset{2e^-}{\frown}}{Zn} + 2H^{\cdot} = Zn^{\cdot\cdot} + H_2$$

Here hydrochloric acid plays the part of an oxidant.

However, when we speak of the oxidizing properties of any acid we do not mean hydrogen-ion, but the atoms of the element from which the acid usually derives its name (for instance, the sulphur atoms in sulphuric acid, the nitrogen atoms in nitric acid, etc.).

The sulphur in sulphuric acid is in a state of maximum oxidation with a valency of +6. But it can be reduced to the state $\overset{+IV}{S}$ (in H_2SO_3 or SO_3''-ion), to S (in free sulphur), or even to $\overset{-II}{S}$ (in hydrogen sulphide).

It should be noted that the oxidative properties of hexavalent sulphur manifest themselves only in concentrated sulphuric acid. For instance, if concentrated sulphuric acid is heated with charcoal, the latter is oxidized to carbon dioxide, while the sulphuric acid is reduced to SO_2:

$$2H_2SO_4 + C = CO_2 + 2SO_2 + 2H_2O$$

This reaction does not take place in the dilute acid.

Now let us examine the action of sulphuric acid on metals.

In the action of dilute sulphuric acid on metals the oxidant is hydrogen-ion. But this ion can oxidize only the metals situated above hydrogen in the electrochemical series, such as magnesium, zinc, iron, etc. As to the metals below hydrogen, such as copper, silver, mercury, dilute sulphuric acid does not act on them. Concentrated sulphuric acid oxidizes almost all the metals *when heated*, but in such cases hydrogen is not evolved, as oxidation in this case is due to the unionized sulphuric acid molecules.

Depending on the activity of the metal, the sulphuric acid molecules may be reduced to SO_2, free sulphur or to H_2S. Mostly sulphuric acid is reduced to SO_2, e.g.:

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O$$
$$Zn + 2H_2SO_4 = ZnSO_4 + SO_2 + 2H_2O$$

Due to the activity of zinc, the following reactions take place simultaneously with the latter:

$$3Zn + 4H_2SO_4 = 3ZnSO_4 + S + 4H_2O$$
$$4Zn + 5H_2SO_4 = 4ZnSO_4 + H_2S + 4H_2O$$

Sulphuric acid is one of the most active acids. In aqueous solution it ionizes mainly into $H^·$ and HSO_4' ions.

A dibasic acid, sulphuric acid forms two series of salts: normal and acid salts. The normal salts of sulphuric acid are called **sulphates** and the acid salts—**acid or hydrogen sulphates.**

Most salts of sulphuric acid are quite soluble in water. Of the salts of the more common metals, barium sulphate $BaSO_4$ and lead sulphate $PbSO_4$ are practically insoluble. Calcium sulphate $CaSO_4$ is very slightly soluble.

Barium sulphate is insoluble not only in water, but in dilute acids as well. And as other barium salts are soluble either in water or in acids, the formation of a white precipitate insoluble in acids as a result of the action of a barium salt on any solution, is an indication

of the presence of sulphuric acid or its salts, i. e., SO_4''-ion, in the solution:

$$Ba^{\cdot\cdot} + SO_4'' = \downarrow BaSO_4$$

Thus, soluble barium salts are test reagents for SO_4''-ion.

The following salts of sulphuric acid are widely used in practice:

1. *Sodium sulphate* Na_2SO_4 crystallizes out of aqueous solution with ten molecules of water ($Na_2SO_4 \cdot 10H_2O$) and in this form is known as *Glauber's salt*, after Glauber, a German physician and chemist who first prepared it by the action of sulphuric acid on common salt and used it as a medicine. The anhydrous salt is used for the preparation of soda by the sulphate method (see p. 425) and in the manufacture of glass.

2. *Magnesium sulphate* $MgSO_4$ is contained in sea water. Crystallizes out of solution in the form of the hydrate $MgSO_4 \cdot 7H_2O$. Is used as a laxative under the name of *Epsom salts*.

3. *Calcium sulphate* $CaSO_4$ occurs in nature in large quantities as the mineral *gypsum* $CaSO_4 \cdot 2H_2O$. When heated to 150 or 170 degrees C, gypsum loses $^3/_4$ of its water of crystallization and passes into what is known as *plaster of Paris* ($2\,CaSO_4 \cdot H_2O$). Mixed with water into a loose dough-like mass, plaster of Paris sets quite rapidly changing back again into $CaSO_4 \cdot 2H_2O$. Owing to this property, gypsum is used to manufacture casting moulds and replicas of various objects, and is a binding agent for plastering walls and ceilings. Gypsum is used in surgery to make plaster bandages for broken bones.

4. *Vitriols*. This is the common name given to the sulphates of copper, iron, zinc and certain other metals containing water of crystallization.

Blue vitriol $CuSO_4 \cdot 5H_2O$ forms blue crystals containing five molecules of crystallization water. Is used for copper-plating metals, for the preparation of certain mineral paints and as a raw material for the preparation of other copper compounds. In agriculture a dilute solution of blue vitriol is used for spraying plants and for pickling grain before sowing to destroy the spores of harmful fungi.

Green vitriol $FeSO_4 \cdot 7H_2O$ crystallizes in the form of light green crystals containing seven molecules of hydration water. Is widely used in industry for preserving wood, for the manufacture of ink and Prussian blue, for freeing illuminating gas from hydrogen sulphide and cyanide compounds, in the dye industry, in agriculture against plant pests, and in photography.

5. *Alums*. If a solution of potassium sulphate K_2SO_4 is added to a solution of aluminium sulphate $Al_2(SO_4)_3$, and the liquid is left standing, beautiful colourless crystals separate out, whose composition can be expressed by the formula $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ or

$KAl(SO_4)_2 \cdot 12H_2O$. This compound is known as ordinary or *aluminium alum*, and is a double salt of sulphuric acid and the metals potassium and aluminium.

Double salts can exist only in the solid form. When alum is dissolved in water the solution contains $K^{\cdot}$, $Al^{\cdot\cdot\cdot}$ and SO_4'' ions.

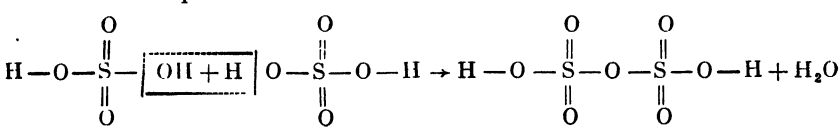
Alums may be of various compositions. Instead of aluminium they may contain other trivalent metals, namely iron or chromium, and instead of potassium they may contain sodium or ammonium. For instance, chrome alum has the composition $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$. Alum is used in tanning leather and in the dye industry.

127. Pyrosulphuric Acid $H_2S_2O_7$. If sulphur trioxide is dissolved in sulphuric acid the SO_3 molecules combine with H_2SO_4 molecules to form a new acid called pyrosulphuric acid:

$$H_2SO_4 + SO_3 = H_2S_2O_7$$

Pyrosulphuric acid separates out from the resulting solution (oleum) upon cooling as colourless crystals with a melting point of 35° C.

Pyrosulphuric acid may be regarded as an incomplete anhydride of sulphuric acid, i.e., as a product of the abstraction of one water molecule from two molecules of sulphuric acid:



pyrosulphuric acid

Indeed, hydration of pyrosulphuric acid results in sulphuric acid:

$$H_2S_2O_7 + H_2O = 2H_2SO_4$$

Pyrosulphuric acid is an oxidizing agent whose action is similar to that of sulphuric acid. Pyrosulphuric acid (oleum) is often used in industry, for instance, for purifying petroleum products, for the manufacture of certain dyes, explosives, etc.

The salts of pyrosulphuric acid—**pyrosulphates**—can be prepared by heating acid sulphates. For instance:

$$2KHSO_4 = K_2S_2O_7 + H_2O$$

If heated above the melting point pyrosulphates decompose, liberating sulphuric anhydride and passing into the sulphates:

$$K_2S_2O_7 = SO_3 + K_2SO_4$$

128. Manufacture of Sulphuric Acid. Sulphuric acid is produced commercially by two methods: the contact process and the lead-chamber process.

The contact process for the production of sulphuric acid is based on the direct union of sulphur dioxide with oxygen in contact with a catalyst and on the reaction between the resulting sulphuric trioxide and water.

The sulphur dioxide for this process is obtained by roasting metal sulphides, chiefly pyrite FeS_2, in special burners, in the presence of air:

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2$$

The ferric oxide obtained in this way ("pyrite cinders") is removed from the burners and can be used for the production of iron, while the mixture of sulphur dioxide and air is passed through, a series of apparatuses to free it from dust and other impurities. Complete removal of impurities is one of the compulsory conditions for this process, as even insignificant traces of certain substances (compounds of arsenic, phosphorus, etc.) "poison" the catalyst, depriving it very rapidly of its activity.

A widely used method of purification for freeing the gases from dust and suspended particles is at present the electrostatic method. The gases to be purified are passed through an electric separator (Fig. 90) which in the simplest case consists of a large diameter iron tube with a thin iron wire at its axis, connected to the negative pole of a source of high tension current. The tube and the positive pole are earthed. Under a difference of potentials as high as 200,000 volts, the field intensity in the vicinity of the wire is so high that the air around it becomes ionized. The negatively charged ions thus formed are attracted to the inner surface of the tube, and the positively charged ions—to the wire. The ions collide with the dust particles and charge them. Since only negative ions move through the space outside the ionization zone, which takes up but an insignificant part of the inside of the tube, most of the dust particles passing through the electric separator are charged negatively and are attracted to the inner surface of the tube, where they deposit. Any dust particles which happen to become positively charged, will deposit on the negative wire. Practically all the dust particles are precipitated in this way.

After the removal of impurities, the sulphur dioxide-air mixture passes through a special pre-heater where it is heated by the gases discharged from the contact apparatus, and then enters the contact apparatus. A diagram of such an apparatus is shown in Fig. 91. It is a large cylinder with four grate-like shelves, inside covered with the catalyst. The gas enters the apparatus at the top, passes charged through the four layers of contact mass, and is discharged at the bottom.

On the catalyst the sulphur dioxide is oxidized into sulphur trioxide, this reaction being accompanied by the liberation of a considerable amount of heat:

$$2SO_2 + O_2 \rightleftarrows 2SO_3 + 46.8\,\text{Cal.}$$

The temperature in the contact apparatus is maintained at about 450° C, as below this temperature the gases combine too slowly, whereas above 450° C the back reaction is accelerated. For instance, at 700° C with the usual composition of the gas mixture obtained by roasting pyrite (7 per cent SO_2, 11 per cent O_2 and 82 per cent N_2),

only 15 per cent SO_2 is converted into SO_3. Raising the oxygen content in the mixture increases the yield of sulphur trioxide by shifting the equilibrium of the reaction to the right. In practice, at 450° C and with an excess of oxygen in the gas mixture the degree of conversion of SO_2 into SO_3 is as high as 95 or 97 per cent.

The sulphur trioxide formed is discharged from the contact apparatus in very finely divided form. As such, water will not absorb it, and so it is passed into concentrated sulphuric acid (96 to 98 per cent) which it saturates, turning it into oleum. Very pure sulphuric acid of any desired concentration can be obtained by diluting the latter with water.

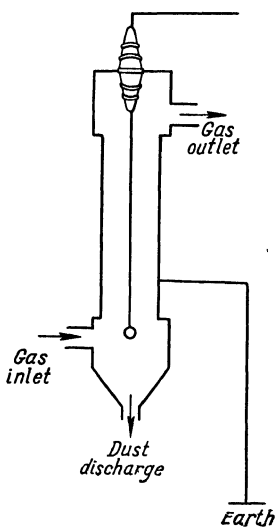


Fig. 90. Diagram of electric separator

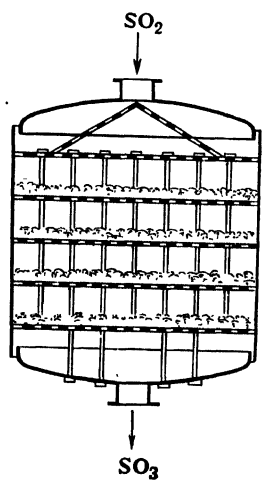


Fig. 91. Diagram of contact apparatus

The catalyst used formerly for oxidizing sulphur dioxide was platinized asbestos. Lately it has been replaced by vanadium pentoxide, V_2O_5, and certain other vanadium compounds. Vanadium catalysts are almost as active as platinum, but are cheaper and are not so easily poisoned, which makes it possible to simplify the purification of the gases considerably.

Sulphuric acid was first produced in Russia by the contact method at the Tentelev Plant (now the Krasny Khimik Plant) in Petersburg. The "Tentelev system" developed by the chemists of this plant was one of the most progressive systems of its time and gained world fame. Contact plants using this system were built in a number of other countries, including Japan and the U.S.A.

Lead-Chamber Method. The contact process for the production of sulphuric acid was introduced comparatively recently. Prior to that, sulphuric acid was manufactured only by the lead-chamber method, which consists essentially in the oxidation of sulphur dioxide by nitrogen dioxide NO_2 in the presence of water.

The nitrogen dioxide is obtained from nitric acid; the reddish-brown gas reacts with sulphur dioxide according to the equation

$$SO_2 + NO_2 + H_2O = H_2SO_4 + NO$$

Yielding part of its oxygen to sulphur dioxide, nitrogen dioxide turns into a colourless gas, namely, nitric oxide NO. The latter is remarkable for its ability to combine with the oxygen of the air to form nitrogen dioxide again:

$$2NO + O_2 = 2NO_2$$

which is used to oxidize further portions of sulphur dioxide.

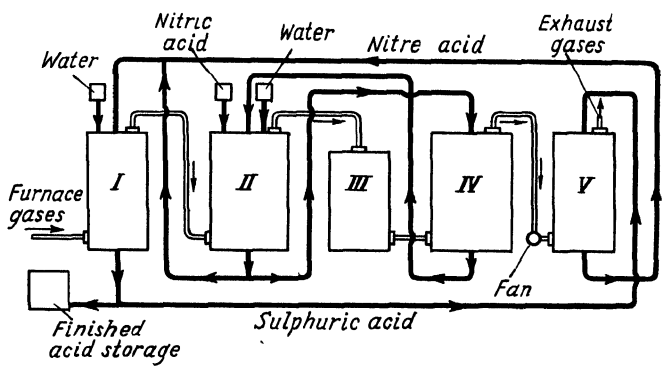


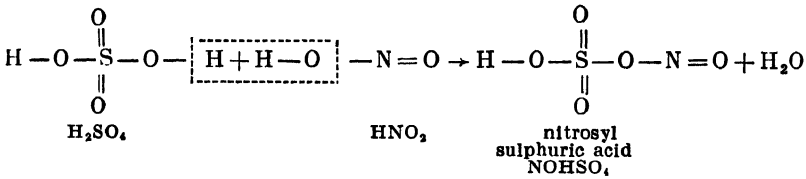
Fig. 92. Diagram of tower plant for manufacture of sulphuric acid

Thus, theoretically, no nitric oxide is used up in the production of sulphuric acid, so that it may be regarded as a catalyst, accelerating the oxidation of sulphur dioxide (§ 130).

The lead-chamber process for the production of sulphuric acid may be accomplished technically in chambers or towers. Since chambers are now practically obsolete, we shall confine outselves to a description of the process as carried out in towers.

Fig. 92 is a diagram of a tower installation. The hot gases from the pyrite burners, containing sulphur dioxide, are freed from dust, and then passed through the Glover or denitrating towers *I* and *II*, filled with acid-proof tiles, down which so-called *nitre acid* trickles. Nitre acid is sulphuric acid solution of *nitrosyl sulphuric acid*

$NOHSO_4$, which is, by structure, a mixed anhydride of sulphuric and nitrous (HNO_2) acids, as can be seen from the following scheme:



Water is also introduced into towers *I* and *II*, besides the nitre acid. Owing to the high temperature of the gases, nitrosyl sulphuric acid hydrolyzes into sulphuric and nitrous acids:

$$NOHSO_4 + H_2O = H_2SO_4 + HNO_2$$

The nitrous acid oxidizes the sulphurous acid, formed by the sulphur dioxide combining with the water, into sulphuric acid:

$$H_2SO_3 + 2HNO_2 = H_2SO_4 + 2NO + H_2O$$

The conditions in the Glover towers are adjusted so as to convert up to 90 per cent of the initial SO_2 into sulphuric acid; the remainder is oxidized in tower *III*, called the stabilizer tower. Then the gases containing NO_2 and NO pass through two Gay-Lussac or "absorption" towers *IV* and *V* filled with pieces of quartz and sprayed with sulphuric acid.

In these towers nitrosyl sulphuric acid is formed:

$$NO_2 + NO + 2H_2SO_4 = 2NOHSO_4 + H_2O$$

Thus, the nitrogen oxides are collected in towers *IV* and *V* and do not pass into the atmosphere.

The gases are circulated through the system by means of a powerful fan installed between towers *IV* and *V*.

Most of the sulphuric acid is formed in Glover tower *I*. Part of this acid is continuously drawn from the system as the finished product, and the rest of it is pumped to Gay-Lussac tower *V*. The nitre acid flowing out of tower *V* is used as a spray in tower *I*.

Part of the acid from tower *II* is delivered to tower *IV*, the rest of it returning to tower *I*. The nitre acid from tower *IV* is used as a spray in tower *II*.

The slight losses of nitrogen oxides occurring during the lead-chamber process are replenished by introducing nitric acid into tower *II*.

Sulphuric acid is one of the most important products of the so-called *fundamental chemical industry*, which includes the production of acids, alkalis, salts, mineral fertilizers and chlorine. Not a single chemical product is produced in such immense quantities as sulphuric acid. The chief consumer of sulphuric acid is the mineral fertilizer industry (for instance, the superphosphate and ammonium sul-

phate industries). Then, it is used for preparation of almost all other acids from their salts, is employed in great quantities for the production of explosives, for the purification of kerosene, mineral oils and coke-oven products (benzene, toluene), for the preparation of various vitriols, for the manufacture of dyes, for etching ferrous metals (scale removal), etc. The output of sulphuric acid in 1952 in the capitalist countries only, was 25 million tons.

Prior to the October Revolution the production of sulphuric acid in Russia was insignificant in comparison with other countries. The small-scale sulphuric acid plants that existed burned almost exclusively imported pyrite. The production of all the plants in 1913 totalled only about 120,000 tons.

The Revolution changed the situation radically. The old plants were extended and re-equipped. A home base of raw materials for the sulphuric acid industry was created and a number of new plants erected. Along with pyrite, the roasting gases of non-ferrous metallurgy containing considerable quantities of SO_2, as well as "flotation tailings"—the waste left over from the concentration of copper and zinc ores—consisting mainly of pyrite, began to be used extensively at Soviet plants as raw materials.

The development of the Soviet sulphuric acid industry involved the erection of new type lead-chamber and contact systems. The former chamber installations were now replaced by tower units. The burner sections of sulphuric acid plants were equipped with powerful mechanical burners. The old contact apparatuses with their platinum catalysts were replaced by more productive apparatuses employing vanadium catalysts.

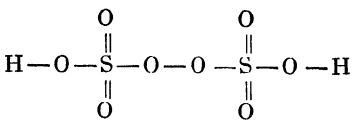
A great deal has been done in the sulphuric acid industry for the intensification of production. If the daily output of lead-chamber systems was formerly 18 to 20 kilograms of acid per cubic metre of tower volume, the average acid yield at present per cubic metre of tower volume exceeds 120 kilograms, and at some plants innovators have brought it up to 200 kg. per cu. m. Another notable achievement is the production of the entire output at lead-chamber installations in the form of oil of vitriol (92 to 92.5 per cent H_2SO_4) instead of 75 to 76 per cent sulphuric acid.

Great opportunities in the manufacture of sulphuric acid are offered by the use of oxygen and by the "fluidized bed" roasting of pyrites (see p. 596).

129. Persulphuric Acid $H_2S_2O_8$. If an electric current is passed through a 50 per cent solution of sulphuric acid, hydrogen is liberated at the cathode, while at the anode HSO_4' ions lose their charges and combine in pairs to form persulphuric acid $H_2S_2O_8$:

$$2HSO_4' - 2e^- = H_2S_2O_8$$

Persulphuric acid is a derivative of hydrogen peroxide and an intermediate product in the production of the latter by the electrochemical method. Its structure is represented by the following formula:



Like in hydrogen peroxide, two of the oxygen atoms are combined here by a covalent bond, forming the characteristic peroxide "chain". Such acids are known under the common name of **peracids** and have been obtained for a number of other elements besides sulphur.

Peracids were studied extensively by the Russian Academician L. Pisarzhevsky, to whom chemistry is obliged for his classical investigations in this field.

Owing to the presence of the peroxide chain in their molecules, all peracids, like peroxides, possess vigorous oxidizing properties.

The salts of persulphuric acid, called **persulphates**, are used for certain technical purposes and as bleaching agents.

130. Catalysis. Our examination of the technical methods for the manufacture of sulphuric acid based on the action of catalysts has given us some idea of the important part catalysis plays in chemistry. In this paragraph we shall deal with catalytic processes in greater detail.

The effect of various "foreign" substances on the rate of chemical reactions was noticed as far back as the beginning of the XIX century. In 1811 the Russian scientist K. Kirchhoff established that sulphuric acid accelerates the saccharification of starch. In 1835 Berzelius suggested the name "catalyst" for such substances, a name which has persisted to our days. As catalysts do not enter into the composition of the reaction products, Berzelius believed that they excite the chemical activity of other substances by their mere presence, without taking direct part in the reaction.

The real explanation of catalytic phenomena should be sought in the properties of matter itself, in the interaction of all the material factors participating in the catalytic process, including the catalysts themselves. A catalyst is no "foreign" substance to the reaction but an active participant, which has in many cases been proved experimentally to interact directly with the reactants.

On these grounds, *the term catalysts is used to denote substances which change the velocity of a reaction, themselves remaining chemically and quantitatively unchanged after the reaction, though they participate in it directly.*

From the above definition it follows that a catalyst cannot cause a reaction which will not take place without it. Indeed, in many cases where reactions appeared not to take place in the absence

of a catalyst, it was subsequently proved that they do take place, albeit at an immeasurably slow rate.

Usually the catalyst has the effect of increasing the rate of the reaction. However, there are reactions which are decelerated in the presence of foreign substances. For instance, if a little glycerine, sugar or alcohol is added to a solution of sodium sulphite, its oxidation by the oxygen of the air is greatly retarded. The same substances have a similar effect on the solutions of certain other salts. Such substances are called *negative catalysts.*

A study of numerous catalytic reactions shows that there are no common catalysts for all reactions; the catalytic effect of catalysts is *strictly specific.* It might be assumed that water is a universal catalyst, as the presence of at least traces of water is indispensable for many reactions. However, there are a number of reactions which are slowed down or stop entirely in the presence of water. For instance, absolutely dry carbon dioxide will decompose under the action of ultra-violet rays into carbon monoxide and oxygen, but the moist gas does not decompose. Thus, even water cannot be considered a universal catalyst.

It has not yet been established just which properties of a catalyst make it suitable for one reaction or another. Sometimes the same process can be accelerated by absolutely different substances which apparently have nothing in common. Such, for instance, are platinum and vanadium pentoxide V_2O_5, used for the oxidation of sulphur dioxide to sulphur trioxide. Nor can any parallelism be detected in the action of catalysts in chemically close reactions. Therefore, the problem of finding a suitable catalyst for any given reaction is often a very difficult one.

Catalysis has so far defied envelopment in strict quantitative laws, but some relationships may be considered already quite well established. Two of the more important of these are: 1) in a homogeneous medium catalytic action is proportional to the concentration of the catalyst; 2) the catalyst does not affect the state of equilibrium of reversible reactions, as it changes the velocity of the forward and the back reaction equally.

At present two kinds of catalysis are usually distinguished, namely, homogeneous and heterogeneous.

If the reactants and the catalyst are in the same phase, the catalysis is *homogeneous.* An example of the latter is the accelerating action of hydrogen (and sometimes other) ions on many reactions between dissolved substances. If the catalyst and the reactants are in different phases, as is the case with the reaction between hydrogen and oxygen in the presence of platinized asbestos, the catalysis is called *heterogeneous.*

In view of the great diversity of phenomena united under the conception of catalysis, it would be difficult to expect them all to

be due to one common cause. Naturally, the causes may be different in different cases. We shall deal here with the two most important theories used most often to explain the action of catalysts.

The accelerating influence of catalysts in homogeneous catalysis is usually explained by the "theory of intermediate reactions". It may, for instance, happen that a reaction of the type

$$A + B = AB$$

takes place very slowly, whereas in the presence of a catalyst K the following rapid reactions take place:

$$A + K = AK \quad (1)$$

$$\underline{AK + B = AB + K} \quad (2)$$

$$A + B + (K) = AB + (K)$$

This scheme affords a good explanation for the catalyst remaining unchanged in the long run, and is in agreement with the fact that catalytic action is proportional to the amount of catalyst present (as the rate of reaction (1) must be proportional to the concentration of K).

In many cases the formation of intermediate compounds such as AK in the above scheme has been proved experimentally, thus testifying to the truth of this theory. A graphic illustration is the lead-chamber process for the production of sulphuric acid. By itself (without the catalyst) the reaction

$$2SO_2 + O_2 + 2H_2O = 2H_2SO_4$$

proceeds very slowly. But in the presence of nitric oxide as catalyst the following reactions take place rapidly:

$$2NO + O_2 = 2NO_2$$

$$\underline{2NO_2 + 2SO_2 + 2H_2O = 2H_2SO_4 + 2NO}$$

$$(2NO) + 2SO_2 + O_2 + 2H_2O = 2H_2SO_4 + (2NO)$$

as a result of which the amount of the catalyst NO remains unchanged.

Some cases of heterogeneous catalysis can also be attributed to the formation of intermediate compounds. It has been established, for instance, that crystalline manganese dioxide, which accelerates the decomposition of potassium chlorate, is converted as a result of the reaction into a fine powder. On this basis it has been assumed that the salt decomposes in two steps:

$$2KClO_3 + 4MnO_2 = 2KCl + 2Mn_2O_7$$

$$\underline{2Mn_2O_7 = 4MnO_2 + 3O_2}$$

$$(4MnO_2) + 2KClO_3 = 2KCl + 3O_2 + (4MnO_2)$$

The intermediate product formed in this case is the unstable highest oxide of manganese, Mn_2O_7.

However, the main role in heterogeneous catalysis, especially if the catalyst is in the solid phase and the reactants are in solution

or in the gaseous state, is played by **adsorption**, i. e., fixation of the molecules of the reactants by the surface of the catalyst. The increase in the concentration of the reactants at the surface of the catalyst should in itself influence the reaction rate, but this influence is not strong enough to explain the great increase in reaction rate observed in such cases. Besides, if the increase in concentration due to adsorption were the only factor, the specificity of catalytic action could not be accounted for. Therefore, it is considered that the main factor accelerating the reaction is the increase in activity of the adsorbed molecules under the action of the outer force field of the catalyst.

Profound studies of the catalytic action of solid amorphous bodies on the course of chemical processes, as well as the dependence of this action on the nature of the contacting bodies and their surface. were carried out by Konovalov.

An explanation of the role of contact in heterogeneous catalysis and the causes of the increase in activity of the adsorbed molecules was given by Mendeleyev (1866) who first suggested the idea that "at the points of contact between bodies the state of internal motion of the atoms in the particles changes, and it is this state that governs chemical reactions". Developing this idea, another prominent Russian scientist Zelinsky worked out and grounded experimentally new views on the nature of heterogeneous catalysis. He attached great importance to the change in shape of the reacting molecules and to the deformation of their bonds due to contact with the catalyst, which is not active all over its surface but only at certain points, called active centres. Adsorption of molecules at definite points on the surface of the crystal lattice of the catalyst is, according to Zelinsky, "an obligatory preliminary stage of heterogeneos catalysis".

Some substances, even if present in insignificant quantities, greatly decrease the activity of the catalyst or even completely preclude its action.

It was pointed out above that in the contact process for the manufacture of sulphuric acid the gases must be thoroughly purified, otherwise the catalyst is quickly poisoned.

Like the catalyst itself, these catalytic poisons are specific in their action: though they may spoil catalysts of one type, they are quite harmless to others. Poisoning is probably due to adsorption of the catalytic poison by the surface of the catalyst, especially at its active centres, as a result of which the catalyst becomes as if enveloped in the poisons, and the reactant molecules are blocked out.

Whereas some substances poison catalysts, others, on the other hand, greatly enhance their activity if added in small quantities, though they themselves are not catalysts for the reaction in question.

Such substances are called **promoters** and serve, so to say, as "catalysts for catalysts". The nature of the action of promoters has not yet been established exactly.

The role of catalysis in chemistry is enormous. The very fact that the impurities in ordinary water may serve as catalysts for many reactions, shows how widespread catalytic phenomena are. If we take into account, besides, that the walls of the vessels in which the chemical reactions take place may also often act as catalysts, it may be considered that catalysis occurs in latent form in almost every chemical reaction.

In our days a great number of very important industrial chemical processes are based on the use of catalysts. And the more the chemical industry progresses, the more it makes use of catalytic action.

131. Compounds of Sulphur with the Halogens. Passing chlorine through melted sulphur results in *sulphur monochloride*, an orange liquid boiling at 138° C. The molecular weight of this substance, as determined by the density of its vapours, corresponds to the formula S_2Cl_2.

Sulphur monochloride can dissolve sulphur up to 66 per cent. Water decomposes S_2Cl_2, forming sulphur dioxide, hydrogen chloride and sulphur:

$$2S_2Cl_2 + 2H_2O = SO_2 + 3S + 4HCl$$

Sulphur monochloride is used for the vulcanization of rubber.

Two more compounds of sulphur and chlorine are known, namely, SCl_2 and SCl_4, which are, however, of no practical importance. With fluorine sulphur forms the gaseous compound SF_6, in which it attains its highest degree of oxidation.

SELENIUM SUBGROUP

This subgroup includes the elements selenium, tellurium and polonium. Of them only selenium and tellurium, greatly resembling sulphur in their properties, have been investigated chemically.

132. Selenium; at. wt. 78.96. Tellurium; at. wt. 127.61. Selenium is quite abundant in nature, but occurs usually in small quantities, namely, as admixtures to natural metal sulphides (PbS, FeS_2, etc.). When pyrite is roasted, selenium accumulates in the dust collecting chambers of sulphuric acid plants. This dust is the chief source for the production of selenium. Tellurium, on the other hand, is one of the very rare elements, its content in the earth's crust being only 1×10^{-6} per cent.

Like sulphur, elemental selenium forms several allotropic modifications of which the best known are: *amorphous selenium*, a reddish-brown powder with a specific gravity of 4.3 and *crystalline selenium*, a grey brittle substance with a metallic lustre and a specific gravity of 4.8. The latter modification possesses a remarkable property: its electrical conductivity, which in itself is very small, increases

greatly under the action of light. This property of selenium is the basis of its use in various optical apparatuses, namely, photometers, light signallers, etc., as well as in television. Tellurium is also known in the form of the amorphous modification and as a crystalline substance of light grey colour with a metallic lustre. Tellurium is a good conductor of heat and electricity, approaching metals in this respect.

The resemblance between selenium and tellurium, on the one hand, and sulphur, on the other, is especially manifest in their compounds.

Hydrogen selenide H_2Se and *hydrogen telluride* H_2Te are colourless poisonous gases with disgusting odours. Their aqueous solutions are acids whose degress of ionization, however, are somewhat higher than that of hydrogen sulphide, as the attraction between the negative ions and the hydrogen ions becomes weaker as the radius of the former increases.

In chemical properties H_2Se and H_2Te greatly resemble H_2S. Like hydrogen sulphide, they are easily oxidized by the oxygen of the air, decompose when heated and possess powerful reducing properties. Their salts, *selenides* and *tellurides*, are prepared, like sulphides, by the action of H_2Se or H_2Te on soluble salts of the metals and are very similar to the sulphides with respect to their solubility in water and in acids. H_2Se and H_2Te can be prepared by the action of strong acids on selenides and tellurides.

Combustion of selenium and tellurium in air or in oxygen results in the solid oxides SeO_2 and TeO_2, the anhydrides of *selenious* and *tellurious* acids, H_2SeO_3 and H_2TeO_3. Unlike sulphur dioxide SeO_2 and TeO_2 are predominantly oxidants, being easily reduced to free selenium and tellurium. By the action of powerful oxidizing agents SeO_2 and TeO_2 can be converted respectively into selenic and telluric acids, H_2SeO_4 and H_2TeO_4.

Selenic acid H_2SeO_4 is a solid crystalline substance melting at 58° C. Like sulphuric acid, it is non-volatile, combines vigorously with water, chars organic substances and possesses powerful oxidative properties.

Selenic acid is one of the strong acids. Its salts, known as *selenates*, bear a striking resemblance to sulphates. Even the same salts are insoluble as in the case of sulphuric acid, e.g., the barium and lead salts. Selenic anhydride is unknown.

Telluric acid, in contradistinction to selenic and sulphuric, is a very weak acid. It separates out of solution as crystals of the composition H_6TeO_6. This is a hexabasic acid, forming a number of salts, such as Ag_6TeO_6. When heated, telluric acid splits off two molecules of water and becomes a dibasic acid, analogous to sulphuric acid, H_2TeO_4. If heated more strongly it turns into telluric anhydride TeO_3.

CHAPTER XVI

The Nitrogen Group

Element	Symbol	Atomic weight	Atomic number	Arrangement of electrons in layers					
Nitrogen . .	N	14.008	7	2	5				
Phosphorus	P	30.975	15	2	8	5			
Arsenic . .	As	74.91	33	2	8	18	5		
Antimony .	Sb	121.76	51	2	8	18	18	5	
Bismuth . .	Bi	209.00	83	2	8	18	32	18	5

133. General Features of the Nitrogen Group. The nitrogen group includes the typical elements of the fifth group of the Periodic Table, *nitrogen* and *phosphorus*, as well as *arsenic*, *antimony* and *bismuth*, elements with atoms of similar structure in the odd series of the large periods. Together these five elements make up the main subgroup of the fifth group called also the **nitrogen group.**

The elements of the nitrogen group, having five electrons in the outer layer of their atoms, may be characterized on the whole as non-metals. However, their capacity for gaining electrons is much weaker than that of the corresponding elements of the sixth and seventh groups. Owing to the presence of five outer electrons, the highest positive valency of the nitrogen group elements equals five, and the highest negative valency, three. Owing to their relatively lower electronegativity, the bond between hydrogen and the elements of the nitrogen group is less polar than that between hydrogen and the elements of the sixth and seventh groups. Therefore, the hydrogen compounds of the nitrogen group elements do not split off hydrogen ions in aqueous solution and hence do not possess acidic properties.

The physical and chemical properties of the elements of the nitrogen group vary with increasing atomic number in the same order as in the groups studied earlier. But since the non-metallic properties of nitrogen are less pronounced than those of oxygen, and the more so than of fluorine, further weakening of these properties in passing to the subsequent elements results in rapid growth of metallic

properties. The latter become perceptible already in arsenic; antimony possesses metallic and non-metallic properties in approximately equal degree, while in bismuth metallic properties predominate considerably over non-metallic.

The most important constants of the nitrogen group elements are given in Table 22.

Table 22

Most Important Physical Constants of the Nitrogen Group Elements

Constants	Nitrogen N	Phosphorus P	Arsenic As	Antimony Sb	Bismuth Bi
Specific gravity	0.81 (liq.)	1.82 (white)	5.73	6.62	9.8
Melting point, degrees C	—210	44.2	817 (36 atm. pressure)	630.5	271.3
Boiling point, degrees C	—195.8	280.5	615 (subl.)	1,635	1,560
Atomic radius, Å . . .	0.71	—	1.48	1.61	1.82

NITROGEN (Nitrogenium); at. wt. 14.008

134. Nitrogen in Nature. Preparation and Properties of Nitrogen. Nitrogen occurs in nature mostly in the free state. Free nitrogen, as is commonly known, is the chief component of air, which contains about 78 per cent nitrogen by volume. The only inorganic nitrogen compound found in nature in considerable quantities is sodium nitrate $NaNO_3$, which occurs in thick deposits on the Pacific coast in Chile. The soil contains insignificant quantities of nitrogen, mainly as nitrates. But as a constituent of the complex organic compounds, known as proteins, nitrogen is found in the body of every plant and animal. Proteins constitute the most important parts of cells, namely, the protoplasm and the nucleus. The wonderful changes which proteins undergo in plant and animal cells form the basis of all vital processes. *Life is impossible without protein*, and as nitrogen is a compulsory constituent of protein it will easily be understood how important is the role played by this element in nature.

The total content of nitrogen in the earth's crust (including the hydrosphere and the atmosphere) is 0.04 per cent.

The preparation of nitrogen from air reduces essentially to its separation from oxygen. In industry this is done by evaporating liquid air in special plants.

Absolutely pure nitrogen can be obtained from its compounds, e.g., from ammonia, by passing the latter over strongly heated cupric oxide:

$$3CuO + 2NH_3 = N_2 + 3Cu + 3H_2O$$

or by heating ammonium nitrite:

$$NH_4NO_2 = N_2 + 2H_2O$$

Pure nitrogen is a colourless gas with no odour, very slightly soluble in water. It is a little lighter than air, one litre of it weighing 1.25 gr. When cooled strongly under high pressure nitrogen becomes a liquid which boils at —195.8° and solidifies into a snow-like mass at —210° C.

Nitrogen is conspicuous for its chemical inertness. At ordinary temperatures it is almost incapable of forming compounds. When heated it combines quite readily with some metals, such as lithium, magnesium, calcium, titanium. Finally, at very high temperatures nitrogen combines directly with oxygen and hydrogen.

Animals placed in an atmosphere of nitrogen soon perish, not as a result of nitrogen poisoning, but due to the absence of oxygen. This property accounts for the old name of nitrogen, azote, from the Greek "azoos", meaning lifeless. The present English name "nitrogen" is derived from the Latin "nitrogenium", meaning "originating saltpetre".

The nitrogen molecule consists of two atoms (N_2). These atoms are tied together very stably, which accounts for the chemical inertness of nitrogen under ordinary conditions.

Nitrogen forms a large number of compounds, which are prepared indirectly and easily undergo various changes.

Free nitrogen is used in electrical engineering to fill "half-watt" lamps. But the greater part of nitrogen obtained from the air is used for the preparation of synthetic ammonia and calcium cyanamide.

135. Ammonia NH_3. Nitrogen forms several compounds with hydrogen, the most important of which is ammonia, a colourless gas with a characteristic pungent odour, well known to everyone as the odour of ammonia spirit.

Ammonia is usually prepared in the laboratory by heating a mixture of ammonium chloride NH_4Cl and slaked lime $Ca(OH)_2$. The reaction is represented by the equation

$$2NH_4Cl + Ca(OH)_2 = CaCl_2 + 2H_2O + 2NH_3$$

The ammonia liberated contains water vapour. To dry it, it is passed through a jar of soda lime (a mixture of lime and caustic soda).

One litre of ammonia at S.T.P. weighs 0.77 gr. As ammonia is much lighter than air, it can be collected in an inverted vessel.

When cooled to —33.4°C at ordinary pressure, ammonia turns into a transparent liquid which solidifies at —77.7° C. Liquid ammonia is kept in steel cylinders under a pressure of 6-7 atm. The comparatively high boiling point of ammonia (—33.4°), contradicting its low molecular weight (M = 17), is due to the active association of liquid ammonia molecules owing to their pronounced polarity.

Ammonia is very soluble in water, one volume of water at ordinary temperatures dissolving 700 volumes of ammonia. A concentrated solution contains 25 per cent NH_3 and has a specific gravity of 0.91. A solution of ammonia in water is sometimes called *ammonia spirit.* Ordinary medicinal ammonia spirit contains 10 per cent NH_3. As the temperature rises, the solubility of ammonia decreases, so that it is liberated if a concentrated solution is heated. This is made use of sometimes in laboratories for the preparation of NH_3 in small quantities.

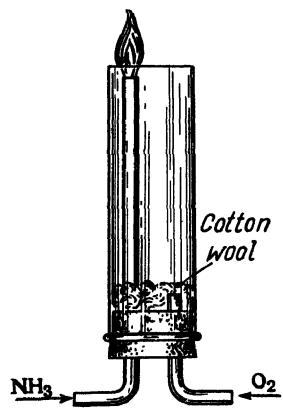


Fig. 93. Apparatus for demonstrating combustion of ammonia in oxygen

At low temperatures the crystal hydrate $NH_3 \cdot H_2O$, having a melting point of —79° C, can be separated out of an ammonia solution. A crystal hydrate of the composition $NH_3 \cdot 2H_2O$ is also known.

Chemically ammonia is quite active; it reacts with many substances. In ammonia nitrogen reaches its highest degree of reduction, corresponding to a valency of —3. Therefore, ammonia will not participate in reactions connected with further lowering of the valency of nitrogen: it possesses only reducing properties. If a stream of ammonia is passed through a tube inside another wider tube (Fig. 93), through which oxygen is delivered, the ammonia can easily be ignited; it burns in oxygen with a pale green flame. Combustion of ammonia leads to the formation of water and free nitrogen:

$$4NH_3 + 3O_2 = 6H_2O + 2N_2$$

$$4 \mid \overset{-III}{N} - 3e^- = \overset{0}{N}$$

$$3 \mid O_2 + 4e^- = \overset{-II}{2O}$$

Under other conditions ammonia can be oxidized to nitrogen oxides.

In contradistinction to the hydrogen compounds of the sixth and seventh group non-metals, ammonia does not possess any distinctly

pronounced acid properties. However, its hydrogen can be displaced by metals, the compounds formed being called *nitrides*. Some of them, such as calcium and magnesium nitrides, can be prepared by combining nitrogen directly with the metals in question at a high temperature:

$$3Mg + N_2 = Mg_3N_2$$

Many nitrides are completely hydrolyzed in water, forming ammonia and the hydroxide of the metal. For instance:

$$Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3$$

If only one hydrogen atom in the ammonia molecule is displaced by a metal the result is a *metal amide*. Thus, if ammonia is passed over molten sodium, *sodium amide*, or *sodamide*, $NaNH_2$ is produced as colourless crystals with a melting point of 210° C:

$$2NH_3 + 2Na = 2NaNH_2 + H_2$$

Water decomposes sodium amide according to the equation:

$$NaNH_2 + H_2O = NaOH + NH_3$$

Possessing strong basic and dehydrating properties, sodium amide has found application in several organic syntheses, e.g., in the synthesis of such an important dye as indigo and in the synthesis of sulphidine.

The product of substitution of one of the hydrogen atoms in ammonia by a hydroxyl group is *hydroxylamine* NH_2OH, a solid with a melting point of 33° C.

Hydroxylamine is prepared by the reduction of nitric acid with nascent hydrogen. It dissolves readily in water forming the hydrate $NH_2OH \cdot H_2O$, which ionizes partially into $[NH_3OH]^+$ and OH^-. Therefore, in aqueous solution hydroxylamine possesses basic properties; when neutralized with acids it produces hydroxylamine salts, such as $[NH_3OH]Cl$ (cf. ammonia below).

Hydroxylamine and its salts are widely used to obtain many organic preparations.

The hydrogen in ammonia can be substituted also by the halogens to form very unstable compounds of nitrogen and the halogens. For example, the action of chlorine on a concentrated solution of ammonium chloride results in *nitrogen chloride* NCl_3:

$$NH_4Cl + 3Cl_2 = NCl_3 + 4HCl$$

in the form of a heavy, oily, very explosive liquid.

Similar properties are possessed by nitrogen iodide, which forms as a solid black substance, insoluble in water, when ammonia is treated with iodine. In the moist state it is harmless, but when dried explodes at the least touch, liberating purple puffs of iodine vapours. The composition of nitrogen iodide varies depending on the temperature at which it is prepared ($NI_3 \cdot NH_3$ at ordinary temperatures).

A solution of ammonia in water has a basic reaction, showing that it contains hydroxyl ions. The appearance of these ions in solution is due to the fact that part of the NH_3 molecules combine with the hydrogen ions of water forming complex singly-charged NH_4^+ ions (ammonium ions) and liberating hydroxyl ions:

$$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^- \qquad (1)$$

the latter, in their turn, combine partly with ammonium-ion to form *ammonium hydroxide* NH_4OH, a base, in which the NH_4 group plays the part of a univalent metal:

$$NH_4^{\cdot} + OH' \rightleftarrows NH_4OH \qquad (2)$$

As a result an equilibrium is established in the solution between ammonium-ion, hydroxyl-ion and molecular ammonium hydroxide, on the one hand, and between the same ions, molecular ammonia and water, on the other:

$$NH_3 + H_2O \rightleftarrows NH_4^{\cdot} + OH' \rightleftarrows NH_4OH$$

Thus, a solution of ammonia contains simultaneously molecular NH_3, $NH_4^{\cdot}$-ion, OH'-ion and molecular ammonium hydroxide.

Since ammonia in solution reacts slightly basic, ammonium hydroxide is usually regarded as a weak base, only slightly dissociated into ions (its ionization constant at 18° C is 1.75×10^{-5}).

There is an opinion that most of the dissolved ammonia is in solution in the form of NH_3 molecules. Under such conditions the existence in solution of unionized ammonium hydroxyde is doubtful, and it is therefore assumed that ammonium hydroxide is a strong, practically completely ionized base, the ions of which cannot, however, be present in solution in any considerable concentration, because equilibrium (1) is greatly displaced to the left.

If a strong acid, say hydrochloric, is added to an ammonia solution, the hydrogen ions of the acid combine both with the hydroxyl ions in solution and with the ammonia molecules (forming ammonium ions with the latter). The result is a neutral solution in which practically only ammonium ions and anions of the acid used remain.

The reactions that take place may be expressed by the following equations:

$$NH_4OH + H^{\cdot} = NH_4^{\cdot} + H_2O$$

and

$$NH_3 + H^{\cdot} = NH_4^{\cdot}$$

136. Ammonium Salts. If neutralized ammonia solutions are evaporated, the ammonium ions combine with the anions of the acids used, to form solid crystalline substances with ionic lattices and all the properties of typical salts. They are called ammonium salts.

Ammonium salts can be formed not only by neutralizing aqueous ammonia solutions, but also by direct union between gaseous ammonia and anhydrous acids.

For example:

$$NH_3 + HCl = NH_4Cl + 42 \text{ Cal.}$$

That is why in the laboratory, where the air always contains gaseous ammonia and acid vapours, the glass panes of hoods, windows, reagent bottles and other objects often become coated with a white layer of ammonium salts.

Ammonium salts greatly resemble the salts of the alkali metals, especially those of potassium, as K^+ ions and NH_4^+ ions have approximately equal radii. Ammonium salts dissolve readily in water, dissociating completely into ions. Solutions of ammonium salts of strong acids react slightly acid, owing to hydrolysis.

Numerous attempts to isolate ammonium in the free state from its salts, i.e., to obtain a substance consisting of electrically neutral NH_4 molecules, have been unsuccessful, as at the moment of formation ammonium immediately decomposes into ammonia and hydrogen. Free ammonium should have possessed the properties of a metal. An indirect indication of its metallic character is the existence of ammonium amalgams, alloys of ammonium and mercury, which are very much like the amalgams of the alkali metals.

To prepare ammonium amalgam an amalgam of sodium is first prepared by adding metallic sodium to mercury in small portions until a semi-liquid mass results. If a saturated solution of ammonium chloride is added to the sodium amalgam prepared in this way, the ammonium and sodium change places and the result is a very voluminous ammonium amalgam which is oily to the touch. Ammonium amalgam is very unstable and can be kept only at low temperatures. If ammonium amalgam is brought into contact with a cold $CuSO_4$ solution, the ammonium displaces part of the copper from the $CuSO_4$, forming $(NH_4)_2SO_4$:

$$2NH_4 + CuSO_4 = Cu + (NH_4)_2SO_4$$

At ordinary temperatures ammonium amalgam decomposes rapidly into mercury, ammonia and hydrogen.

A characteristic feature is the attitude of ammonium salts to the alkalis.

If an aqueous solution of any ammonium salt is treated with an alkali the following reaction takes place:

$$NH_4^+ + OH' \rightleftarrows NH_3 + H_2O$$

If the solution is heated ammonia is given off and can easily be detected by its odour and by means of a moistened piece of litmus paper which changes its colour. Thus, the presence of any ammonium salt in solution can be detected by heating the solution with an alkali (test for ammonium-ion).

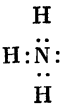
When heated, dry ammonium salts dissociate quite readily into ammonia and an acid. For instance:

$$NH_4Cl \rightleftarrows NH_3 + HCl$$

If the acid forming the salt is volatile, as in the above case, it comes off together with the ammonia and recombines with it upon cooling to form with the salt again. For example, if dry ammonium chloride is heated in a test tube the salt apparently sublimes, forming a white deposit on the cold walls of the test tube.

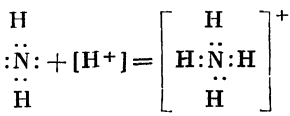
But if the acid is not volatile, only ammonia comes off, the acid remaining in the vessel in which the salt was heated. Examples of this are the heating of $(NH_4)_2SO_4$, $(NH_4)_3PO_4$, etc.

The formation of ammonium ions in the reactions between ammonia and water and between ammonia and solutions of acids is due to the structure of the ammonia molecule, which can be represented as follows:

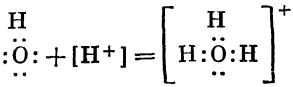


It can be seen from this formula that besides the three electrons forming pairs with the hydrogen electrons, nitrogen has one more "free" electron pair left. The addition of a hydrogen ion to the nitrogen takes place at the expense of this pair, after which both electrons become common to nitrogen and hydrogen.

If the hydrogen ion, which does not contain a single electron, is represented by $[H]^+$, the above can be expressed by the following scheme:



This is analogous to the formation of an oxonium ion from a molecule of water and a $[H]^+$ ion:



137. Uses of Ammonia and Ammonium Salts. Ammonia and ammonium salts are widely used in practice. As has been stated, ammonia can easily be liquefied, and the boiling point of the liquid is about —33° C. At ordinary temperatures ammonia can be liquefied at a pressure of only 7 to 8 atm. Since the evaporation of liquid ammonia involves the absorption of a large amount of heat (327 Cal. per gr.), liquid ammonia has found wide application in refrigeration engineering for cooling storehouses and storerooms in which perishables are kept, as well as for the preparation of artificial ice.

Fig. 94 is a diagram of a refrigerator used for artificial cooling. Compressor *1* compresses the ammonia under its piston to 9 atm. The compressed ammonia passes through valve *2* at the top into coil *3* cooled by running water. Here the ammonia condenses into a liquid and through cock *4* passes into a long coil *5* inside vessel *6* containing a concentrated salt solution. Due to the large volume of coil *5* the liquid ammonia evaporates rapidly, removing heat from the salt solution. The evaporated ammonia is then drawn back into the compressor through valve *7* which opens only upwards, and thus keeps

going through a continuous cycle. If metal boxes filled with water are lowered into vessel *6*, the water will freeze into bars of ice. If the salt solution cooled in vessel *6* is circulated through pipes laid in storerooms where products are kept, the low temperature required can be maintained in those rooms.

Aqueous ammonium solutions are used in chemical laboratories and plants as a weak volatile base; they find application also in medicine and in the home. But most of the ammonia produced commercially at present is employed for the preparation of nitric acid and artificial nitrogenous fertilizers.

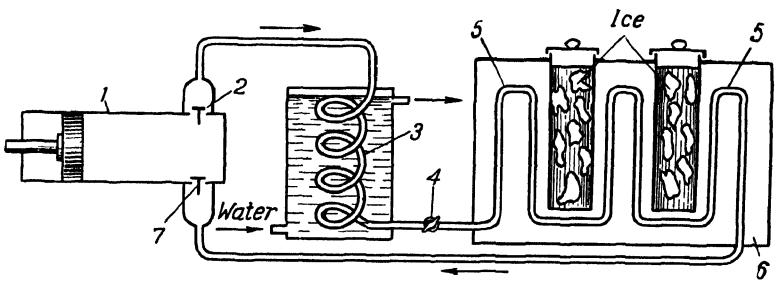


Fig. 94. Diagram of refrigerator:
1—compressor *2* and *7*—valves; *3*—ammonia condensation coil; *4*—cock; *5*—ammonia evaporation coil; *6*—vessel containing concentrated salt solution

A very important ammonium salt is *ammonium sulphate* $(NH_4)_2SO_4$. It is a good fertilizer and is manufactured in immense quantities as such. Of even greater importance is *ammonium nitrate* NH_4NO_3, a fertilizer which can be made entirely from air and water. *Ammonium chloride* or *sal ammoniac* NH_4Cl is used in the dyeing industry, in textile printing, in soldering and tin plating, as well as in galvanic cells. The action of ammonium chloride in soldering is based on the fact that when it comes into contact with the hot metals it decomposes into ammonia and hydrogen chloride. The latter dissolves metal oxides forming volatile chlorides, and thus cleans the metal surface, enabling the solder to adhere well.

138. Preparation of Ammonia. Up to the end of the last century ammonia was prepared commercially only as a by-product of the carbonization of coal. Coal contains between 1 and 2 per cent nitrogen. During the dry distillation of coal almost all this nitrogen escapes as ammonia and ammonium salts. The latter are separated from the other gaseous dry distillation products by passing the coke-oven gas through water. Ammonia is liberated from this *ammonia* (or *gas*) *liquor* by heating with lime. The ammonia thus produced is passed into sulphuric acid with which it forms ammonium sulphate

$(NH_4)_2SO_4$. To produce pure ammonia the ammonium sulphate is heated with lime.

For a long time ammonia liquor was the only source of ammonia. But in the early XX century several new methods were discovered for the commercial production of ammonia, based on the binding or fixation, as it is called, of atmospheric nitrogen. To evaluate the immense importance of these discoveries for mankind, we must first get a clear idea of the role of nitrogen in vital processes.

As was stated above, nitrogen is an obligatory constituent of proteins, and as such is indispensable for the nourishment of any living creature. However, in spite of the immense, practically inexhaustible supply of free nitrogen in the atmosphere, neither animals nor plants (with very few exceptions) can make any direct use of this nitrogen for nourishment.

Plants get their nitrogen from the soil, where it is contained mainly as various organic compounds which gradually change into nitrates and ammonium salts. Dissolved in soil waters, these salts are drawn up by the roots of plants and transformed in their cells into proteins and other complex nitrogen compounds.

Animals cannot assimilate nitrogen even in the form of salts. They need for their nourishment the proteins produced by plants or other animals. Proteins cannot be substituted by any other compounds. That is why the existence of animals depends entirely on plants; they can obtain the nitrogen they need only through plants.

The soil usually contains very insignificant quantities of nitrogen which is continuously being extracted from it by plants. When crops are harvested the nitrogen extracted by the plants from the soil goes with the crop. Thus, the soil is rapidly exhausted and becomes less and less fertile. Therefore, to obtain good crops the deficiency of nitrogen must be continually replenished by adding nitrogen compounds to the soil in the form of various fertilizers.

Before World I War (1914-18) the chief nitrogenous fertilizer was sodium nitrate (Chile saltpetre), imported to Europe from South America. It was also the only raw material for the manufacture of the nitric acid required for the production of explosives and other nitrogen compounds.

The limited supplies of natural saltpetre, their remoteness from the chief consumers and mainly the tendency to relieve the necessity of importing raw materials, confronted the chemical industry of many countries with the problem of utilizing atmospheric nitrogen for the preparation of nitrogen compounds. The successful solution of this problem was one of the greatest victories scored by chemistry in the early XX century. In the course of a single decade not one, but several technical methods of "binding" atmospheric nitrogen were

invented. Two of these methods, which are at the same time methods of production of ammonia, are examined below.

The first discovery (1904) was the *cyanamide process for the production of ammonia*, based on the ability of nitrogen to combine directly with calcium carbide CaC_2.

Calcium carbide is produced by heating a mixture of quicklime with coal in an electric furnace. At a high temperature calcium carbide reacts with nitrogen to form a solid called *calcium cyanamide* $CaCN_2$ and free carbon.

The reaction proceeds according to the equation

$$CaC_2 + N_2 = CaCN_2 + C + 69.2 \text{ Cal.}$$

The reaction is accomplished by passing a stream of nitrogen through the calcium carbide, which is heated at one point. The nitrogen begins to combine at this point liberating a large amount of heat. The heat raises the temperature of the surrounding mass of carbide, and the nitrogen continues to combine until all the carbide is used up.

The calcium cyanamide obtained in this way is a dark grey powder, its colour being due to the presence of carbon. If treated with steam at a temperature of 110 to 115° C and a pressure of about 6 atm. calcium cyanamide decomposes readily into ammonia and calcium carbonate:

$$CaCN_2 + 3H_2O = CaCO_3 + 2NH_3 + 18 \text{ Cal.}$$

The first calcium cyanamide plant with a capacity of 4,000 tons per year was built in 1906 in Italy. By 1921 the world production of calcium cyanamide had reached 500,000 tons yearly. But after this the erection of new plants stopped almost entirely, as another method for the commercial production of ammonia took the upper hand. This was the *direct synthesis of ammonia from hydrogen and nitrogen** suggested by F. Haber in 1908.

At ordinary temperatures nitrogen will not combine with hydrogen. But it has long been known that if electric sparks are passed through a mixture of these gases a small quantity of ammonia forms. A detailed study of this reaction showed that the sparks cause not only the formation of ammonia, but its decomposition back into nitrogen and hydrogen as well. Thus, the reaction between nitrogen and hydrogen is reversible and leads to a state of equilibrium:

$$N_2 + 3H_2 \rightleftarrows 2NH_3$$

---

* At present the greater part of the calcium cyanamide produced is used directly as a nitrogenous fertilizer suitable for many crops, mainly on podzol soil. Some calcium cyanamide is used for the manufacture of urea and cyanide compounds.

At the high temperature caused by the electric sparks the equilibrium is displaced greatly to the left, so that the quantity of ammonia produced is very small. For a long time all attempts to increase the ammonia yield were unsuccessful. Only in the beginning of the present century, after long, painstaking work, were conditions at last found, under which the ammonia yield becomes high enough to warrant carrying out the reaction on a plant scale. One of the chief conditions for this reaction was found to be high pressure. Indeed, it can be seen from the above equation that the formation of ammonia leads to a decrease in the volume of the nitrogen-hydrogen mixture; therefore, according to Le Châtelier's Principle, increasing the pressure should favour the formation of ammonia. This was borne out by experiment.

On the other hand, it was found that the combination of nitrogen and hydrogen is accompanied by the liberation of heat:

$$N_2 + 3H_2 \rightleftarrows 2NH_3 + 22 \text{ Cal.}$$

Hence, the higher the temperature, the lower the ammonia yield. Therefore the reaction must be carried out at as low a temperature as possible. But at low temperatures the reaction rate is so low that it would take too long to obtain appreciable quantities of ammonia. The reaction was finally accelerated by the use of catalysts. Of the various metals and their oxides, the most suitable catalyst proved to be metallic iron (in the form of a spongy mass) with insignificant admixtures of aluminium and potassium compounds.

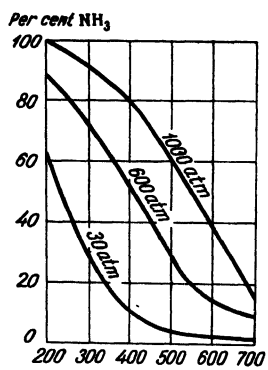


Fig. 95. Dependence of ammonia yield on temperature and pressure

In practice the reaction is accomplished at a temperature of about 500° C, compensating the consequent shift of equilibrium to the left by high pressure. Fig. 95 is a graphic illustration of how the amount of ammonia at equilibrium changes depending on the temperature and pressure. Examining the curves presented in the figure, we find that the same yield of ammonia can be obtained both at low and at higher temperatures, if the pressure is raised accordingly.*

A diagram of synthetic ammonia plant is shown in Fig. 96. The mixture, consisting of one volume of nitrogen and three of hydrogen, is compressed by means of compressor *1* to 200 or 300 atm. (in some plants to 1,000 atm.) and after passing through a filter (not shown in the diagram) to purify the gases, passes into synthesis column *2*,

* At a pressure of 4,000 to 5,000 atm. the synthesis of ammonia takes place with a yield of 100 per cent in the absence of any catalyst.

holding the catalyst, where the formation of ammonia takes place. Before starting up the whole system, the synthesis column is heated internally by an electric current to 500 or 550° C. This temperature is sustained afterwards automatically, at the expense of the heat given off during the reaction. After passing over the catalyst, the gases, which now contain up to 20 per cent ammonia, enter cooler *3* where the gaseous ammonia liquefies due to the high pressure.

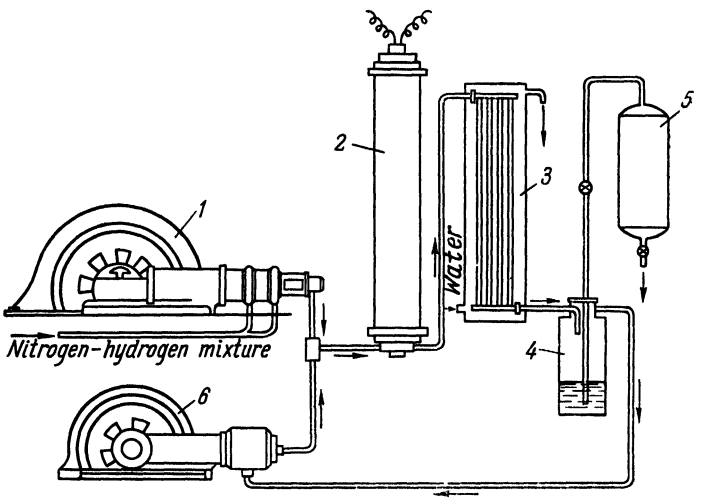


Fig. 96. Diagram of synthetic ammonia plant:
1—compressor; *2*—synthesis column; *3*—cooler; *4*—separator; *5*—liquid ammonia collector; *6*—circulation pump

Then the liquid ammonia is removed from the unchanged nitrogen and hydrogen in separator *4*. From here the ammonia is transferred by batches into low-pressure collector *5*, from which it goes to storage. The residual gases are drawn out of the separator by circulation pump *6*, mixed with a new portion of the nitrogen-hydrogen mixture discharged by compressor *1*, and pass back into synthesis column *2*. Thus, a certain amount of nitrogen-hydrogen mixture keeps circulating continuously through the system.

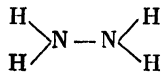
Various types of synthetic ammonia plants are employed in industry, using different methods for preparing the nitrogen-hydrogen mixture, instruments of various designs, different catalytic compositions, different pressures, etc.

At present the synthesis of ammonia is the principal method of binding atmospheric nitrogen. The chief advantage of this method over all others is its comparative cheapness.

139. Hydrazine N_2H_4. Hydrazoic Acid HN_3. Nitrogen forms two more compounds with hydrogen, much inferior in importance, however, to ammonia

Hydrazine N_2H_4 is a colourless liquid boiling at 113.5° C, prepared by the action of NaClO on a concentrated ammonia solution.

The structural formula of hydrazine is



With water hydrazine forms a stable hydrate $(N_2H_5)OH$ which possesses slightly basic properties and forms salts resembling those of ammonium, such as hydrazine hydrochloride N_2H_5Cl, etc. Hydrazine is used as an active reducing agent.

Hydrazoic acid HN_3 can be prepared by the action of nitric acid HNO_3 on an aqueous solution of hydrazine; it is a colourless liquid with a pungent odour and a boiling point of 36° C.

Hydrazoic acid is classed as a weak acid ($K = 3 \times 10^{-5}$). In aqueous solution it dissociates into H^+-ion and N_3^--ion. Its salts, called **azides**, are, like the acid itself, very explosive.

Lead azide $Pb(N_3)_2$ is used to fill detonating fuses.

140. Oxides of Nitrogen. Nitrogen forms six oxides, namely: nitrous oxide N_2O, nitric oxide NO, nitrogen dioxide NO_2, nitrogen tetroxide N_2O_4; nitrogen trioxide N_2O_3 and nitrogen pentoxide N_2O_5. They can all be obtained from nitric acid and its salts.

Nitrous oxide N_2O is prepared by heating ammonium nitrate:

$$NH_4NO_3 = N_2O + 2H_2O$$

In this reaction one of the nitrogen atoms of NH_4NO_3 loses electrons and the other gains them, both of them becoming positively univalent.

$$\left|\begin{array}{l} \overset{-III}{N} - 4e^- = \overset{+I}{N} \\ \overset{+V}{N} + 4e^- = \overset{+I}{N} \end{array}\right.$$

Nitrous oxide is a colourless, odourless gas which liquefies at 0° C under a pressure of 30 atm. It is rather soluble in water: at 0°C one volume of water will dissolve 1.3, and at 25° C, 0.6 volumes of N_2O. Upon dissolving nitrous oxide does not combine with the water.

Nitrous oxide is an endothermal compound, easily decomposed by heat into nitrogen and oxygen:

$$2N_2O = 2N_2 + O_2 + 17.7 \text{ Cal.}$$

therefore it supports combustion well. A glowing splint lowered into nitrous oxide bursts into flame, like in pure oxygen; phosphorus, sulphur and other substances also burn vigorously in nitrous oxide, liberating nitrogen.

Inhalation of small quantities of nitrous oxide deadens pain, so that the gas is sometimes used in mixture with oxygen as an anaesthetic during light operations. Large quantities of nitrous oxide excite the nervous system, for which reason it was formerly called "laughing gas".

Nitric Oxide NO. Under ordinary conditions nitrogen and oxygen will not react with one another. But at very high temperatures, for instance, when electric sparks are passed through air, nitrogen is capable of combining directly with oxygen to form nitric oxide. That is why nitric oxide always forms in the atmosphere during thunderstorms.

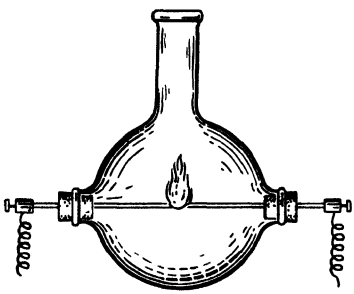


Fig. 97. Apparatus for demonstrating combustion of nitrogen in oxygen

The formation of nitric oxide by an electrical discharge can be illustrated by the following experiment. Two thick copper wires are passed through stoppers in the side necks of a large flask (Fig. 97) and connected to the poles of a large induction coil. When current is passed through the coil a continuous spark appears between the ends of the wire and above it there appears a yellowish flame of nitrogen "burning" in oxygen.

The reaction of formation of nitric oxide from nitrogen and oxygen is reversible and is accompanied by the absorption of a large quantity of heat:

$$N_2 + O_2 \rightleftarrows 2NO - 43.2 \text{ Cal.}$$

At low temperatures the equilibrium of this reaction is practically shifted completely to the left, that is, the amount of nitric oxide formed is infinitesimal. As the temperature rises the equilibrium begins to shift to the right, but so slowly that even at 1,000° C the gas mixture contains only about 1 per cent nitric oxide. If the temperature is lowered the nitric oxide again decomposes into nitrogen and oxygen, but if the gas mixture is cooled very quickly the equilibrium does not get a chance to shift immediately and does not shift afterwards due to the very slow rate of the reaction at low temperatures, so that almost the entire quantity of NO formed at the high temperature remains in the mixture. The practical application of this reaction will be discussed in § 143.

Nitric oxide is usually prepared in the laboratory by the action of dilute nitric acid on copper:

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O$$

or in the ionic form

$$3Cu + 2NO_3' + 8H^{\cdot} = 3Cu^{\cdot\cdot} + 2NO + 4H_2O$$

Nitric oxide is a colourless gas, very difficult to condense. Liquid nitric oxide boils at —151.8° C and solidifies at —163.7° C. It is slightly soluble in water: one volume of water will dissolve only 0.07 volume of NO at 0° C.

As to chemical properties, nitric oxide is classed as an indifferent oxide, since it forms no acid.

Nitric oxide loses its oxygen with greater difficulty than the other oxides of nitrogen. That is why the only substances that can burn in it are those capable of combining vigorously with oxygen, such as phosphorus. But a burning candle, splint or piece of sulphur are extinguished if lowered into nitric oxide.

The most characteristic property of nitric oxide is its ability to combine with oxygen very readily, without being heated, giving brown nitrogen dioxide:

$$2NO + O_2 = 2NO_2 + 27 \text{ Cal.}$$

If, for instance, a cylinder filled with nitric oxide is opened, a brown cloud of nitrogen dioxide immediately appears at its mouth.

Nitrogen dioxide is a brown poisonous gas with a characteristic odour. It can easily be condensed into a reddish liquid (b.p. 21.3°C), the shade of which gradually becomes lighter as it is cooled. At —10° C it freezes into a colourless crystalline mass. On the other hand, when heated, gaseous nitrogen dioxide grows darker and at 140° becomes almost black. The change in colour of nitrogen dioxide with rising temperature is accompanied by a change in the density of its vapours. At a low temperature the vapour density corresponds approximately to the double formula N_2O_4. As the temperature rises the vapour density decreases and at 140° exactly corresponds to the formula NO_2. Hence it follows that the colourless crystals existing at —10° and lower probably consist entirely of N_2O_4 molecules and may be called nitrogen *tetroxide*. When heated, the colourless nitrogen tetroxide gradually dissociates to form molecules of dark brown nitrogen dioxide NO_2; complete dissociation occurs at 140° C. Therefore, at temperatures between —10 and +140° this substance is always a mixture of NO_2 and N_2O_4 molecules in equilibrium with each other:

$$\underset{\substack{100 \text{ p. c.} \\ \text{at } -10°C}}{N_2O_4} \rightleftarrows \underset{\substack{100 \text{ p. c.} \\ \text{at } +140°C}}{2NO_2} - 13.6 \text{ Cal.}$$

Above 140° NO_2 begins to dissociate into NO and oxygen.

Nitric dioxide is a very active oxidant. Many substances can burn in nitrogen dioxide, abstracting oxygen from it. Sulphur dioxide is

oxidized by it into sulphuric anhydride, this being the basic principle of the lead-chamber process for the manufacture of sulphuric acid (see § 128).

Nitrogen dioxide vapours are quite poisonous. Inhaling them irritates the respiratory tract badly and may lead to serious poisoning.

When dissolved in water nitrogen dioxide, or rather tetroxide, reacts with the water to form nitric and nitrous acids:

$$N_2O_4 + H_2O = HNO_3 + HNO_2$$

But nitrous acid is very unstable and decomposes rapidly into nitric acid, nitric oxide and water:

$$3HNO_2 = HNO_3 + 2NO + H_2O$$

Therefore, practically the reaction between nitrogen dioxide (tetroxide) and water, especially warm water, proceeds according to the equation

$$3N_2O_4 + 2H_2O = 4HNO_3 + 2NO$$

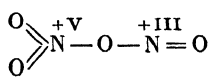
which can easily be obtained by multiplying the first of the two foregoing equations by 3 and adding the second to it.

The oxygen of the air immediately oxidizes the nitric oxide thus formed into nitrogen dioxide, so that in the presence of air the NO_2 changes completely into nitric acid. This reaction is of very great technical importance and is utilized in modern processes for the production of nitric acid.

If nitrogen dioxide (tetroxide) is dissolved in alkalis, a mixture of nitrates and nitrites results:

$$N_2O_4 + 2NaOH = NaNO_3 + NaNO_2 + H_2O$$

The above reactions of nitrogen tetroxide with water and with alkalis show that the valency of one of the nitrogen atoms in its molecule is +5, and that of the other +3. Thus, nitrogen tetroxide may be regarded as a mixed anhydride of nitrous and nitric acids, its structural formula being written as follows:



If we count up the total number of valency electrons of all the atoms in the molecules NO and NO_2, we find that it equals respectively 11(5+6) and 17(5+ +2×6), i. e., is an odd number in both cases. Nitric oxide and nitrogen dioxide belong to the limited number of molecules having an odd number of electrons. Such molecules behave chemically like free atoms, which also contain unpaired electrons. Molecules with unpaired electrons are called **free radicals.**

Nitrogen trioxide or *nitrous anhydride* N_2O_3 is a dark blue liquid boiling at +4° C and decomposing thereupon into nitric oxide and

nitrogen dioxide. A mixture of equal volumes of nitric oxide and nitrogen dioxide forms nitrogen trioxide again when cooled:

$$N_2O_3 \rightleftarrows NO + NO_2$$

Nitrogen trioxide corresponds to nitrous acid.

Nitrogen pentoxide or *nitric anhydride* N_2O_5 is a solid crystalline substance melting at 30° C. It can be obtained by the action of phosphorus pentoxide on nitric acid:

$$2HNO_3 + P_2O_5 = N_2O_5 + 2HPO_3$$

Nitrogen pentoxide is a very active oxidant. Many organic substances burst into flame upon coming into contact with it. Nitrogen pentoxide dissolves readily in water to form nitric acid.

141. Nitrous Acid HNO_2. If potassium or sodium nitrate are heated they lose part of their oxygen and pass into salts of nitrous acid HNO_2. The decomposition takes place more readily in the presence of lead, which binds the oxygen liberated:

$$KNO_3 + Pb = KNO_2 + PbO$$

The salts of nitrous acid, called **nitrites**, are crystalline substances, quite soluble in water (except the silver salt). Sodium nitrite $NaNO_2$ is widely used for the manufacture of various dyes.

If a solution of any nitrite is treated with dilute sulphuric acid the result is free nitrous acid:

$$2NaNO_2 + H_2SO_4 = Na_2SO_4 + 2HNO_2$$

It is classed as a weak acid ($K = 5 \times 10^{-4}$) and is known only in very dilute aqueous solution. If the solution is concentrated or heated the nitrous acid decomposes, forming nitric oxide and nitrogen dioxide:

$$2HNO_2 = NO + NO_2 + H_2O$$

Nitrous acid is an active oxidizing agent, but at the same time, under the action of other more active oxidants, can itself be oxidized into nitric acid.

142. Nitric Acid. Pure nitric acid is a colourless liquid with a specific gravity of 1.53, boiling at 86°C and freezing at —41°C into a transparent crystalline mass. In the air it "fumes", like concentrated hydrochloric acid, as its vapours form minute mist drops with the moisture of the air.

Nitric acid is miscible with water in all proportions. A 68 per cent solution boils at 120.5°C and can be distilled without alteration. This is the composition of the usual nitric acid of commerce, which has a specific gravity of 1.4. The concentrated acid, containing 96 to 98 per cent HNO_3, and coloured reddish-brown due to the nitrogen dioxide dissolved in it, is known as *fuming* nitric acid.

Nitric acid is chemically not very stable. Under the influence even of light it decomposes gradually into water, oxygen and nitrogen dioxide:

$$4HNO_3 = 2H_2O + 4NO_2 + O_2$$

The higher the temperature and the more concentrated the acid, the more rapidly it decomposes. That is why nitric acid prepared from saltpetre is always yellowish in colour, due to the presence of nitrogen dioxide. To avoid decomposition, the acid is distilled under a pressure low enough for the nitric acid to boil at a temperature of about 20°C.



Fig. 98. Ignition of turpentine in nitric acid

Nitric acid is one of the strongest acids; in dilute solution it is dissociated completely into H^+- and NO_3^--ion.

The most characteristic property of nitric acid is its pronounced oxidizing capacity. *Nitric acid is one of the most powerful oxidants.* Many non-metals are oxidized readily by it into the corresponding acids. For instance, if sulphur is boiled with nitric acid, it gradually oxidizes into sulphuric acid, phosphorus into phosphoric acid, etc. A glowing coal lowered into nitric acid not only fails to extinguish but, on the contrary, begins to burn brightly, decomposing the acid into reddish-brown nitrogen dioxide.

Sometimes so much heat is liberated during oxidation that the substance oxidized ignites spontaneously without having to be preheated.

For instance, pour a little fuming nitric acid into an evaporating dish, put the dish on the bottom of a wide beaker and add some turpentine from a pipette, drop by drop, to the acid in the dish. As each drop falls into the acid it ignites and burns with a large flame, forming a cloud of soot (Fig. 98). Heated sawdust can also be ignited with a drop of fuming nitric acid. Nitric acid attacks almost all the metals except gold, platinum and a few rare metals, converting them into nitrates. As the latter are soluble in water, nitric acid is constantly used in practice to dissolve metals, especially such as copper, silver, lead which are not attacked or are attacked very feebly by other acids.

It is noteworthy that some metals (iron, aluminium, etc.), which dissolve readily in dilute nitric acid, will not dissolve in cold con-

centrated nitric acid, as was discovered by Lomonosov. This is apparently due to the formation of a thin, very dense film of oxide on their surface, protecting the metal from the further action of the acid. After treatment with concentrated nitric acid such metals become "passive", i.e., lose their capacity for dissolving in dilute acids as well.

The oxidizing properties of nitric acid are due to the instability of its molecules and the presence of nitrogen in its highest state of oxidation, corresponding to a positive valency of 5. When oxidizing, nitric acid is reduced successively into the following compounds:

$$\overset{+V}{HNO_3} \rightarrow \overset{+IV}{NO_2} \rightarrow \overset{+III}{HNO_2} \rightarrow \overset{+II}{NO} \rightarrow \overset{+I}{N_2O} \rightarrow \overset{0}{N_2} \rightarrow \overset{-III}{NH_3}$$

The degree of reduction of nitric acid depends both on its concentration and on the activity of the reductant. The more dilute the acid, the greater it is reduced. Concentrated nitric acid is always reduced to NO_2. Dilute nitric acid reduces usually to NO, or, under the action of the more active metals, such as Fe, Zn, Mg, to N_2O. But if the acid is very dilute the chief reduction product is NH_3, which forms ammonium nitrate NH_4NO_3 with the excess acid.

By way of illustration the equations (unbalanced) of several oxidation reactions involving nitric acid are given below:

1) $Pb + \underset{\text{conc.}}{HNO_3} \rightarrow Pb(NO_3)_2 + NO_2 + H_2O$

2) $Cu + \underset{\text{dil.}}{HNO_3} \rightarrow Cu(NO_3)_2 + NO + H_2O$

3) $Mg + \underset{\text{dil.}}{HNO_3} \rightarrow Mg(NO_3)_2 + N_2O + H_2O$

4) $Zn + \underset{\text{very dil.}}{HNO_3} \rightarrow Zn(NO_3)_2 + NH_4NO_3 + H_2O$

We leave it to the student to balance the equations of these reactions.

It should be noted that *the action of dilute nitric acid on metals does not, as a rule, lead to the liberation of hydrogen.*

When oxidizing non-metals, nitric acid is usually reduced to NO. For example:

$$S + 2HNO_3 = H_2SO_4 + 2NO$$

The above equations illustrate the most typical cases of the oxidizing action of nitric acid. Generally, however, it should be noted that all oxidation reactions involving nitric acid are very complex, due to the simultaneous formation of various reduction products, and cannot be considered quite clear as yet.

A mixture consisting of one volume of nitric and three volumes of hydrochloric acids is called *aqua regia.* Aqua regia dissolves certain metals which do not dissolve in nitric acid, including gold, the "king

of metals." Its action is due to the fact that nitric acid oxidizes hydrochloric acid, liberating free chlorine and forming *nitrosyl chloride* NOCl:

$$\overset{+V}{HNO_3} + 3HCl = Cl_2 + 2H_2O + \overset{+III}{NOCl}$$

Nitrosyl chloride is an intermediate reaction product and decomposes into nitric oxide and chlorine:

$$2NOCl = 2NO + Cl_2$$

The chlorine liberated combines with the metals forming metal chlorides, and therefore, when metals are dissolved in aqua regia they are converted to chlorides, and not nitrates:

$$Au + 3HCl + HNO_3 = AuCl_3 + NO + 2H_2O$$

Nitric acid attacks many organic substances, substituting one or several hydrogen atoms in the molecule of the organic compound by nitro-groups, NO_2. This process, known as *nitration*, is of great importance in organic chemistry.

If nitric acid is treated with phosphorus pentoxide, the latter abstracts the elements of water from the nitric acid, forming nitrogen pentoxide and metaphosphoric acid.

$$2HNO_3 + P_2O_5 = N_2O_5 + 2HPO_3$$

Nitric acid is the most important compound of nitrogen owing to its diverse applications in the national economy.

Nitric acid is used in large quantities for the manufacture of nitrogen fertilizers and organic dyes. It is used as an oxidant in many chemical processes, is employed in the manufacture of sulphuric acid by the lead-chamber process, serves for dissolving metals, for the preparation of nitrates, is used in the manufacture of cellulose varnishes, cinema film and in a number of other chemical processes. Nitric acid is also employed for the production of smokeless gunpowder and explosives used widely in mining and various earth work (construction of canals, dams, etc.), as well as for military purposes.

143. Industrial Preparation of Nitric Acid. Nitric acid can be manufactured by three methods which will be described in the chronological order of their use in industry.

1. *Preparation of Nitric Acid from Chile Saltpetre.* The oldest method of preparation of nitric acid, employed as far back as the middle of the XVII century, consists in heating Chile saltpetre with concentrated sulphuric acid:

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$$

The vapours of nitric acid liberated upon heating are passed into a water-cooled receptacle, where they condense into a liquid. If

gently heated in an excess of sulphuric acid, the reaction leads to the formation of the acid salt. But if saltpetre is taken in sufficient quantity and the mixture is heated more strongly, the normal salt results:

$$2NaNO_3 + H_2SO_4 = Na_2SO_4 + 2HNO_3$$

However, in this case a considerable amount of nitric acid is lost during the reaction due to decomposition. For this reason the process is adjusted to take place according to the first equation.

Up to the beginning of the present century this was the only process used commercially for the manufacture of nitric acid. It has since been almost completely replaced by other methods based on the fixation of atmospheric nitrogen.

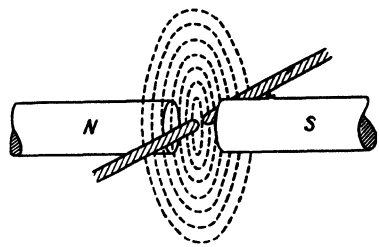


Fig. 99. Electric arc in magnetic field

2. *Production of Nitric Acid from Air by the Arc Method.* This method, suggested by Birkeland and Eyde, and first employed industrially in Norway in 1905, is based on the direct union of nitrogen with oxygen, as described in § 140. The high temperature required for this reaction is obtained by means of an electric arc fed by a powerful source of electric current. If the flame of the electric arc is brought between the two poles of a strong electromagnet (Fig. 99) it becomes disc-shaped, greatly increasing the surface of the flame. Such a fiery disc, up to three metres in diameter, is struck in a special furnace, built of refractory brick, in which the temperature rises as high as 3,000 or 3,500°C. Air is blown into the furnace through channels in its walls. Coming into contact with the flame of the electric arc, the air is strongly heated and part of it combines into nitric oxide.

The gases discharged from the furnace, containing 2 to 3 per cent nitric oxide, are cooled rapidly to 1,000 or 1,100° C to keep the nitric oxide formed from decomposing back into nitrogen and oxygen. When the gas mixture is further cooled, the nitric oxide combines with oxygen to form nitrogen dioxide, which is absorbed by water and changes into nitric acid.

The manufacture of nitric acid by the above method requires a great amount of electric power, and it developed mostly in Norway, which possesses vast resources of cheap electric power. By 1925 the world production of nitrogen compounds by the arc process had reached 42,000 tons per year (recalculated for nitrogen). Lately, however, the arc process has been employed on a considerably smaller

scale, as it was found that nitric acid could be manufactured more economically by the oxidation of synthetic ammonia.

3. *Production of Nitric Acid by Oxidation of Ammonia.* The most important method of nitric acid production nowadays is the catalytic oxidation of ammonia by the oxygen of the air. It was indicated, when describing the properties of ammonia (see p. 372), that the latter burns in oxygen, forming water and free nitrogen. But in the presence of catalysts the oxidation of ammonia may take a different course. If, for instance, a mixture of ammonia and air in definite proportions is passed through a red-hot platinum wire gauze, which serves as a catalyst, at 750°C the ammonia is transformed almost quantitatively into nitric oxide:

$$4NH_3 + 5O_2 = 4NO + 6H_2O + 215.8 \text{ Cal.}$$

The nitric oxide is easily transformed into nitrogen dioxide which combines with water to form nitric acid.

The catalytic oxidation of ammonia into nitric acid has been known for a long time, but only in the early XX century was this process used successfully for the commercial production of nitric acid. In early apparatuses for the oxidation of ammonia the catalyst was platinum. At present an alloy of platinum and rhodium containing five to ten per cent rhodium is used more often. The yield of nitric oxide is 96 to 98 per cent.

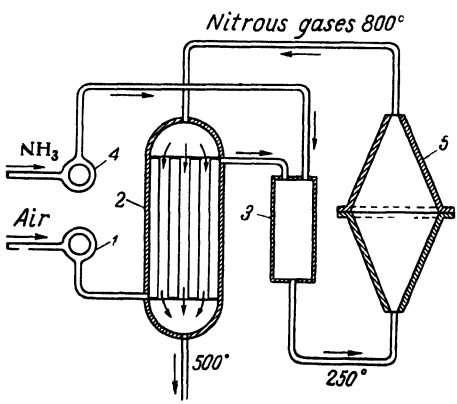


Fig. 100. Diagram of ammonia oxidation plant:
1 and *4*—fans; *2*—heat exchanger; *3*—mixer; *5*—contact apparatus

Fig. 100 is a diagram of an ammonia oxidation plant operated at atmospheric pressure. Air, freed by filtration from mechanical impurities, is blown by means of fan *1* into heat exchanger *2* where it is heated by the gases discharged from the contact apparatus to a temperature of about 300°C, after which it passes into mixer *3*. Fan *4* blows gaseous ammonia into the same mixer. From here the ammonia-air mixture, containing 10 to 11 per cent ammonia, enters contact apparatus *5*, consisting of two hollow cones placed base to base. Several screens of thin platinum-rhodium wire, used as the catalyst, are fixed horizontally in the wide part of the apparatus. In the contact apparatus the ammonium is oxidized into nitric oxide. The hot gas

mixture discharged from the contact apparatus goes through the heat exchanger, where it is cooled to 500-550°C, and then passes consecutively through a steam boiler (to utilize the heat), special coolers and, finally, absorption towers, in which mainly the nitric oxide is oxidized into nitrogen dioxide, and the nitric acid is formed.

The acid obtained in the towers usually contains about 50 to 55 per cent HNO_3. It is concentrated by distillation with sulphuric acid, which serves as a means of holding back the water. Besides, a method has been developed lately for the manufacture of concentrated nitric acid by the reaction between liquid nitrogen dioxide and water (or dilute nitric acid) in the presence of oxygen at 50 atm. pressure and a temperature of 75°C. The reaction proceeds according to the following summary equation:

$$2N_2O_4 + O_2 + 2H_2O = 4HNO_3 + 14.2 \text{ Cal.}$$

By this method, called "direct synthesis", 98 per cent nitric acid is obtained directly.

At present most of the vast quantities of nitric acid produced is obtained by the oxidation of ammonia. And since most of the ammonia is prepared by synthesis from the elements, this method in the long run, like the previous one, is based on the fixation of atmospheric nitrogen.

The founder of the Russian home manufacture of synthetic nitric acid was I. Andreyev, an engineer, who in 1914 first raised the question of the organization in Russia of nitric acid production by the oxidation of ammonia obtained during the carbonization of coal. Andreyev made a thorough study of the oxidation of ammonia over catalysts prepared under his supervision, and built a pilot plant. The experimental data obtained at this plant were used in designing the first Russian synthetic nitric acid plant which was started up in July 1917. The experience gained at that plant was widely used by Soviet engineers in designing new plants built during the years of the first five-year plans.

144. Salts of Nitric Acid. The salts of nitric acid are known under the generic name of **nitrates**. They are usually obtained by the action of nitric acid on the corresponding metals or metal oxides.

Nitrates are very soluble in water. When heated dry all nitrates decompose, liberating oxygen, the nitrates of the most active metals splitting off only part of the oxygen and passing into **nitrites**, salts of nitrous acid:

$$2KNO_3 = 2KNO_2 + O_2$$

But the nitrates of the majority of other metals decompose into the metal oxide, oxygen and nitrogen dioxide. For example:

$$2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2$$

Splitting off oxygen readily, nitrates are very powerful oxidants at high temperatures. On the other hand, their aqueous solutions are almost devoid of oxidizing properties. The most important are the nitrates of sodium, potassium, ammonium and calcium, which are sometimes known by the common name of **nitres.**

Sodium nitrate or *sodium nitre* $NaNO_3$, known also as *Chile saltpetre*, occurs in large quantities in nature only at one point of the globe, in the Republic of Chile, whence it received its name.

Potassium nitrate or *potassium nitre* KNO_3, known also as *saltpetre*, found in nature in minor quantities, is mostly prepared artificially by the exchange reaction between sodium nitrate and potassium chloride.

Potassium nitrate is used for the manufacture of *black gunpowder*, which is a specially treated mixture of saltpetre, sulphur and charcoal. It usually contains 75 per cent saltpetre, 10 per cent sulphur and 15 per cent charcoal.

The combustion of gunpowder is a complicated process involving several reactions. The gases formed during this process, of which the most important are nitrogen, carbon dioxide and carbon monoxide, occupy a volume approximately 2 thousand times as large as that of the powder burnt, which accounts for its explosive power. Besides gaseous substances, the combustion of gunpowder results in solid substances, namely, K_2CO_3, K_2SO_4, K_2S, etc., which form smoke and leave a deposit in the gun barrel. Under the action of the moisture of the air K_2S decomposes partly, liberating hydrogen sulphide. That is why the odour of hydrogen sulphide can always be detected coming out of the muzzle of a gun after using black gunpowder. Sodium nitrate is not used to prepare gunpowder as it is very hygroscopic.

Ammonium nitrate or *ammonium nitre* NH_4NO_3 is prepared by neutralizing nitric acid with ammonia. Is used as a fertilizer. Forms explosive mixtures, known as *ammonals*, with various combustible substances. Ammonals are used extensively for industrial blasting.

Calcium nitrate or *calcium nitre* $Ca(NO_3)_2$ has been manufactured in large quantities since the beginning of the present century by neutralizing nitric acid with lime; is used as a fertilizer.

145. Development of the Nitrogen Industry in the U.S.S.R. The nitrogen industry embraces chiefly the production of ammonia, nitric acid and nitrogenous fertilizers. Its development in the U.S.S.R. was initiated in 1927 by the start-up of the first synthetic ammonia plant in the Soviet Union at the Chernorechensk Chemical Mill. Although the technology of ammonia production at this mill was far from perfect and the capacity of the plant not large, the Chernorechensk Mill played an important role in the founding of the Soviet nitrogen industry, as a school for mastering the new complex process of ammonia synthesis under high pressure.

During the years of the First and Second Five-Year Plans, several plants were built in which the synthesis of ammonium was combined with the manufacture of nitric acid and nitrogenous fertilizers. Such chemical industry giants as the Berezniki, Novomoskovsk, Chirchik and other nitrogenous fertilizer combines put into operation during this period, were not inferior technically to analogous plants in foreign countries. The entire complex equipment of these plants, including gas compressors, circulation pumps, ammonia synthesis columns and other apparatuses working under high pressure, was manufactured at Soviet machine-building plants and designed by Soviet engineers.

Extensive research work carried out in the U.S.S.R. brought a number of important improvements in the technology and equipment of nitrogen plants. New catalytic compositions were developed both for the synthesis of ammonia and for its oxidation into nitric acid. The management and operating personnel of nitrogen plants have made great progress by way of intensifying production processes, particularly by the use of oxygen for oxidizing ammonia into nitric acid. Methods of production of concentrated nitric acid by "direct synthesis" have been developed and introduced into industry. A new, simpler, highly productive method of preparing ammonium nitrate has been developed. At the same time, the production of another important nitrogen fertilizer, namely, ammonium sulphate, from the ammonia of coke-oven gas plus lead-chamber sulphuric acid, has been considerably extended. The production of calcium cyanamide, urea, sodium, potassium and calcium nitrates has been mastered.

The mighty nitrogen industry which grew up in the U.S.S.R. before the Great Patriotic War supplied the home agriculture with scores of times more nitrogenous fertilizers than it received in pre-revolutionary times. During the war the production of nitrogenous fertilizers was almost completely discontinued, but by 1946 the pre-war level had already been re-established and lately has been surpassed severalfold.

146. Nitrogen Cycle in Nature. During the decay of organic substances a considerable part of the nitrogen contained in them turns into ammonia which is subsequently oxidized into nitric acid by **nitrifying** bacteria, which live in the soil. The nitric acid thus produced reacts with the salts of carbonic acid contained in the soil, for instance, with $CaCO_3$, to form calcium nitrate:

$$2HNO_3 + CaCO_3 = Ca(NO_3)_2 + CO_2 + H_2O$$

But during decay part of the organic nitrogen always escapes as elemental nitrogen into the atmosphere. Nitrogen is liberated also during the combustion of organic substances, when wood, coal, peat or other fuels are burnt. Besides, there are bacteria which are capable,

in a limited supply of oxygen, of abstracting oxygen from nitrates, liberating free nitrogen. As a result of the activities of these **denitrifying** bacteria, part of the combined nitrogen passes from the form assimilable by green plants (nitrates) into an inaccessible form (free nitrogen). Thus, by no means all the nitrogen contained in dead plants is returned to the soil; some of it is constantly evolved in the free form and is therefore lost for the plants.

The continuous depletion of mineral nitrogen compounds should have long since resulted in complete cessation of life on the earth, were it not for the existence in nature of other processes replenishing

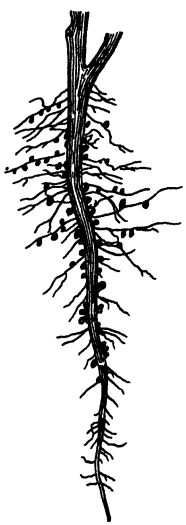


Fig. 101. Nodule-forming bacteria on roots of bean plant

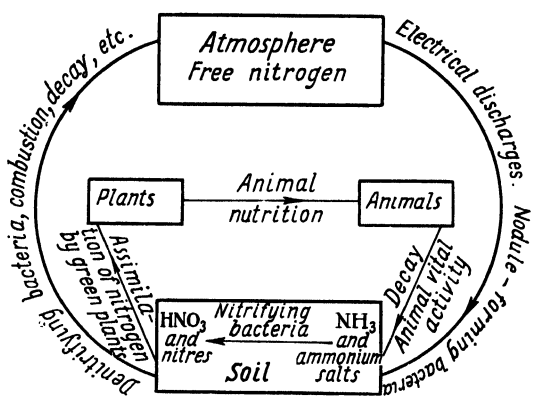


Fig. 102. Nitrogen cycle in nature

the nitrogen losses. These processes include primarily the electric discharges occurring in the atmosphere, always leading to the formation of a certain amount of nitrogen oxide; the latter combines with water giving nitric acid, which is transformed into nitrates in the soil. Another source which keeps continuously supplementing the nitrogen compounds in the soil is the vital activities of the so-called *nitrobacteria*, capable of assimilating atmospheric nitrogen. Some of these bacteria inhabit the roots of plants of the bean family causing the formation of characteristic swellings, called "nodules." Hence, the name *nodule bacteria* (Fig. 101). Assimilating atmospheric nitrogen, nodule bacteria convert it into nitrogen compounds, and plants, in their turn, convert the latter into proteins and other

complex substances. That is why bean plants, contrary to others, thrive excellently in soils which are almost devoid of nitrogen compounds.

The activities of bacteria which assimilate atmospheric nitrogen are the main reason for the quantity of combined nitrogen in the soil remaining more or less constant despite its losses due to the decomposition of nitrogen compounds. This decomposition is balanced by the formation of new nitrogen compounds, and thus there is a continuous nitrogen cycle in nature (Fig. 102).

PHOSPHORUS: at. wt. 30.975

147. Phosphorus in Nature. Preparation and Properties of Phosphorus. Phosphorus is one of the more abundant elements, its content in the earth's crust being about 0.12 per cent. Owing to its high oxidizing ability phosphorus does not occur in nature in the free state.

Of the compounds of phosphorus, the most important is the calcium salt of phosphoric acid $Ca_3(PO_4)_2$, which forms vast deposits in places as the mineral *phosphorite*. The largest deposits of phosphorites in the U.S.S.R. are in Southern Kazakhstan in the Kara-Tau Mountains. Another frequently occurring mineral is *apatite*, containing CaF_2 or $CaCl_2$ besides $Ca_3(PO_4)_2$. Immense deposits of apatite were discovered in the twenties of this century on the Kola Peninsula in the Khibiny Mountains. The resources of this deposit are the largest in the world.

Like nitrogen, phosphorus is quite indispensable to all living creatures. It is contained in various proteins both of plant and animal origin. In plants phosphorus is contained mainly in the seed proteins; in animal organisms—in the proteins of milk, blood, brain and nerve tissues. Besides, a large amount of phosphorus is contained as calcium phosphate $Ca_3(PO_4)_2$ in the bones of vertebrates. When bones are burnt all the organic substances are driven off, the residue consisting mainly of calcium phosphate.

Free phosphorus was first isolated from urine as far back as the XVII century by the alchemist Brand. At present phosphorus is prepared from calcium phosphate. For this purpose calcium phosphate is mixed with sand and coal and calcined without access of air in special furnaces by means of electric current.

To understand the reaction that takes place we must conceive calcium phosphate as a compound of calcium oxide and phosphoric anhydride ($3CaO \cdot P_2O_5$); sand, as we know, is silicon dioxide or silicic anhydride SiO_2. At a high temperature silicon dioxide displaces phosphorus pentoxide, and combining with calcium oxide, forms the calcium salt of silicic acid $CaSiO_3$, while phosphorus pentoxide

is reduced by the charcoal to elemental phosphorus:

$$P_2O_5 \cdot 3CaO + 3SiO_2 = 3CaSiO_3 + P_2O_5$$
$$P_2O_5 + 5C = 2P + 5CO$$

Adding up these two equations, we get:

$$Ca_3(PO_4)_2 + 3SiO_2 + 5C = 3CaSiO_3 + 2P + 5CO$$

The phosphorus liberated vapourizes and is condensed in a collector under water.

Phosphorus has several allotropic modifications.

White phosphorus results when phosphorus vapours are cooled rapidly. It is crystalline solid with a specific gravity of 1.82. When pure, white phosphorus is quite colourless; the commercial product, however, is usually yellow in colour and greatly resembles wax in appearance. In the cold white phosphorus is brittle, but above 15°C it softens and can easily be cut with a knife. White phosphorus melts at 44.2°C and begins to boil at 280.5°C. In the vapour form below 800°C the phosphorus molecule consists of four atoms (P_4). In the air white phosphorus oxidizes very rapidly and glows in the dark. Hence its name phosphorus which literally means "light bearing." The slight amount of heat evolved by mere friction is sufficient to make phosphorus burst into flame and burn, evolving a large amount of heat. Phosphorus may ignite spontaneously in the air due to the liberation of heat during its oxidation. To prevent white phosphorus from oxidizing it is kept under water. White phosphorus is insoluble in water, but dissolves readily in carbon disulphide.

White phosphorus is a strong poison, mortal even in small doses.

If white phosphorus is heated for a long time out of contact with air at 250 to 300°C, it turns into another modification of phosphorus, having a purple-red colour and called red phosphorus. The same transformation takes place, though much more slowly, under the action of light.

Red phosphorus differs greatly in properties from white. It oxidizes very slowly in the air, does not glow in the dark, ignites only at 260°C, does not dissolve in carbon disulphide and is not poisonous. The specific gravity of red phosphorus is 2.20. If heated strongly red phosphorus vapourizes without melting and upon cooling turns into white phosphorus.*

Black phosphorus forms from red phosphorus if the latter is heated to 350°C under several hundred atmospheres pressure. In appearance it greatly resembles graphite, is greasy to the touch, conducts elec-

* Red phosphorus is apparently not quite a homogeneous substance, but consists of several modifications of phosphorus, which have not as yet been studied thoroughly.

tricity well and is much heavier than the other modifications of phosphorus. The specific gravity of black phosphorus is 2.70 and its ignition temperature is 490°C.

The chief field of application of phosphorus is the manufacture of matches. Matches have become such a necessity in everyday life that it is difficult to imagine how people ever got along without them. Meanwhile, matches have existed only for 150 years.

The first matches, which appeared in 1805, were wooden splints one end of which was coated with a mixture of potassium chlorate, sugar and gum arabic. These matches were ignited by wetting their heads with concentrated sulphuric acid. For this purpose the splints were dipped into a tiny phial containing asbestos moistened with sulphuric acid. The reason for the ignition of the mixture was explained on page 324.

Phosphorus matches, ignited by friction, were invented in the thirties of the last century. The match heads consisted of sulphur coated with a mixture of white phosphorus and certain substances rich in oxygen (minium Pb_3O_4 or manganese dioxide MnO_2) held together with glue. These matches were called *sulphur* matches and were in use in Russia until the end of the XIX century. They ignited easily when rubbed on any surface, which, though convenient, made these matches very dangerous from the point of view of fire hazards. Besides, owing to the poisonousness of white phosphorus, their manufacture was very injurious to the health of the workers at match factories. Cases of poisoning by matches were also common. At present the manufacture of sulphur matches has been discontinued in almost all countries, having been forced out by *safety* matches. These matches were first manufactured in Sweden, for which reason they are sometimes known as Swedish matches.

Only red phosphorus is used in the manufacture of safety matches, and it is contained not in the match head but only in the composition coating the side of the match box. The head of the match consists of a mixture of combustible substances with potassium chlorate and compounds catalyzing its decomposition (pyrolusite, Fe_2O_3 and others). The mixture ignites readily if rubbed against the coated side of a match box.

Besides the match industry, phosphorus is used for military purposes. As the combustion of phosphorus results in a thick white smoke, white phosphorus is used to fill smoke screen shells and hand grenades.

Free phosphorus is very active. It combines directly with many simple substances, liberating a large amount of heat. Phosphorus combines the most readily with oxygen, then with the halogens, sulphur and many metals, forming in the latter case phosphides, analogous to nitrides, such as Ca_3P_2, Mg_3P_2, etc.

All these properties are especially pronounced in white phosphorus; red phosphorus reacts less vigorously, while black phosphorus generally enters into chemical reactions with great difficulty.

148. Phosphorus Compounds with Hydrogen and the Halogens. Phosphorus forms three compounds with hydrogen, namely gaseous hydrogen phosphide PH_3, liquid hydrogen phosphide P_2H_4, and solid hydrogen phosphide $P_{12}H_6$.

Gaseous hydrogen phosphide or phosphine PH_3 can be prepared by boiling white phosphorus with KOH solution or, more simply, by the action of hydrochloric acid on calcium phosphide Ca_3P_2:

$$Ca_3P_2 + 6HCl = 3CaCl_2 + 2PH_3$$

Gaseous hydrogen phosphide is a colourless gas with the odour of garlic, very poisonous. The preparation of gaseous hydrogen phosphide is sometimes accompanied by the formation of small amounts of liquid hydrogen phosphide, the vapours of which ignite spontaneously in the air. The presence of P_2H_4 accounts for the spontaneous combustion of gaseous hydrogen phosphide observed sometimes during its preparation.

The combustion of hydrogen phosphide results in phosphorus pentoxide and water:

$$2PH_3 + 4O_2 = P_2O_5 + 3H_2O$$

Like ammonia, hydrogen phosphide combines with hydrohalic acids (but not with oxyacids), forming salts in which the part of the metal is played by PH_4, called the **phosphonium** group, for instance, *phosphonium chloride* PH_4Cl. Phosphonium salts are very unstable compounds; when brought into contact with water they decompose into the hydrogen halide and PH_3.

Phosphorus combines directly with all the halogens liberating a great amount of heat. Of practical importance are mainly its compounds with chlorine.

Phosphorus trichloride PCl_3 is prepared by passing chlorine over melted phosphorus. It is a liquid, boiling at 76°C.

In water PCl_3 undergoes complete hydrolysis into hydrogen chloride and phosphorous acid:

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl$$

If chlorine is passed through phosphorus trichloride the result is *phosphorus pentachloride* PCl_5, a white solid, also hydrolyzing in water into hydrogen chloride and phosphoric acid. Phosphorus forms similar compounds with bromine, iodine and fluorine; however, in the case of iodine no compound of the composition PI_5 is known.

Phosphorus trichloride and pentachloride are widely used in the synthesis of various organic substances.

149. Oxides and Acids of Phosphorus. Phosphorus forms three compounds with oxygen, viz., phosphorus anhydride or phosphorus

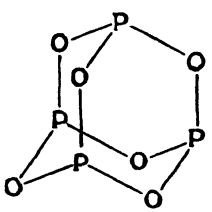
trioxide P_2O_3, phosphoric anhydride or phosphorus pentoxide P_2O_5 and phosphorus tetroxide P_2O_4.

Phosphorus trioxide P_2O_3 is prepared by the slow oxidation of phosphorus or by burning phosphorus in a limited supply of oxygen. It is a white crystalline substance melting at 23.8°C and boiling at 173°C. Its molecular weight at low temperatures corresponds to the formula P_4O_6. When treated with cold water phosphorus trioxide combines with it slowly, forming *phosphorous acid* H_3PO_3. Both phosphorus trioxide and phosphorous acid are active reducing agents.

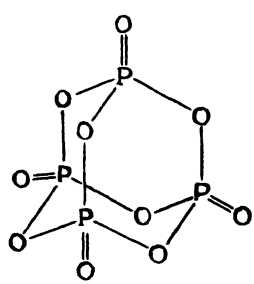
Phosphorus pentoxide P_2O_5 results from the combustion of phosphorus in air or in oxygen, as a white voluminous snow-like mass with a melting point of 563°C. Its vapour density corresponds to the formula P_4O_{10}.

Phosphorus pentoxide combines avidly with water and is thus a good dehydrating agent. It is also capable of removing the elements of water from other compounds, such as sulphuric and nitric acids (see p. 389). In the air phosphorus pentoxide deliquesces, turning rapidly into a sticky mass of metaphosphoric acid.

The molecular structure of phosphorus trioxide and pentoxide can be represented by the following structural formulas:



Phosphorus trioxide



Phosphorus pentoxide

Phosphorus tetroxide P_2O_4 is a colourless shiny crystalline substance. This oxide, like N_2O_4, may be regarded as a mixed oxide. When dissolved in water it forms equimolecular quantities of phosphoric and phosphorous acids:

$$P_2O_4 + 3H_2O = H_3PO_4 + H_3PO_3$$

The phosphoric acids. Depending on the temperature phosphorus pentoxide is capable of combining with different quantities of water to form *meta-*, *pyro-* and *ortho*phosphoric acids:

$P_2O_5 + H_2O = 2HPO_3$ (*meta*phosphoric acid)
$P_2O_5 + 2H_2O = H_4P_2O_7$ (*pyro*phosphoric acid)
$P_2O_5 + 3H_2O = 2H_3PO_4$ (*ortho*phosphoric acid)

When phosphorus pentoxide is dissolved in cold water the result is *metaphosphoric acid*, the simplest formula of which is HPO_3; the actual composition of its molecule is expressed by the formula $(HPO_3)_x$, where $x=3$, 4, 5, 6, etc. If a solution of *meta*phosphoric acid is evaporated, the latter separates out as a vitreous mass, readily soluble in water. *Meta*phosphoric acid is very poisonous. The salts of *meta*-phosphoric acid are used to soften water.

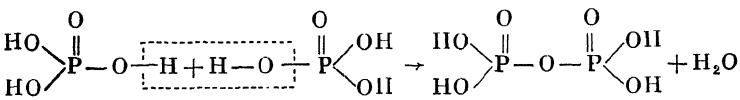
If a solution of *meta*phosphoric acid is boiled, molecules of water unite with it to form tribasic *ortho*phosphoric acid H_3PO_4:

$$(HPO_3)_x + xH_2O = xH_3PO_4$$

Orthophosphoric acid H_3PO_4 forms colourless crystals melting at 42°C. It is very soluble in water.

*Ortho*phosphoric acid is not poisonous.

When heated dry to 215°C every two molecules of *ortho*phosphoric acid split off one molecule of water forming tetrabasic *pyrophosphoric acid* as a vitreous mass, soluble in water:



or

$$2H_3PO_4 = H_4P_2O_7 + H_2O$$

The most important of the above three acids is *ortho*phosphoric acid and it is usually the one meant when phosphoric acid is mentioned.

*Ortho*phosphoric acid can be prepared not only by boiling a solution of *meta*phosphoric acid, but also by oxidizing red phosphorus with nitric acid:

$$\overset{0}{3P} + 5\overset{+V}{H}NO_3 + 2H_2O = 3\overset{+V}{H_3}PO_4 + 5\overset{+II}{N}O$$

*Ortho*phosphoric acid is prepared for technical purposes mostly by the action of sulphuric acid on calcium phosphate:

$$Ca_3(PO_4)_2 + 3H_2SO_4 = \downarrow 3CaSO_4 + 2H_3PO_4$$

As the calcium sulphate formed is almost insoluble in water, the phosphoric acid solution can easily be separated from it and then concentrated by evaporation.

Phosphoric acid is an acid of moderate strength. Its primary ionization constant equals 7.5×10^{-3}. In aqueous solution phosphoric acid ionizes mainly into H^+- and $H_2PO_4^-$-ion.

A tribasic acid, *ortho*phosphoric acid forms three series of salts: normal salts, acid salts with one hydrogen atom in the acid radical and acid salts with two hydrogen atoms in the acid radical. The

normal salts of phosphoric acid are called *phosphates*, the acid salts, *hydrogen* or *acid phosphates.*

Na_3PO_4; $Ca_3(PO_4)_2$—normal, or tertiary, phosphates
Na_2HPO_4; $Ca_2(HPO_4)_2$—secondary, hydrogen, or acid, phosphater
NaH_2PO_4; $Ca(H_2PO_4)_2$—primary, dihydrogen, or diacid, phosphates

All the primary phosphates are soluble in water; of the secondary and tertiary phosphates only those of sodium, potassium and ammonium are soluble.

150. Phosphate Fertilizers. The salts of phosphoric acid are of especially great importance in agriculture. As was mentioned above, phosphorus is contained in the proteins of plants. Therefore, it is just as important an element for plants as nitrogen. Plants receive their phosphorus from the soil, in which it is contained as phosphoric acid salts. But the phosphorus content in soils is very low and a deficiency lowers the crop yield, especially of grain cultures and tubers (sugar beet). To increase the crops various phosphate fertilizers are introduced into the soil.

Natural phosphorus compounds, phosphorites and apatites, contain phosphorus in the form of the insoluble tertiary phosphate $Ca_3(PO_4)_2$, which is difficult for plants to assimilate. To obtain readily assimilated fertilizers, phosphorites are treated chemically to convert the normal salt into an acid one. This is how the most important phosphate fertilizers, called superphosphate and precipitate, are prepared.

To produce *superphosphate*, finely ground natural phosphorite is mixed with enough sulphuric acid to total two molecules of H_2SO_4 for every molecule of $Ca_3(PO_4)_2$. The mixture is vigorously mixed and charged into special continuous action chambers, where the following reaction is completed:

$$Ca_3(PO_4)_2 + 2H_2SO_4 = 2CaSO_4 + Ca(H_2PO_4)_2$$

The reaction results in a mixture of gypsum and the primary phosphate $Ca(H_2PO_4)_2$, which is comparatively soluble in water. This mixture, ground or granulated, is known as superphosphate.

The manufacture of superphosphate is one of the largest branches of the basic chemical industry, closely connected with the production of sulphuric acid. Most of the sulphuric acid produced is used for the manufacture of superphosphate. The output of superphosphate in the capitalist countries alone amounted to 22 million tons in 1953.

Precipitate is a phosphate fertilizer containing secondary calcium phosphate $Ca_2(HPO_4)_2$ or $CaHPO_4$, which is insoluble in water but dissolves in the acids contained in soils.

To prepare precipitate free phosphoric acid is first evolved from phosphorite by treating the latter with a greater quantity of sulphuric

acid than is necessary for the production of superphosphate:

$$Ca_3(PO_4)_2 + 3H_2SO_4 = \downarrow 3CaSO_4 + 2H_3PO_4$$

The phosphoric acid solution is decanted from the precipitate, which contains gypsum and other insoluble admixtures, and milk of lime, i.e., a suspension of lime in water, is added to it in sufficient quantity to form the secondary phosphate:

$$H_3PO_4 + Ca(OH)_2 = \downarrow CaHPO_4 \cdot H_2O + H_2O$$

The crystalline precipitate is separated from the liquid and carefully dried, so as not to drive off the water contained in the crystals. This salt is assimilated readily by plants if it has not lost its water of crystallization.

A third type of phosphate fertilizer, produced lately in large quantities, are the ammonium phosphates, known as *ammophoses*. The most important of these is *diammophos* $(NH_4)_2HPO_4$. Ammophoses are complex fertilizers, containing nitrogen besides phosphorus.

Before the Revolution the phosphate fertilizer industry was in its embryonic stage in Russia. In 1913 the output of the few existing superphosphate plants totalled only 70 or 80 thousand tons.

The construction of new plants began only in 1925-26 and immediately assumed a large scale. During the pre-war five-year periods a number of large plants for the production of phosphate fertilizers were erected. By 1938 the U.S.S.R. occupied the first place in Europe for the production of superphosphate.

The production of mineral fertilizers now occupies first place in the output of the chemical industry of the U.S.S.R.

In 1955 the total output of all mineral fertilizers (including phosphate fertilizers) amounted to 9.6 million tons. It will grow even higher during the Sixth Five-Year Plan. The output of various mineral fertilizers in 1960 will reach 19.6 million tons, including a considerable increase in the production of the most effective fertilizers. For instance, the yearly output of concentrated phosphate fertilizers will be about one million tons.

ARSENIC SUBGROUP

151. Arsenic (Arsenicum); at. wt. 74.91. Arsenic occurs in nature mainly as compounds with metals and sulphur and but rarely in the native state. The content of arsenic in the earth's crust amounts to 0.00005 per cent by weight.

Arsenic is usually obtained from *mispickel* (*arsenopyrite*) FeAsS. When heated out of contact with the air, this mineral decomposes into iron sulphide and arsenic, which sublimates, owing to its vola-

tility. The resulting product is usually impure and has to be refined. Pure arsenic is a dark grey crystalline substance with a metallic lustre and a specific gravity of 5.73. It is very brittle and is quite a good conductor of heat and electricity, its electrical conductivity being only 22 times less than that of copper.

Like phosphorus, arsenic forms several allotropic modifications. Besides grey crystalline arsenic mention should be made of *black amorphous arsenic*, obtained by the decomposition of hydrogen arsenide. All the allotropic modifications of arsenic sublime when heated, without melting.

Arsenic is insoluble in water. In the air it oxidizes very slowly at ordinary temperatures, but burns if heated strongly, forming white

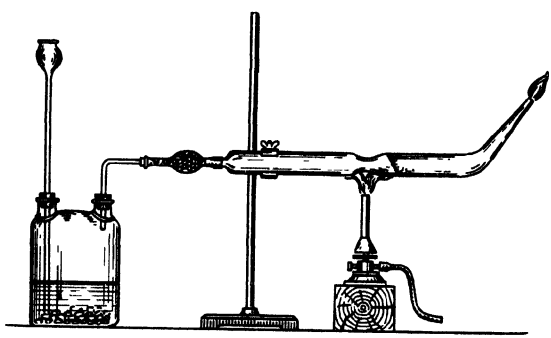


Fig. 103. Apparatus for detection of arsenic

arsenious anhydride As_2O_3 and giving rise to a characteristic garlic-like odour. At a high temperature arsenic will combine directly with many elements.

Arsenic is tri- and pentavalent in its compounds.

Elemental arsenic and all its compounds are poisonous.

Arsenic trihydride, hydrogen arsenide, or *arsine*, AsH_3, is a colourless, very poisonous gas with a characteristic garlic-like odour, slightly soluble in water. Hydrogen arsenide forms when *any* arsenious compound is reduced by nascent hydrogen. For instance:

$$As_2O_3 + 6Zn + 6H_2SO_4 = 2AsH_3 + 6ZnSO_4 + 3H_2O$$

Hydrogen arsenide is rather unstable, and when heated decomposes readily into hydrogen and elemental arsenic.

Advantage is taken of the ability of hydrogen arsenide to decompose when heated for the detection of arsenic in various substances. For this purpose the apparatus shown in Fig. 103 is employed. It consists of a double-necked bottle for the preparation of hydrogen and a refractory tube with its end drawn out and upwards and with

a kink in the middle. Between the bottle and the tube is a small bulb containing calcium chloride for drying the hydrogen liberated.

Several pieces of pure zinc are placed in the bottle and dilute hydrochloric acid is poured over them; when all the air has been forced out of the apparatus, the hydrogen is ignited at the drawn-out end of the tube. Then a portion of the substance under test is added to the bottle through a thistle tube and heat is applied to the kink of the horizontal tube. If the substance contains arsenic, hydrogen arsenide will form in the bottle and decompose again on passing through the heated part of the tube. The arsenic thus liberated deposits on the cold parts of the tube as a shiny black deposit ("arsenic mirror").

This method enables detection of even insignificant quantities of arsenic.

Arsenic has two oxides, viz., arsenic trioxide or arsenious anhydride As_2O_3 and arsenic pentoxide or arsenic anhydride As_2O_5.

Arsenic trioxide As_2O_3 results when arsenic burns in air or arsenic ores are calcined. It is a white crystalline substance, commonly known as *white arsenic* or just *arsenic*. Arsenic trioxide is only slightly soluble in water, a saturated solution at 15°C containing only 1.5 per cent As_2O_3. When dissolved, arsenic trioxide combines with water to form the hydroxide $As(OH)_3$ or H_3AsO_3:

$$As_2O_3 + 3H_2O = 2As(OH)_3$$

It is amphoteric but with predominating acid properties and for that reason is called arsenious acid.

Arsenious acid H_3AsO_3 has not been obtained in the free state and is known only in aqueous solution. It is a very week acid ($K = 6 \times \times 10^{-10}$). Its salts are called **arsenites**. The arsenites of the alkali metals can easily be obtained by the action of alkalis on As_2O_3:

$$As_2O_3 + 6KOH = 2K_3AsO_3 + 3H_2O$$

Many arsenites are derivatives of *meta*arsenious acid $HAsO_2$.

Arsenious acid and its salts are very active reducing agents.

If arsenic or arsenic trioxide is oxidized by nitric acid, arsenic acid results:

$$\overset{+III}{3As_2O_3} + \overset{+V}{4HNO_3} + 7H_2O = \overset{+V}{6H_3AsO_4} + \overset{+II}{4NO}$$

Arsenic acid H_3AsO_4 is a solid, readily soluble in water. The strength of this acid is about the same as phosphoric acid. Its salts, called **arsenates**, greatly resemble the corresponding phosphates. *Meta-* and *pyro*arsenic acids are also known. If arsenic acid is calcined it turns into *arsenic pentoxide* As_2O_5, a white vitreous mass.

A comparison of the properties of arsenious and arsenic acids shows that the acid properties are more pronounced in the latter. Such a gradation of properties is a general law characteristic of all elements,

namely, *as the valency of an element increases, the nature of its hydroxide changes, its acid properties becoming more, and basic properties less, pronounced.*

Sulphides of Arsenic. If hydrogen sulphide is passed through a solution of H_3AsO_3 acidified with hydrochloric acid, a yellow precipitate of *arsenic trisulphide* As_2S_3, insoluble in hydrochloric acid, is formed. The reactions that take place can be expressed by the equations:

$$H_3AsO_3 + 3HCl \rightleftarrows AsCl_3 + 3H_2O$$
$$2AsCl_3 + 3H_2S = \downarrow As_2S_3 + 6HCl$$

Yellow *arsenic pentasulphide* As_2S_5 can be obtained in a similar way by the action of hydrogen sulphide on a solution of H_3AsO_4 in hydrochloric acid:

$$H_3AsO_4 + 5HCl \rightleftarrows AsCl_5 + 4H_2O$$
$$2AsCl_5 + 5H_2S = \downarrow As_2S_5 + 10HCl$$

The sulphides of arsenic react with the sulphides of the alkali metals Na_2S, K_2S and with $(NH_4)_2S$ to form soluble salts of *thioarsenious acid* H_3AsS_3 and *thioarsenic acid* H_3AsS_4, which differ from the oxyacids of arsenic in that all the oxygen in them is substituted by sulphur:

$$As_2S_3 + 3Na_2S = \underset{\text{sodium thioarsenite}}{2Na_3AsS_3}$$

$$As_2S_5 + 3Na_2S = \underset{\text{sodium thioarsenite}}{2Na_3AsS_4}$$

Thioarsenic acid salts can be obtained also by the action of the alkali *polysulphides* on As_2S_3:

$$As_2S_3 + Na_2S_3 + 2Na_2S = 2Na_3AsS_4$$
$$\overset{+III}{2As} - 4e^- = \overset{+V}{2As}$$
$$S_3^{--} + 4e^- = \overset{-II}{3S}$$

Thioacids are very unstable in the free state and decompose readily into hydrogen sulphide and the corresponding sulphide. For example:

$$2H_3AsS_4 = As_2S_5 + 3H_2S$$

Therefore, if arsenic thiosalts are treated with strong acids, hydrogen sulphide is liberated and the thiosalts break down into the sulphides:

$$2Na_3AsS_3 + 6HCl = 6NaCl + As_2S_3 + 3H_2S$$
$$2Na_3AsS_4 + 6HCl = 6NaCl + \downarrow As_2S_5 + 3H_2S$$

The decomposition of the thioacids into hydrogen sulphide and the sulphides is analogous to the decomposition of the corresponding oxyacids into water and the anhydride:

$$2H_3AsO_4 = As_2O_5 + 3H_2O$$
$$2H_3AsS_4 = As_2S_5 + 3H_2S$$

For this reason sulphides which form thioacids are called the *thioanhydrides* of those acids.

The uses of elemental arsenic are very limited. It is added in small quantities to various alloys of non-ferrous metals to make them harder and more resistant to corrosion. But arsenic compounds are very widely used in connection with the pronounced physiological action of arsenic on almost all plant and animal organisms.

Arsenic compounds have long been used as medicines, small doses of arsenic stimulating metabolism and strengthening the organism. Dilute solutions of potassium arsenide are usually used for this purpose. Arsenic is contained also in many organic medicinals, such as novarsanol, salvarsan, etc.

Another extensive field of application of arsenic compounds is agriculture, where many salts of arsenious and arsenic acids are employed as "insecticides" (substances which destroy insect pests).

Arsenic trioxide is used as a poison for destroying rats, mice and other rodents.

Arsenic sulphides are used as yellow paints, as well as in the tanning industry for removing hair from hides.

The world production of white arsenic As_2O_3 (not counting the U.S.S.R.) is 60 to 70 thousand tons per year and is concentrated mainly in the U.S.A. and Sweden.

152. Antimony (Stibium); at. wt. 121.76. Antimony occurs in nature usually as compounds with sulphur, in the form of *desmine* Sb_2S_3. In spite of the fact that the content of antimony in the earth's crust is comparatively low (0.00005 per cent by weight) it has been known since ancient times. This is due to the frequent occurrence of desmine in nature and the ease with which pure antimony can be extracted from it. If calcined (roasted) in the presence of air desmine is converted into antimony tetroxide Sb_2O_4, from which antimony is obtained by reduction with coal.

In the free state antimony is a silver-white solid with a metallic lustre, a specific gravity of 6.62 and a melting point of 630.5°C. It is very much like a metal in appearance but is brittle and a much worse conductor of heat and electricity than ordinary metals. Besides this "metallic" form of antimony, other allotropic modifications are known.

Metallic antimony is used in many alloys to make them harder. An alloy consisting of antimony and lead with a little tin added is called *type metal* and is used for making type.

The world production of antimony (not counting the U.S.S.R.) is about 40,000 tons per year. Its main producers are Mexico, Bolivia, Yugoslavia and China. Tsarist Russia had no antimony industry in spite of the fact that it possessed the necessary raw material base.

Antimony began to be extracted from domestic ores only in Soviet times.

Antimony resembles arsenic greatly in its compounds but has more pronounced metallic properties.

Hydrogen antimonide SbH_3 is a poisonous gas formed under the same conditions as hydrogen arsenide. When heated it decomposes even more readily than AsH_3, forming antimony and hydrogen.

Antimony trioxide or *antimonious anhydride* Sb_2O_3 is a typical amphoteric oxide with somewhat predominating basic properties. Antimony trioxide dissolves in strong acids, such as sulphuric and hydrochloric, forming salts, in which antimony behaves like a trivalent metal:

$$Sb_2O_3 + 3H_2SO_4 = Sb_2(SO_4)_3 + 3H_2O$$

Antimony trioxide dissolves also in alkalis, resulting in salts of antimonious acid H_3SbO_3 or *meta*antimonious acid $HSbO_2$. For example:

$$Sb_2O_3 + 2NaOH = 2NaSbO_2 + H_2O$$

Antimonious acid or *antimony hydroxide* $Sb(OH)_3$ falls out as a white precipitate when salts of trivalent antimony are treated with alkalis:

$$SbCl_3 + 3NaOH = \downarrow Sb(OH)_3 + 3NaCl$$

The precipitate dissolves readily both in acids and in an excess of alkali.

The salts of trivalent antimony, as salts of a weak base, hydrolyze in aqueous solution forming basic salts:

$$SbCl_3 + 2H_2O \rightleftarrows Sb(OH)_2Cl + 2HCl$$

But salts of this kind can easily split off one molecule of water and pass into basic salts of another type:

$$Sb(OH)_2Cl = SbOCl + H_2O$$

In the latter salt the SbO group plays the part of a univalent metal and is known as *antimonyl*. The salt produced is called antimony oxychloride or *antimonyl chloride*.

Antimony pentoxide or *antimonic anhydride* Sb_2O_5 is predominantly acidic in properties; it has three corresponding acids: *ortho-*, *meta-* and *pyro*antimonic acids (H_3SbO_4, $HSbO_3$ and $H_4Sb_2O_7$). Salts of all three acids are known.

Antimony tetroxide Sb_2O_4 is a mixed oxide in which one antimony atom is trivalent and the other pentavalent. It is prepared by heating either Sb_2O_3 or Sb_2O_5 in the presence of air. It is the most stable oxide of antimony. Usually antimony tetroxide is regarded as the antimony salt of *ortho*antimonic acid $SbSbO_4$.

The *sulphides of antimony* Sb_2S_3 and Sb_2S_5 are quite analogous in properties to the sulphides of arsenic. They are orange-red substances, which dissolve in

the alkali sulphides, to form thiosalts. Antimony sulphides are used in the manufacture of matches and in the rubber industry.

153. Bismuth (Bismuthum); at. wt. 209.00. The last member of the arsenic subgroup, bismuth, is characterized by a pronounced predominance of metallic properties over non-metallic, and may be regarded as a metal.

Bismuth occurs rarely in nature (the content of bismuth in the earth's crust constitutes 0.00001 per cent by weight). It is found both in the native state and in the form of the compounds *bismuth ochre* Bi_2O_3 and *bismuthite* Bi_2S_3. The world production of bismuth is 1,000-1,500 tons per year.

In the free state bismuth is a shiny reddish-white brittle metal having a specific gravity of 9.8 and melting at 271.3°C. It is contained in many fusible alloys used in printing, various fire protection devices, etc.

At ordinary temperatures bismuth does not oxidize in the air but burns if heated strongly, forming bismuth oxide Bi_2O_3. Bismuth can be dissolved in nitric acid.

Bismuth hydride BiH_3 was first obtained in insignificant quantities in 1918 by treating an alloy of bismuth and magnesium with hydrochloric acid. It is very unstable and decomposes slowly even at ordinary temperatures.

Bismuth trioxide Bi_2O_3 results when bismuth is calcined in air and also from the decomposition of bismuth nitrate. It is basic in nature and dissolves in acids to form salts of trivalent bismuth. Besides it, three more oxides are known, namely, BiO, Bi_2O_4 and Bi_2O_5, of which Bi_2O_5 possesses slightly acidic properties.

Bismuth hydroxide $Bi(OH)_3$ separates as a white precipitate when soluble bismuth salts are treated with alkalis:

$$Bi(NO_3)_3 + 3NaOH = \downarrow Bi(OH)_3 + 3NaNO_3$$

Bismuth hydroxide is a very weak base. That is why bismuth salts are easily hydrolyzed, forming the basic salts which are very slightly soluble in water.

Among the salts of bismuth the following are worthy of mention:

Bismuth nitrate $Bi(NO_3)_3 \cdot 5H_2O$. This salt can be crystallized out of a solution of bismuth in nitric acid. It dissolves readily in a small quantity of water acidified with nitric acid. If the solution is diluted with water, hydrolysis occurs, and a basic salt of the composition $Bi(OH)_2NO_3$ precipitates out:

$$Bi(NO_3)_3 + 2H_2O \rightleftarrows \downarrow Bi(OH)_2NO_3 + 2HNO_3$$

The reaction, however, is reversible, and therefore an excess of acid redissolves the precipitate, changing it back into $Bi(NO_3)_3$.

Basic bismuth nitrate is used in medicine to cure certain gastric diseases.

Bismuth chloride $BiCl_3$ can be prepared by heating bismuth in a stream of chlorine or by dissolving it in aqua regia. $BiCl_3$ decomposes in water, forming a white precipitate of the basic salt *bismuth oxychloride* or *bismuthyl chloride* BiOCl.

Bismuth sulphide Bi_2S_3 is formed as a blackish-brown precipitate by the action of hydrogen sulphide on bismuth salts. The precipitate does not dissolve in the alkali sulphides; contrary to arsenic and antimony, bismuth does not form thiosalts.

CHAPTER XVII

The Carbon Group

Name of element	Symbol	Atomic weight	Atomic number	Arrangement of electrons in layers					
Carbon	C	12.011	6	2	4				
Silicon	Si	28.09	14	2	8	4			
Germanium . .	Ge	72.60	32	2	8	18	4		
Tin	Sn	118.70	50	2	8	18	18	4	
Lead	Pb	207.21	82	2	8	18	32	18	4

154. General Features of the Carbon Group. *Carbon* is the first element of the fourth group in the Periodic Table. The second box of this group is occupied by *silicon*, situated in the third short period. The atoms of both elements have four electrons in their outer layer and form covalent bonds quite readily with four atoms of hydrogen, which characterizes them as non-metals, though less typical than the corresponding elements in the fifth group. *Germanium*, *tin* and *lead* are similar to carbon and silicon in atomic structure. Together these five elements form the main subgroup of the fourth group called also the **carbon group.**

In view of the increase in atomic volume from carbon to lead, the capacity for gaining electrons, and therefore the non-metallic properties of the carbon group elements, should be expected to weaken and their ability to yield electrons, to become stronger in the same sequence. Indeed, germanium already possesses pronounced metallic properties, while the metallic properties of tin and lead predominate greatly over their non-metallic properties. Thus, only the first two members of this group are non-metals, the other three usually being classed as metals.

Owing to the presence of four electrons in the outer layer of the atom, the highest valency of all the elements of the carbon group, both positive and negative, equals four. The elements of the carbon group also manifest a positive valency of two, but bivalent compounds of carbon and silicon are scarce and comparatively unstable.

This chapter will deal only with carbon and silicon; the rest of the elements of the carbon group will be discussed later on, together with the other metals.

CARBON (Carboneum); at. wt. 12.011

155. Carbon in Nature. Carbon is found in nature both in the elemental state and in numerous compounds. Native carbon occurs in the form of two simple substances, diamond and graphite. A third simple substance consisting also of carbon, namely, charcoal, can be obtained only artificially. However, there are substances in nature very close in composition to charcoal. Such, for instance, are various kinds of mineral coal, forming huge deposits at many points of the globe. Some mineral coals contain as much as 99 per cent carbon.

Carbon compounds are very widespread. Besides mineral coal, the depths of the earth contain large accumulations of mineral oil, which is a complex mixture of various carboniferous compounds, mainly hydrocarbons. Salts of carbonic acid occur in immense quantities in the earth's crust, particularly the calcium salt, which frequently forms whole mountains of limestone and chalk. The air always contains carbon dioxide. Finally, plants and animal organisms consist of substances, the main constituent of which is carbon. Thus, carbon is one of the most abundant elements on the earth, although its total content in the earth's crust has been estimated at not over 0.35 per cent by weight.

Carbon occupies quite a specific position among other elements with regard to the abundance and diversity of its compounds. The number of carbon compounds already known is well over a million, while the compounds of all the rest of the elements taken together do not total more than 25 or 30 thousand.

The diversity of carbon compounds is due to the ability of its atoms to unite with one another into long chains or rings consisting sometimes of scores or even hundreds of atoms (see § 168).

156. Allotropy of Carbon. Elemental carbon is known in three allotropic modifications: *diamond*, crystallizing in the isometric system; *graphite*, belonging to the hexagonal system, and *amorphous carbon*, usually called coal or charcoal. The latter modification is apparently but a peculiar cryptocrystalline form of graphite. It has not been established for certain to the present day whether an amorphous modification of carbon really exists or not.

Diamond is a colourless substance which refracts light rays very strongly. Diamonds occur rarely in nature, usually in the form of small crystals embedded in rocks or disseminated through placer deposits. The largest diamond ever found weighed 620

diamond deposits have been found in Congo and South Africa. Rich diamond deposits have been discovered recently in the Yakut A.S.S.R (Eastern Siberia).

The specific gravity of diamond is 3.5. Diamond is harder than any other known substance and it is employed to work various hard materials, to cut glass and to drill rocks. Being very hard, diamond is at the same time very brittle. The powder left over when cutting diamonds is used to manufacture gems and cut other diamonds. Finely cut and perfectly transparent diamonds are called *brilliants.*

In 1954 the world production of diamonds was about 4 tons, of which 82 per cent were used for technical purposes.

Owing to the great value of diamonds there have been many attempts to obtain them artificially from graphite. But until recently these attempts were fruitless. Only in 1955 did American, and simultaneously Swedish, scientists succeed in producing artificial diamonds, by using very high pressures (around 70 or 100 thousand atm.) and prolonged heating at about 3,000°C. The procedures were based on precise theoretical calculations. The diamonds obtained were small yellow crystals, the cost of which is as yet much higher than that of natural diamonds.

If heated strongly in oxygen diamond will burn up, the only product of its combustion being carbon dioxide. If heated strongly without access of air it turns into graphite.

Graphite is a dark grey crystalline substance with a slight metallic lustre. Its specific gravity varies from 2.17 to 2.3. Contrary to diamond, graphite is a very soft substance. If a piece of graphite is drawn across a sheet of paper minute graphite crystals in the form of scales adhere to the paper, leaving a grey mark. This is the basis of the use of graphite for the manufacture of lead pencils.

Graphite will not burn in air even if heated very strongly but burns readily in pure oxygen, turning into CO_2.

Graphite conducts electricity; it is used in electrical engineering for the manufacture of electrodes. Mixed with clay, graphite is used to make refractory crucibles for melting metals. Mixed with oil, graphite makes an excellent lubricant, as its scales fill the irregularities of the material, resulting in a smooth surface which facilitates sliding. Graphite is used also as a moderator in nuclear reactors.

In 1952 the output of graphite by the capitalist countries amounted to 134,000 tons. A considerable part of this was mined in Mexico, Austria and Madagascar. In the U.S.S.R. large deposits of graphite have been found in Eastern Siberia, in the Altai Mountains, along the banks of the River Kureika, a tributary of the Enisei, and elsewhere.

At present graphite is obtained artificially by passing an alternating current of great intensity through a mass of granulated coke

mixed with pitch and a small quantity of sand. The mixture between the electrodes becomes very hot due to its great resistance, and in about 24 to 36 hours the carbon turns into graphite. Artificial graphite surpasses natural graphite in purity and homogeneity.

Graphite forms also when molten pig iron is cooled (the carbon dissolved in the pig iron is partly liberated as graphite, which accounts for the grey colour of the pig iron).

The great difference between the properties of diamond and graphite is due to the difference in their internal structure. The arrangement of the carbon atoms in the crystals of these substances was established by means of X-rays. It was found that in diamond crystals all the carbon atoms are at equal distances (1.54 Ångströms) from one another. Each atom is in the centre of a regular tetrahedron

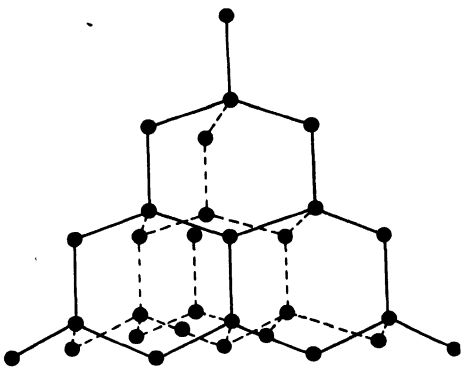


Fig. 104. Arrangement of carbon atoms in diamond

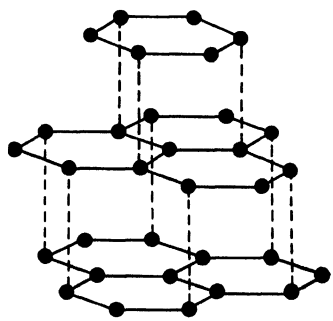


Fig. 105. Arrangement of carbon atoms in graphite

with other atoms located at its four apices (Fig. 104). Judging by the hardness of diamond, the forces acting between its atoms are very strong and are probably chemical valency forces, the entire crystal being a single huge carbon molecule.

Graphite crystals are of an entirely different structure. The carbon atoms in this substance are located at the corners of regular hexagons arranged in parallel planes (Fig. 105). The distance between the adjacent planes (3.4 Ångströms) is greater than that between the adjacent atoms of the hexagon (1.45 Ångströms), as a result of which the bond between atoms lying in the same plane is much stronger than that between the planes. Whereas the diamond crystal is a single huge three-dimensional molecule, the structure of the graphite crystal corresponds to an accumulation of immense flat two-dimen-

sional molecules piled onto one another comparatively loosely. The weakness of the bonds between the planes manifests itself every time we use a lead pencil, the mark left on the paper being composed of minute scales split off the graphite.

Amorphous Carbon (charcoal). If carboniferous compounds are heated without access of air, carbon is evolved from them in the form of a black mass called amorphous carbon or charcoal. It has been proved by X-raying that such carbon consists in many cases of tiny crystals, invisible even under the microscope, but having the same structure as graphite. It is possible, however, that alongside these crystals charcoal contains really amorphous modifications of carbon.

Charcoal is one of the most refractory substances. Charcoal can be observed to melt only if a very intense electric current is passed through a graphite rod. The drops of molten charcoal thus formed solidify into pure graphite. The melting point of charcoal is about 3,500°C.

Amorphous carbon is insoluble in ordinary solvents but dissolves in many molten metals such as iron, nickel and platinum. Upon cooling it precipitates out of these solutions as graphite. The specific gravity of charcoal varies between 1.8 and 2.1.

Charcoals differ considerably in properties depending on the substance from which they are obtained and on the method of their preparation. Besides, they always contain impurities which greatly influence their properties. The most important technical types of amorphous carbon are: *coke*, *wood charcoal*, *bone charcoal* and *carbon black*.

Coke is obtained by dry distillation of mineral coal. It is used chiefly in metallurgy for reducing metals from their ores.

Wood charcoal is obtained by heating wood out of contact with air. Formerly this used to be done in a very crude manner: the wood would be piled up in large heaps, "bonfires," covered with turf, leaving small holes for air, and ignited. Part of the wood would be burnt, but the greater part would turn into charcoal. Nowadays charcoal is usually prepared in large iron retorts, making it possible to collect the valuable products of dry distillation, namely, methyl alcohol, acetic acid, etc.

Charcoal is used in metallurgy, in forge-smithing, for the preparation of gunpowder, as well as for the absorption of vapours and gases.

Bone charcoal is prepared by charring degreased bones. It contains from 7 to 11 per cent carbon, about 80 per cent calcium phosphate and other mineral salts. A distinguishing feature of bone charcoal is its very high absorptive capacity, especially with respect to organic dyes, and it is used to remove various kinds of colouring matter from solutions.

Carbon black (lampblack) is the purest form of amorphous carbon. It is prepared in industry by burning pitch, turpentine or other substances rich in carbon in a limited supply of air. It is widely used as black paint (India ink, printer's ink, etc.) and as an important component of rubber in the rubber industry.

157. Adsorption. As indicated above, charcoal possesses the property of retaining various substances on its surface. This property is called adsorption. Both solids and liquids may serve as adsorbents, but the best adsorbents are solid substances.

Adsorption is due to the fact that the surface particles of a substance are in a different state than the particles in the bulk. Inside the substance all the forces acting between the particles are mutually balanced, while on the surface of the substance only the forces within the surface plane are balanced. Therefore the surface layer is capable of attracting particles from the adjoining liquid or gaseous phase. In many cases the adsorbed layer of particles is monomolecular, i. e., one molecule thick.

Adsorbed molecules oscillate in a definite way. Some of the molecules may detach themselves and return to the surrounding medium,

Table 23

Increase in Surface Area of a Substance Due to Crushing

Length of cube edge	Number of cubes per cu. cm.	Total surface area	Length of cube edge	Number of cubes per cu. cm.	Total surface area
1 cm.	1	6 cm^2	1 μ	10^{12}	6 m^2
1 mm.	10^3	60 cm^2	1 mμ	10^{21}	6,000 m^2
0.1 mm.	10^6	600 cm^2	0.1 mμ	10^{24}	60,000 m^2
0.01 mm.	10^9	6,000 cm^2			

their place being taken by other molecules; as a result a definite state of **adsorption equilibrium** is established, during which the number of molecules adsorbed by the surface is the same as that leaving it.

The state of adsorption equilibrium depends both on the concentration of the adsorbed substance in the phase adjacent to the adsorbent, and on the temperature. As the concentration increases, the absolute quantity of adsorbed molecules grows, although the percentage adsorbed is lower than at low concentrations.

Shifts of equilibrium due to changes in temperature are governed by the fact that adsorption is accompanied by the liberation of heat.

Therefore, according to Le Châtelier's Principle, a rise in temperature shifts the adsorption equilibrium in the direction of **desorption**, i. e., liberation of the adsorbed molecules. A drop in temperature, on the other hand, increases the amount of substance adsorbed.

Since adsorption takes place only on the surface of a substance, it is clear that the greater the total surface area of the adsorbent, the more molecules it can adsorb. Therefore, porous and powdered substances, as a rule, are of higher adsorptive capacity than nonporous substances. Table 23 shows graphically how rapidly the surface of a substance grows as it is crushed. It shows the increase in the surface area of a cube with an edge one centimetre long when subdivided into cubes with edges of one millimetre, 0.1 mm., etc. The especially high adsorptive capacity of ordinary charcoal is largely due to its porous structure.

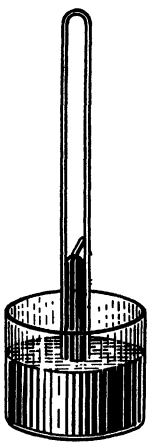


Fig. 106. Apparatus for demonstrating adsorption of ammonia by charcoal

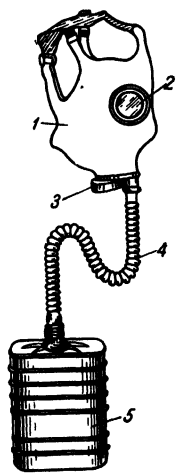


Fig. 107. Gas mask: *1*—rubber mask; *2*—goggles; *3*—exhale valve; *4*—corrugated tube; *5*—adsorption box

The following experiment may be carried out to observe the adsorption of gases by charcoal. Fill a glass cylinder with ammonia and invert it into a vessel containing mercury (Fig. 106). Then heat a piece of charcoal with a gas burner, immerse it in the mercury to cool it and then bring it under the mouth of the cylinder. The charcoal will float to the surface of the mercury in the cylinder, and the mercury will immediately begin to rise, due to adsorption of the ammonia by the charcoal.

The amount of gas adsorbed by an adsorbent depends both on the properties of the adsorbent and on the nature of the gas. A definite relationship is observed in this respect, namely, the higher the critical temperature of a gas, i. e., the easier it can be condensed, the better, as a rule, it is adsorbed.

Table 24 gives the quantities of different gases in millilitres that one gram of charcoal can adsorb at 15°C and normal pressure.

Gases are especially readily adsorbed by *activated* charcoal. One of the best methods of preparing activated charcoal is by heating ordinary birch charcoal strongly in a stream of water vapour. After

Table 24

Adsorption of Gases by Charcoal

Adsorbed gas	B. p., degrees C	Quantity of gas adsorbed, ml.	Adsorbed gas	B. p., degrees C	Quantity of gas adsorbed, ml.
Sulphur dioxide. .	—10.1	380	Carbon dioxide	— 78.5	47.6
Chlorine	—34	235	Methane	—161.5	16.2
Ammonia	—33.4	181	Oxygen	—183	8.2
Hydrogen sulphide	—60.7	99	Hydrogen	—252.7	4.7

such treatment the charcoal becomes very porous and its adsorptive capacity greatly increases.*

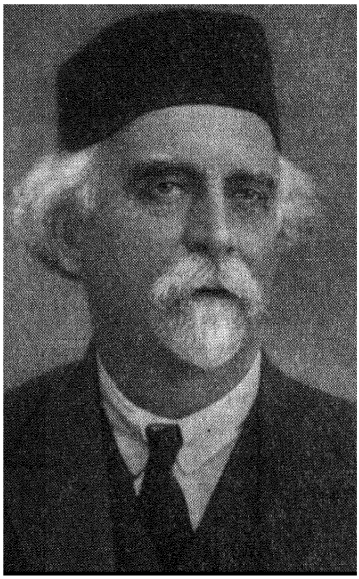
Activated charcoal is used for adsorbing the vapours of volatile liquids from air and gas mixtures. For instance, benzine can be collected by activated charcoal from the natural gases evolved in great quantities in oil-bearing districts. Adsorption of volatile liquids by charcoal and other adsorbents, and their subsequent desorption, is a process which has found wide application in industry, as it saves considerable quantities of valuable solvents.

Strongly cooled activated charcoal is an excellent means for obtaining high degrees of evacuation, as the charcoal adsorbs the last traces of gases which cannot be removed by the vacuum pump. Activated charcoal is used also as a catalyst in certain chemical processes.

During World War I (1914-18) activated charcoal was employed, on the suggestion of N. Zelinsky, to protect the respiratory organs from toxic gases. "Zelinsky's gas masks," filled with activated charcoal, saved thousands of Russian soldiers from agonizing death during the First World War. Activated charcoal is still used in modern gas masks (Fig. 107).

Nikolai Dmitriyevich Zelinsky was born in 1861 in the town of Tiraspol. After graduating the Novorossiisky University (in Odessa) in 1884 he was invited to stay on at the University for research work. In 1891 Zelinsky maintained his Doctor's thesis on stereoisomerism. In 1893 he was appointed head of the chair of inorganic and analytical chemistry at the Moscow University where he continued to work to the end of his life.

* Activated charcoal contains pores of two kinds: a) relatively large pores, visible under the microscope, with diameters between 10^{-3} and 10^{-4} cm. and b) ultrapores, invisible under the microscope, with diameters between 9.2×10^{-7} and 2.8×10^{-7} cm. The latter are the most important in adsorption processes. The total surface of such pores in one gram of activated charcoal may be as high as 1,000 sq. m.



Nikolai Dmitriyevich Zelinsky
(1861-1953)

In 1929 Zelinsky was elected Member of the U.S.S.R. Academy of Sciences. The range of scientific interests of N. Zelinsky was very extensive, and his work very fruitful. The works of Zelinsky and his pupils in the field of organic catalysis occupy a prominent place in world science. Of very great interest are N. Zelinsky's works on mineral oils and on the hydrolysis of proteins, in which he was the first to point out the cyclic structure of protein molecules.

The adsorption of dissolved substances by charcoal was discovered in the latter part of the XVIII century by the Russian Academician T. Lovits, who used charcoal to purify ethyl alcohol. Since that time ethyl alcohol is freed from the impurities it contains (so-called fusel oils) at alcohol factories by filtration through charcoal. At sugar refineries sugar is purified from the substances which account for its yellow colour, in the same way.

There are several other substances besides charcoal which possess a pronounced capacity for adsorption. The dyeing of fabrics, the tanning of leather and some other processes are based on the adsorption of dissolved substances by vegetable and animal fibres.

Various substances are adsorbed differently by the same adsorbent. On the basis of this phenomenon the Russian scientist and botanist M. Tsvet (1872-1919) developed the method of chromatographic ("colour") analysis and used it successfully for resolving chlorophyll, the green pigment of plant leaves, into its two component parts, the structures of which are almost identical.

M. Tsvet extracted chlorophyll from the leaves with benzine and passed the solution through a glass column packed tightly with calcium carbonate. In passing through the column the benzine lost its colour, and the component pigments, adsorbed successively by the calcium carbonate, formed a series of coloured rings in the cylindrical column. Removing the calcium carbonate column from the glass cylinder, Tsvet separated the rings from one another and extracted the adsorbed substance from each of them by means of a suitable solvent. In this way he obtained the chemically pure forms of chlorophyll.

In founding the exceedingly accurate method of adsorption analysis, Tsvet realized the chemists' long-cherished dream of separating mixtures of related chemical compounds into their component parts without drastic chemical or physical treatment. The chromatographic method is now used extensively in all kinds of investigations. By its means purest preparations of various vitamins, hormones, penicillin and other substances are obtained in present-day industry.

Academician P. Rehbinder established the influence of adsorption on the mechanical strength of various materials. He showed that when surface-active substances, i. e., substances capable of lowering the surface tension of liquids considerably, are adsorbed by solids, the adsorbed molecules "wedge apart" the minute cracks in the solids and thus lower their strength. This phenomenon is of great importance for rock drilling practice, in the mechanical treatment of alloys, etc.

158. Chemical Properties of Carbon. Carbides. At ordinary temperatures carbon is inert and reacts only with very active oxidants. When heated, the activity of carbon increases; it unites readily with oxygen and is a good reducing agent. The most important process in metallurgy, the smelting of metals from their ores, is carried out by reducing the oxides of metals with coal (or carbon monoxide).

Carbon forms two principal oxides with oxygen, viz., carbon dioxide, or carbonic acid gas, CO_2, and carbon monoxide CO. Besides them oxides of the compositions C_3O_2 and $C_{12}O_9$ are known.

At very high temperatures carbon combines with hydrogen, sulphur, silicon, boron and many metals.

The most reactive of the allotropic modifications of carbon is amorphous carbon.

Compounds of carbon with metals and other elements, which are electrically positive with respect to carbon, are called **carbides.** They are obtained by heating either the metals or their oxides strongly with coal.

Carbides are crystalline solids with very high melting points. Their composition is very diverse and frequently does not correspond at all to the valencies of the combining elements. Some carbides are

easily decomposed by water to form hydrocarbons; others are not attacked even by dilute acids.

Of great practical importance is calcium carbide CaC_2, obtained by calcining a mixture of coal and lime:

$$CaO + 3C = CaC_2 + CO$$

This reaction is usually accomplished in an electric furnace.

Recently a new method of production of calcium carbide has been developed, which does not require the expenditure of comparatively expensive electric power. According to this method, the carbide is obtained in simple vertical furnaces of the same type as blast furnaces, in which the high temperature needed for the formation of the carbide (up to 2,000°C and more) is attained by blowing air, enriched with oxygen, through the furnace.

The pure carbide is quite colourless, but the technical product consists of hard opaque lumps of a dark grey colour. Calcium carbide is used to prepare acetylene by the action of water (see § 170). Acetylene is widely used in many industries; a considerable amount of calcium carbide is consumed by plants manufacturing calcium cyanamide, a valuable fertilizer.

Other practically important carbides are silicon and tungsten carbides (see §§ 180 and 245).

159. Carbon Dioxide CO_2 and Carbonic Acid H_2CO_3. *Carbon dioxide* or carbonic acid gas forms continuously in nature during all kinds of processes of oxidation of organic substances (decay of vegetable and animal remains, burning of fuel, respiration). Carbon dioxide escapes in large quantities from cracks in the earth's crust in volcanic regions, and from the waters of many mineral springs.

Carbon dioxide is usually prepared in the laboratory by the action of hydrochloric acid on marble $CaCO_3$:

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$$

Large quantities of carbon dioxide are produced in industry as a by-product in the manufacture of lime by roasting limestone:

$$CaCO_3 = CaO + CO_2$$

Under ordinary conditions carbon dioxide is a colourless gas about one and a half times as heavy as air, so that it can be poured like a liquid from one vessel into another. One litre of carbon dioxide at S.T.P. weighs 1.98 gr. Water will dissolve a considerable quantity of carbonic acid gas. At 20°C one volume of water can dissolve 0.88 volumes of CO_2 and at 0°C—1.7 volumes. Carbon dioxide is used mainly for the production of soda by the Solvay process (p. 426), in the sugar-beet industry, and for gasifying soft and mineral drinks, wines, beer and other beverages.

At a pressure of about 60 atm. carbon dioxide can be converted into a liquid at ordinary temperatures. Liquid carbon dioxide is stored in steel cylinders. If let out of the cylinder rapidly, so much heat is absorbed due to its evaporation that the carbon dioxide turns into a solid white snow-like mass which sublimates without melting at —78.5°C.

Known as "dry ice," solid carbon dioxide is used for cooling perishables, for the manufacture and storage of ice cream and in many other cases where low temperatures are required.

A solution of carbon dioxide in water has a slightly sour taste and reacts slightly acid with litmus, this being due to the presence in the solution of small quantities of carbonic acid H_2CO_3, formed as a result of the following reversible reaction:

$$CO_2 + H_2O \rightleftarrows H_2CO_3$$

The equilibrium of this reaction is shifted greatly to the left, so that not more than 1 per cent of the CO_2 dissolved is converted into carbonic acid.

Carbonic acid H_2CO_3 can exist only in aqueous solution. If the solution is heated the carbon dioxide escapes, the equilibrium shifts to the left and at length only pure water remains.

The formula of carbonic acid has been established by analyzing its salts.

Carbonic acid is a very weak acid. In solution it ionizes mainly into $H^{\cdot}$ and HCO_3', forming CO_3''-ion in very small quantities:

$$H_2CO_3 \rightleftarrows H^{\cdot} + HCO_3' \rightleftarrows 2H^{\cdot} + CO_3''$$

A dibasic acid, carbonic acid forms two series of salts, normal and acid; the normal salts are called **carbonates** and the acid, **hydrocarbonates, acid carbonates** or **bicarbonates.**

The *salts of carbonic acid* can be prepared either by the action of carbon dioxide on alkalis or by exchange reactions between the soluble salts of carbonic acid and the salts of other acids. For instance:

$$NaOH + CO_2 = NaHCO_3$$
$$NaHCO_3 + NaOH = Na_2CO_3 + H_2O$$
$$BaCl_2 + Na_2CO_3 = \downarrow BaCO_3 + 2NaCl$$

With weak bases carbonic acid mostly gives only basic salts, an example of which is basic copper carbonate $Cu_2(OH)_2CO_3$. A mineral of this composition occurs in nature and is known as *malachite.*

Under the action of acids, even such weak ones as acetic acid, all the salts of carbonic acid decompose, liberating carbon dioxide. This reaction is very characteristic and is often employed as a test for carbonates, as the liberation of carbon dioxide can easily be detected by the hissing sound accompanying it or by means of a burning splint.

When heated more or less strongly all the salts of carbonic acid except those of the alkali metals decompose, liberating carbon dioxide. The decomposition products are mostly the oxides of the corresponding metals. For instance:

$$MgCO_3 = MgO + CO_2$$
$$CaCO_3 = CaO + CO_2$$

The hydrocarbonates of the alkali metals are converted by heating into carbonates:

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O$$

Potassium, sodium and ammonium carbonates and most hydrocarbonates are soluble in water, but the carbonates of the other metals are insoluble.

Solutions of potassium and sodium carbonates react strongly alkaline owing to hydrolysis:

$$Na_2CO_3 + H_2O \rightleftarrows NaHCO_3 + NaOH$$

or

$$CO_3'' + H_2O \rightleftarrows HCO_3' + OH'$$

This accounts, by the way, for their use in washing clothes (alkalis help to remove grease from dirty clothes). The same effect is displayed by an infusion of ashes in water (called "lye") due to the presence of potassium carbonate.

One of the most abundant salts of carbonic acid in nature is *calcium carbonate* $CaCO_3$. It occurs as limestone, chalk and marble, all of which are modifications of calcium carbonate. This salt is contained also in almost all types of soil.

Calcium carbonate is insoluble in water. That is why lime water becomes turbid if carbon dioxide is passed through it:

$$Ca(OH)_2 + CO_2 = \downarrow CaCO_3 + H_2O$$

However, if carbon dioxide is passed through lime water for a long time, the liquid first becomes turbid, then gradually begins to clear, and finally becomes quite transparent. The precipitate dissolves owing to the formation of the acid salt, calcium hydrocarbonate:

$$CaCO_3 + H_2O + CO_2 = Ca(HCO_3)_2$$

Calcium hydrocarbonate is unstable. If its solution is boiled or just left standing for a long time in the air the hydrocarbonate decomposes, liberating carbon dioxide and forming the normal salt.

The solubility of hydrocarbonates in water accounts for the constant migration of carbonates in nature. When rain water containing carbon dioxide absorbed from the air seeps through the soil, and especially through limestone strata, it dissolves calcium carbonate and carries it as the hydrocarbonate into streams, rivers and seas.

Here it is assimilated by the organisms of sea animals and goes to build up their skeletons, or, losing carbon dioxide, it changes back into calcium carbonate and is deposited in layers.

Another carbonate occurring in nature in large quantities is *magnesium carbonate* $MgCO_3$, the mineral being known as *magnesite*. Magnesium carbonate, like calcium carbonate, dissolves readily in water containing carbon dioxide, turning into the soluble acid salt.

Some carbonates are valuable ores and are used for the extraction of metals (for instance, iron spar $FeCO_3$, smithsonite $ZnCO_3$, etc.).

Sodium and potassium carbonates and hydrocarbonates are widely used in industry and in the home.

Sodium carbonate Na_2CO_3, or *soda*, is one of the chief products of the basic chemical industry. Soda is used in immense quantities by the glass, soap, pulp and paper, textile, mineral oil and other industries and serves also for the preparation of various sodium salts. The domestic uses of soda are well known to everybody.

Up to the end of the XVIII century all the soda used in industry was obtained only from natural sources. Such were the natural deposits of sodium carbonate found in Egypt and several other places, the ashes of seaweeds and plants grown on saline soils, and soda lakes. In 1775, the deficiency of alkalis in France led the French Academy of Sciences to announce a prize for the best method of preparing soda from common salt. However, sixteen years passed before the French physician Nicolas Le Blanc developed an economical method of obtaining soda, now known as the Le Blanc, or sulphate, process, and put it into practice on an industrial scale in 1791.

The *sulphate*, or *Le Blanc*, *process* consists essentially of the following reactions. First, common salt is converted into sodium sulphate by the action of sulphuric acid:

$$2NaCl + H_2SO_4 = 2HCl + Na_2SO_4$$

The sodium sulphate is mixed with limestone and coal, and the mixture is heated to redness. The coal reduces the sulphate into sodium sulphide:

$$Na_2SO_4 + 2C = Na_2S + 2CO_2$$

The sodium sulphide reacts with the limestone to form calcium sulphide and soda:

$$Na_2S + CaCO_3 = Na_2CO_3 + CaS$$

The fusion, consisting of soda, calcium sulphide and the excess coal and lime, is treated with water to dissolve the sodium carbonate. The presence of an excess of lime, due to the decomposition of $CaCO_3$, prevents hydrolysis of the calcium sulphide and its conversion into the soluble acid salt $Ca(HS)_2$, permitting the sodium carbonate to be extracted completely from the fusion. The carbonate solution is condensed by evaporation until crystallization sets in. At a low temperature the highly efflorescent crystals of the decahydrate $Na_2CO_3 \cdot 10H_2O$ are formed; at a higher temperature the monohydrate $Na_2CO_3 \cdot H_2O$ crystallizes out.

The by-products of the sulphate process for the manufacture of soda are: hydrogen chloride, which previously used to be discharged into the air, but is now used to make hydrochloric acid, and calcium sulphide, which is of no commercial importance.

In the 1860's a Belgian chemist Solvay suggested a new method of preparing soda from common salt, known as the *Solvay* or *ammonia process.*

This process is based on the formation of sodium hydrocarbonate by the reaction between common salt and ammonium hydrocarbonate in aqueous solution.

In industry this reaction is accomplished as follows. A concentrated solution of common salt is cooled and saturated with ammonia; then carbon dioxide, obtained by roasting limestone, is passed through under pressure. The interaction between the ammonia, carbon dioxide and water leads to the formation of ammonium hydrocarbonate:

$$NH_3 + CO_2 + H_2O = NH_4HCO_3$$

which enters into an exchange reaction with the salt to form ammonium chloride and sodium hydrocarbonate:

$$NH_4HCO_3 + NaCl = \downarrow NaHCO_3 + NH_4Cl$$

This reaction takes place due to sodium hydrocarbonate being but sparingly soluble in cold water and falling out as a precipitate, which can be separated by filtration.

When heated strongly, sodium hydrocarbonate decomposes into the carbonate, water and carbon dioxide, the latter being re-used:

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O$$

The solution containing ammonium chloride is heated with lime to recover the ammonia:

$$2NH_4Cl + Ca(OH)_2 = 2NH_3 + CaCl_2 + 2H_2O$$

Thus, in the ammonia process for the production of soda the only industrial waste is the calcium chloride which remains in solution after the ammonia is driven off; calcium chloride is a product of but limited importance.

Soda prepared by the ammonia method contains no crystallization water and is called *soda ash.*

Part of the sodium hydrocarbonate is marketed, being employed in medicine and as a substitute of yeast (under the name of "baking soda").

At present the ammonia process has forced the Le Blanc sulphate process almost completely out of use. The chief advantage of the former over the latter is its low fuel consumption.

The output of soda ash in the U.S.S.R. was 1,437 thousand tons in 1955. In the course of the Sixth Five-Year Plan it is to be increased by 68 per cent and reached 2,420 thousand tons in 1960.

Potassium carbonate K_2CO_3, or *potash.* Formerly potash was obtained only from plant ashes by leaching them with water and evaporating the resulting solution. Nowadays potash is prepared chiefly by the action of carbon dioxide on a solution of caustic potash formed by electrolysis of a potassium chloride solution

$$KOH + CO_2 = KHCO_3$$
$$KHCO_3 + KOH = K_2CO_3 + H_2O$$

Potash is a white powder-like substance, deliquescent in humid air and very soluble in water. It is used in soap manufacturing, in the production of refractory glass, in photography, etc.

160. Carbon Monoxide CO. Carbon monoxide is a colourless poisonous gas which liquefies only at —192°C and solidifies at —207°C. Carbon monoxide is very slightly soluble in water and does not react with it chemically.

Carbon monoxide forms whenever coal or carboniferous compounds are burnt with an insufficient supply of oxygen at high temperatures (at low temperatures the result is always carbon dioxide). Carbon monoxide forms also when carbon dioxide comes into contact with red-hot coal:

$$CO_2 + C \rightleftarrows 2CO - 38.3 \text{ Cal.}$$

This reaction is reversible and proceeds from left to right with the absorption of heat. As long as the temperature is not over 400 or 450°C, the equilibrium of the reaction is practically shifted completely to the left, but if the temperature is raised still higher it begins to shift to the right and by 800°C the degree of conversion of CO_2 into CO reaches about 90 per cent. Thus, by passing carbon dioxide through a layer of red-hot coal, the CO_2 can be converted almost entirely into carbon monoxide.

Pure carbon monoxide is usually prepared in the laboratory by adding formic acid HCOOH in small portions to hot sulphuric acid. The latter abstracts the elements of water from formic acid, liberating carbon monoxide:

$$HCOOH = CO + H_2O$$

This reaction shows that carbon monoxide may be regarded as the anhydride of formic acid. Although formic acid cannot be obtained directly from carbon monoxide and water, its salts can be formed by the reaction between alkalis and carbon monoxide at 150-200° C:

$$NaOH + CO = NCOONa$$

Carbon monoxide burns in air with a bluish flame, turning into carbon dioxide:

$$2CO + O_2 = 2CO_2 + 136 \text{ Cal.}$$

As a large amount of heat is liberated during this reaction, carbon monoxide is widely used in mixture with other gases as a gaseous fuel. In particular, coke-oven gas contains about 4 per cent carbon monoxide.

In the sunlight or in the presence of activated charcoal (as a catalyst), carbon monoxide unites directly with chlorine forming an exceedingly poisonous gas known as *phosgene*:

$$CO + Cl_2 = COCl_2$$

Phosgene is used in various organic syntheses.

At high temperatures carbon monoxide is an active reducing agent and plays an important part in metallurgy in the reduction of metals from their oxides.

Carbon monoxide is very poisonous and is especially dangerous because it has no odour; for this reason carbon monoxide poisoning may occur quite unnoticed. Carbon monoxide poisoning occurs frequently due to furnace dampers being closed too early, when there are still red-hot coals left in the furnace; this may lead to the formation of carbon monoxide, which then penetrates into the heated premises.

The poisonous action of carbon monoxide, known as *coal gas* or *charcoal fume poisoning*, is due to the fact that CO combines readily with haemoglobin of the red blood corpuscles, rendering them incapable of carrying oxygen from the lungs to the tissues. If fresh air is inhaled this compound is gradually decomposed, and the haemoglobin recovers its ability to absorb oxygen.

161. Compounds of Carbon with Sulphur and Nitrogen. Of the compounds of carbon with sulphur and nitrogen the most important, practically, are: carbon disulphide CS_2 and hydrocyanic acid HCN.

Carbon disulphide CS_2 is prepared by passing sulphur vapours through red-hot coal. It is a colourless volatile liquid with a high index of refraction, boiling at 46° C and possessing an ethereal odour in the pure form. After standing for some time carbon disulphide turns yellow and acquires a disgusting odour.

Carbon disulphide is poisonous and very inflammable. It readily dissolves sulphur, phosphorus, iodine, various fats and resinous substances. Carbon disulphide is consumed in large quantities to destroy various agricultural pests, but most of it is used to prepare rayon, which is employed for the manufacture of one of the types of artificial silk.

Hydrocyanic Acid HCN. At the temperature of an electric arc carbon will unite directly with nitrogen to form a colourless poisonous gas, *cyanogen*, the molecular weight of which corresponds to the formula C_2N_2. In chemical properties cyanogen resembles the halogens. Like them, it forms a hydrogen compound HCN with acid properties, called hydrocyanic acid.

Hydrocyanic acid is a colourless, very volatile liquid, boiling at 26.5°C and possessing a characteristic odour of bitter almond. It is usually prepared by the action of sulphuric acid on its salts, for instance on KCN:

$$2KCN + H_2SO_4 = K_2SO_4 + 2HCN$$

In aqueous solution hydrocyanic acid ionizes insignificantly ($K = 4.7 \times 10^{-10}$).

Hydrocyanic acid is one of the most powerful poisons and is mortal even in very small doses (under 0.05 gr.).

Free hydrocyanic acid is one of the best means of fighting parasitic insects, rodents and orchard pests. It is used also in industry for organic syntheses. Hydrocyanic acid should be handled very carefully due to its high toxicity.

Hydrocyanic acid salts are called **cyanides.** The most important cyanides in practice are those of the alkali metals, potassium and sodium, obtained by various methods, for instance, by heating a mixture of coke and potash or soda in an atmosphere of nitrogen. The most widely used is potassium cyanide.

Potassium cyanide KCN is a colourless crystalline substance, readily soluble in water. Potassium cyanide is just as poisonous as hydrocyanic acid. It decomposes quite rapidly in the air under the action of carbon dioxide, liberating hydrocyanic acid and turning into potash:

$$2KCN + H_2O + CO_2 = K_2CO_3 + 2HCN$$

A salt of a very weak acid, potassium cyanide is greatly hydrolyzed in water:

$$CN' + H_2O \rightleftarrows HCN + OH'$$

Therefore its solution reacts alkaline and smells strongly of hydrocyanic acid. Sodium cyanide possesses similar properties.

Potassium and sodium cyanides are capable of dissolving gold and silver in the presence of atmospheric oxygen. This is the basis of their use for the extraction of these metals from their ores. Besides they are used for the preparation of hydrocyanic acid, in organic syntheses, in galvanic gold and silver plating, in photography, etc.

162. Thermochemistry. As we know, during chemical changes energy may be evolved or absorbed in various forms: as heat, light,

electricity, etc. Quantitative investigation of the thermal changes accompanying chemical reactions makes the subject of a special branch of chemistry known as **thermochemistry.**

The thermal effects of chemical reactions are measured by means of special apparatuses called calorimeters. The simplest type of calorimeter is a vessel with good thermal insulation containing an accurately weighed quantity of water. The reaction is carried out in a reaction chamber placed inside the calorimeter. The heat evolved during the reaction is transferred to the water, the temperature of which is measured before and after the reaction by means of a delicate thermometer. The product of the temperature increase by the specific heat of the water and the calorimeter is a measure of the heat liberated during the reaction.

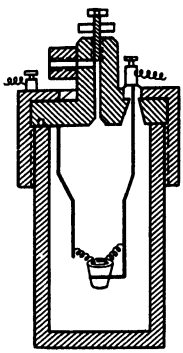


Fig. 108. Calorimetric bomb

Especially important in practice is the determination of the amount of heat evolved during the combustion of various substances. These determinations are carried out with the aid of a *calorimetric bomb* (Fig. 108), which is a closed vessel made of strong steel and capable of withstanding a pressure of several score atmospheres.

The bomb is placed in a calorimeter. The substance to be burnt is put into the bomb, which is filled with oxygen under pressure, and the reaction is brought about by means of an electric ignition device. The amount of heat evolved is determined by the rise in temperature of the water in the calorimeter.

The main principle underlying all thermochemical calculations was established by the Russian Academician G. Hess in 1840. This principle, known as **Hess's Law**, may be formulated as follows:

> *The thermal effect of a reaction depends only on the initial and final conditions of the reacting substances, but not on the intermediate stages of the process.*

This can be explained by an example. A dilute solution of sodium sulphate Na_2SO_4 can be prepared from sulphuric acid, sodium hydroxide and water in various ways, for instance: 1) by mixing a dilute solution containing two gram-molecules of NaOH with a solution containing one gram-molecule of H_2SO_4; 2) by adding a solution containing one gram-molecule of NaOH to a solution containing one gram-molecule of H_2SO_4, thus forming first a solution of the acid salt $NaHSO_4$, and then adding one more gram-molecule of NaOH to the acid salt solution.

The thermal effect for these two cases will be *:

First way:

$$2NaOH\ (aq.) + H_2SO_4\ (aq.) = Na_2SO_4\ (aq.) + 2H_2O\ (liq.) + 31.4\ Cal.$$

* The symbol (aq.) indicates that the substance is in aqueous solution.

Second way:

$$NaOH\ (aq.) + H_2SO_4\ (aq.) = NaHSO_4\ (aq.) + H_2O\ (liq.) + 14.75\ Cal.$$
$$NaHSO_4\ (aq.) + NaOH\ (aq.) = Na_2SO_4\ (aq.) + H_2O\ (liq.) + 16.65\ Cal.$$

Total 31.4 Cal.

Thus, the total amount of heat evolved during the formation of one gram-molecule of sodium sulphate is the same in both cases, although the reaction took place in two stages in the second case.

Hess's Law makes it possible to calculate the thermal effect of reactions in cases when they cannot be measured directly for some reason or other. The usual method used in such calculations is to break up the complex reaction into separate stages. Calculation of the thermal effect sought is based on the fact that the total amount of heat evolved (or absorbed) during the reaction in question equals the algebraic sum of the heat evolved (or absorbed) during the successive stages of the reaction. When carrying out such calculations it should be kept in mind that the heat of formation of a complex substance from simple substances equals its heat of decomposition with the opposite sign.

A good example of the use of Hess's Law is calculation of the heat of formation of carbon monoxide from the simple substances—coal and oxygen. The thermal effect of this reaction cannot be determined directly by experiment, as coal, when burnt, forms carbon dioxide and not carbon monoxide. But knowing the heat of formation of carbon dioxide from carbon and oxygen (97.7 Cal.) and the heat of combustion of carbon monoxide (68 Cal.), the heat of formation of carbon monoxide can be calculated.

The combustion of carbon can be represented by the following thermochemical equation:

$$C\ (s.) + O_2\ (g.) = CO_2\ (g.) + 97.7\ Cal.$$

We break this reaction up into stages, assuming that the carbon burns to form carbon monoxide, which then burns in its turn, forming carbon dioxide. Denoting the heat of formation of carbon monoxide by x, we write the equations for the individual stages of the reaction and add them up:

$$C + \frac{1}{2} O_2 = CO + x\ Cal.$$
$$CO + \frac{1}{2} O_2 = CO_2 + 68\ Cal.$$
$$C + O_2 = CO_2 + x\ Cal. + 68\ Cal.$$

Comparing the resulting equation with that written above we find:

$$x + 68 \text{ Cal.} = 97.7 \text{ Cal.}$$

hence

$$x = 29.7 \text{ Cal.}$$

Therefore, the heat of formation of carbon monoxide from carbon and oxygen equals 29.7 Cal.

The result obtained is very interesting. It shows that the addition of the second oxygen atom to the carbon atom is accompanied by the evolution of a much larger quantity of heat than the addition of the first atom. This is due probably to the fact that the first bond that has to be ruptured during the oxidation of carbon is that between the carbon atoms. This work consumes the greater part of the energy liberated during the union of the carbon atom with the first oxygen atom, so that only the energy left after this is liberated as heat.

When coal burns to form carbon monoxide it evolves only a little over a quarter of the amount of heat produced by its complete combustion. Hence the economic importance of complete combustion of fuel. The presence of a large amount of carbon monoxide in the flue gases discharged into the air shows that a considerable part of the energy, contained in the coal burnt, was lost.

To help the student to master thermochemical calculations, we shall calculate the thermal effect of the reaction of combustion of methane CH_4, proceeding from the following data: the heat of formation of methane is 21.7 Cal., of water 68.4 Cal., and of carbon dioxide 97.7 Cal.

Denoting the thermal effect sought by x, we write down the reaction of combustion of methane:

$$CH_4\,(g.) + 2O_2\,(g.) = CO_2\,(g.) + 2H_2O\,(liq.) + x \text{ Cal.}$$

We break the reaction up into stages. Suppose the methane decomposes first into hydrogen and carbon, and then the carbon and hydrogen unite with oxygen to form water and carbon dioxide respectively. Considering that the heat of formation of methane equals 22.7 Cal. and therefore the same amount of heat must be absorbed during its decomposition, we write out the equations for the individual stages of the reaction and add them up:

$$\begin{aligned} CH_4 &= C + 2H_2 - 22.7 \text{ Cal.} \\ C + O_2 &= CO_2 + 97.7 \text{ Cal.} \\ 2H_2 + O_2 &= 2H_2O + 2 \cdot 68.4 \text{ Cal.} \\ \hline CH_4 + 2O_2 &= CO_2 + 2H_2O + 211.8 \text{ Cal.} \end{aligned}$$

The above example is an illustration of the following general corollary derived from Hess's Law:

The thermal effect of a chemical reaction equals the sum of the formation heats of the resulting substances minus the sum of the formation heats of the reactants.

This corollary simplifies many thermochemical calculations. For instance, the above problem can be solved in the following way. Writing out the equation of the combustion of methane and denoting the thermal effect sought by x, we write the respective heat of formation under the formula of each substance:

$$\underset{22.7\ \text{Cal.}}{CH_4\,(g)} + \underset{}{2O_2\,(g)} = \underset{97.7\ \text{Cal.}}{CO_2\,(g)} + \underset{2\cdot 68.4\ \text{Cal.}}{2H_2O\,(\text{liq.})} + x\ \text{Cal.}$$

hence

$$x = 97.7 + 2\cdot 68.4 - 22.7 = 211.8\ \text{Cal.}$$

163. Fuel and Types of Fuel. Amorphous carbon, as charcoal and coke, mineral coal, and many carbon compounds, play a very important part in modern life as sources of various kinds of energy. When coal and carboniferous compounds are burnt, heat is evolved which can be employed for heating, preparing food and for many industrial processes. Most of the heat obtained, however, is converted into other kinds of energy and is used to do mechanical work.

True, to put various machines into motion we use, besides thermal power, the power of falling water ("white coal") and wind power; there have also been attempts to make direct use of solar energy; however, these are all as yet but a small fraction of the power obtained by burning fuel.

The chief types of fuel are: mineral coal, peat, wood, mineral oil and natural gas.

Mineral coal is the most widely used type of fuel. It is used both directly for burning and for the production of more valuable types of fuel, namely, coke, liquid fuel, gaseous fuel.

The world's resources of mineral coal are estimated at 7,900,000 million tons. The coal resources of the U.S.S.R. are the second largest in the world.

The coal mined in tsarist Russia could not cover the requirements of even the underdeveloped industry of that time, and mineral coal was imported additionally from abroad. The only source of coal in the whole country at that time was the Donets Basin. Russia occupied the sixth place in world coal mining.

After the October Revolution great changes took place in the coal industry. During the pre-war five-year plan periods new coal basins were put into operation in Central Asia, in the Caucasus, in Eastern Siberia. Coal mining was started in a number of other districts as well. The output of coal in 1959 amounted to 506.5 million tons. By 1965 it will be 600 to 612 million tons per year. But the share of coal

in this country's fuel production will gradually decrease, as the output of oil and natural gas makes headway.

Mineral coal is the remains of the vegetable kingdom which existed on our planet in the long past periods of its life. The older the coal, the more carbon it contains.

Three main types of mineral coal are distinguished:

1. *Anthracite*, the oldest of mineral coals. It has a high density and bright lustre, contains an average of 95 per cent carbon and gives a large amount of heat when burnt. The resources of anthracite in the U.S.S.R. constitute about 5.5 per cent of its total coal resources.

2. *Bituminous coal* is a compact black substance containing between 75 and 90 per cent carbon. It is the most widely used of all mineral coals.

3. *Brown coal* or *lignite* contains 65 to 70 per cent carbon. Is brown in colour. The youngest of all mineral coals, it often bears traces of the structure of the wood from which it originated. Brown coal is very hygroscopic, has a high ash content (from 7 to 38 per cent), and for that reason is used only as local fuel.

Recently larger and larger quantities of brown coal have been employed as a raw material for the production of valuable types of liquid fuel, gasoline and kerosene. For this purpose the powdered coal is *hydrogenated*, i. e., heated under high pressure with hydrogen in the presence of catalysts. Under the action of hydrogen the very complex organic molecules split apart and form simpler molecules of saturated hydrocarbons (see § 169). The products resulting from the hydrogenation of coal are again split and converted into gasoline and kerosene.

Of great importance in many districts of the U.S.S.R. is the use of peat.

Peat is a product of the first stage of formation of mineral coals. It forms in immense quantities at the bottoms of marshes from the dead parts of marsh lichens. In explored peat resources the U.S.S.R. is the richest country in the world. The carbon content of peat does not exceed 65 per cent. Its chief disadvantage as a fuel is its high ash content. Peat is burnt as a local fuel at a number of large power stations.

Dry distillation of peat results in *peat coke*, which contains very little sulphur, making it suitable for smelting high quality iron. Besides, upon dry distillation peat yields a number of valuable chemical products.

Wood occupies a secondary place in the total fuel balance.

In recent years the use of wood as fuel in industry has been continuously decreasing, as timber can be utilized to greater advantage for other purposes.

Mineral oil has been used widely as fuel ever since the end of the XIX century when the internal-combustion engine was invented. This engine burns oil and makes it possible to utilize a much greater

part of heat evolved during the combustion of the fuel than the steam engine. Oil products, gasoline and kerosene, are used as fuel for tractors, automobiles, aeroplanes, etc. The great importance of internal-combustion engines in modern life makes oil, and especially its products, a fuel of prime importance. The explored oil resources of the Soviet Union are the largest in the world.

The Russian oil industry began to develop extensively under Soviet power. By 1940 the production of oil had increased 3.4 times compared to 1913. In 1959 the oil output of the Soviet Union was 129.5 million tons, while by 1965 it is to reach 230 to 240 million tons per year.

Oil is not only a convenient and highly calorific fuel, but also a most important raw material for the production of a wide range of chemical products. Of great importance as a raw material for the chemical industry are also casing head and refinery gases.

Natural gas, consisting of methane and other saturated hydrocarbons, is a very cheap and convenient fuel. The importance of natural gas is evident from the fact that in the course of 12 years (1940-52) its extraction in the capitalist countries increased threefold and reached 259,000 million cubic metres, whilst the coal output of these countries hardly increased at all during the same period.

Natural gases began to be utilized in our country practically only after the war. In 1947 the Saratov-Moscow gas line, 843 kilometres long, was completed, and this increased the supply of gaseous fuel to the capital by about five times. In 1948 the Dashava-Kiev gas line was put into operation, bringing gas to the Ukrainian capital from Dashava, a very rich source of natural gas in the Carpathian foothills.

During recent years a great number of new gas mains have been built in the Soviet Union. The largest is the Stavropol-Moscow gas main. Huge deposits of natural gas have been discovered in the Ukraine, the Krasnodar Territory, Middle Asia and a number of districts of Siberia.

The gas industry is one of the most rapidly developing branches of the country's heavy industry. In 1955, 10,400 million cubic metres of gas were produced by coal and slate processing, while in 1959 this figure had risen to 37,200 million cubic metres. In 1965 the total gas output is to reach 150,000 million cubic metres.

Natural gas is an exceedingly valuable and economical raw material for the organic synthesis industry and for the manufacture of many synthetic products. A number of new chemical plants now in construction are to be based on natural gas; besides, several operating chemical enterprises are being switched to this raw material.

Equal quantities of fuel give different quantities of heat when burnt. Therefore, to evaluate the quality of a fuel, its **heat value** is

determined, this being the maximum amount of heat evolved upon complete combustion of one kilogram of the fuel.

The various types of fuel consist mainly of the three elements: carbon, hydrogen and oxygen. It may be considered that the higher the carbon and hydrogen content in the fuel, the greater its heat value.

The average composition of the organic mass of various kinds of fuel and their heat values are given in Table 25.

Table 25

Elemental Composition and Heat Values of Various Kinds of Fuel

Fuel	Content, per cent			Heat value Cal./kg.
	Carbon	Hydrogen	Oxygen (nitrogen, sulphur)	
Wood, air-dry	50	6	44	4,500
Peat, air-dry	59	6	35	5,400
Brown coal	69	5.5	25.5	6,700
Bituminous coal	82	4.3	13.7	8,400
Anthracite	95	2.2	2.8	8,100
Charcoal	100	—	—	8,080
Mineral oil	85.5	14.2	0.3	10,500

164. Gaseous Fuel. Of essential importance for many industries is not only the heat value of a fuel, but also the highest temperature that can be obtained with the fuel, if burnt rationally. This temperature is called the **pyrometric burning effect** and, besides the calorific power of the fuel, it depends to a considerable extent on the physical state of the latter.

Experience shows that for complete combustion of a solid fuel, approximately one and a half times the amount of air needed theoretically must be introduced into the furnace where it is being burnt. This excess air absorbs part of the heat evolved and greatly lowers the pyrometric burning effect.

A higher pyrometric effect is obtained when a liquid fuel, such as crude oil, is burnt. The oil is introduced into the stoker by means of special atomizers, called *burners*, which mix it thoroughly with air, so that it does not require such an excess of the latter as solid fuel.

But only gaseous fuel can be mixed perfectly with air and therefore it burns up completely with almost the theoretical quantity of air and gives the highest pyrometric effect.

Another important advantage of gaseous fuel is the possibility of utilizing the heat of the combustion products formed for pre-heating

the fuel and the air mixed with it, thus increasing the temperature developed during combustion still more.

The heat of the hot combustion products is utilized in regenerative furnaces, a diagram of which is shown in Fig. 109. The furnace consists of four regenerative chambers filled with refractory bricks laid in squares. Air is introduced into regenerator *IV* through pipe *1*, and the fuel gas into regenerator *III* through pipes *2* and *3*. The

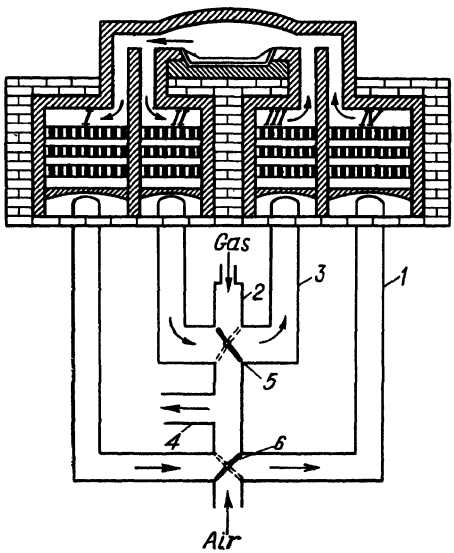


Fig. 109. Diagram of regenerative furnace:
1, *2*, *3* and *4*—piping; *5* and *6*—valves

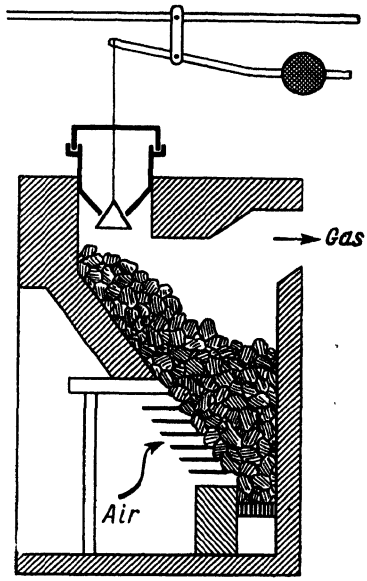


Fig. 110. Diagram of producer

gases mix under the roof of the furnace and burn. The combustion products pass through regenerators *I* and *II*, transferring their heat to the bricks in these chambers. The cooled gases are discharged through pipe *4* into the chimney stack. If valves *5* and *6* are turned into the position indicated by dotted lines on the diagram, the direction of the gases changes: now the air and the fuel gas pass into regenerators *I* and *II*, where they are preheated, while the combustion products are discharged through regenerators *III* and *IV*.

In regenerative furnaces the temperature may rise as high as 1,800°C. In such furnaces not only iron and steel, but even platinum, can be melted.

Of course, part of the fuel must be expended on converting the solid fuel into gaseous. Calculations show that about one-third of the total heat that the fuel can yield is lost in this way. However,

this loss is made up for by the high temperature developed in burning the resulting gases, especially if it is taken into account that they can be produced from such materials as peat, slack coal, etc., which will not give high temperatures if burned in ordinary furnaces.

The most important types of gaseous fuel are: natural gas (see § 163), producer gas, water gas and coal or coke-oven gas.

Producer gas is obtained by blowing air through a layer of red-hot coal. This process is carried out in tall cylindrical furnaces, called producers (Fig. 110). The fuel, say coal, is dumped into the producer at the top, while air is forced in at the bottom. As the coal burns, carbon dioxide forms in the lower part of the producer and upon rising is reduced by the hot coal to carbon monoxide; the latter is discharged from the furnace together with the nitrogen of the air, which had not taken part in the reaction, through an opening in the side wall of the producer. A mixture of these two gases, containing theoretically two volumes of nitrogen per volume of carbon monoxide (or more precisely 34.7 per cent CO and 65.3 per cent N_2) is known as producer gas. Producer gas usually contains a little carbon dioxide (2.5 to 5 per cent).

The reactions taking place in the producer may be expressed by the following equations:

$$C + O_2 = CO_2 + 97.7 \text{ Cal.}$$
$$CO_2 + C = 2CO - 38.3 \text{ Cal.}$$

More heat is liberated during the first of these reactions than is absorbed during the second, so that in the long run some excess heat is obtained, which keeps the coal in the producer hot.

Water gas is made by passing steam through a layer of red-hot coal in a producer:

$$C + H_2O = CO + H_2 - 28.1 \text{ Cal.}$$

As can be seen from the equation, water gas consists of equal volumes of carbon monoxide and hydrogen. As both component parts are combustible, water gas gives a higher temperature, when burnt, than producer gas.

As the formation of water gas is accompanied by absorption of heat, the passing of steam through the coal in the producer soon makes it cold. Therefore the production of water gas is usually alternated with the production of producer gas, making it possible to keep the coal at red heat.

Water gas is used not only as a gaseous fuel but also as a raw material for the preparation of hydrogen for the synthesis of ammonia (see p. 200).

A gas close in composition to water gas can be obtained by passing a mixture of steam and oxygen through the producer.

Coke-Oven or *coal gas* is the gas obtained by heating bituminous coal to a high temperature out of contact with air. Large quantities of this gas are used pure or mixed with natural gas in industry, in laboratories and for domestic purposes.

Coal gas is a mixture of various combustible gases. Its composition depends on the raw materials, but on the average it may be expressed by the following figures:

Hydrogen	55 p. c.
Methane	30 p. c.
Carbon monoxide	4 p. c.
Other hydrocarbons	3 p. c.
Incombustible impurities (CO_2, N_2, O_2)	8 p. c.

When using coal gas or its mixtures with natural gas for domestic purposes, it should be handled with care, as it contains a considerable percentage of carbon monoxide. Special precautions should be taken to prevent leakage. When the gas is not burning, the gas cocks should always be turned off.

Underground Gasification of Coal. Coal can be converted into gaseous fuel by gasification right in the seams in which it occurs (under the earth).

The possibility of underground gasification of coal in Russia was first suggested by D. Mendeleyev in 1888 after a trip to the Donets Basin, where he made a thorough study of the state of the coal industry.

In an article entitled "The Future Might Lying on the Banks of the Donets," published in the journal *Severny Vestnik*, Mendeleyev wrote: "...There will probably even come a time when coal will no longer be extracted from the earth but will be converted right there, in the earth, into combustible gases which will be sent over long distances through pipes."

Later Mendeleyev repeatedly returned to the idea of underground gasification of coal. In particular, with respect to the underground fires of coal seams occurring at that time in the Urals, he wrote: "...As to these coal seam fires, it seems to me that they could be utilized by getting them under control and directing them to make the coal burn like in a producer, i.e., with a limited supply of air. Then carbon monoxide should form and producer gas would be produced in the seams."

For a number of years Mendeleyev persistently put forth his ideas of underground gasification, deeply convinced of the possibility of their realization. But all Mendeleyev's appeals to coal manufacturers to experiment with underground coal gasification were in vain. His suggestions were considered too fantastic and unreal at that time.

The English chemist Ramsay worked on the problem of underground gasification of coal between 1910 and 1915.

However, only in the U.S.S.R. has D. Mendeleyev's idea begun to be realized. Numerous experiments carried out in the Donets and Moscow coal basins have shown the technical possibility of solving this problem.

165. Carbon Cycle in Nature. When various types of fuel are burnt and, in general, during the combustion of organic substances, as well as the decay of animal and plant remains, all the carbon contained in them passes finally into carbon dioxide, a substance incapable of further combustion and devoid of the energy contained in the organic substances. If, despite combustion, organic substances, animals and plants still exist in nature, there obviously must somewhere be a process opposite to combustion, during which the carbon dioxide forms organic substances again. This process, as is known, takes place in plants, in their leaves, in those green corpuscles which account for the green colour of the leaves and are called chlorophyll granules.

Plants abstract carbon dioxide from the air, evolving an equal volume of oxygen back into the atmosphere. In the presence of chlorophyll carbon dioxide reacts with water, turning into more complex carbonaceous compounds, such as carbohydrates. Schematically the formation of carbohydrates may be represented by the equation

$$6CO_2 + 6H_2O = \underset{\text{glucose}}{C_6H_{12}O_6} + 6O_2$$

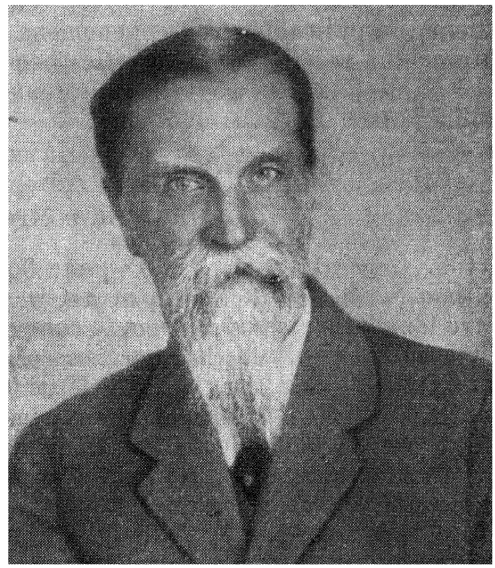
At the same time, starch and the various other substances contained in plants are formed. These substances serve as food for animals and the chief source of the energy consumed by human beings.

Thus, carbon goes through a definite cycle in nature: carbon dioxide is withdrawn from the atmosphere by plants and converted into organic matter; combustion or decay of this matter, as well as the respiration of people and animals lead again to the formation of carbon dioxide which is discharged into the atmosphere, whence it is again withdrawn by plants, etc.

However, the transformation of carbon dioxide and water into organic compounds can take place only if energy is absorbed from the surroundings. This energy is supplied by the sun. Solar rays, falling on the green plants, are absorbed in cells of the latter by the chlorophyll granules and give rise to the changes mentioned above. Since this process takes place under the influence of light it is called **photosynthesis.**

Science is indebted to the Russian scientist K. Timiryazev for the explanation of the formation of organic substances in plants, on which the existence of the entire organic world depends. Timiryazev devo-

Kliment Arkadyevich Timiryazev (1843-1920)



ted his whole life to the solution of the problem of the air nutrition of plants.

Prior to Timiryazev's studies the green colouring of plants was not thought to have any special significance. As a result of prolonged and painstaking work Timiryazev first proved that the entire process of plant nutrition is closely connected precisely with the green colouring of the chlorophyll granules. Studying the influence of various spectral rays on the decomposition of carbon dioxide by plants, Timiryazev established that this process takes place the most intensively under the action of red rays, i.e., the rays which are completely absorbed by the green chlorophyll and possess the greatest amount of energy. On the other hand, carbon dioxide hardly decomposes at all under the rays which are not absorbed by chlorophyll.

Timiryazev's exceedingly refined and delicate experiments left no doubt of the fact that the assimilation of carbon dioxide by plants is due to their absorbing solar energy, which is thereupon transformed into the chemical energy of the organic substances formed. Thus, all the energy we consume, whether in using organic substances as food, or in burning them as fuel, comes, in the long run, from the sun.

Having ascertained the fundamentals of the process of plant nutrition by air, having established the part played by chlorophyll

in this process, Timiryazev proved that the Law of Conservation of Energy is applicable also to phenomena of live nature. This positively refuted the reactionary idealistic theory of "vital force" (see § 166) which blocked the way to a profound investigation of processes taking place in live organisms.

ORGANIC COMPOUNDS

166. General Features of Organic Compounds. The compounds of carbon (with the exception of a few of the most simple of them) have long been classed as **organic compounds**, as they occur in nature almost exclusively in the organisms of animals and plants, being an indispensable and the chief constituent part of these organisms. In contradistinction to organic compounds, such substances as sand, clay, various minerals, water, carbon dioxide and others occurring in "inanimate nature" are called **inorganic** or **mineral compounds.**

The classification of substances into organic and inorganic was due to the fact that for a long time it was considered impossible in principle to obtain organic substances by synthesis from simple substances. The formation of organic substances was attributed to the influence of a special "vital force," active only in live organisms and not taking any part in the formation of inorganic compounds. The adherents of this theory were called vitalists (from the Latin *vis vitalis*—vital force). The vitalists attempted to find in the phenomena of animate nature proof of the existence of certain mysterious forces in the world, which cannot be accounted for or studied, and are not governed by ordinary physico-chemical laws. The vitalists were headed by one of the most authoritative chemists of the first half of the XIX century, the Swedish scientist Berzelius.

Vitalism received its first blow when in 1828 the German chemist Wöhler obtained urea in the laboratory from ammonium cyanate NH_4CNO, which, in its turn, could be synthesized from simple substances. One of the products of the vital activity of animals, urea, was undoubtedly an "organic" substance and, according to previous views, could be produced only under the influence of "vital force." Now urea had been obtained artificially in the laboratory. However, vitalistic views were so widespread among scientists, that no great importance was attached to Wöhler's discovery.

Chemistry was freed from vitalistic ideas only in the middle of the last century, after the French chemist Berthelot succeeded in synthesizing a number of simple organic compounds (carbohydrates, alcohol, etc.), and the Russian chemist A. Butlerov first synthesized a substance belonging to the saccharide group. This proved that no mysterious vital force existed and that the formation of organic

compounds takes place according to the same laws as inorganic substances.

It does not follow from this, however, that a live organism can be regarded as a system determined entirely by only physico-chemical laws.

The biological processes occurring in live organisms are higher, more complex forms of the motion of matter and cannot be reduced entirely to the forms of matter motion studied by physics and chemistry.

After organic substances had been synthesized, the demarcation line between organic and inorganic substances disappeared; however, the name "organic substances" persisted. Now this name refers to all carbon-containing compounds in general; the majority of these compounds do not even occur in organisms but have been obtained artificially in the laboratory.

One of the important features of organic compounds, which leaves its mark on their entire chemical behaviour, is the nature of the interatomic bonds in their molecules. In the great majority of cases these bonds are of a pronounced atomic nature. That is why organic compounds, as a rule, do not ionize and react with one another comparatively slowly. While reactions between electrolytes in solution take place almost instantaneously, the time necessary for any reaction between organic substances to be completed usually amounts to hours and sometimes days. That is why the use of various catalysts is of great importance in organic chemistry.

Another characteristic feature of organic compounds is their tendency to undergo profound changes when heated, forming new substances with entirely new properties. For instance, if wood or coal is heated without access of air, a number of new, practically very important, products result. If heated, on the other hand, in the presence of air or oxidants, organic substances burn up, the carbon and hydrogen contained in them being converted completely into carbon dioxide and water, while the nitrogen is usually liberated in the free state. This forms the basis of the elementary analysis of organic compounds: the carbon and hydrogen content in the substances burnt is determined by the quantity of carbon dioxide and water formed, the nitrogen evolved is measured directly, while the oxygen content is established by the difference between the weight of the substance burnt and the weight of the other elements it contained.

The molecular formula of an organic substance can be derived from analysis data and determination of its molecular weight. However, contrary to inorganic compounds the molecular formula of an organic substance gives no idea of its nature or its properties. The trouble is that very many organic compounds are known to possess

identical compositions and identical molecular weights, but nevertheless to have entirely different physical and even chemical properties. For example, though the composition of ethyl alcohol and of dimethyl ether are represented by the same molecular formula C_2H_6O, they are entirely different substances. Ethyl alcohol is a liquid boiling at 78°C, miscible with water in all proportions, while dimethyl ether is a gas, almost insoluble in water; their chemical properties also have very little in common.

This phenomenon, very common among organic compounds, is known as **isomerism**, and substances responding to the same molecular formula, but differing in properties, are called **isomeric** substances or **isomers**.

The various cases of isomerism are explained by the theory of the structure of organic compounds founded in the sixties of the last century by A. Butlerov.

167. A. M. Butlerov and His Theory of Chemical Structure. Alexander Mikhailovich Butlerov was born in 1828 in the town of Chistopol, Kazan Gubernia. In 1849 he graduated from the Kazan University, where he studied under the prominent Russian chemists K. Klaus and N. Zinin.

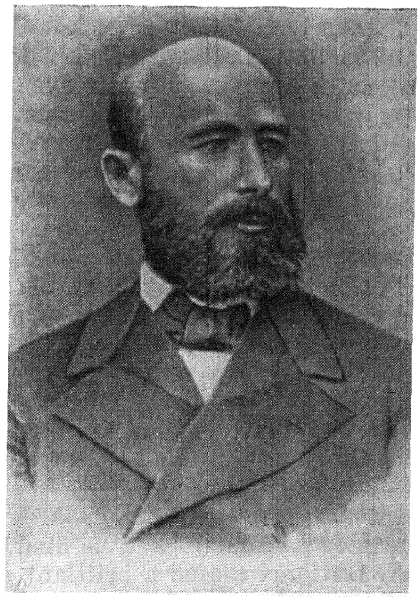
After graduation Butlerov was left at the University to prepare for the title of professor, and soon began to deliver lectures in chemistry. In 1851 Butlerov submitted a thesis "On the Oxidation of Organic Compounds" for which he received his master's degree, and in 1854, after submitting a dissertation "On Ethereal Oils," he was admitted to a doctor's degree and the same year was elected professor of the Kazan University, where he instructed for a period of 20 years.

In May 1868, the Council of the Petersburg University, on D. Mendeleyev's suggestion, elected Butlerov professor in the chair of chemistry, after which his entire scientific and pedagogical activities were transferred to Petersburg. For his prominent scientific merits Butlerov was in 1871 elected an extraordinary, and in 1874, a full member of the Russian Academy of Sciences.

From the very first steps of his scientific activities Butlerov showed himself to be a brilliant experimenter and carried out a number of remarkable syntheses, in particular the synthesis of the first artificial saccharide substance which he called *methylenitan*, and the synthesis of *urotropin*, a compound now widely used in medicine.

Butlerov's talent as an experimenter was supplemented by his power of broad theoretical generalization and scientific prediction. While still a comparatively young scientist, Butlerov put forth a number of profound and daring ideas in the field of theoretical chemistry, for instance, with respect to expressing the structure of molecules and their interatomic bonds by formulas. At that time many chemists thought that science would never be able to penetrate

Alexander Mikhailovich
Butlerov
(1828-86)



into the structure of the molecule, but Butlerov was confident that the structure of the molecules of organic compounds could be expressed by formulas, and that this could be done by studying their chemical changes.

In 1861, during a commission abroad, Butlerov spoke at a congress of German scientists and physicians on "The Chemical Structure of Substances," ushering in a new epoch in the chemistry of organic compounds. Back in Kazan, he elaborated this new science and together with his numerous pupils undertook extensive experimental investigations to confirm his theoretical theses. These works of Butlerov not only led to a number of new important syntheses but also confirmed his theory, which, under the name of the theory of chemical structure, became the guiding theory in organic chemistry.

The essence of Butlerov's theory consists in the statement that the properties of substances depend not only upon their qualitative and quantitative composition, as was thought previously, but on their internal molecular structure as well, and on how the atoms, making up the molecule, are linked with each other. Butlerov called this internal arrangement "chemical structure."

"The chemical nature of a complex particle," wrote Butlerov, "is determined by the nature of its elementary composite parts, by their quantity and chemical structure."

Of especial importance was Butlerov's idea that when atoms combine chemically in a definite order, according to their valencies, they influence each other in such a way as to partially change their own nature, their "chemical content." "One and the same element," wrote Butlerov, "in combination with various other elements displays a different chemical essence." For this reason changes in the internal structure of molecules lead regularly to the appearance of new qualities.*

In 1862-63 Butlerov wrote his outstanding work "Introduction to a Complete Study of Organic Chemistry," in which he arranged the entire aggregate of facts of organic chemistry on the basis of a strict scientific classification deduced from the theory of chemical structure. In force of thought, scientific depth, clarity of form and richness in new ideas, Butlerov's "Introduction" resembles Mendeleyev's "Principles of Chemistry." The classification of organic compounds used in his book has remained intact in its main features to this day.

Intense scientific and pedagogical work broke down Butlerov's health and strength, and he died, 58 years of age, in 1886.

A. Butlerov reared a brilliant pleiad of pupils who developed his ideas further. His school gave such prominent scientists as V. Markovnikov, A. Favorsky and many others.

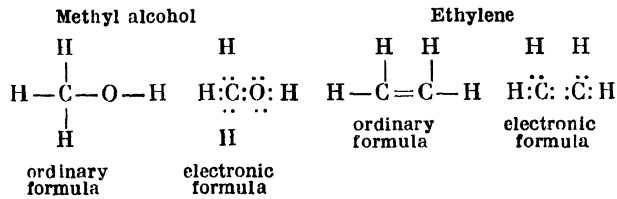
The importance of Butlerov's works and his prominent role in the development of science were characterized excellently by Mendeleyev in presenting Butlerov to the chair of organic chemistry at the Petersburg University. "A. Butlerov is a professor of the Kazan University, one of the most prominent Russian scientists. He is Russian both in scientific education and in originality of his works. A pupil of our prominent Academician N. Zinin, he became a chemist not in foreign lands, but in Kazan, where he continues to develop an independent chemical school of his own. The trend of Butlerov's scientific works is neither a continuation nor a development of the ideas of his predecessors, but belongs entirely to himself. Chemistry knows Butlerov's school and Butlerov's trend."

Butlerov's theory of the chemical structure of molecules is the theoretical foundation of organic chemistry. It enables the chemist to orient himself in the vast diversity of carbon compounds, to determine the structure of molecules by studying their chemical properties, to predict the properties of substances from their molecular structure, to outline methods of synthesis for any substances required.

Over ninety years have passed since the theory of chemical structure was founded, but the fundamental ideas of this theory have not

* Butlerov's ideas of the mutual influence of the atoms constituting a molecule were elaborated by his pupil V. Markovnikov, a professor of the Moscow University.

only failed to lose their force in time, but, on the contrary, have become more consolidated and profound. In particular, present-day data on the electronic structure of molecules has fully confirmed all the conclusions obtained on the basis of Butlerov's theory. At the same time, the physical sense of his "valency lines" turned out to be the pairs of electrons common to both linked atoms. This becomes obvious if we compare structural formulas in their ordinary and electronic forms.



When using ordinary structural formulas it must always be kept in mind that each "valency line" connecting two atoms represents one common pair of electrons.

168. Fundamentals of the Classification of Organic Compounds. The modern classification of organic compounds is based on the following principles of the theory of chemical structure:

1. The atoms in molecules are linked to one another in a definite order. Any change in this order results in a new substance with new properties.

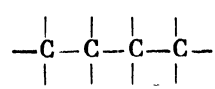
2. Atoms combine according to their valencies. The valencies of all the atoms in the molecule are mutually saturated. No free valencies are left in atoms constituting molecules.

3. The properties of substances depend on their "chemical structure," i.e., on the arrangement of the atoms in their molecules and their mutual influence. Directly linked atoms exert the greatest influence on each other. Therefore, molecules having similar atomic groupings possess similar properties.

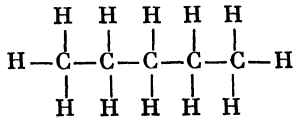
4. Carbon is a tetravalent element. Each carbon atom has four valency units by means of which it can combine with other atoms or atomic groups, such as H, Cl, OH, NO_2, NH_2, CN, etc.

5. Carbon atoms are capable of combining with each other to form an atomic "chain" or the "carbon skeleton" of a molecule.

Denoting the valency bonds of carbon atoms by straight lines and keeping in mind the physical sense of this denotation, the simplest chain may be represented as follows:

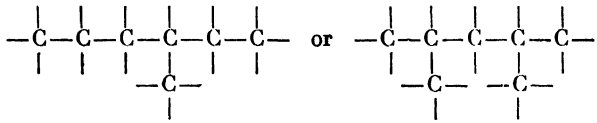


The free valency units serve to combine with other atoms or atomic groups. For instance:

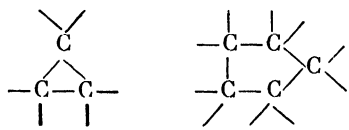


pentane, a hydrocarbon

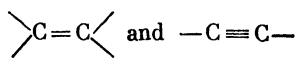
Chains may be simple, such as those shown above, or branched, as, for instance:



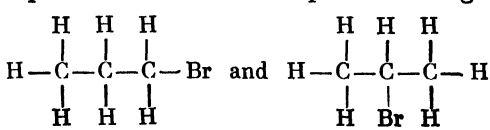
Chains may be "open," as above, or "closed," in which the carbon atoms are linked together to form a ring or "cycle." For example:



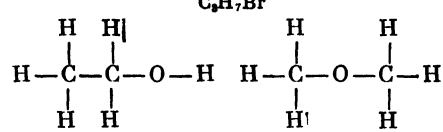
These rings, in their turn, may combine with open chains and other rings. Finally, carbon atoms may use up two or three valency units on the bond between each other instead of one. Then we get chains with "double" or "triple" bonds, the simplest of which may be represented as follows:



The formation of different chains consisting of the same number of carbon atoms, as well as different positions of other atoms in molecules of identical composition, account for the numerous cases of isomerism among organic compounds. To illustrate, the structural formulas of two pairs of isomeric compounds are given below:



isomeric propyl bromides
C_3H_7Br



ethyl alcohol
C_2H_6O

methyl ether
C_2H_6O

Isomerism may be due not only to the atoms being linked in different orders, but also to differences in their spatial arrangement. The fact is that the covalent bonds of the atoms have quite a definite direction in space. When the carbon atom forms simple bonds they are at an angle of 109°28′ to each other, as if the carbon were in the centre of a tetrahedron and the atoms combined with it, at its corners. Fig. 111 shows a tetrahedral model of methane, the simplest compound of carbon and hydrogen.

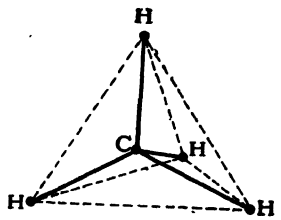


Fig. 111. Tetrahedric model of methane molecule

If four different atoms or groups of atoms are combined with the carbon atom, molecules with two different configurations are possible, as shown in Fig. 112. The two models shown here cannot be matched in space; they represent the configurations of molecules of substances which differ from one another in some of their physical properties. It can easily be seen that one model is the mirror image of the other.

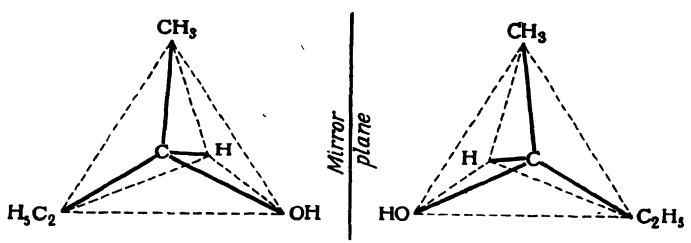
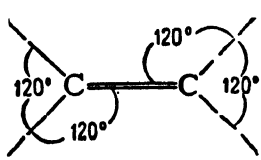
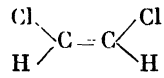


Fig. 112. Tetrahedric model of secondary *n*-butyl alcohol molecules

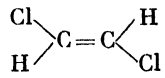
If the carbon atoms are combined by a double bond they are both in the same plane and the other bonds are also in the same plane at an angle of 120° to each other:



If two different atoms or radicals are combined with each of the carbon atoms, geometrical or cis-trans-isomerism becomes possible. An example of this is dichloroethylene:



cis-dichloroethylene



trans-dichloroethylene

In the molecules of one of isomers the chlorine atoms are both on the same side of the double bond axis, while in the molecules of the other, they are on different sides. The first configuration is called the cis-configuration, and the second, the trans-configuration. Cis- and trans-isomers differ in physical and chemical properties.

According to the structure of their carbon chains, all organic compounds fall into three large groups:

1. Compounds with open carbon atom chains, called also acyclic compounds or compounds of the fatty series, as they include fats and substances related to them. Depending on the nature of the carbon atom bonds in the "chains," these compounds are divided into **saturated** compounds, containing only simple bonds in their molecules, and **unsaturated** compounds, which have double or triple bonds between some of the carbon atoms in their molecules.

2. Compounds with closed carbon atom chains, or carbocyclic compounds. These compounds form two subgroups:

a) *compounds of the aromatic series*, characterized by the presence in their molecules of rings consisting of six carbon atoms with a specific alternation of simple and double bonds; a ring of this kind is contained in the benzene molecule, and it is called the *benzene ring*;

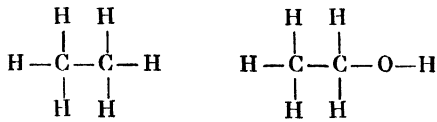
b) *alicyclic compounds*—all the rest of the carbocyclic compounds. Alicyclic compounds have different numbers of carbon atoms in their cycles and different kinds of bonds between them.

3. *Heterocyclic compounds.* Heterocyclic compounds are those whose rings, besides carbon atoms, contain atoms of other elements (oxygen, nitrogen, sulphur, etc.).

In classifying organic compounds, the substances belonging to the hydrocarbon class, i. e., consisting only of carbon and hydrogen,* are considered the basic substances. All other compounds are regarded as derived from hydrocarbons by substitution in their molecules of other atoms or atomic groups for part or all of the hydrogen atoms. For instance, alcohols are obtained by substituting one or several hydrogen atoms in the molecules of hydrocarbons by hydroxyl groups. Therefore, alcohols may be regarded as *hydroxyl derivatives*

* In the case of heterocyclic compounds—of carbon, hydrogen and the other elements contained in the cycle (the heteroatom).

of hydrocarbons. For example,



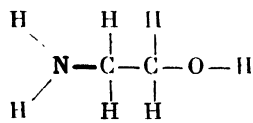
ethane, a hydrocarbon

ethyl alcohol or ethanol

Groups of atoms accounting for the generic chemical properties of substances belonging to the same class are called functional groups. The hydroxyl radical is the functional group of alcohols.

The functional group of nitrocompounds is the group NO_2 (nitrogroup), the functional group of primary amines, the NH_2 group (aminogroup), etc.

If there are several different functional groups in the molecule of a substance, the substance is called a *mixed function compound.* An example of such a substance is aminoethanol, a representative of the aminoalcohol class:



Aminoalcohols possess properties characteristic of amines and alcohols, but both sets of properties are slightly modified, owing to the influence of the functional groups on one another.

The classes of organic substances are very diverse and in the present course of general chemistry we can dwell but briefly only on the most important of them.

169. Saturated Hydrocarbons. The simplest representative of the saturated hydrocarbons is *methane* CH_4. It is a colourless, light, combustible gas with no odour, almost insoluble in water. The boiling point of methane is —161.5°C and its freezing point, —184°C.

Methane occurs quite frequently in nature. The so-called *natural gases*, escaping at certain points of the globe, consist mainly of methane.

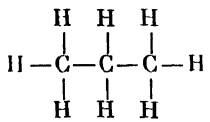
This gas is liberated from the bottoms of marshes, ponds and stagnant water bodies, as a result of the decomposition of plant remains out of contact with air, for which reason it is known also as *marsh gas.* Finally, methane accumulates constantly in coal mines, where it is called *mine gas* or *firedamp.* As it forms an explosive mixture with air, methane has more than once been the cause of mine hazards.

Methane is one of the main component parts of coal gas, produced by heating coal without access of air and containing about 25 to 30 per cent CH_4.

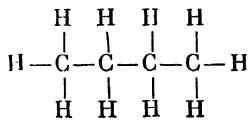
The methane molecule is comparatively stable. Under ordinary conditions methane will react only with chlorine, and especially vigorously with fluorine. The reaction is accelerated by light, the hydrogen atoms being substituted successively by chlorine atoms:

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$
$$CH_3Cl + Cl_2 \longrightarrow CH_2Cl_2 + HCl, \text{ etc.}$$

There are very many hydrocarbons with properties similar to those of methane. Some of them are: ethane C_2H_6, propane C_3H_8, butane C_4H_{10} and others. In the molecules of these compounds all the bonds between the carbon atoms are simple ones:



propane



butane

or

$CH_3-CH_2-CH_3$ $\qquad$ $CH_3-CH_2-CH_2-CH_3$

If we arrange the formulas of the above hydrocarbons in orde. of increasing numbers of carbon atoms in their molecules, we get the following series:

CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}	etc.
methane	ethane	propane	butane	pentane	hexane	

Comparing these formulas, we see that each subsequent member of the series contains one carbon and two hydrogen atoms more than the preceding member. *A series of organic compounds, all the members of which are similar in chemical properties and structure, each subsequent member differing from the one preceding it by a CH_2 group of atoms, is called a homological series and its individual members are called homologues.* The hydrocarbons mentioned above form the *homological methane* or *saturated hydrocarbon series*, known also as the *paraffins* (from the Latin *parum affinis*—of low affinity) due to their low activity. Other organic substances can also be grouped into similar homological series.

Homological series are an especially striking manifestation of one of the universal laws of nature, namely, the Law of Transformation of Quantity into Quality. The addition or abstraction of one carbon and two hydrogen atoms from the hydrocarbon molecule results in an entirely different substance which, though it has much in common with the adjacent members of its series, differs qualitatively from them. The qualitative difference between homologues is especially pronounced in their physical properties. The lowest members of the saturated hydrocarbon series (from CH_4 to C_4H_{10}) are gases, and

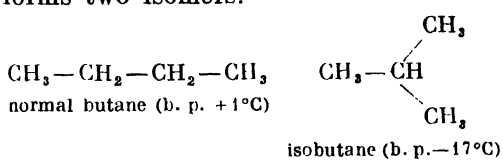
the larger their molecular weights, the higher their boiling points; the intermediate members of the series (from C_5H_{12} to $C_{16}H_{34}$) are liquids at temperatures up to 20° and the rest are solids.

Special credit for the study of the homological paraffin series is due to the German scientist C. Schorlemmer (1834-1892).

The saturated hydrocarbons are composite parts of crude oil and oil products. Petroleum ether contains hydrocarbons with formulas from C_5H_{12} to C_7H_{16}, gasoline, from C_7H_{16} to C_9H_{20}, kerosene, from $C_{10}H_{22}$ to $C_{16}H_{34}$. Solar oil and other heavy oils used as Diesel fuel are also mixtures of hydrocarbons; some of them contain as many as 20 carbon atoms in their molecules. Still heavier hydrocarbons are contained in greases, vaseline and paraffin.

As the number of atoms in the molecules of the saturated hydrocarbons increases, another qualitative feature arises, namely, the number of isomers becomes larger and larger.

Methane CH_4, ethane C_2H_6 and propane C_3H_8 have no isomers. Butane C_4H_{10} forms two isomers:



Pentane C_5H_{12} has three isomers, the number of isomeric heptanes C_7H_{16} is nine, while the formula $C_{14}H_{30}$ represents as many as 1,818 different hydrocarbons, etc.

Isomerism in the saturated hydrocarbon series was predicted by A. Butlerov. He also synthesized the first isomers with branched carbon atom chains.

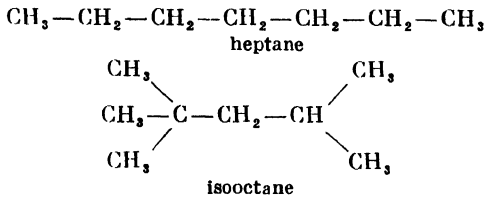
The individual homologues and their isomers differ not only in physical properties, but in chemical properties as well. The difference in chemical properties, particularly, tells on the tendency of some of the hydrocarbons contained in motor fuel to cause **knocking**.

Knocking is due to very rapid decomposition (explosion) of hydrocarbons, taking place suddenly when the fuel mixture is compressed in the motor cylinder. Knocking prevents a high degree of compression of the fuel mixture from being attained,* leads to excessive fuel consumption and to rapid wear of the motor. The anti-knock characteristics of a fuel depend greatly on the structure of the carbon chains in its hydrocarbon molecules. Branched chain isomers cause knocking much less than straight-chain isomers.

The anti-knock properties of a motor fuel are characterized by its so-called **octane number**. The usual standard samples used for

* The higher the degree of compression, the greater the power of the motor.

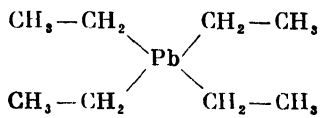
determining the octane number are the straight-chain hydrocarbon *heptane* C_7H_{16}, with a high tendency for knocking, and a highly branched chain isomer of octane, which is almost non-knocking. The structure of these hydrocarbons is represented by the following formulas:



Heptane has been given the octane number 0, and *iso*octane, the octane number 100. If we say that the octane number of a fuel equals 80 we mean that when mixed with air its tendency to cause knocking is the same as that of a mixture containing 80 per cent isooctane and 20 per cent heptane (under the same degree of compression).

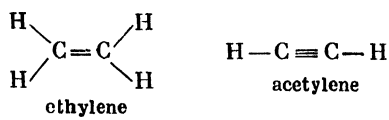
The octane number of a fuel is raised by increasing the percentage of branched chain hydrocarbons in it, and/or by adding tetraethyl lead, a small amount of which greatly decreases knocking.

Tetraethyl lead is a heavy poisonous liquid, the molecular structure of which can be represented by the following formula:



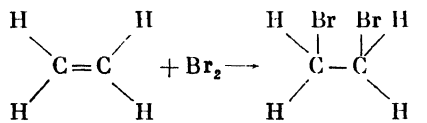
Compounds in which the hydrocarbon radicals are combined directly with any metal as, for instance, in tetraethyl lead, are called **metal-organic compounds**. They are of immense importance and are becoming more so from year to year. Metal-organic compounds include, for instance, one of the most effective preparations for fighting plant pests and diseases, *granosan*, or *ethylmercuric chloride* $C_2H_5—Hg—Cl$.

170. Unsaturated Hydrocarbons. The unsaturated hydrocarbons are those which contain double or triple bonds between some of the carbon atoms in their molecules. The simplest representatives are ethylene and acetylene:



Ethylene C_2H_4 is a colourless gas with a feeble pleasant odour, rather soluble in water. It burns in air with a slightly luminous flame. If burnt in special torches it will give high temperatures.

Ethylene is a very important raw material for the preparation of a number of synthetic products. The use of ethylene is based on its high chemical activity, manifested in its ability to enter into addition reactions. The double bond in ethylene molecules is readily ruptured by the action of various substances, leaving a simple bond, while new atoms or atomic groups are added at the expense of the freed valencies. For instance, ethylene easily adds bromine in place of its double bond, passing into the saturated compound *dibromoethane* or *ethylene bromide* $C_2H_4Br_2$:



Addition reactions are characteristic of all hydrocarbons with double and triple bonds in their molecules.

Ethylene molecules are capable not only of adding other atoms or groups of atoms but also of combining with each other. This process takes place, for instance, if ethylene is greatly compressed (to above 1,000 atm.) and heated to 200° C. Under such conditions the ethylene molecules combine with one another, as shown in the following scheme:

$$CH_2=CH_2+CH_2=CH_2+CH_2=CH_2+\ldots \longrightarrow$$
$$\longrightarrow [-CH_2-CH_2-+-CH_2-CH_2-+-CH_2-CH_2-+\ldots] \longrightarrow$$
$$\longrightarrow -CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-\ldots$$

The reaction may be regarded as rupture of the double bonds in a large number of ethylene molecules followed by union of the resulting particles with free valencies (bivalent radicals) to form a single giant molecule.

The combination of several molecules into a larger one, due solely to union at the double or triple bond, is called polymerization, and the product of such a reaction is called a polymer.

The polymer of ethylene is called *polythene*. It is a soft, pliable substance resembling gutta-percha and retaining its elasticity at quite low temperatures. One of the most valuable properties of polythene is its high electrical insulating properties which account for its use in present-day electrical and radio engineering.

Polymerization of various compounds containing multiple bonds is widely used in the chemical industry for the preparation of various kinds of artificial resins, elastic materials, artificial fibres, lubricants, plastics, etc.

Ethylene is the first member of the ethylene hydrocarbon or *olefin series.* The subsequent members of this series are propylene C_3H_6, butylene C_4H_8, etc.

The main source of ethylene and its homologues are the gases formed during the *cracking* of oil products. Cracking is the process of splitting large hydrocarbon molecules into smaller ones, accomplished by heating saturated hydrocarbons to 400 or 500° C under high pressure. For instance:

$$CH_3—CH_2—CH_2—CH_3 \rightarrow CH_2=CH_2+CH_3—CH_3$$

The cracking of oil products, first accomplished on an industrial scale by the Russian engineer V. Shukhov (who patented his apparatus in 1891), makes it possible to obtain low-boiling hydrocarbons (such as gasoline) from hydrocarbons with high boiling points. Cracking always leads to the formation of unsaturated hydrocarbons as well as saturated.

The unsaturated hydrocarbons, formed during the cracking process, serve as raw materials for the organic synthesis industry, which puts out high-octane gasolines, alcohols, various solvents, insulators and rubber-like materials, plastics and other valuable substances.

A very important unsaturated hydrocarbon with a large number of double bonds in its molecule is *rubber.* The composition of rubber molecules may be expressed by the formula $(C_5H_8)_x$, where x may equal from 1,000 to 3,000.

Rubber is a polymer of the hydrocarbon *isoprene* and forms according to the scheme

$$x\underset{\text{isoprene}}{CH_2=CH—\overset{\overset{CH_3}{|}}{C}=CH_2} \rightarrow [—CH_2—\underset{\text{rubber}}{CH=\overset{\overset{CH_3}{|}}{C}—CH_2}—]x$$

As can be seen from this scheme, polymerization of isoprene results in a shift of the double bond.

Rubber latex is contained in the milky fluid of certain plants. Another natural product, *gutta-percha,* is also a polymer of isoprene, but its molecules have a different configuration.

Raw rubber latex is sticky, and a very slight drop of temperature makes it brittle. To render the rubber suitable for the manufacture of various products, it is first vulcanized (heated with sulphur). After vulcanization it becomes what we usually call rubber.

The absence of natural rubber in the U. S. S. R. made it necessary to develop a method of obtaining this very important product artificially. Soviet chemists discovered a method of producing *synthetic rubber* and were the first to effect it on an industrial scale. In the process proposed by S. Lebedev (1874-1934) the raw material for the

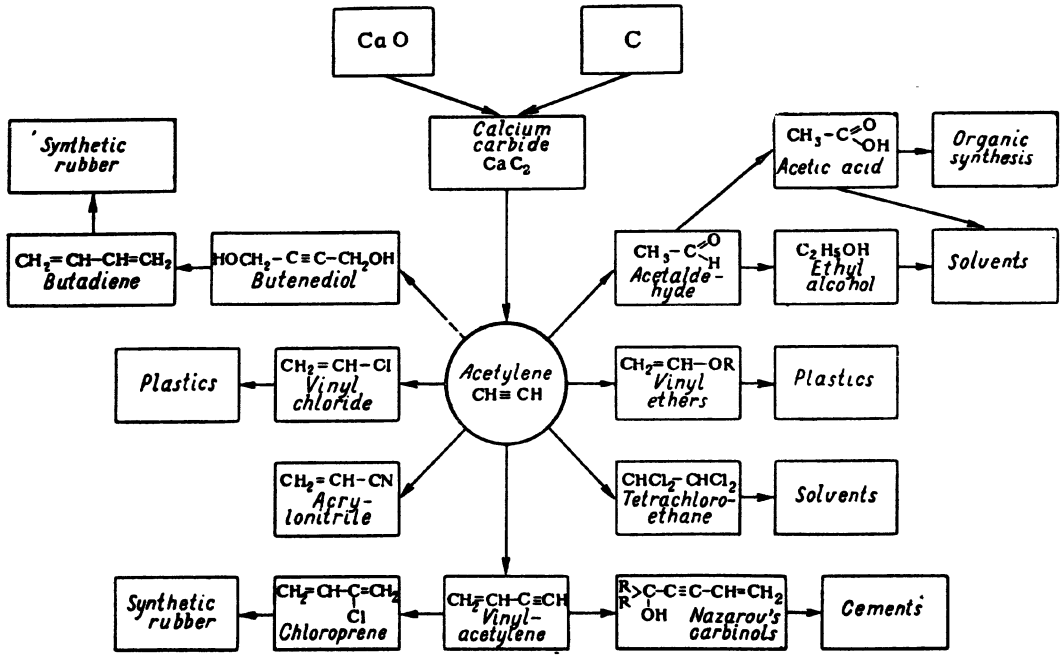
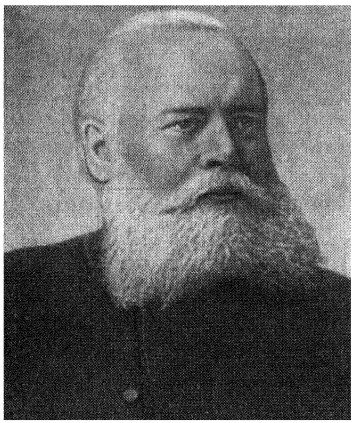


Fig. 113. Syntheses based on acetylene



Vladimir Vasilyevich
Markovnikov
(1838-1904)

production of synthetic rubber is the hydrocarbon *butadiene* $CH_2=CH-CH=CH_2$ obtained from alcohol and from petroleum butane. Polymerization of butadiene results in synthetic rubber:

$$\underset{\text{butadiene}}{xCH_2=CH-CH=CH_2} \longrightarrow \underset{\text{synthetic rubber}}{[-CH_2-CH=CH-CH_2-]_x}$$

Other types of synthetic rubber besides butadiene rubber are now produced in the U. S. S. R.

Acetylene C_2H_2. The most important of the hydrocarbons with triple bonds in their molecules is acetylene $H-C\equiv C-H$, a colourless gas prepared by the action of water on calcium carbide:

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$$

Acetylene is an endothermal compound, and a large amount of heat is therefore released during its combustion. The high temperature developed when acetylene is burnt makes it suitable for gas welding.

Acetylene enters into a great variety of reactions, including addition, polymerization and others. Many industrial syntheses of such important products as acetic acid, synthetic rubber, various plastics, etc. (see Fig. 113, p. 457) depend on the use of acetylene as the raw material.

Of great theoretical and practical importance in the field of unsaturated, and especially acetylene, hydrocarbons are the works of A. Favorsky (1860-1945) and his pupils. Favorsky discovered a large number of different molecular regroupings taking place during

chemical reactions, studied their regularities and pointed out methods of controlling these processes.

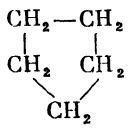
171. Cyclic Hydrocarbons. In the seventies of the last century V. Markovnikov showed that, unlike American crude oil, Baku crudes consist mainly of cyclic hydrocarbons with five or six carbon atoms in their cycles. Markovnikov called these hydrocarbons **naphthenes.** The carbon atoms of naphthene molecules are connected by simple bonds, like in the molecules of the paraffins, so that the properties of the naphthenes resemble those of saturated hydrocarbons.

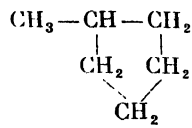
Vladimir Vasilyevich Markovnikov was born in 1838. After graduating the Kazan University in 1860, Markovnikov was offered a position at the chair of Butlerov. In 1869 Markovnikov maintained his doctor's thesis entitled "Data on the Mutual Influence of Atoms in Chemical Compounds," in which he developed the ideas set forth in Butlerov's theory of chemical structure.

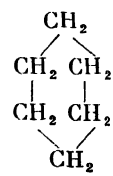
In 1873 Markovnikov was offered a position at the University of Moscow, where he remained as a professor to his very death. Attaching great importance to scientific investigations "on materials related to Russian nature," Markovnikov undertook in 1881 an extensive study of Russian mineral oils.

This study led to a number of discoveries, the most important of which was a new class of organic compounds called naphthenes.

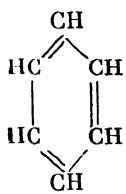
Some examples of naphthenes are:

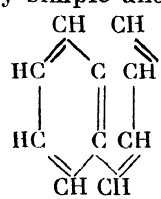

cyclopentane

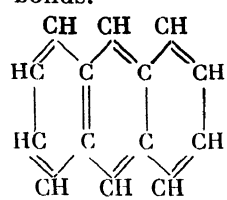

methyl cyclopentane


cyclohexane

Another very important group embraces hydrocarbons whose molecules contain cycles (one or several) consisting of six carbon atoms connected alternately by simple and double bonds:


benzene C_6H_6

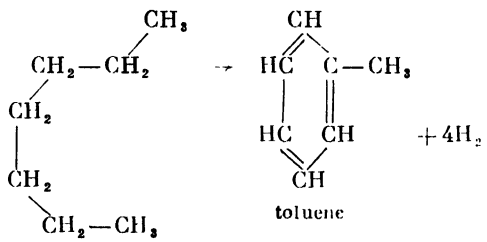

naphthalene $C_{10}H_8$


anthracene $C_{14}H_{10}$

Hydrocarbons with such molecular structures have long been known as aromatic hydrocarbons. They are present in large quantities in the coal tar obtained by carbonization of bituminous coal. The industrial importance of aromatic hydrocarbons is so great that it became necessary to prepare them from the hydrocarbons contained in mineral oils. This problem was successfully solved by N. Zelinsky

and his pupils B. Kazansky and A. Platé, who transformed many saturated hydrocarbons into aromatic.

For instance, if heptane C_7H_{16}, obtained from mineral oil, is heated in the presence of a catalyst, the aromatic hydrocarbon toluene results, according to the equation:



Aromatic hydrocarbons enter into a great variety of reactions. However, with the combination of bonds peculiar to their molecules,

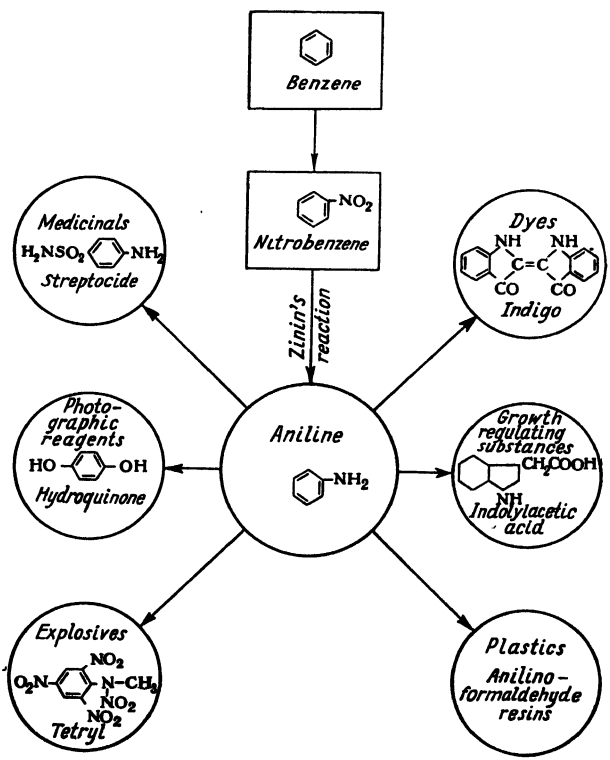
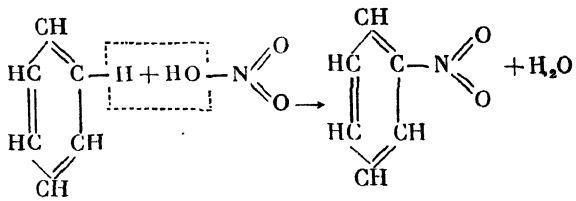


Fig. 114. Syntheses based on aniline

reactions characteristic of double bonds, i. e., addition reactions, are rare. On the other hand, reactions of hydrogen displacement by other atoms or atomic groups are common in aromatic compounds.

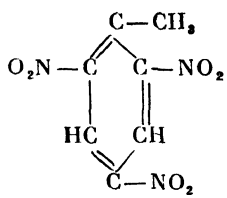
For instance, benzene and other aromatic hydrocarbons react readily with concentrated nitric acid according to the reaction:



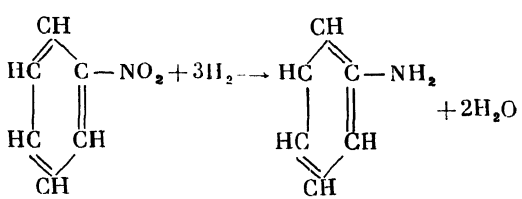
benzene nitrobenzene

Reactions of this kind are called nitration.

Nitration of toluene gives an explosive called *trinitrotoluene* (TNT), which has the following structure:



In 1842 Zinin discovered the reduction of nitrocompounds into amines, a reaction known ever since as the "Zinin reaction." By reducing nitrobenzene he obtained the aromatic amine *aniline* $C_6H_5NH_2$:



nitrobenzene aniline

Zinin's discovery can hardly be overappreciated. Aniline and other aromatic amines are used for the preparation of a great variety of synthetic dyes. Numerous syntheses of pharmaceuticals, photographic reagents, explosives and other valuable materials have been developed and accomplished on the basis of aromatic amines (see Fig. 114, p. 460).

Nikolai Nikolayevich Zinin, a prominent Russian chemist, founder of the famous Kazan school of organic chemists, was born in 1812. Zinin's scientific



Nikolai Nikolayevich Zinin
(1812-80)

and pedagogical activities were connected at first with the Kazan University, where in 1842 he discovered the reaction of the preparation of aniline. A small quantity of aniline obtained personally by Zinin is kept and cherished to this day in the chemical laboratory of the University. In 1847 Zinin moved to Petersburg, where he headed a chair at the Academy of Medicine and Surgery, and in 1867 he was elected to full membership in the Russian Academy of Sciences.

Besides the discovery of the reaction of transformation of nitrobenzene into aniline, which brought Zinin world fame, he also accomplished a number of other organic syntheses of great practical importance.

Zinin was the first President of the Russian Chemical Society, founded in 1868 (now the All-Union Mendeleyev Chemical Society). This Society played a great part in the development of chemistry and the propagation of chemical knowledge in Russia. Zinin remained its President for ten years.

"Zinin's name will always be honoured by those to whom the progress and might of Russian science are dear" (A. Butlerov).

172. Halogen Derivatives of Hydrocarbons. Halogen derivatives of hydrocarbons are compounds which may be regarded as products of the substitution of one or several hydrogen atoms in the hydrocarbon molecule by halogen atoms. The following substances exemplify compounds of this class:

Chloroform $CHCl_3$ (or trichloromethane), a liquid boiling at 61.2° C, used as an anaesthetic during surgical operations.

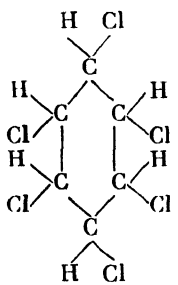
Carbon tetrachloride CCl_4, a heavy non-inflammable liquid (b. p. 76.7° C), is used as a solvent for extracting fats and oils from plants, for removing fatty spots from clothing, etc.

Difluorodichloromethane CF_2Cl_2 (freon) boils at 30° C, is non-poisonous and does not react at ordinary temperatures with metals; when evaporated absorbs a large amount of heat. Used in refrigerators.

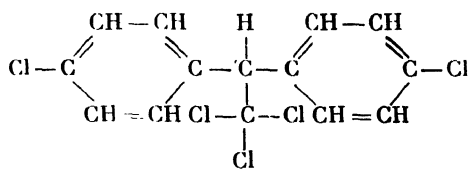
Vinyl chloride $CH_2=CHCl$, a derivative of ethylene. A colourless gas, easily polymerized into an elastic mass known as polyvinyl chloride $(-CH_2-CHCl-)_x$, very stable against acids and alkalis. Polyvinyl chloride is widely used for lining pipes and vessels in the chemical industry. It is used also for insulating electric wires, for the preparation of artificial leather, very light, transparent raincoats, etc.

Tetrafluoroethylene $CF_2=CF_2$. Its polymer $[-CF_2-CF_2-]_x$ known as "teflon" is a very valuable plastic, stable against alkalis, concentrated acids and other reagents. Teflon is used in the production of chemical apparatus.

Hexachlorocyclohexane (hexachlorane) and *dichlorodiphenyltrichloromethylmethane* (DDT) are widely used to destroy insects and agricultural pests.



hexachlorocyclohexane
(hexachlorane)



dichlorodiphenylthrichloromethylmethane
(DDT)

173. Alcohols. Alcohols are hydroxyl derivatives of hydrocarbons, obtained by substituting hydroxyl groups for one or more hydrogen atoms in the hydrocarbon molecule. For instance, methyl alcohol CH_3OH is a hydroxyl derivative of methane CH_4, ethyl alcohol CH_3-CH_2-OH, a hydroxyl derivative of ethane CH_3-CH_3, etc.

If alcohols are acted upon by alkali metals, the hydrogen of the hydroxyl group linked directly to the oxygen is displaced by the metal to form solid compounds soluble in alcohol and known as **alcoholates**:

$$2CH_3CH_2-OH + 2Na \longrightarrow 2CH_3CH_2-ONa + H_2$$

In this respect alcohols are similar to many inorganic compounds containing hydroxyl groups in their molecules, such as water, oxyacids and other compounds, in which the hydroxyl groups are linked to non-metal atoms.

Like water, alcohols are associated liquids (see § 72) for which reason they have higher boiling points than other organic substances having equal molecular weights, but not containing hydroxyl groups in their molecules.

All alcohols react with acids, splitting off a molecule of water and forming compounds known as *esters*, e. g.:

$$\underset{\text{methyl alcohol}}{CH_3-O-H} + \underset{\text{nitric acid}}{HO-NO_2} \rightleftarrows \underset{\text{methyl nitrate}}{CH_3-O-NO_2} + H_2O$$

The ability to form esters is a characteristic property common to all alcohols and all acids.

At first sight, esters resemble salts in structure. Actually, however, the resemblance is only formal. The bond between the hydrocarbon radical (the radical obtained by abstracting one hydrogen atom from a hydrocarbon molecule) and the rest of the ester molecule is atomic and not ionic, as in salts.

Unlike most salts, esters are insoluble in water, but dissolve in organic solvents. Their solutions do not conduct electricity.

The formation of an ester from an alcohol and an acid is a reversible reaction, the forward reaction being called **esterification** and the back reaction **ester hydrolysis** or **saponification.**

Methyl alcohol or *methanol* CH_3OH is a colourless liquid (b. p. 65° C), highly poisonous; causes blindness if drunk, and may even be fatal if taken in large doses. Is obtained in large quantities by synthesis from carbon monoxide and hydrogen at a high pressure and high temperature in the presence of a catalyst:

$$CO + 2H_2 \rightleftarrows CH_3OH$$

Methyl alcohol is produced by the dry distillation of wood and for that reason is known also as *wood alcohol.* It is used as a solvent and for the preparation of other organic substances.

Ethyl alcohol or *ethanol* CH_3CH_2OH (b. p. 78° C) is one of the most important initial substances in the present-day organic synthesis industry. It has been prepared since ancient times from various sugar-containing substances, such as grape sugar, or glucose, which is converted into alcohol by fermentation under the action of ferments (enzymes) produced by yeast fungi.

The reaction takes place according to the equation:

$$\underset{\text{glucose}}{C_6H_{12}O_6} \rightleftarrows 2C_2H_5OH + 2CO_2$$

The raw material for the preparation of alcohol by fermentation may be the starch contained in potato tubers, or in the grains

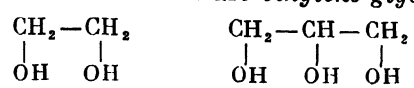
of rye, wheat, maize, etc. To convert the starch into saccharide substances, the flour or finely divided potatoes are scalded with hot water and cooled, after which *malt*, i. e., germinated barley grains ground with water, is added to it. The malt contains a special enzyme, called diastase, which acts catalytically on the saccharization of starch. After saccharization is complete yeast is added to the resulting liquid, and under the action of its enzymes (zimases) alcohol is formed. The latter is then distilled off and purified by redistillation.

At present cellulose, the chief constituent of wood, is also saccharized by the action of concentrated acids. The product obtained in this way is fermented into alcohol by means of yeast.

Finally, alcohol can be prepared by synthesis from ethylene. The reaction consists, in the long run, in the addition of water to ethylene (in the presence of a catalyst):

$$CH_2=CH_2+H_2O \longrightarrow CH_3-CH_2-OH$$

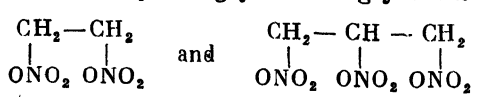
Besides alcohols with one hydroxyl group in their molecule, there are also alcohols whose molecules contain two or more hydroxyl groups. Examples of such alcohols are *ethylene glycol* and *glycerine*:



ethylene glycol glycerine

Ethylene glycol and glycerine are high-boiling liquids with a sweet taste, miscible with water in all proportions. Ethylene glycol is used as a composite part of *antifreezes*, i. e., substances substituting water in automobile and aircraft motor radiators in winter. A 65 per cent solution of ethylene glycol in water freezes at as low a temperature as $-40°$ C.

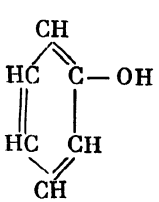
The nitrate esters of ethylene glycol and glycerine



and

incorrectly called *nitroethylene glycol* and *nitroglycerine*, are very explosive and are used for the preparation of dynamite.

Phenol C_6H_5OH is a hydroxyl derivative of the aromatic hydrocarbon benzene C_6H_6. Its structural formula is:



Pure phenol is a colourless crystalline substance melting at 41° C. It possesses a characteristic odour and antiseptic properties. The acid properties of the hydroxyl hydrogen are much more pronounced in phenol than in alcohols; this hydrogen can be displaced by a metal not only by the action of alkali metals, but by the action of alkalis as well. That is why phenol is otherwise called *carbolic acid.*

Phenol is contained in coal tar and can be prepared also synthetically from benzene. It is used in large quantities for the synthesis of medicinals, dyes and plastics.

174. Ethers. Ethers are organic compounds, whose molecules consist of two hydrocarbon radicals connected by an oxygen atom. An example is diethyl ether $C_2H_5—O—C_2H_5$.

Ethers are usually prepared by abstracting a molecule of water from two alcohol molecules. For instance:

$$C_2H_5—O—H + H—O—C_2H_5 \longrightarrow C_2H_5—O—C_2H_5 + H_2O$$

Most ethers are liquids, almost insoluble in water. The most important of them is *diethyl ether* $(C_2H_5)_2O$, a very mobile liquid with a characteristic odour and a boiling point of 34.5° C. It is widely used in laboratory practice as a solvent and in medicine as an anaesthetic and as a composite part of certain medicines.

175. Aldehydes. The functional group of aldehydes is the univalent group $—C\overset{O}{\diagdown\!\!\!\diagup H}$. Examples of aldehydes are:

$H—C\overset{O}{\diagdown\!\!\!\diagup H}$ formaldehyde

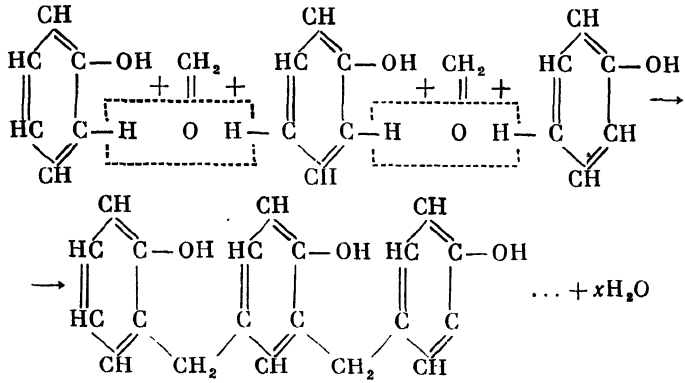
$CH_3—C\overset{O}{\diagdown\!\!\!\diagup H}$ acetaldehyde

Aldehydes are prepared by oxidizing the corresponding alcohols. For instance, formaldehyde is formed by passing a mixture of methyl alcohol vapour and air over a hot catalyst:

$$2CH_3OH + O_2 \longrightarrow 2H—C\overset{O}{\diagdown\!\!\!\diagup H} + 2H_2O$$

Formaldehyde is a gas with a pungent, disagreeable odour, very soluble in water. It possesses excellent antiseptic and tanning properties. A 40 per cent solution of formaldehyde in water under the name of formalin is widely used for disinfection, for preserving anatomical preparations, for pickling seeds before sowing, etc. Considerable quantities of formaldehyde are used for the preparation of its reaction

products with phenol. The reaction taking place may be represented as follows:



The formation of large molecules from molecules of lower molecular weight accompanied by the splitting off (or shifting) of atoms or groups of atoms, is called condensation.

The condensation products of phenol and formaldehyde are known as *phenol-formaldehyde* resins, which possess a remarkable property: when heated they at first soften, and then, if further heated (especially in the presence of suitable catalysts), become hard again. Phenol-formaldehyde resins are mixed with various fillers (wood pulp, finely divided paper, asbestos, graphite, etc.), with plasticizers and dyes, and the wares required are manufactured from the resulting mass by hot pressing. About 40 per cent of all the wares made of plastics are obtained on the basis of phenol-formaldehyde resins.

Acetaldehyde CH_3CHO (b.p. 21° C) is prepared in industry by the combination of water and acetylene in the presence of mercury salts, which act as catalysts for this reaction:

$$H-C\equiv C-H + H_2O \longrightarrow CH_3-C\begin{matrix}=O\\ \diagdown H\end{matrix}$$

This industrially important reaction was discovered by the Russian scientist M. Kucherov (1850-1911).

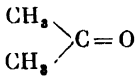
Aldehydes oxidize very readily into carboxylic acids. For instance, oxidation of acetaldehyde results in the formation of acetic acid, which is of great economic importance:

$$2CH_3-C\begin{matrix}=O\\ \diagdown H\end{matrix} + O_2 \longrightarrow 2CH_3-C\begin{matrix}=O\\ \diagdown O-H\end{matrix}$$

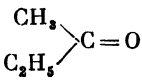
acetaldehyde — acetic acid

Owing to their ready oxidizability aldehydes are potent reducing agents.

176. Ketones. Ketones are compounds whose molecules contain the atomic group $>C=O$, linked to two hydrocarbon radicals. For example:



dimethyl ketone (acetone)

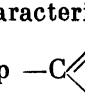


methylethyl ketone

The group  , known as the **carbonyl** group, is present also in aldehyde molecules. This accounts for the resemblance in the chemical properties of aldehydes and ketones. However, they are not identical, as in aldehyde molecules one of the bonds of the carbonyl group is combined with hydrogen, while in ketone molecules both bonds are linked to hydrocarbon radicals. In particular, ketones are much more difficult to oxidize than aldehydes, and are not such powerful reducing agents.

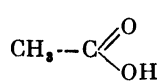
The most important ketone, practically, is dimethyl ketone, or acetone.

Acetone $CH_3—CO—CH_3$ is a colourless liquid with a characteristic odour, boiling at 56° C and miscible with water in any proportions. Acetone is an excellent solvent for many organic substances, which accounts for its wide use in the paint and varnish industry, in the manufacture of certain types of artificial silk, shatterproof organic glass, cinema film, etc. It is also used for the synthesis of a number of organic compounds.

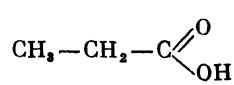
177. Carboxylic Acids. Carboxylic acids are characterized by the presence in their molecules of the atomic group  , which is the functional group of this class of compounds and is known as the carboxyl group. Examples of acids are



formic acid



acetic acid



propionic acid

It can be seen from the above formulas that carboxylic acid molecules, like those of alcohols, contain hydroxyl groups, for which reason acids resemble alcohols in some respects. But in acids the hydroxyl group is under the influence of the atomic group  , while in alcohols it is influenced only by the hydrocarbon radical. The influence of the carbonyl group on the hydroxyl manifests itself particularly in the fact that the hydrogen atom of the hydroxyl

group in acids is much more "acidic" than in alcohols: it is displaced much more readily by metals and splits off as a cation, for instance:

$$CH_3COOH \rightleftarrows CH_3COO' + H^+$$

With bases these acids form salts:

$$CH_3COOH + NaOH = CH_3COONa + H_2O$$

However, carboxylic acids are weak acids and therefore their salts are hydrolyzed.

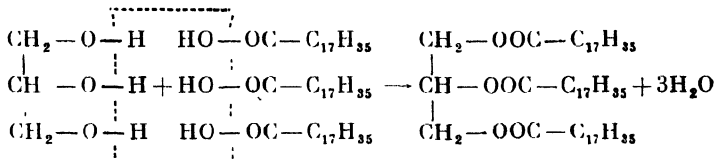
Depending on the number of carboxylic groups in the molecule, carboxylic acids fall into *unibasic*, *dibasic*, etc., acids.

Acetic acid CH_3COOH (b. p. 118.1° C) was the first acid ever known to man. It forms during the fermentation of wine and during the dry distillation of wood. It is prepared in industry in large quantities by the oxidation of acetaldehydes obtained from acetylene by the Kucherov reaction.

Acetic acid is used in very many chemical processes: in the manufacture of various dyes, medicinals, artificial fibres, certain types of plastics, etc.

Acids with higher molecular weights, such as the solid saturated acids *palmitic* $C_{15}H_{31}—COOH$ and *stearic* $C_{17}H_{35}—COOH$, and liquid, unsaturated *oleic* acid $C_{17}H_{33}—COOH$, are widely disseminated in animal and plant organisms as esters. Natural *fats* are mixtures of the glycerine esters of these acids.

The following equation represents the formation of one of these esters:



Solid fats contain chiefly esters of palmitic and stearic acids, while liquid vegetable oils are esters of oleic acid. Under the action of hydrogen (in the presence of nickel as a catalyst) liquid fats can be converted into solids as a result of the addition of hydrogen at the double bond between the carbon atoms in the esterified molecules of the unsaturated acid.

Like all esters, fats undergo hydrolysis (saponification). The saponification of fats is in itself a slow reaction but can be catalyzed by strong acids, alkalis, metal oxides or enzymes formed in live organisms.

The hydrolysis of a fat in a neutral or acid medium results in glycerine and the above-mentioned acids; if they are hydrolyzed in

alkaline solution the result is not the free acids, but their salts, called **soaps** (e. g., $C_{17}H_{35}COONa$ — sodium soap).

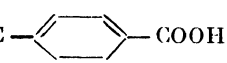
Some oils such as *linseed oil* consist of esters of still more unsaturated acids than oleic, containing two or three double bonds in their molecules. Such oils, on being applied to a surface, possess the property of forming solid durable films in the air. They are known as *drying oils*, and are used for the preparation of oil paints. To make them dry more rapidly the oils are preliminarily boiled in the presence of metal oxides (oxides of cobalt, manganese or lead), which act as catalysts for the formation of the film. They are then called *boiled oil*.

Many esters of carboxylic acids and saturated hydrocarbons possess pleasant odours and are often found in plants, accounting for the fragrance of flowers and the flavour of fruits and berries. Some of these esters can be prepared artificially and are widely used under the name of "fruit essences" in confectionery, in the manufacture of soft drinks, perfumes, etc. *Isoamyl acetate* $CH_3COOC_5H_{11}$ (oil of pears) is used as a solvent for celluloid.

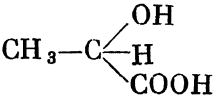
In recent years certain derivatives of *acrylic acid* $CH_2=CH-$ $-COOH$, an easily polymerized unsaturated acid, have acquired great importance. One of them is *methyl methacryalate* $CH_2=C(CH_3)-$ $-COOCH_3$. The polymers of this ester are transparent solids, resistant to heat and light. They are used to prepare sheets of strong and light *plexiglass*, widely used for aeroplanes and for the manufacture of various goods.

Oxalic acid HOOC—COOH is the simplest representative of dibasic carboxylic acids. It is a crystalline solid, readily soluble in water. It is contained in many plants (e.g., sorrel) in the form of the acid potassium salt, and is used for dyeing fabrics.

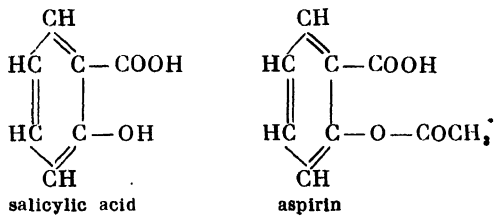
Teraphthalic acid, a dibasic carboxylic acid of the aromatic series, has the structural formula



The condensation product of the dimethyl ester of this acid with ethylene glycol (p. 465) is used for the manufacture of *lavsan*, an artificial fibre.

Lactic acid  is an example of a compound possessing different functional groups and manifesting the properties of both acids and alcohols (alcohol-acid). It is formed during the olactic fermentation of sugar-containing substances caused by special bacteria. It is contained in sour milk, sauerkraut, siloed fodder, etc.

A similar compound of the aromatic series is *salicylic acid* $C_6H_4(OH)COOH$, the acetate of which, known as *aspirin*, is widely used as a febrifuge.



salicylic acid aspirin

178. **Carbohydrates.** Carbohydrates include various sugars and substances which turn into sugars when hydrolyzed. Carbohydrates fall into three groups: *monosaccharides*, *disaccharides* and *polysaccharides*.

A representative of the simplest carbohydrates, the monosaccharides, is *glucose*, or *grape sugar*, a white crystalline substance with a sweet taste, readily soluble in water. Glucose is contained in large quantities in grape juice, in many fruits, as well as in the blood of animals and man. The work of the muscles depends mainly on the energy released due to the oxidation of glucose.

Glucose is an aldehyde-alcohol. The following structure is attributed to its molecules:

$$CH_2OH—CHOH—CHOH—CHOH—CHOH—C\begin{matrix}O\\H\end{matrix}$$

However, the properties of aldehyde-alcohols show that it would probably be more correct to represent their molecules as cyclic compounds; for instance, the structural formula of glucose would be

$$CHOH—CHOH—CHOH—CHOH—CH—CH_2OH$$
$$\underbrace{\qquad\qquad\qquad\qquad\qquad\qquad}_{O}$$

Glucose is used to finish fabrics, in the manufacture of mirrors and as a medicine.

Ordinary *beet sugar* $C_{12}H_{22}O_{11}$ is a disaccharide. It is contained in sugar beet (up to 15 per cent), in sugar cane, in birch and maple sap and in some fruit juices.

If heated in acid solution disaccharides hydrolyze into monosaccharides:

$$C_{12}H_{22}O_{11} + H_2O \rightarrow 2C_6H_{12}O_6$$

The polysaccharides form the third class of carbohydrates. These compounds differ in many respects from mono- and disaccharides:

they have no sweet taste and most of them are insoluble in water. The molecules of polysaccharides are built up of numerous $-C_6H_{10}O_5-$ groups, so that their composition is expressed by the generic formula $(C_6H_{10}O_5)_x$. Polysaccharides include such substances as starch and cellulose.

Starch $(C_6H_{10}O_5)_x$ forms as a result of photosynthesis in plant leaves. It is also deposited "as a reserve" in tubers, roots and grains. In the digestive tract of man and animals starch is hydrolyzed and converted into glucose, which is assimilated by the organism.

In industry starch is converted into glucose by boiling for several hours with dilute sulphuric acid (Kirchhoff process, p. 364). The sulphuric acid is removed from the resulting solution by adding chalk, which forms insoluble $CaSO_4$ with the sulphuric acid. The precipitate is filtered off and the solution evaporated. The result is a thick sweet mass known as *starch molasses*, which, besides glucose, contains considerable quantities of other starch hydrolysis products. Molasses is used for the preparation of confectionery goods and for various technical purposes.

If pure glucose is required, the starch is boiled for a longer time to convert it more completely into glucose. The solution obtained after neutralization and filtration is condensed until glucose crystals begin to separate out.

If dry starch is heated to 200 or 250° C it partly decomposes, yielding a mixture of polysaccharides of less complex composition than starch. This mixture is called *dextrin* and is used for finishing fabrics and for the preparation of pastes. The conversion of starch into dextrin accounts for the formation of the shiny crust on baked bread, as well as the lustre of starched linen.

Cellulose $(C_6H_{10}O_5)_x$ is the chief constituent of the shells of plant cells. In some types of cellulose the value of x is about 1,500. The purest cellulose found in nature is cotton fibre, which contains 85 to 90 per cent cellulose. The wood of coniferous trees contains about 50 per cent cellulose.

The importance of cellulose is very great. Suffice it to mention the immense quantity of cotton fibre used to manufacture cotton fabrics. Cellulose is made into paper and cardboard, and, by chemical treatment, into a large number of diverse products, such as artificial fibre, plastics, varnishes, smokeless gunpowder, ethyl alcohol (see p. 464), etc.

In industry cellulose is produced from wood by various methods. The most common method consists in treating the wood pulp at high temperature and pressure with a solution of calcium acid sulphite $Ca(HSO_3)_2$. The wood is decomposed, the lignin contained in it passing into solution, while the cellulose remains unchanged. Then the cellulose is separated from the solution, washed with water, dried and further treated. Cellulose obtained by this method is often called *sulphite cellulose*.

Cellulose is insoluble in water, ether and alcohol; it is very stable to the action of dilute acids, alkalis and weak oxidants.

When treated for a short time with concentrated sulphuric acid cellulose partly hydrolyzes, turning into what is known as *amyloid*, a substance close in properties to starch. If unsized paper is dipped into concentrated sulphuric acid for a short time and then immediately washed, the amyloid formed cements the paper fibres together, making the paper denser and stronger. This is how *parchment paper* is made.

Under the prolonged action of mineral acids cellulose passes into hydrocellulose, a mixture of unchanged cellulose and the products of its decomposition and hydrolysis. More vigorous action of acids causes hydrolysis of the hydrocellulose, resulting finally in glucose.

Cellulose contains hydroxyl groups in its molecules, and therefore forms ethers and esters. The esters of cellulose and nitric acid (nitro-cellulose) are used for the manufacture of smokeless gunpowder, celluloid, various kinds of films (for photography and cinema) nitro-varnishes, etc.

The acetate esters of cellulose (cellulose acetates) are used to manufacture non-inflammable photographic and cinema films, various transparent plastics and varnishes.

Of great industrial importance is the production of artificial fibre * by the chemical treatment of cellulose.

Three methods are used for the manufacture of artificial fibre from cellulose, namely, the viscose, acetate and copper-ammonia methods.

To obtain fibre by the *viscose method* the cellulose is treated with sodium hydroxide, and then with carbon bisulphide. The resulting orange mass, known as *xanthogenate*, is dissolved in a dilute solution of sodium hydroxide to form *viscose*. The latter is forced through special caps with minute apertures, called *dies*, into a precipitation bath consisting of an aqueous solution of sulphuric acid. Under the action of the sulphuric acid the viscose decomposes, splitting off sodium hydroxide and carbon bisulphide and forming threads of a somewhat modified cellulose known as *cellulose hydrate*. These threads are viscose or rayon fibres.

The viscose method is the most widespread method for the manufacture of artificial fibres. It will suffice to mention that in 1954, 78.4 per cent of all the artificial and synthetic fibre produced in the capitalist countries was obtained by this method.

In the *acetate method* an acetone solution of acetyl cellulose is forced through dies into a current of warm air. The acetone evaporates, and the jets of solution change into fine threads of acetate fibre. In 1954 the share of acetate fibre in the total output of artificial and synthetic fibres in the capitalist countries was 10.6 per cent.

The least common method is the *copper-ammonia method*, which makes use of a characteristic property of cellulose, namely, its ability to dissolve in an ammonia solution of cupric oxide $[Cu(NH_3)_4]$ $(OH)_2$. The cellulose is precipi-

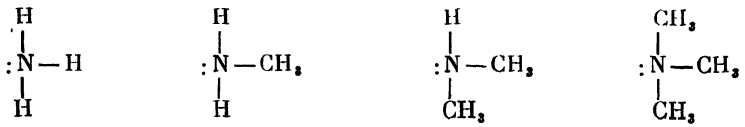
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* *Artificial fibre* is fibre produced by the chemical treatment of natural fibres (mainly cellulose), while *synthetic fibre* is the name given to fibre prepared from specially synthesized chemical materials.

tated from this solution as cellulose hydrate by treating it with acids. The fibrous threads are obtained by forcing the copper-ammonia solution through dies into a precipitation bath.

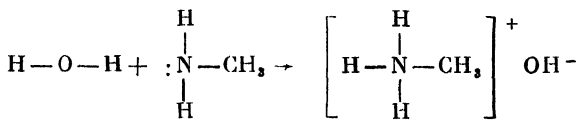
179. Amines, Aminoacids and Proteins. In molecular structure amines are derivatives of ammonia. They may be regarded as products of the displacement of one, two, or all three hydrogen atoms in ammonia by hydrocarbon radicals.

For the sake of comparison the formulas of ammonia and some amines are given below:

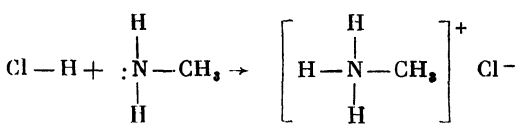


ammonia | methyl amine | dimethyl amine | trimethyl amine

The resemblance in structure accounts for the resemblance in properties. Like ammonia, amines are capable of combining with protons, abstracting them from other molecules, for instance, from water or acid molecules:



methylammonium hydroxide

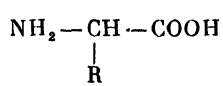


methylammonium chloride

One of the most important amines, aniline $C_6H_5NH_2$ has been mentioned above (p. 461).

Of great importance in natural processes are the *aminoacids*, the molecules of which contain aminogroups $-NH_2$ and carboxyl groups $-COOH$.

An example of the simplest aminoacid is *aminoacetic acid* NH_2-CH_2-COOH. The structure of other natural aminoacids may be represented by the formula



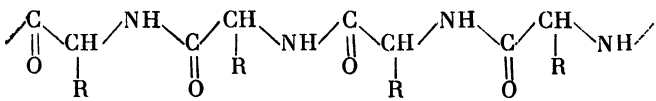
where R is a hydrocarbon radical.

Aminoacids form as a result of the hydrolysis of proteins, exceedingly complex organic compounds without which life is impossible.

The composition of proteins includes carbon, hydrogen, oxygen, nitrogen and frequently other elements as well, such as sulphur, phosphorus, iron. The molecular weights of proteins are very high, from 15,000 to several million. Proteins are contained in all the tissues of organisms, in the blood and in bones. All enzymes are complex proteins. Skin, hair, wool, feathers, horns, hoofs, claws—all consist of proteins.

The problem of the structure and synthesis of proteins is not quite solved as yet. Very important investigations have been carried out in this field in the U.S.S.R. by Zelinsky and his pupils.

It has been established at present that protein molecules consist of a large number of radicals of 25 to 30 different aminoacids, which in many proteins are linked as follows:



Such is the structure, for instance, of silk proteins.

The data obtained have made it possible to synthesize new substances with links of the same kind as in proteins between the individual structural units of their molecules.

It was thus that the synthetic polyamine fibres *capron* and *nylon* were obtained. These fibres are superior to natural silk in certain properties.

Capron is a polycondensate of aminocapronic acid

$$NH_2-CH_2-CH_2-CH_2-CH_2-CH_2-COOH$$

Part of the molecule of this substance is represented below:

$$-NH-(CH_2)_5-CO-NH-(CH_2)_5-CO-$$

Nylon, or *anide*, is obtained by the condensation of dibasic adipic acid HOOC—$(CH_2)_4$—COOH and hexamethylenediamine NH_2—$(CH_2)_6$—NH_2.

The structure of the nylon molecule can be represented as follows:

$$[-CO-(CH_2)_4-CO-NH-(CH_2)_6-NH-]_x$$

The brief information on organic compounds given in this section reflects but a small fraction of the great achievements made by synthetic organic chemistry in the course of its development on the basis of Butlerov's theory of chemical structure.

SILICON (Silicium); at. wt. 28.09

Silicon is situated in the fourth group of the Periodic Table directly below carbon, and is a complete analogue of the latter. Like carbon, silicon can both yield and accept electrons; but its capacity for gaining electrons, and therefore its non-metallic properties, are somewhat less pronounced than those of carbon. The most typical compounds of silicon are those in which it is positively tetravalent.

180. Silicon in Nature. Preparation and Properties of Silicon. Silicon is one of the most abundant elements in nature. It constitutes 26 per cent of the part of the earth's crust accessible to investigation and occupies the second place among the elements in abundance.

Silicon occurs in nature only in the form of compounds: as the oxide SiO_2, called *silicon dioxide* or *silica*, and in the form of *silicic acid* salts.

Just as carbon, a constituent of all organic substances, is the most important element in the animal and vegetable kingdoms, so is silicon the principal element in the kingdom of minerals and rocks forming the earth's crust and consisting almost entirely of silicon compounds. Besides the earth's crust, silicon compounds are found in the stems of certain plants (such as horsetails, cereals, etc.), in the shells of many infusorians and lower seaweeds, in the bodies of sponges, in birds' feathers and in the fur of animals.

Free silicon can be prepared both in the amorphous and in the crystalline form.

Amorphous silicon is prepared by strongly heating magnesium with fine white sand of a chemical composition corresponding to almost pure silicon dioxide:

$$SiO_2 + 2Mg = 2MgO + Si$$

It has the appearance of a brown powder and a specific gravity of approximately 2.35. Amorphous silicon dissolves in molten metals. When cooled slowly, a solution of silicon in zinc or in aluminium will deposit well-formed octahedral crystals of silicon having a specific gravity of 2.5.

Crystalline silicon has a steely metallic lustre and conducts electric current perceptibly. Its boiling point is about 1,415° C.

Silicon is used mainly in various alloys. Iron containing 4 per cent silicon has a high magnetic permeability and is employed for the manufacture of electric transformers. Iron alloys rich in silicon are excellent acid-resistant materials. Of great importance are alloys of silicon with aluminium and copper. Silicon is used also for the reduction of some of the metals from their oxides.

Lately silicon, alongside of germanium (see § 233), has found wide application in radio and electrical engineering for the manufacture of semi-conductor apparatuses.

Silicon is obtained commercially by reducing silicon dioxide SiO_2 with coal in electric furnaces:

$$SiO_2 + 2C = Si + 2CO$$

Silicon produced by this process always contains a certain amount of impurities. Much purer silicon can be obtained by reducing silicon dioxide with aluminium or by reducing silicon tetrachloride $SiCl_4$ with zinc. Very pure silicon is produced by decomposing silicon tetrachloride on a red-hot tantalum band.

In chemical properties silicon (especially the crystalline modification) is rather inactive; at ordinary temperatures it will combine directly only with fluorine. If heated, amorphous silicon combines readily with oxygen, the halogens, sulphur and many metals.

Acids, with the exception of hydrofluoric, do not attack silicon, but the alkalis react with it vigorously, liberating hydrogen and forming salts of silicic acid:

$$Si + 2KOH + H_2O = K_2SiO_3 + 2H_2$$

As silicon will displace hydrogen even from water in the presence of traces of alkali (which evidently acts as a catalyst), this reaction may be represented as proceeding in two steps:

$$\overset{0}{Si} + 3H_2O = \overset{+IV}{H_2SiO_3} + 2H_2$$
$$H_2SiO_3 + 2KOH = K_2SiO_3 + 2H_2O$$

Adding up these equations we get the summary equation of the reaction as written above.

If a mixture of sand and coke in definite proportions is heated in an electric furnace, the result is silicon carbide SiC, commonly known as *carborundum*:

$$SiO_2 + 3C = SiC + 2CO$$

Pure carborundum is a colourless crystalline substance (specific gravity 3.2) close to diamond in hardness. The technical product is usually dark grey, due to impurities.

The internal structure of carborundum is that of a diamond in which half the carbon atoms have been uniformly replaced by silicon atoms. Each carbon atom is in the centre of a tetrahedron with silicon atoms at its corners; in its turn, each silicon atom is surrounded in a similar manner by four carbon atoms. The covalent bonds linking all the atoms in this structure are very strong, like in a diamond. That is why carborundum is so hard.

Carborundum is prepared nowadays in large quantities. It is used to make grinding wheels and whetstones, and as a refractory material.

At a high temperature silicon unites with many metals forming silicides. For instance, if SiO_2 is heated with an excess of metallic magnesium, the reduced silicon unites with the magnesium to form magnesium silicide Mg_2Si:

$$4Mg + SiO_2 = Mg_2Si + 2MgO$$

181. Compounds of Silicon with Hydrogen and the Halogens. If magnesium silicide Mg_2Si is treated with hydrochloric acid the result is silicon hydride SiH_4, an analogue of methane:

$$Mg_2Si + 4HCl = 2MgCl_2 + SiH_4$$

Silicon hydride SiH_4 is a colourless gas igniting spontaneously in the air and burning to form silicon dioxide and water:

$$SiH_4 + 2O_2 = SiO_2 + 2H_2O$$

Besides SiH_4, several more silicon hydrides, Si_2H_6, Si_3H_8, etc., are known, under the generic name of silanes. Silanes are analogous to hydrocarbons, but are much less stable. Apparently, the bond between the silicon atoms is much weaker than that between carbon atoms, so that —Si—Si—Si—etc. chains are easily broken up. The bond between silicon and hydrogen is also unstable, showing that the non-metallic properties of silicon are much weaker than those of carbon.

Silicon tetrachloride $SiCl_4$ is prepared by heating a mixture of silica and coal in a stream of chlorine:

$$SiO_2 + 2C + 2Cl_2 = SiCl_4 + 2CO$$

It is a liquid, boiling at 57° C. In water $SiCl_4$ undergoes complete hydrolysis, forming silicic and hydrochloric acids:

$$SiCl_4 + 3H_2O = H_2SiO_3 + 4HCl$$

When evaporated in moist air, $SiCl_4$ produces a thick smoke according to the above reaction. This property accounts for the use of silicon tetrachloride for smoke screens.

Silicon tetrafluoride SiF_4 is produced by the action of hydrogen fluoride on silica:

$$SiO_2 + 4HF = SiF_4 + 2H_2O$$

It is a colourless gas with a pungent odour. When cooled strongly it passes directly from the gaseous state into the solid.

If silicon tetrafluoride is passed into water a solution of fluosilicic acid H_2SiF_6 results:

$$3SiF_4 + 3H_2O = 2H_2SiF_6 + \downarrow H_2SiO_3$$

If the concentrated solution is cooled, crystals of the composition $H_2SiF_6 \cdot 2H_2O$ separate out.

Fluosilicic acid H_2SiF_6 is a strong acid. Its degree of ionization in 0.1 N solution is 75 per cent. Even at very low concentrations it is a powerful disinfectant. The salts of fluosilicic acid, known as **fluosilicates**, are mostly soluble in water. Sodium and barium fluosilicates are widely used to kill agricultural pests. Sodium fluosilicate is used also for the preparation of various enamels. Magnesium and zinc fluosilicates are employed to make cement waterproof.

182. Silicon Dioxide or Silica SiO_2. The most characteristic and stable compound of silicon is silicon dioxide, usually known as silica. It is found both in the crystalline and in the amorphous form.

Crystalline silica occurs in nature mainly as the mineral *quartz*. Transparent colourless crystals of quartz having the form of hexagonal prisms with hexagonal pyramids on their ends are called *rock crystal* (Fig. 115). Rock crystal coloured violet by impurities is called *amethyst*, whereas if it is brownish it is known as *smoky topaz*. But more frequently quartz is found in the form of a compact semitransparent mass, colourless or of various colours. One of the varieties of quartz is called *flint*. *Agate* and *jasper* are very finely crystalline varieties of quartz. Quartz also forms part of many complex rocks, such as granite, gneiss, etc.

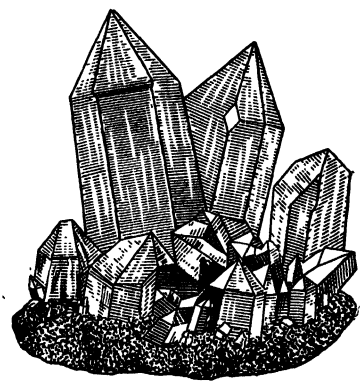


Fig. 115. Rock crystals

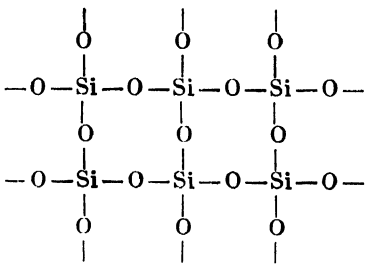
Ordinary *sand* consists of tiny grains of quartz. Pure sand is white in colour, but more often it is coloured yellow or reddish by iron compounds.

Crystalline silica is very hard, insoluble in water and melts only in the flame of detonating gas or in an electric furnace, turning into a colourless liquid. When this liquid cools, it solidifies into a transparent vitreous mass of amorphous silica, quite similar in appearance to ordinary glass.

Amorphous silica is much less abundant in nature than the crystalline modification. The testae of some of the lower seaweeds are of amorphous silica. Accumulations of such testae form rather large deposits in some places and are known as tripoli (diatomite) or infusorian earth. Silicon can be prepared artificially as a white amorphous mobile powder by strongly heating silicic acid.

The pronounced difference between the physical properties of silica and carbon dioxide is due to the fact that the latter consists of separate CO_2 molecules,

while the former is a polymer $(SiO_2)_x$. The structure of this polymer, for instance, the structure of quartz, can be represented as follows:



Each silicon atom is in the centre of a tetrahedron with oxygen atoms at its corners; each of the oxygen atoms is in its turn connected with two atoms of silicon. To destroy a quartz crystal a large number of strong bonds between silicon and oxygen must be ruptured, which accounts for the great hardness of quartz.

Silica is not attacked by acids, except hydrofluoric acid. The latter, as has been mentioned above, reacts readily with it, forming SiF and water

$$SiO_2 + 4HF = SiF_4 + 2H_2O$$

No other acid will act like this on the oxide of a typical non-metal.

183. Silicic Acids and Their Salts. Silicon dioxide is an acid oxide, corresponding to *orthosilicic acid* H_4SiO_4. This acid condenses very readily, forming high molecular *metasilicic acid* $(H_2SiO_3)_x$. In simplified form the formula of metasilicic acid is written as H_2SiO_3. The salts of silicic acid are called **silicates.**

Potassium and sodium silicates are prepared by fusing silica with the alkalis or carbonates of potassium and sodium, as:

$$SiO_2 + 2NaOH = Na_2SiO_3 + H_2O$$
$$SiO_2 + K_2CO_3 = K_2SiO_3 + CO_2$$

The fusions formed are vitreous masses and, contrary to all the other silicates, are soluble in water. That is why potassium and sodium silicates are known as *soluble glass.*

The above formulas of potassium and sodium silicates are simplified. Actually these silicates are of a variable composition, expressed by the generic formula $R_2O \cdot nSiO_2$, where R stands for potassium or sodium.

Aqueous solutions of soluble glass are called *water glass* and are used for the preparation of acidproof cement and concrete (see § 186), for kerosene proof plasters on concrete, for impregnating fabrics, for preparing fireproof wood paints, for chemical consolidation of weak soils.

The reaction between a solution of Na_2SiO_3 or K_2SiO_3 and hydrochloric or sulphuric acid results in free metasilicic acid, which, depending on the concentration of the initial solutions, either falls out of solution, as a jelly-like precipitate (in some cases the entire liquid turns into a jelly) or remains in solution in the *colloidal* state (see § 188).

The reaction of formation of silicic acid may be expressed by the following equation:

$$Na_2SiO_3 + 2HCl = H_2SiO_3 + 2NaCl$$

The jelly-like precipitate of silicic acid falling out of the solution contains an immense amount of water which can be removed by heating. However, no definite acid of a composition expressible by a formula is obtained: the precipitate gradually loses water until it is finally converted, when calcined, into pure anhydrous silicon dioxide. It is assumed that silicon dioxide forms many silicic acids, differing, like the phosphoric acids, in water content. The fact that they exist is borne out by the great number of salts corresponding to the following acids: $H_2SiO_3(SiO_2+H_2O)$, $H_4SiO_4(SiO_2+2H_2O)$, $H_4Si_3O_8(3SiO_2+2H_2O)$, etc.

The composition of the silicic acids may be expressed by the generic formula: $mSiO_2 \cdot nH_2O$, where m and n are whole numbers. Acids in which $m > 1$ are known as **polysilicic acids.**

Up to the present date the existence of three acids has been established beyond doubt, namely, *orthosilicic* H_4SiO_4, *metasilicic* H_2SiO_3, or rather $(H_2SiO_3)_x$, and *bimetasilicic* $(H_2Si_2O_5)_x$. When silicic acid is formed in any reaction, its composition is usually expressed by the simplified formula of metasilicic acid H_2SiO_3.

If the greater part of the water is removed from a jelly-like precipitate of silicic acid (without, however, completely dehydrating it), a solid white slightly translucent mass results, having numerous very tiny pores and possessing an immense adsorptive capacity. This product is known as *silica gel.* It is prepared in great quantities in industry and is widely used for absorbing various vapours and gases, for purifying mineral oils, as a catalyst in many reactions, etc. Silica gel is used also as a base for catalysts in the production of sulphuric acid by the contact method.

Silicic acid is a very weak acid and therefore Na_2SiO_3 and K_2SiO_3 are greatly hydrolyzed in solution and react alkaline.

The salts of silicic acid, silicates, are very abundant in nature. As has already been said, the earth's crust consists mainly of silica and different kinds of silicates. The natural silicates include feldspars, micas, clays, asbestos, talc and many other minerals. Silicates are composite parts of a large number of rocks, such as granite, gneiss,

basalt, various schists, etc. Many precious stones, such as emerald, topaz, aquamarine, are well-formed crystals of natural silicates.

The composition of natural silicates is, in the majority of cases, expressed by rather complex formulas. Owing to the complexity of these formulas, and to the fact that the existence of the corresponding polysilicic acids has not been proved, they are conventionally written somewhat differently than the formulas of ordinary salts.

Any salt of an oxyacid may be regarded as a compound of an acid and a basic oxide (or even two basic oxides, if it is a double salt). For instance, $CaCO_3$ may be regarded as a compound of CaO and CO_2, $Al_2(SO_4)_3$, as a compound of Al_2O_3 and $3SO_3$, etc. On these grounds the composition of silicates is usually expressed by writing the formulas of silicon dioxide and all the oxides forming the silicate separately, without combining them into a single salt formula.

The formulas of some of the natural silicates are given below:

Kaolin $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, or $H_4Al_2Si_2O_9$
White mica $K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$, or $H_4K_2Al_6Si_6O_{24}$
Asbestos $CaO \cdot 3MgO \cdot 4SiO_2$, or $CaMg_3Si_4O_{12}$

The most widely dispersed silicates in nature are the so-called *alumosilicates*, i.e., those containing aluminium. The most important of them are the *feldspars*.

Besides silicon and aluminium oxides, feldspars contain also oxides of potassium, sodium or calcium. Ordinary feldspar, *orthoclase*, contains potassium oxide; its composition is expressed by the formula $K_2O \cdot Al_2O_3 \cdot 6SiO_2$. The most common colour of feldspars is white or red. They are found both as compact deposits and as composite parts of complex rocks.

Alumosilicates include also the quite commonly known minerals called *micas*, distinguished by their ability to split into thin flexible flakes or sheets. The composition of micas are very complex; besides silicon and aluminium, they contain hydrogen, potassium or sodium; some micas contain also calcium, magnesium and iron. Ordinary white mica, which, due to its refractory properties, is frequently used in the form of large transparent sheets to cover apertures in various furnaces, is a silicate of potassium and aluminium. Micas high in iron and magnesium are black in colour. Micas do not occur very often in separate deposits, but are composite parts of very many complex rocks. Some of the most abundant complex rocks, *granites* and *gneisses*, consist of minute crystals of quartz, feldspar and mica.

On coming into contact with the atmosphere and being subjected to the mechanical and chemical action of water and air, minerals and rocks on the earth's surface are gradually altered and broken down. Such destruction caused by the combined action of water and air is called *erosion*. Of special importance is the erosion of feldspars.

for instance, orthoclase. Water containing carbon dioxide erodes orthoclase by leaching out K_2O, the latter combining with CO_2 to form potash K_2CO_3; part of the SiO_2 is also leached out, and the remainder combines with water, forming a new silicate, *kaolin*, which is a composite part of various *clays*.

The decomposition of orthoclase may be expressed by the following equation:

$$K_2O \cdot Al_2O_3 \cdot 6SiO_2 + CO_2 + nH_2O = K_2CO_3 + 4SiO_2 \cdot mH_2O + Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$$

Micas decompose similarly to feldspars, but more slowly.

The process of erosion of feldspars and other alumosilicates into kaolin is called *kaolinization*. As feldspars are very abundant, immense quantities of clay are formed in nature as a result of their decomposition.

Pure kaolin with minor impurities of quartz sand is found comparatively rarely. It is white in colour and is valued as a material for the preparation of porcelain. There are rich deposits of kaolin in many parts of the Soviet Union, especially in the South. The best kaolin comes from the deposits of the Glukhov District, Ukrainian S.S.R. Ordinary clay is a mixture of kaolin and other substances, which account for its yellowish-brown or bluish colour. Some types of clays, intensely coloured by iron oxides, are used as mineral paints (ochre, etc.).

Silicon compounds play an important part in the national economy. Silica and the natural silicates serve as raw materials for the manufacture of glass, ceramics, porcelain, majolica, building and binding materials. All these industries constitute a large branch of the national economy, known as the *silicate industry*.

184. Glass. If mixtures of many silicates (with each other or with silica) are heated, they form transparent amorphous fusions, called glasses.

The chief property of any glass, which is of great importance for the manufacture of glassware, is that the molten glass does not solidify immediately upon cooling, but thickens gradually, becoming viscous and finally changing into a solid, homogeneous, transparent mass.

Many other properties of glass depend largely on its composition. By changing not only the composite parts of glass, but their relative proportions as well, glasses of a wide range of properties can be obtained.

Ordinary *window glass*, as well as the glass in most of the glassware used for domestic purposes (bottles, tumblers, etc.), consists mainly of sodium and potassium silicates, fused with silica. The composition of such glass is expressed approximately by the formula $Na_2O \cdot CaO \cdot 6SiO_2$. The raw materials for its manufacture are, however, not the silicates themselves, but white sand, soda and lime or chalk. A

mixture of these substances is fused in regenerative furnaces heated usually by producer gas. When they are melted, the following reactions ensue:

$$CaCO_3 + SiO_2 = CaSiO_3 + CO_2$$
$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2$$

Sodium sulphate and coal are often used instead of soda. The coal reduces the Na_2SO_4 to Na_2SO_3, which reacts with the sand, forming Na_2SiO_3:

$$2Na_2SO_4 + 2SiO_2 + C = 2Na_2SiO_3 + 2SO_2 + CO_2$$

Glassware is manufactured by blowing, casting, pressing and drawing. Not so very long ago glassware used to be blown only by lung power, and its manufacture was a very laborious job. Today the glass industry is considerably mechanized. There are machines which manufacture the simplest glass articles (such as bottles) mechanically, and other machines for the direct production of sheet glass by drawing an endless glass sheet from the viscous vitreous mass.

If potash is employed instead of soda in glass-making, refractory glass results. The latter is used for manufacturing special kinds of chemical glassware capable of withstanding more intense heating than ordinary glassware.

If silica is fused with potash and plumbic oxide, a bright heavy glass is obtained, known as *crystal glass* and containing potassium and lead silicates. Such glass possesses high refractive properties and acquires a bright lustre when ground; it is used to make optical glasses and decorative dishes.

Substitution of the particles of silica by boron oxide B_2O_3 (see § 228) greatly influences the properties of glass. The addition of boron oxide increases the hardness of the glass, makes it more resistant to chemicals and less sensitive to abrupt changes of temperature. This glass is used to prepare high-quality chemical glassware.

The sand used in manufacturing ordinary glass often contains iron compounds as impurities, which impart a greenish tint to the glass. To prevent the formation of this tint, minute quantities of selenium are added to the fusion, this causing a pink colour. Pink and green are complementary colours and together give white. Manganese dioxide causes a similar effect.

Sometimes various substances are added to the glass fusion purposely to obtain coloured glasses. Thus, for instance, chromic oxide Cr_2O_3 gives glass a green colour; manganese dioxide, a reddish-purple colour; cobaltous oxide, a blue colour, etc. In most cases the colour of the glass depends on the formation of coloured silicates (of iron, manganese, cobalt, etc.). But sometimes it is due to the fact that the substance added is present in the glass in the form of very finely divided particles. Thus, if a very small quantity of gold is added to glass, it acquires a ruby-red colour, due to the presence of minute particles of gold, invisible even under the microscope,

which form when the melted glass is cooled slowly. Ruby glasses transmit only red rays and are therefore used in photography wherever red illumination is required.

The manufacture of coloured glass in Russia was founded by M. Lomonosov who developed and put into practice a method of producing coloured glass, beads, bugles, mosaic smalt and a number of other substances. The famous mosaic pictures by Lomonosov which have come down to us, are made up of thousands of tiny pieces of variously coloured glass (smalt) prepared according to his recipes. For the manufacture of coloured glass Lomonosov built a small glass factory near Petersburg in 1753. This was the first plant in Russia which manufactured, besides the above named articles, also variously coloured glassware and various minor fancy glass articles (cuff buttons, snuffboxes, cane heads, etc). Somewhat later coloured glass and coloured crystal were manufactured according to Lomonosov's recipes at the state glass factory in Petersburg.

Glass is usually considered insoluble in water. However, if ordinary sodium glass is subjected to the action of water for a long time, the latter extracts part of the sodium silicate from it. If, for instance, powdered glass is shaken with water and then several drops of phenolphthalein are added, the liquid turns definitely red, showing an alkaline reaction (due to hydrolysis of the Na_2SiO_3).

Besides the above brands of glass, which are mostly fusions of various silicates and silica, another very important type of glass is that manufactured directly from quartz by melting in an electric furnace.

Quartz glass has many advantages over ordinary glass. Since the melting point of quartz is around 1,500° C, quartz glass can be subjected to high temperatures without fear of its softening. Quartz glass transmits ultra-violet rays, which ordinary glass does not. A very valuable quality of quartz glass is its exceedingly small coefficient of expansion. This means that heating or cooling hardly changes the volume of quartz glass. That is why articles made of it can be heated strongly and then immersed quickly in cold water without shattering.

Quartz glass is used for the manufacture of laboratory apparatus (crucibles, evaporating dishes, flasks, etc.) and in the chemical industry. In lighting engineering, quartz glass is used for the manufacture of electric mercury lamps, which emit light high in ultra-violet rays. Mercury lamps are employed in medicine, for scientific purposes and especially in filming motion pictures. The disadvantages of quartz glass, accounting for its rather limited use, are difficulty of working, brittleness and high cost.

Ordinary glass does not transmit ultra-violet rays owing to the iron oxides contained in it, especially Fe_2O_3. This shortcoming of glass can be eliminated by using pure raw materials for its manufacture. Glass prepared in this way is called *uviol glass*. It transmits ultra-violet rays almost as well as quartz glass, but is much cheaper

and easier to work. The Fe_2O_3 content in this glass does not exceed 0.02 to 0.08 per cent. Uviol glass is used in medicine for ultra-violet raying and in some cases for the manufacture of window glass.

Glass manufacture is one of the largest branches of the silicate industry.

Molten glass can be drawn through dies into fibres 2 to 10 μ in diameter, and is then known as *fibre glass*. Fibre glass is not brittle like ordinary glass and possesses high tensile strength. Fabrics made of this fibre are non-flammable, conduct neither heat nor electric current, are poor conductors of sound and chemically inactive.

The valuable properties of materials made of fibre glass warrant their wide use in various branches of technology, especially in electrical engineering. Of great importance in this connection are the availability and cheapness of the chief raw materials and the simple technology of production of this type of glass.

Fibre glass mixed with various synthetic resins gives new types of building materials, known as *glass fibre laminates*. They are three or four times lighter than steel but are just as strong, which makes them eligible as substitutes both for metal and for wood in mechanical engineering, construction work, etc. Glass fibre laminates are widely used for the manufacture of automobile and aircraft parts. A striking illustration of the importance of glass fibre laminates in modern engineering is the fact that in the course of twelve years (from 1938 to 1954) the output of these materials in the U.S.A. increased about sixtyfold.

185. Ceramics. Ceramics include various wares made of clay. The *ceramic industry* manufacturing these wares embraces the production of brick, tiles, refractories, earthenware pottery and pipes (crude ceramics), as well as the manufacture of chinaware (fine ceramics). All these industries are based on the ability of clay when mixed with water to form a putty which after baking turns into a hard porous mass that will not soften in water. To increase the mechanical strength of the wares, various substances are added to the clay, the most important of which are quartz and feldspar.

Ceramic objects are shaped from the wet clay either mechanically or by hand on potter's wheels, then dried in the air or in special driers and baked in kilns. During the last named operation the water with which the clay was mixed and the water contained in the clay itself is driven off. As a result, the clay becomes porous, shrinks a little and turns into aluminium silicate $3Al_2O_3 \cdot 2SiO_2$.

Crude ceramic ware such as bricks, drainage pipes, tiles, flower pots, etc., are manufactured at brick factories. These wares are made of low-quality clays, baked at comparatively low temperatures (not over 1,000° C), are porous and capable of absorbing large amounts of water. Ordinary pottery is manufactured in the same way. To make the pot waterproof it is *glazed*, for which purpose common salt is thrown into the baking kiln; its vapours react with part of the silica in the wares. As a result of this process the pots become coated with a glass-like layer of fusible silicate.

Finer ceramic wares and *majolica* are made of the purest iron-free grades of clay and are baked at a higher temperature. The glaze is applied by coating the baked objects, or *bisques*, as they are called, with fusible mixtures, which may

consist of various substances (feldspar, boric acid, stannic oxide, etc.) and then reheating them in a kiln.

Porcelain wares are shaped from pure elutriated kaolin mixed with an approximately equal quantity of quartz and feldspar. The objects are baked at a high temperature (about 1,200° C). After the first baking the bisques are immersed in a gruel of finely ground feldspar and water, where they become coated with a layer of feldspar, and are then put back into the kiln. The bisques are baked at about 1,400° C, whereupon the feldspar in the glaze and in the bulk of the bisques melts and almost completely fills their pores. The resulting chinaware is translucent and has a dense, lustrous glaze.

Porcelain was invented in China in ancient times, but the secret of its production remained unknown for a long time. Porcelain was first obtained in Russia in the XVIII century by D. Vinogradov. Thanks to the persistent, painstaking work of Vinogradov, who, together with Lomonosov, carried out a great number of experiments on the preparation of porcelain mixtures, the porcelain he produced was not inferior to the Chinese.

186. Cement. One of the most important materials produced by the silicate industry is cement, employed in enormous quantities in all kinds of construction work.

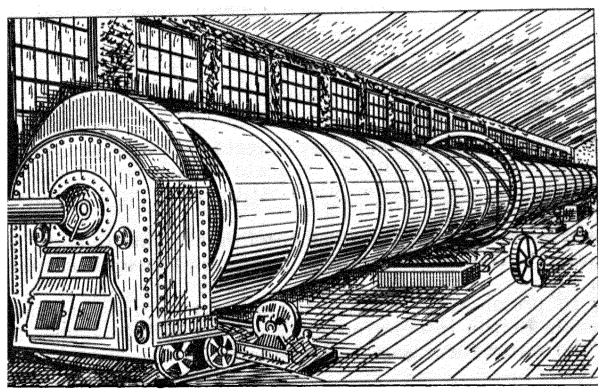


Fig. 116. Rotary cement kiln

Cement is prepared by roasting clay together with limestone until they cake. For this purpose the clay and limestone are first thoroughly mixed, dry or wet, and then strongly heated. When the cement mixture is roasted, the calcium carbonate decomposes into carbon dioxide and calcium oxide, which reacts with the clay, forming calcium silicates and aluminates. In the latter, aluminium oxide plays the part of a weak acidic oxide.

The cement mixture is roasted in special cylindrical rotary kilns. A kiln of this kind (Fig. 116) is a large tube made of thick sheet steel, 40 to 150 m. long, and 2.5 to 3.5 m. in diameter, slightly inclined and lined on the inside with refractory materials. The cement

mixture is added at the higher end of the furnace and burning coal dust or atomized heavy fuel oil is blown into the lower. Due to the incline and the slow rotation of the kiln, the mixture travels slowly towards the flame and the lower end of the furnace, from which it emerges in the form of tiny grains called *cement clinker*. The clinker is ground to a fine greyish-green powder and marketed under the name of *silicate cement* (otherwise called *Portland cement*).

The cement mixture is usually prepared artificially from limestone and clay. But nature has provided lime-clay rocks called *marls*, which correspond exactly in composition to the cement mixture. Deposits of marls used for the production of cement are found, for instance, in the mountains surrounding Novorossiisk.

The chemical composition of cements is usually expressed as percentages of the oxides they contain, the most important of these being CaO, Al_2O_3, SiO_2 and Fe_2O_3. The weight ratio between calcium oxide and the other three oxides is called the *hydraulic module* of the cement and characterizes its technical properties. By way of illustration, the average content of the chief composite parts in various grades of silicate cement is given below (in per cent):

CaO	62	Fe_2O_3	2.5
SiO_2	22	MgO	2.5
Al_2O_3 . . .	7.5	SO_3	1.5

It has recently been established that silicate cement has the following mineralogical composition: tricalcium silicate $3CaO \cdot SiO_2$, dicalcium silicate $2CaO \cdot SiO_2$, tricalcium aluminate $3CaO \cdot Al_2O_3$ and tetracalcium alumoferrite $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$.

When mixed with water silicate cement forms a plastic mass which hardens after some time. Its transition from the plastic to the solid state is called "setting".

According to present-day theories the cement hardens in three steps. The first step consists in the interaction between the surface layers of the cement particles and the water according to the equation

$$3CaO \cdot SiO_2 + nH_2O = 2CaO \cdot SiO_2 \cdot 2H_2O + Ca(OH)_2 + (n-3)\,H_2O$$

The calcium hydroxide, contained as a saturated solution in the plastic cement, begins to separate out in the amorphous state and, surrounding the cement grains, binds them into a coherent mass. This is the second step, that of setting proper. The third step is crystallization or the initial hardening. The particles of calcium hydroxide increase in size, turning into long, needle-like crystals which grow into the amorphous mass of calcium silicate and make it more compact. This is accompanied by an increase in the mechanical strength of the cement.

When cement is used as a binding material it is usually mixed with several parts by weight of sand. A mixture of cement, sand and water is called *mortar*.

Cement is one of the most important building materials in modern engineering. As it is inert towards water it is absolutely irreplaceable

in all port and submarine structures, for the construction of dams, for the erection of buildings in damp places, etc.

If mortar is mixed with gravel, crushed rock, etc., we get *concrete*. Concrete is very widely used to build vaults, arches, bridges, cisterns, tanks, residential houses, etc. Structures made of concrete based on iron beams and rods are called *reinforced concrete* structures.

The continuously growing demands of the national economy for building materials led to a considerable growth of the cement industry in the Soviet Union. In 1955, 22.5 million tons of cement were produced in the U.S.S.R., and by 1960 the cement output was 55 million tons.

Other types of cement besides silicate cement are also manufactured in the U.S.S.R.

Alumina cement is prepared by fusing a finely pulverized mixture of bauxite (natural aluminium oxide) and limestone. The mixture is fused in vertical or special electric kilns. Alumina cement contains a smaller percentage of CaO, but more Al_2O_3, than silicate cement. Its approximate composition is 40 per cent CaO, 10 per cent SiO_2 and 50 per cent Al_2O_3. The chief compounds constituting this cement are various calcium aluminates. Alumina cement hardens much more rapidly than silicate cement. Besides, it resists sea water more effectively. As alumina cement is much more expensive than silicate cement, it is used for construction purposes only in special cases.

Acid-resistant cement is a mixture of finely ground quartz sand and an "active" silica substance possessing a highly developed surface. The latter is usually either chemically treated tripoli or artificially produced silicon dioxide. When sodium silicate solution is added to this mixture it becomes plastic and hardens subsequently into a stable mass resisting all acids except hydrofluoric.

Acid-resistant cement is used mainly as a binder when lining chemical apparatuses with acid-resistant tiles. In some apparatuses deficient lead is replaced by acid-resistant cement.

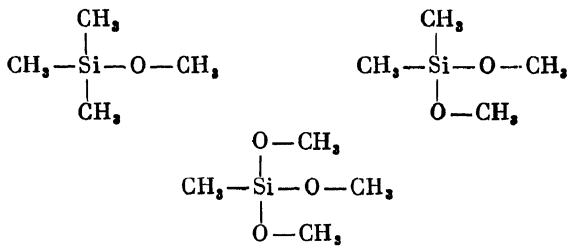
187. Silico-Organic Compounds. There has long been known a considerable number of various silicon compounds in which the silicon atoms are combined with carbon atoms. These compounds are known as silico-organic compounds.

For a long time silico-organic compounds were of no practical importance.

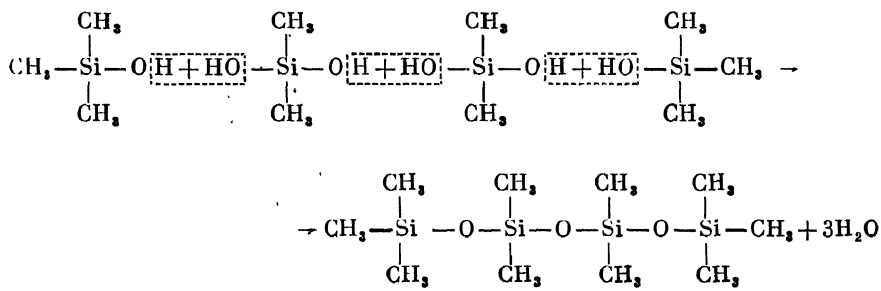
In 1936 the Soviet scientist K. Andrianov developed a method of synthesis of high molecular silico-organic compounds which now forms the basis of the industrial method for the preparation of a number of products possessing very valuable properties.

K. Andrianov synthesized esters of derivatives of orthosilicic acid $Si(OH)_4$ in which one, two, or three hydroxyl groups were replaced

by hydrocarbon radicals. For example:



Hydrolysis of these esters should have resulted in the corresponding hydroxyl-containing silicon compounds, but they immediately condense, splitting off water molecules and forming polycondensates. For instance, the substances resulting from the hydrolysis of a mixture of $(CH_3)_2Si(OCH_3)_2$ and $(CH_3)_3SiOCH_3$ may condense further according to the following equation:



If condensation proceeds to a minor degree (so that the molecules contain about ten atoms of silicon) the resulting liquids can be used as lubricants. Their valuable properties are: insignificant change in viscosity over a wide range of temperatures and chemical stability with respect to metals. Compared to ordinary lubricants, which are mixtures of saturated hydrocarbons, they are much more stable against high temperatures.

If condensation is more extensive the resulting substances are of a resinous nature. Such resins are very heat resistant owing to the high strength of their Si—O bond, and are excellent dielectrics. They are used for insulating electric conductors in cases where ordinary insulation is unsuitable due to high temperatures. Rubber-like materials can be obtained on the basis of silico-organic resins, which retain their elasticity at temperatures from —60 to +200° C and do not break down even at 300° C.

COLLOIDS

188. Crystalline and Colloid States of Substances. If a solution of sodium silicate is added to concentrated hydrochloric acid, the resulting silicic acid does not separate out as precipitate but remains in solution together with the sodium chloride formed during the reaction.

The hydrochloric acid and sodium chloride can be removed from the solution in the following way. The solution is placed in a bottomless cylinder with a membrane of parchment paper or an animal bladder bound over its end. The cylinder is submerged in a wider vessel containing water which is continuously renewed (Fig. 117). The sodium chloride and hydrochloric acid diffuse freely through the membrane into the outer vessel, but the silicic acid cannot penetrate the membrane and remains in solution. As a result, the cylinder will be found after some time to contain a pure solution of silicic acid.

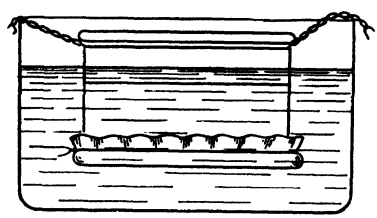


Fig. 117. Dialyzer

The method of separating dissolved substances based on the fact that one of them will not diffuse through a membrane, is known as **dialysis**, and the apparatus described is called a **dialyzer.**

Many other dissolved substances, besides silicic acid, viz., glue, gelatine, egg albumen, etc., cannot penetrate a membrane of parchment paper or bladder.

In the sixties of the last century the diffusion of dissolved substances through vegetable and animal membranes was studied in detail by the English chemist Graham.

Graham found that all substances capable of diffusing in solution are crystalline in the solid state. On the contrary, substances which could not diffuse through membranes were found to be amorphous, and formed shapeless (and to a certain degree plastic) masses when isolated from solution. On this basis Graham called the former **crystalloids** and the latter **colloids** (from the Greek "colla"—glue).

However, as early as 1869, the Russian botanist I. Borshchov put forth the assumption that the particles of certain colloids may also be of crystalline structure. Further investigations confirmed this assumption and led to the conclusion that Graham's division of substances into crystalloids and colloids should be rejected, as not only such typical colloids as albumen could be obtained in the form of crystals, but many indisputable crystalloids, such as common salt, could be obtained in the form of colloids.

Finally, it was proved that the same substance could behave like a colloid in some solvents and like a crystalloid in others. For instance, ordinary soap dissolved in water diffuses very slowly and cannot penetrate a membrane, showing it to be a colloid; but in alcohol solution the same soap possesses the properties of a crystalloid.

Thus, the sharp demarcation line between crystalloids and colloids gradually disappeared, and at present we can speak only of the crystalloid or colloid states of substances, just as we have spoken above of their solid and liquid states.

The colloid state of substances plays a very important part not only in chemistry, but also in biology, medicine, technology and agriculture, and therefore we shall dwell on it in some detail.

189. Dispersed Systems. If a fine powder of any insoluble substance, say clay, is shaken with water, the larger particles will soon settle at the bottom while the finest will remain in a "suspended" state in the water for a considerable length of time, so that the liquid may remain turbid sometimes for weeks. Liquids with particles of a solid substance suspended in them are called **suspensions.**

If minute drops of a liquid are suspended in another liquid the system is called an **emulsion.** An emulsion can easily be obtained by shaking an oil vigorously with water in the presence of substances capable of lowering the surface tension of the oil. Ordinary milk is an emulsion of minute drops of butter fat in water (see Fig. 1, p. 15).

Particles suspended in liquids can be separated from them by filtration. Ordinary filter paper will detain particles down to 5 μ, i.e., 0.005 mm., in diameter, specially prepared filter paper down to 1 μ, while clay filters detain particles as small as 0.2 μ.

As long as particles above 0.1 μ in diameter are present in a liquid, it will not seem quite transparent, and the suspended particles can be detected in a drop of the liquid with the aid of an ordinary microscope.

A substance can be divided artificially into such tiny particles, that the liquid containing them will seem quite transparent and homogeneous, although actually it is not homogeneous. For instance, if we dip two silver wires into distilled water, connect them to a sufficiently powerful source of electric current (Fig. 118) and bring their ends together under the water, an electric arc will be struck and a brownish cloud will appear. Soon the entire liquid will turn brown, though remaining quite transparent. This colouring is due to minute particles of silver sent into the water by the electric arc. If gold wires are used instead of the silver ones, the liquid will turn purple and will contain minute particles of gold. The particles obtained in this manner cannot be detected even with the most powerful magnification possible in an ordinary microscope, but their presence can be revealed by means of the so-called Tyndall effect.

The *Tyndall effect* may be explained as follows. If a beam of converging rays, say, from a projection lantern, is passed through a liquid containing minute particles in suspension, each of these particles scatters the light rays that fall on it, becoming, in a sense, a

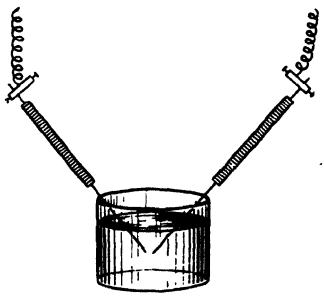


Fig. 118. Diagram of apparatus for preparation of colloidal solution of silver

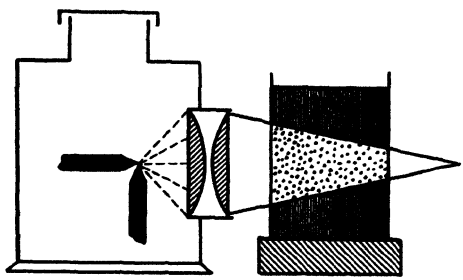


Fig. 119. Tyndall cone

luminous point. Thus, the entire path of the rays through the liquid becomes visible, having the appearance of a bright cone, if viewed in a darkened room.

The Tyndall effect is the underlying principle of the instrument known as the *ultra-microscope*; with this instrument, particles less

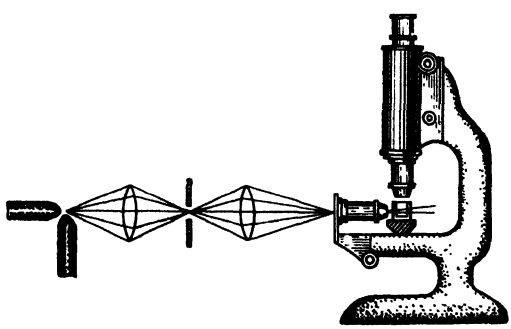


Fig. 120. Diagram of ultra-microscope

than 0.1 μ in diameter, and invisible under an ordinary microscope, can be detected in a liquid. The difference between an ultra-microscope (Fig. 120) and an ordinary one is that in the former the light falls laterally on the liquid under study, instead of from below. If the liquid is perfectly homogeneous, all the fields of vision will appear dark, as no light rays enter the tube of the microscope. But if the liquid contains minute suspended particles, say, silver particles

formed by an electric arc, the rays scattered by them come to the observer's eye and the dark background will appear studded with luminous specks in continuous motion (Brownian movement).

If the particles are much less than 0.1 μ in size, they may be difficult to discern even with an ultra-microscope, but the beam of rays passing through the liquid will still be observed. Finally, if the particles are as small as 1 mμ, the light scattering becomes so insignificant that this phenomenon also disappears and the liquid appears quite homogeneous or, as we say, "optically void." Such, for instance, are ordinary solutions of various substances.

Any system in which one substance is finely divided and distributed as more or less minute particles through another substance is called a dispersed system; the divided substance is known as the **dispersed phase** of the system while the substance around it is called the **dispersion medium**. For instance, in the case of a suspension of clay in water, the dispersed phase consists of the clay particles, while the dispersion medium is water.

Dispersed systems, as we have seen, may have different degrees of dispersion. Suspensions and emulsions are classed as coarsely dispersed systems, as the particles of their dispersed phases are comparatively large. On the other hand, ordinary solutions are systems with very high, one may say ultimate, degrees of dispersion, as the distributed substance is broken down into molecules and/or ions. In this limit case there is no dispersed phase to speak of, as the entire solution is one single phase. An intermediate position is occupied by dispersed systems, in which the size of the dispersed particles is larger than in ordinary solutions, but still so small that they are discernible only with the aid of an ultra-microscope. Such systems are called **colloidal solutions** or **sols**.

A close study of colloidal solutions shows that no sharp boundary can be drawn between such solutions and ordinary, or, as they are called, "true" solutions, on the one hand, and suspensions or emulsions, on the other. Therefore, the division of dispersed systems with liquid dispersion media into the three above classes is rather conventional. The demarcation line between these classes is determined approximately by the limits of visibility with an ordinary microscope and with an ultra-microscope.

Suspensions and *emulsions* contain particles visible under an ordinary microscope. Their size exceeds 100 mμ (0.1 μ). The heterogeneity of such a system can be detected by the naked eye.

Colloidal solutions. Size of dispersed particles between 100 and 1mμ. The particles are discernible only under the ultra-microscope; they pass unhindered through the pores of ordinary filters, but can be detained by membranes of parchment paper, bull bladder or special "ultra-filters." In transmitted light colloidal solutions appear quite

transparent and homogeneous, in reflected light—slightly turbid, especially if the size of their particles is close to 100 mμ.

Modern electron microscopes, which give magnifications of tens and hundreds of thousands of times, enable not only detection of colloidal particles, but determination of their size and shape as well.

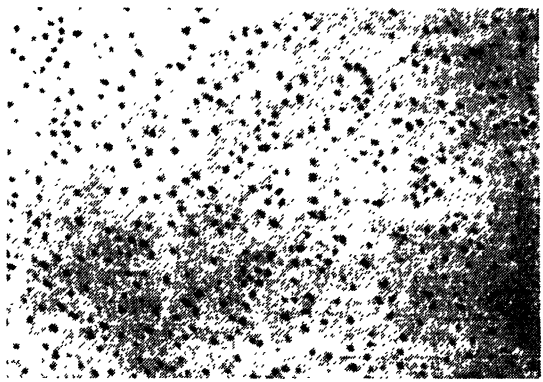


Fig. 121. Silver sol (magnification 18,000X)

Fig. 121 shows a silver sol photographed with the aid of an electron microscope.

True solutions. Size of dispersed particles below 1 mμ. Such particles cannot be detected by optical means.

If we arrange liquid dispersed systems in order of increasing dispersity of the solid or liquid particles they contain, we get the following series:

Suspensions and emulsion — Colloidal solutions — True solutions

100 mμ — 1 mμ

Increasing degree of dispersity

Fig. 122 gives a good idea of the relative particle size in different dispersed systems.

190. Composition of Colloidal Particles. Thus, the difference between colloidal and true solutions is that the dispersed particles in the former are much larger. In true solutions the dispersed particles are molecules or ions of the solute, while in colloidal solutions the particles are evidently whole aggregates consisting of numerous molecules. An idea of the size of these aggregates (of the number of molecules forming them) can be had by determining the relative weight of colloidal particles. For instance, the relative weights of the soap

particles contained in a colloidal solution of soap in water ranges from 7,000 to 15,000 oxygen units, depending on the concentration. But if the same soap is dissolved in alcohol it forms a true solution, and determination of the boiling point of such a solution gives a molecular weight of 306 for soap, corresponding to the formula $C_{17}H_{35}COONa$, obtained by analysis. Hence, the soap particles contained in the colloidal solution are aggregates consisting of 20 to 50

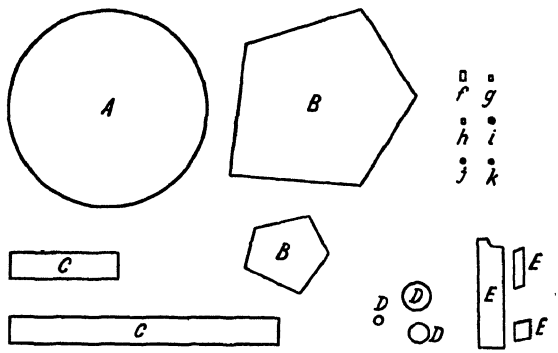


Fig. 122. Relative sizes of various particles:
A—arythrocytes of human blood, diameter about 7.5 μ; *B*—fragments of starch grains 3 to 8 μ; *C*—anthrax bacilli, length 4 to 10 μ; *D*—cocci, 0.1 to 1μ; *E*—particles of kaolin suspension; *f*, *g*, *h*—particles of gold suspension, 0.075 to 0.2μ; *i*, *j*, *k*—particles of colloidal gold, 0.006 to 0.015 μ

molecules each. Likewise, particles of metals contained in colloidal solutions like those obtained by dispersing silver in water, are found to consist of scores and hundreds of atoms, while the molecules of the metals in the gaseous state or in mercury solution consist of only one atom each.

In some cases the molecules themselves are so large that they form a colloidal solution without combining into larger aggregates. For instance, the molecule of the red substance of blood corpuscles, haemoglobin, weighs approximately 68,100 oxygen units, while the molecular weights of some other proteins may be as high as several million units.

191. Preparation of Colloidal Solutions. Colloidal solutions can be obtained by various methods.

Some substances having a complex composition and large molecules, such as proteins, gelatine, gum arabic, form colloidal solutions if merely left in contact with water for a sufficient length of time. Others can be converted to the colloidal state by grinding them with the liquid. Coarse particles can also be ground to colloidal size in so-called *colloid mills*. Such mills are widely used in practice for the

preparation of various paints, paper and rubber fillers, in the pharmaceutical industry, in the food industry, etc. Substances can be ground by colloid mills to particles as small as 0.01 μ in diameter.

The above methods are based on the conversion of large particles into smaller ones and are for this reason classed as **dispersion** methods. But colloids can be prepared also in the opposite way, by setting up conditions that promote the combination of simple molecules into larger aggregates which will not, however, exceed a certain limit. Such methods are known as **condensation** methods; they are based on chemical reactions taking place in aqueous solutions. By adjusting the conditions appropriately, the insoluble substance formed during the reaction can in many cases be made to assume the form of colloidal particles of one size or another, giving rise to a colloidal solution. For instance, the colloidal gold solution described above can easily be obtained by reducing auric chloride with formalin.

Add several drops of a 1 per cent solution of $AuCl_3$ to a test tube containing distilled water. Heat the solution to boiling and then add 2 or 3 ml. of a very weak solution of formalin. The liquid turns a beautiful purple colour due to the formation of colloidal particles of gold:

$$2AuCl_3 + 3HC\begin{matrix}O\\H\end{matrix} + 3H_2O = 2Au + 6HCl + 3HC\begin{matrix}O\\OH\end{matrix}$$

Of course, in this case gold is evolved first in the form of individual atoms which, however, combine into larger aggregates immediately afterwards.

Several more examples of the formation of colloidal solutions during chemical reactions are given below.

1. Heat some distilled water to boiling in a beaker and then add a solution of ferric chloride $FeCl_3$ drop by drop.

As a result of hydrolysis, a large part of the ferric chloride is converted into ferric hydroxide:

$$FeCl_3 + 3H_2O \rightleftarrows Fe(OH)_3 + 3HCl$$

At the same time a certain quantity of the basic salt FeOCl will be formed.

Though ferric hydroxide is insoluble in water, it does not form a precipitate under the above conditions but remains in solution as very minute particles. The result is a transparent $Fe(OH)_3$ sol, of the colour of strong tea.

2. Pass hydrogen sulphide for some time through a solution of arsenious acid:

$$2H_3AsO_3 + 3H_2S = As_2S_3 + 6H_2O$$

A transparent golden-yellow sol of arsenic trisulphide results.

Another condensation method is that of the production of metal sols with the aid of an electric arc. A study of this phenomenon showed that when the arc is struck the metal is converted directly to the gaseous form, where it is divided into separate atoms; the colloidal particles of the metal form as a result of condensation of its vapour.

192. Stability of Colloidal Solutions. Like the molecules of true solutions, the colloid particles of sols are in a state of continuous unorderly movement (Brownian movement). Although the intensity of this movement falls rapidly as the particle size increases, in the case of colloidal solutions it is still high enough to counteract gravity and to keep the colloid particles from settling to the bottom, as in the case of coarse suspensions. It would seem that as the Brownian movement leads to incessant collisions between the colloid particles, it should inevitably result in their combining into larger aggregates and precipitating, thus breaking up the sol. But this is not so; colloidal systems are quite stable and in many cases are capable of standing for years without undergoing any visible change. Obviously, they are under the action of some forces which hinder particle growth and destruction of the sols. These forces are the electric charges on the colloid particles.

If two electrodes connected to the poles of a current source of sufficiently high voltage are dipped into a colloidal solution, the colloid particles begin to migrate slowly towards the anode or the cathode. This phenomenon, discovered as far back as 1809 by Professor F. Reiss of the Moscow University, is known as **electrophoresis,** i.e., electrical transfer of particles. The movement of the colloid particles under the influence of current shows that they carry a definite electrical charge. The particles of metal hydroxides, many organic paints, haemoglobin, etc., are positively charged; negative charges occur on metal particles, sulphur, sulphides and gum arabic.

The origin of these charges is attributed to the adsorption of ions from solution by the colloid particles. In most cases colloidal particles are formed in media containing electrolytes of some kind, and if the particles are capable of adsorbing predominantly or exclusively ions of one type, i.e., either cations or anions, they acquire the charge of those ions. For instance, the colloidal particles of arsenic trisulphide formed by the action of hydrogen sulphide on an H_3AsO_3 solution adsorb HS' ions from the solution and turn into large negatively charged anions, the composition of which can be represented by the following conventional formula:

$$\{[As_2S_3]_m \cdot xHS'\}$$

Of course, charged colloid particles can exist in solution only if the latter contains at the same time ions of the opposite charge, called **counter-ions.** In this case the counter-ions are hydrogen ions.

A system consisting of a charged colloidal particle and the ions neutralizing it is known as a micelle. Its structure is shown in Fig.123.

The micelle of arsenic trisulphide can be represented as follows:

$$\{[As_2S_3]_m \cdot xHS'\} + xH^{\cdot}$$

When a current is passed through the solution, the negatively charged ions of the micelles are drawn towards the anode, where they deposit gradually as yellow arsenic trisulphide. Careful analysis always detects a certain excess of sulphur in this deposit relative to the formula As_2S_3. At the same time hydrogen is observed to be liberated at the cathode.

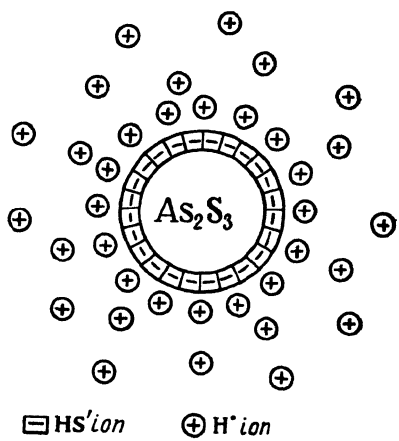


Fig. 123. Structure of As_2S_3 micelle

Other colloid particles become charged in a way similar to that described for arsenic trisulphide particles. For instance, a gold solution obtained by dispersing metallic gold in water contains the colloidal anions $\{[Au]_n \cdot xOH'\}$, formed as a result of adsorption of hydroxyl ions from the water; a colloidal solution of ferric hydroxide obtained by hydrolysis of ferric chloride contains the colloidal cations $\{[Fe(OH)_3]_m \cdot xFeO^{\cdot}\}$ or $\{[Fe(OH)_3]_m \cdot xFe^{\cdots}\}$, etc.

The capacity of colloid particles for adsorbing ions accounts for the stability of colloidal solutions. The adsorbed ions impart like electrical charges to the particles, keeping them from approaching each other and clustering into larger aggregates. Besides, the charged colloid particles and their counter-ions may be highly solvated in solution, which also impedes close contact and cohesion of the particles.

The mechanism of formation of colloidal solutions during chemical reactions may be pictured as follows.

The molecules of the insoluble substance, say $Fe(OH)_3$, produced as a result of a reaction, immediately begin to cluster into larger and larger particles. Usually the growth of these particles is very rapid (practically almost instantaneous) and results in precipitation. But under suitable conditions the particles begin at a definite stage of their growth to adsorb the ions contained in the solution, as a result of which they acquire a definite charge. The appearance of the charge on the particles checks or greatly retards their further growth and they remain in the liquid, forming a colloidal solution.

193. Coagulation. Since the stability of colloidal solutions is due to the presence of electrical charges and solvate shells on the colloid particles, any factor causing such charges to decrease or disappear must obviously decrease the stability of colloidal solutions, promoting cohesion of their particles and the formation of larger aggregates. This process of growth of colloidal particles is known as **coagulation** or **curdling**. It takes place very slowly in any colloidal solution. When the particles reach a certain size, rapid precipitation or **sedimentation** sets in.

The chief method of accelerating coagulation is by adding small quantities of various electrolytes to the colloidal solution. The introduction of an electrolyte into the solution greatly increases the total concentration of ions in it, creating favourable conditions for the charged colloid particles to absorb ions of the opposite sign. Thus, the initial charge of the particles decreases or is neutralized altogether, after which rapid coagulation of the sol sets in.

Take, for instance, a colloidal solution of arsenic trisulphide As_2S_3, a transparent light yellow liquid, and add some hydrochloric acid or some salt solution to it; coagulation begins immediately, and arsenic trisulphide separates out of the liquid in a form of yellow precipitate. Coagulation can be caused in other colloidal solutions in a similar way.

Not only the particles contained in colloidal solutions, but also the coarser particles of suspensions, are always charged. Therefore, the addition of electrolytes to suspensions promotes rapid precipitation. The formation of deltas at the mouths of rivers as they fall into the sea may be attributed to the precipitation of suspended clay and sand particles due to the river water mixing with the salt sea water.

Coagulation can be brought about not only by electrolytes but also by other colloids with opposite charges on their particles. For instance, if a solution of arsenic trisulphide is mixed with a solution of ferric hydroxide, a precipitate immediately appears, although no chemical reaction has taken place between the two substances: the positively and negatively charged particles neutralize each other's charges, leading to mutual coagulation of the colloids. The same phenomenon can often be observed when variously coloured inks are mixed, these inks usually being colloidal solutions of organic dyes. If one of the dyes is positively charged and the other negatively, mixing them will cause the formation of a flaky precipitate and the liquid above it becomes colourless.

The coagulation of colloids by one another has found a very important use in the purification of drinking water. The settling tanks and sand and coke filters used for the purification of river water before it is delivered to the water mains cannot detain particles of the fine suspensions and colloids contained in large quantities in any natural

waters. In most cases these particles are negatively charged. To coagulate them a positively charged sol of aluminium hydroxide $Al(OH)_3$ is used. In practice this is done as follows: a precalculated quantity of aluminium sulphate is added to the water in the settling tank. Part of it reacts with the calcium and magnesium carbonates in the water, forming aluminium carbonate which is immediately completely hydrolyzed. Another part is directly hydrolyzed by water. The result is an aluminium hydroxide sol which coagulates the colloids contained in the water, forming a precipitate that cannot pass through the filter.

Although adding electrolytes is the chief means of coagulating sols, it is not the only one. Many sols coagulate when heated. Heating increases the velocity of the colloid particles and at the same time decreases the adsorption of ions and therefore the charges on the colloid particles, promoting the formation of clusters where they collide. For instance, if a sol of arsenic trisulphide is heated to boiling, a yellow precipitate of As_2S_3 falls out immediately. The setting of egg albumen when heated, the turning of milk, etc., are commonly known facts. Finally, all methods of concentrating sols (evaporation or freezing out of the solvent, etc.) also lead to coagulation.

194. Lyophilic and Lyophobic Colloids. The precipitates formed by the coagulation of colloids may be of various structures. Some colloids form jelly-like precipitates, retaining immense quantities of the solvent, others precipitate in the form of powders or flakes which hardly carry any solvent with them at all.

On this basis, the former are called **lyophilic colloids** and the latter **lyophobic.*** In particular, when the solvent is water, the colloids may be **hydrophilic** or **hydrophobic**. Hydrophilic colloids include proteins, glue, starch, silicic acid and generally high-molecular compounds; hydrophobic colloids include metallic colloids, metal sulphides, various salts, etc. The hydroxides of metals occupy a somewhat intermediate position between these two classes.

The difference between lyophilic and lyophobic colloids is manifested in many respects.

1) Sols of lyophilic colloids are much more viscous than the pure solvent, whereas the viscosity of sols of lyophobic colloids hardly differs from that of the pure solvent.

2) The coagulation of lyophilic colloids is, as a rule (but not always), a reversible process. The precipitate of a lyophilic colloid will pass back into the sol if the cause of coagulation is removed. On the contrary, a precipitate formed by a lyophobic colloid will not usually redissolve if treated with a new portion of the solvent.

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* From the Greek *lyo*—I dissolve, *phileo*—I love, and *phobos*—fear.

3) Sols of lyophilic colloids are much more stable than those of lyophobic colloids. Whereas the latter coagulate in the presence of very small quantities of electrolytes, coagulation of lyophilic colloids requires the addition of considerable quantities of electrolytes. In this case the process is usually called **salting out**. An example of the latter is the salting out of soap from its colloidal solution in water.

The high stability of the sols of lyophilic colloids is due to their ability to solvate. The influence of solvation on the stability of the lyophobic colloids is comparatively small and is manifested chiefly in solvatation of their counter-ions. In lyophilic colloids, on the other hand, the entire particle is solvated, due, probably, not simply to electrostatic attraction of the dispersion medium molecules, but to a more profound interaction between them and the disperison medium, as in the case of a molecular solution. Thus, the particles of a lyophilic colloid are surrounded by a dense solvate shell which keeps them from clustering. To cause coagulation, these solvate shells must be removed, which is done by adding large amounts of electrolytes. The ions of the latter themselves become solvated, abstracting the solvent molecules from the particles of the colloid, and thus cause its coagulation. The solvate shell can be destroyed also by other means. For instance, a glue sol can be coagulated by adding alcohol to it, as the latter also binds water molecules. In general, it should be noted that the main stability factor of lyophobic colloids is the charge on their particles, while that of lyophilic colloids is solvatation.

It is noteworthy that easily coagulated sols of lyophobic colloids can be made very stable with respect to electrolytes by adding a small quantity of some lyophilic colloid, say, gelatine, gum arabic, etc. A similar "protective influence" is displayed by lyophilic colloids over suspensions, their presence greatly retarding the settling of the suspended particles.

The important phenomenon of "colloidal protection" can be illustrated by the following experiment.

Pour some dilute hydrochloric acid into two test tubes and add a little gelatine solution to one of them. Then add some silver nitrate solution to both test tubes and shake them well. In the test tube not containing gelatine characteristic curd-like flakes of silver chloride form after shaking; in the other test tube the entire liquid becomes turbid, but no precipitate falls out. Owing to the presence of the gelatine, the minute particles of silver chloride do not cluster into flakes, but remain in solution in the form of a very fine suspension.

This principle is utilized in the preparation of photographic bromogelatine plates, the gelatine layer of which contains a very fine suspension of silver bromide.

The mechanism of colloid protection consists apparently in the fact that the lyophilic colloid coats the particles of the lyophobic

colloid, protecting them from the penetration of ions and the formation of clusters.

195. Formation of Jellies. The sols of many lyophilic colloids are capable, under certain conditions, of coagulating in such a way that the entire sol is converted into a rather dense mass called a **jelly** or **gel**. This process is called **jellification** or **gelatination**. A commonly known example is that of gelatine, a two or three per cent solution of which in warm water turns after some time into a rather thick jelly. When heated the jelly again becomes a sol.

Similar jellies are formed by colloidal solutions of silicic acid, with the only difference that in this case coagulation is irreversible.

According to present-day views, jellies are formed by high-molecular compounds, the molecules of which are capable of uniting into long chains or threads. These threads intertangle to form an intricate space lattice or screen (jelly skeleton), the cells of which are filled with liquid (Fig. 124). This structure accounts for the jelly having the properties of a solid. The cohesion of the particles in the lattice may be so weak that it is sometimes sufficient to shake the jelly for its structure to break down and a sol to form.

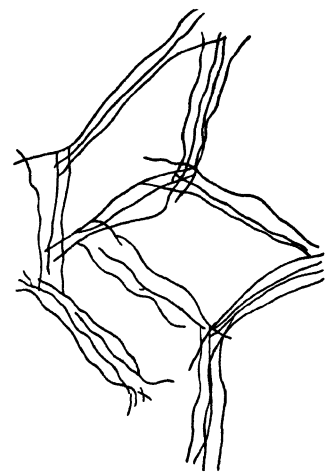


Fig. 124. Schematic structure of a jelly

It is obvious that jellification of the entire sol requires a sufficient concentration of the colloid, as it must bind the entire amount of solvent present. In this respect jelly-forming colloids differ greatly from one another. Thus, gelatine will form a jelly at a concentration of 1 to 1.5 per cent, agar-agar, at a concentration of only 0.25 per cent, while other colloids require higher concentrations.

Jellification depends greatly on the temperature. For instance, a 10 per cent gelatine jelly, which is quite solid at room temperature, liquefies rapidly if heated to 40 or 50° C, passing into a sol.

The consistence of a jelly depends greatly on the amount of solvent contained in it. For instance, a silicic acid jelly containing 94 to 97 per cent water has the appearance of a jelly and quivers if shaken; if it contains 90 to 92 per cent water it can be cut with a knife. A jelly containing 75 per cent water is breakable.

Jellies may undergo profound changes in time, decreasing in volume and separating out their liquid. This phenomenon is called **syneresis** and is observed during many processes of everyday life. A well-known

example of syneresis is the curdling of sour milk to form curds and whey.

When dried, some jellies change little in volume, their skeleton remaining intact, but become harder and harder until they turn entirely into a brittle mass which can easily be ground to a powder. Such jellies usually contain numerous pores and, like charcoal, are excellent adsorbents. These include the dried jelly of silicic acid, called silica gel (see § 183). Other jellies, such as those of gelatine, various proteins, rubbers, etc., on the contrary, contract greatly when dried but are afterwards still capable of bending without breaking. Such jellies are referred to as *elastic* jellies.

A remarkable peculiarity of elastic jellies is their ability to *swell*, i.e., absorb liquid, greatly increasing in volume and exerting high pressures. Sometimes the liquid can be imbibed by the jelly only to a certain limit, after which swelling ceases (for instance wood). In other cases (such as glue or gelatine in hot water) the jelly continues to swell indefinitely and finally passes into a sol.

Investigation of the properties of substance in the colloidal state is of immense practical importance. Colloids are encountered in various branches of industry and technology. Such are the leather, rubber, textile, soap, glass, photographic, and ceramic industries, the production of artificial fibres, plastics, etc. In many of these industries colloid chemical investigations have led to considerable progress in technological processes.

CHAPTER XVIII

General Properties of Metals

We shall begin our discussion of the metals by examining their general properties and the methods by which they are obtained from their natural compounds, and shall then pass over to a survey of the individual metals in the order of their arrangement by groups in the Periodic Table.

196. Physical Properties of Metals. One of the most commonly known characteristic features of metals is their peculiar "metallic" lustre, which is due to their high capacity for reflecting light rays. However, the lustre of a metal can usually be observed only when it is in the form of a compact mass. True, magnesium and aluminium retain their lustre even in powder form, but most metals are black or dark grey when pulverized. Besides, typical metals are good conductors of heat and electricity, their order in both of these capacities being the same: the best conductors are silver and copper and the worst, lead and mercury. With rising temperature the electrical conductivity of metals decreases, and vice versa.

A very important property of metals is their relatively easy mechanical deformability. Metals are plastic, they can be readily forged, drawn into wire, rolled into sheets, etc.

The characteristic physical properties of metals are related to the peculiarities of their internal structure. According to present-day views, the crystals of metals consist of positively charged ions and free electrons, split away from the corresponding atoms. The crystal as a whole can be pictured as a space lattice with ions at its points and mobile electrons in the interstices between them. These electrons keep constantly passing from atom to atom and moving about the nucleus now of one, now of another atom. As the electrons are not bound up with any definite ions, a very small difference of potentials is sufficient to make them move in a definite direction, thus giving rise to electric current. Thus, the high electrical conductivity of metals is due to the presence of free electrons ("electron gas") in them. If it is taken into account that the ions at the points of the lattice are not absolutely immobile either, but are capable of minor oscillations, the reason for the decrease in electrical conductivity due to heating will be readily understood. As the temperature rises, the

oscillatory motion of the ions increases, impeding the motion of electrons between them.

The presence of free electrons accounts also for the high thermal conductivity of metals. In continuous motion, the electrons keep constantly colliding with the ions and exchanging energy with them. Therefore, the more intense oscillation of the ions in any heated portion of the metal is immediately transmitted to the adjacent ions, from them to the next, and so on, rapidly equalizing the thermal state of the metal, until at length the entire mass of the metal acquires the same temperature.

The above conception of metals being built up of positive ions and free electrons agrees also with the types of crystal lattices found in

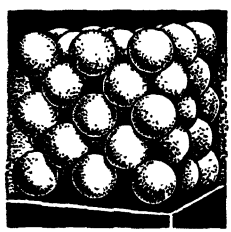


Fig. 125. Cube of densely packed spheres



Fig. 126. Prism of densely packed spheres

metals. Contrary to salts, where the points of the lattice are occupied alternately by anions and cations, the lattices of metals are made up of identical positive ions. Since the electrons, owing to their insignificant size, require very little space, the metal ions are usually arranged according to one of the types of densest packing of equal diameter spheres. There are only two such types. In one the spheres occupy the corners of cubes and the centres of their faces, as shown in Fig. 125. Such is the structure of the crystals of silver, gold, rhodium, platinum, nickel, aluminium, lead, and iron. The other type of densest sphere packing is shown in Fig. 126. Such is the arrangement of the ions in the crystals of beryllium, magnesium, zinc, cadmium, osmium, titanium and others.

The packing is of the same denseness in both cases, i. e., the same volume is taken up by a given number of spheres. Each sphere is surrounded by twelve others. Hence the coordination number of such lattices is 12.

The plasticity of metals is also directly related to their internal structure, which permits ready slippage of the ion layers with respect to one another under the influence of external forces. Some alloys which, like metals, have face-centred cubic lattices, are also highly

plastic (brass, bronze). However, when addition of the alloying metal disturbs the structural homogeneity of the principal metal, the resulting alloy is hard and brittle.

Repeated displacement of the ionic layers of a metal due to mechanical treatment disturbs the arrangement of its ions; the metal becomes amorphous, as it were; its plasticity decreases and its hardness increases. However, plasticity can be restored to a mechanically treated metal (for instance, a drawn iron wire) by "annealing," i. e., heating to a temperature at which it regains its crystalline structure.

Metals are conventionally divided according to specific gravity into two large groups: **light metals**, the specific gravity of which does not exceed 5, and **heavy metals**—all the rest. The specific gravities and melting points of some of the metals are given in Table 26. The data in this table show that all the metals, except mercury, are solids at ordinary temperatures. The light metals are generally the more fusible. Among the heavy metals, on the contrary, there are many very refractory ones. The lowest melting point after mercury is that of caesium (28° C) and the highest is that of tungsten (3,380° C).

The boiling points of metals are very high in the majority of cases. For instance, copper boils at 2,595° C, iron at 2,740° C, platinum at about 4,400° C.

The vapours of metals are monatomic.

197. Chemical Properties of Metals. The chief chemical property of metals is the ability of their atoms to part readily with their valency electrons and form positively charged ions. Typical metals never gain electrons; their ions are charged only positively. That is why metals are referred to as "electropositive" elements in contradistinction to non-metals, which are termed "electronegative" and are characterized rather by their capacity for gaining electrons.

Typical metals part readily with their valency electrons in chemical reactions and *are thus powerful reducing agents.*

The capacity for yielding electrons is by no means equal in different metals. The more easily a metal yields electrons, the more active it is and the more vigorously it will react with other substances.

Various reactions can serve for a comparative study of the activity of metals. Especially convenient for this purpose is the displacement of metals from their salts by other metals. For instance, drop a piece of zinc into a solution of some lead salt. The zinc will begin to dissolve, while lead will deposit from the solution. The reaction may be expressed by the equation

$$Zn + Pb(NO_3)_2 = Pb + Zn(NO_3)_2$$

the ionic equivalent of which is

$$Zn + Pb^{\cdot\cdot} = Pb + Zn^{\cdot\cdot}$$

It can be seen from the equation that this reaction is a typical oxidation-reduction reaction. It consists, essentially, in the zinc atoms yielding their valency electrons to Pb^{++} ions, themselves becoming Zn^{++} ions, while Pb^{++} ions are discharged and deposit as metallic lead. If the reverse is tried, i. e., a piece of lead is dropped

Table 26

Specific Gravities and Melting Points of Some Metals

Name	Atomic weight	Specific gravity	Melting point, degrees C
Light metals			
Lithium	6.940	0 53	186
Potassium	39.100	0.86	63
Sodium	22.991	0.97	97.7
Calcium	40.08	1.54	851
Magnesium	24.32	1.74	651
Caesium	132.91	1.9	28
Aluminium	26.98	2.70	660.1
Barium	137.36	3.5	704
Heavy metals			
Chromium	52.01	7.14	1,800
Zinc	65 38	7.14	419 5
Tin	118.70	7.30	231 9
Manganese	54.94	7.4	1,250
Iron	55.85	7.87	1,539
Cadmium	112.41	8.65	320.9
Nickel	58.69	8.9	1,453
Copper	63.54	8.9	1,083.2
Bismuth	209.00	9.8	271.3
Silver	107.880	10.49	960.8
Lead	207.21	11.34	327.4
Mercury	200.61	13.55	—38.87
Tungsten	183.92	19.3	3,380
Gold	197.0	19.3	1,063
Platinum	195.23	21.45	1,769
Osmium	190.2	22.6	2,700

into a solution of a zinc salt, no reaction will occur. This shows that zinc is more active than lead, that its atoms yield electrons more readily and its ions gain them less readily than the atoms and ions of lead.

By comparing the activities of lead and copper in a similar manner, it can easily be found that lead is more active than copper, as it displaces the latter from its salts, while copper cannot displace lead:

$$Pb + Cu^{\cdot\cdot} = Cu + Pb^{\cdot\cdot}$$

Therefore, of the three metals compared above, namely, zinc, lead and copper, the most active, the one that parts most readily with its electrons, is zinc; lead is less active and copper still less active.

The displacement of metals by one another from their compounds was studied in detail by N. Beketov (1865) who arranged the metals in order of decreasing chemical activity in the so-called "displacement series." At present Beketov's displacement series is known as the **electromotive force series**, as the position of each metal in this series can be determined exactly by the magnitude of the electromotive force or difference of potentials which arises if the metal is dipped into a solution of its salt. Methods of measuring these values and their importance will be dealt with a little later.

The electromotive force series for the most important metals, given once already in § 69, is as follows:

Decreasing chemical activity of neutral atoms

$$\xrightarrow{\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad}$$

K, Na, Ca, Mg, Al, Mn, Zn, Fe, Ni, Sn, Pb, H_2, Cu, Hg, Ag, Au

$$\xleftarrow{\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad}$$

Decreasing capacity of ions for gaining electrons

This series includes hydrogen, as it is also capable of displacing some of the metals from solutions of their salts and is, in its turn, displaced by many metals from acid solutions.

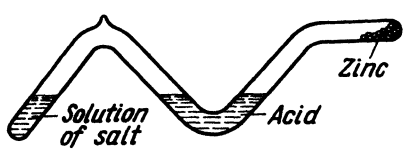


Fig. 127. Tube for experiments in displacing metals by hydrogen under pressure

To determine the position of hydrogen in the "displacement series," Beketov carried out the following experiments.

A solution of a metal salt, an acid and some zinc were placed separately in the arms of a bent glass tube (Fig. 127). The tube was then sealed and inclined so that the zinc fell into the acid and the hydrogen thus liberated acted under pressure on the salt solution.

By observing the arm with the salt solution, Beketov could judge whether the metal was displaced by the hydrogen or not. On the basis of these experiments he came to the conclusion that hydrogen should follow lead in the "displacement series" and that it is capable of displacing (reducing) the metals below it, namely: copper, mercury, silver and gold, from solutions of their salts.

Beketov was certain that the displacement of hydrogen by metals was a reversible reaction and that there must exist a pressure for each metal at which the reaction would reverse its direction, i. e., where the hydrogen would begin to displace the metal from a solution of its salt.

Beketov's views were fully confirmed at a later date.

Consider, for instance, the displacement of hydrogen by zinc:

$$Zn + 2H^{\cdot} \rightleftarrows Zn^{\cdot\cdot} + H_2$$

The equilibrium constant of this reaction is:

$$K = \frac{[Zn^{\cdot\cdot}] \cdot P_{H_2}}{[H^{\cdot}]^2}$$

where the concentration of hydrogen may be substituted by its pressure P_{H_2} in atmospheres. Calculation shows that at ordinary temperatures $K = 36 \times 10^{24}$. Hence, the pressure of hydrogen required to make the reverse reaction, i. e., the displacement of zinc by hydrogen, perceptible, is not attainable at the present level of technique. At ordinary pressures the equilibrium of the reaction is practically displaced completely to the right.

However, in the case of the reaction

$$Sn + 2H^{\cdot} \rightleftarrows Sn^{\cdot\cdot} + H_2$$

the equilibrium constant

$$K = \frac{[Sn^{\cdot\cdot}]\, P_{H_2}}{[H^{\cdot}]^2} = 4 \times 10^4$$

Therefore equilibrium could be attained, say, with the concentrations: $[Sn^{\cdot\cdot}] = 1$ gram-ion/l., $[H^{\cdot}] = 0.01$ gram-ion/l. and with a pressure of hydrogen $P_{H_2} = 4$ atm. Hence, hydrogen is capable of displacing tin from solutions of its salts at a comparatively low pressure.

The electromotive force (e.m.f.) series provides many general hints as to the chemical behaviour of the individual metals during reactions taking place in solution:

1. Each metal of the series, as well as hydrogen under pressure, will displace (reduce) all the metals after (below) it, from solutions of their salts. In its turn it will be displaced (reduced) itself by any of the metals before (above) it.

2. Only the metals before (above) hydrogen in the e.m.f. series can displace it from dilute acids ("hydrogen salts"). Metals to the right of (below) hydrogen are incapable of displacing hydrogen from acids.

3. The farther to the left (the higher up) a metal is in the e.m.f. series, the more active it is, the greater its reducing capacity with respect to ions of other metals, the easier it turns into ions itself and the more difficult its ions are to reduce.

198. Galvanic Cells. The displacement of metals by one another from solutions of their salts is the underlying principle of most galvanic cells, i.e., devices for changing chemical energy into electrical. Apart from their importance as sources of electric current, these devices are of interest to us at this juncture inasmuch as by measuring the electromotive force of each metal we can characterize its activity quantitatively and thus establish its relative position in the e.m.f. series. In order to understand this question better we must first become acquainted with the structure and operation of galvanic cells.

If a metal is submerged in a solution of a salt of another metal, say, a zinc plate in a solution of $Pb(NO_3)_2$, electrons will begin to pass from the zinc atoms to the lead ions owing to the direct contact between the two. The chemical energy liberated during the reaction is in this case transformed into thermal energy. However, the interaction can be accomplished between the zinc and the lead salt out of contact with one another, the only necessary condition for this being the possibility of electrons passing from the zinc to the lead ions.

Pour some $Zn(NO_3)_2$ solution into one beaker and some $Pb(NO_3)_2$ solution into another. Dip a zinc plate into the first and a lead plate into the second (the latter only plays the part of a conductor, and may therefore be replaced by a graphite rod). The solutions in the beakers are connected by means of an inverted U-tube, filled with a solution of some electrolyte, say KNO_3 (Fig. 128). Now, if the plates are connected with a metal wire an electric current will immediately arise, its direction indicating that the electrons are moving from the zinc to the lead salt solution. At the same time, the zinc begins to dissolve, while lead is deposited on the lead plate.

The purpose of the U-tube is to provide a free passage-way for the salt ions from solution to solution; otherwise the zinc salt solution would become positively charged as a result of the $Zn^{\cdot\cdot}$ ions passing into it from the plate, while the lead salt solution, from which $Pb^{\cdot\cdot}$ ions are being removed, would acquire a negative charge. These charges would impede the movement of electrons from the zinc to the lead salt, and the reaction would cease. Obviously, as the reaction proceeds, the negative ions move towards the zinc and the

positive towards the lead, maintaining electrical equilibrium in the solutions.

Thus, under the conditions set up in the above experiment, the reaction caused earlier by simply dipping a piece of zinc into a solution of a lead salt, now occurs remotely. The only difference is that in the first case the electrons could pass from the zinc atoms to the $Pb^{\cdot\cdot}$ ions when the latter collided with the zinc surface, so that the motion of the electrons was of an unorderly nature and the energy released during the reaction changed into thermal energy. In the

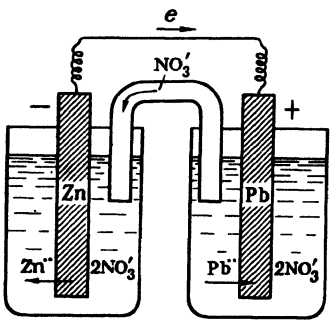


Fig. 128. Apparatus for remote reaction between zinc and lead salt

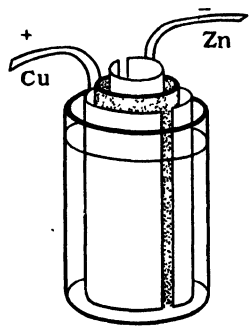


Fig. 129. Copper-zinc cell

latter case, however, by eliminating direct contact between the zinc and the lead salt solution the electrons were forced to travel some distance through a wire to reach the lead ions, so that the unorderly movement of the electrons was replaced by a more or less intense flow of electrons, known as electric current.

The apparatus just described is a galvanic cell, in which the chemical energy of an oxidation-reduction reaction is transformed into electrical energy. Its negative pole is the zinc and its positive, the lead electrode. At the negative electrode zinc is oxidized:

$$Zn - 2e^- = Zn^{\cdot\cdot}$$

at the positive, lead ions are reduced:

$$Pb^{\cdot\cdot} + 2e^- = Pb$$

Adding up these two equations we get the total equation of the reaction taking place in the cell:

$$Zn + Pb^{\cdot\cdot} = Pb + Zn^{\cdot\cdot}$$

or, in the molecular form,

$$Zn + Pb(NO_3)_2 = Zn(NO_3)_2 + Pb$$

Other galvanic cells are of a design similar to that described. Their negative electrode is always the more active metal, which yields its electrons to ions of the less active metal, transforming them into neutral atoms. In the course of operation of the cell the negative electrode gradually disappears, its substance passing into solution as ions.

Fig. 129 shows the copper-zinc cell familiar to most readers from the course of physics. This cell consists of a copper and a zinc plate immersed in solutions of the corresponding sulphates. The zinc sulphate solution is contained in a porous clay cylinder inserted in a glass jar holding the copper sulphate solution. The porous partition keeps the solutions from mixing, but at the same time allows the ions to pass freely from solution to solution when current is tapped from the cell. When the cell is working the following reaction takes place:

$$Zn + Cu^{\cdot\cdot} = Cu + Zn^{\cdot\cdot}$$

Sometimes the displacement of hydrogen from an acid by zinc is utilized in galvanic cells: $Zn+2H^{\cdot}=Zn^{\cdot\cdot}+H_2$.

The first galvanic element, invented by the Italian physicist Volta, consisted of a zinc and a copper plate dipped into a solution of sulphuric acid. If the plates of such an element are connected by means of a conductor, the electrons travel through it from the zinc to the copper, and from the latter are transferred to the hydrogen ions in solution, which are thus discharged. That is why hydrogen is liberated at the copper plate and not at the zinc.

199. Mechanism of Current Induction in Galvanic Cells. Electrode Potentials of Metals. Several theories have been suggested to explain the induction of current in galvanic cells. The simplest was suggested by the German physicist Nernst (1888) and later elaborated by the Russian Academician L. Pisarzhevsky on the basis of the conceptions according to which metals are built up of positively charged ions and free electrons.

Lev Vladimirovich Pisarzhevsky was born in 1874 in the town of Kishinev. After graduating the Natural Science Department of the Novorossiisk University (in Odessa) L. Pisarzhevsky was asked to stay on at the University and later accept professorship. In 1902 he got his Master's Degree and in 1913 was appointed Professor of the Yekaterinoslav Mining Institute (in Dnepropetrovsk). In 1930 Pisarzhevsky was elected Member of the Academy of Sciences of the U.S.S.R.

A great scientist and brilliant teacher, Pisarzhevsky made bold use of the achievements of physics for the study and explanation of chemical processes. His most important works were devoted to investigations of peroxides and peracids, to the development of the theory of solutions, to the application of the electron theory to chemistry and the development of the theory of current induction in galvanic cells.



Lev Vladimirovich Pisarzhevsky
(1874-1938)

The theory of current induction is essentially as follows. If any metal is dipped into water, its ions begin to pass into solution, being attracted by the polar water molecules. This leaves an excess of electrons in the metal, which thus becomes negatively charged, while the solution becomes positively charged. However, the number of ions passing into solution from the metal, as experiment shows, is very small. The negative charge arising on the metal as the ions leave it, attracts those ions back again, so that very soon a state of equilibrium is set up, where the number of ions leaving the metal per unit time equals the number of ions returning to it:

$$\text{metal} \rightleftarrows \underset{\text{(in solution)}}{\text{metal ions}}$$

The ions which have passed into solution are not distributed evenly through the bulk of the solution, but remain near the surface of the negatively charged metal, attracted by the latter and forming a *double electric layer* (Fig. 130). As a result, a difference of potentials arises between the metal and the solution.

Now, suppose some salt of the metal submerged is added to the water. The increase in concentration of metal ions in the solution will disturb the equilibrium between them and the metal, and part of the ions will pass back into the metal. Therefore, the metal should send less ions into a solution of its salt than it does into pure water; moreover, the higher the concentration of the ions in solution, the less of them the metal will emit. If the concentration of the salt is

high enough, ions may not pass at all from the metal into the solution, so that neither the metal, nor the solution will be charged.

Finally, if the concentration of the metal ions in solution is high enough and the activity of the metal is comparatively low, the metal will not only fail to send ions into the solution but, on the contrary, some of the ions will pass from the solution into the metal. This will also result in a difference of potentials being established between the metal and the solution, but now the solution will be charged negatively due to the excess of negative ions from the salt, while the metal will be charged positively. In practice, some metals (the more active) are always charged negatively in solutions of their salts, while others (the less active) are charged positively.

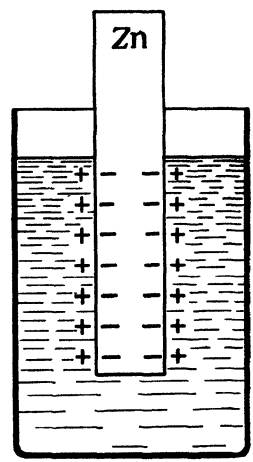


Fig. 130. Double electric layer

It should be noted that when a metal is dipped into a solution of its salt, the quantity of ions passing into solution or deposited from solution is often so small that they cannot be detected by chemical means. However, the charge is large enough to create a measurable difference of potentials.

The theory described above gives a very simple explanation of the mechanism of action of galvanic cells. Consider, for instance, a copper-zinc cell (Fig. 129 on p. 512). In this cell a negative charge arises on the zinc plate submerged in the $ZnSO_4$ solution and a positive charge on the copper submerged in the $CuSO_4$ solution. If the metals are not connected to one another by a conductor, the appearance of these charges, as we have seen above, should immediately check any further passage of zinc ions into solution and deposition of copper ions from solution. But if the plates are connected with a wire, the electrons accumulating on the zinc will flow continuously towards the copper plate where there is a shortage of them. Thus, the zinc is able to send more and more $Zn^{\cdot\cdot}$ ions into the solution, while $Cu^{\cdot\cdot}$ ions continue to be discharged at the copper plate and to deposit as metallic copper. This process continues until all the zinc is dissolved or the copper salt is used up completely.

In galvanic cells, the electrode which is used up during the operation of the cell by emitting ions into the solution is called the anode, and the electrode at which the positive ions are discharged is called the cathode.

A galvanic cell can be made of any two metals dipped into solutions of their salts. There is no necessity at all for one of the metals to

become negatively charged and the other positively. The only condition for the passage of electrons from one charged body to another is the existence of difference of potentials between them. But the latter should arise, no matter which metals we take, as the capacity for splitting off electrons and passing into ions is different in all metals. If, for instance, the galvanic cell is made of zinc and iron dipped in normal solutions of their salts, both metals will be negatively charged in their solutions, but nevertheless, a definite difference of potentials will arise between them. If the metals are connected with a conductor, the electrons will pass from the zinc, the more active metal, to the iron. The zinc will dissolve and the iron will deposit from solution. The reaction taking place in the cell can be represented by the equation

$$Zn + Fe^{\cdot\cdot} = Fe + Zn^{\cdot\cdot}$$

The difference of potentials arising between a metal and the solution of its salt is called the **electrode potential** of the metal and can serve as a measure of its capacity for yielding electrons or, which is the same, a measure of its chemical activity during reactions taking place in solution. Therefore, if the potentials of all the metals with equal concentrations of their ions were measured, the activities of all the metals could be characterized quantitatively.

Unfortunately, direct measurement of these values is very difficult and does not give exact results. This will be clear if it is remembered that a voltmeter, for instance, cannot be connected to the solution without dipping a metallic conductor into it. But this gives rise to a difference of potentials between the conductor and the solution, so that the e.m.f. shown by the voltmeter will depend on two differences of potentials, namely, on the difference of potentials between the metal in question and the solution of its salt and that between the metallic conductor and the solution.

It is much easier to measure the difference of potentials (difference of electron pressures) between two different metallic electrodes dipped into solutions of their corresponding salts, i.e., to find out how much the potential of one of the metals is greater or smaller than that of the other. If the relative potentials of all the metals are thus measured by comparing their potentials with that of one of them, used as a standard, the resulting values can characterize the activity of the metals just as well as the absolute values of their potentials.

The accepted standard electrode with which the potentials of all the other metals are compared, is known as the **normal hydrogen electrode.** The latter consists of a platinum plate coated with a thin layer of finely divided spongy platinum and submerged in a binormal solution of sulphuric acid. A current of pure hydrogen is passed continuously through the solution under a pressure of 1 atm. Coming into

contact with the platinum, the hydrogen is absorbed by it to a considerable degree. A platinum plate saturated with hydrogen behaves as if it were made entirely of hydrogen. When it is in contact with the sulphuric acid solution, a definite difference of potentials (the potential of the hydrogen electrode) arises, this value being accepted as the zero point when measuring relative potentials.

The difference of potentials between a metal in a solution of its salt, containing 1 gram-ion of the metal per litre, and a normal hydrogen electrode, is called the **normal potential of the metal**.

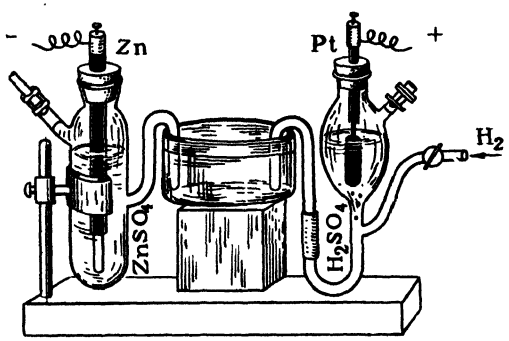


Fig. 131. Apparatus for measuring normal potential of a metal

Normal potentials are usually measured with the aid of arrangements similar to that shown in Fig. 131. This arrangement is essentially a galvanic cell, in which one of the electrodes is the metal under test, and the other, a hydrogen electrode. As the potential of the hydrogen electrode is assumed to be zero, the electromotive force measured between the poles of such a cell is the normal potential of the metal.

Table 27 shows the normal potentials of the most important metals.* They are written with a minus sign when the potential of the metal is smaller, and with a plus sign if it is higher than that of the hydrogen.

If the metals, including hydrogen, are written out in order of decreasing electronic pressures, i.e., decreasing negative (and increasing positive) normal potentials, we get the same e.m.f. series as that shown on p. 509.

Knowing the normal potential of the metals, we can easily determine the electromotive force of any cell consisting of two metals dipped

* Some of them, such as the normal potentials of K, Na, Ca, cannot be measured directly, but are calculated by indirect methods.

Table 27

Normal Potentials of Metals

Metal	Ion	Potential, volts	Metal	Ion	Potential, volts
K	$K^{\cdot}$	−2.92	Ni	$Ni^{\cdot\cdot}$	−0.23
Ca	$Ca^{\cdot\cdot}$	−2.84	Sn	$Sn^{\cdot\cdot}$	−0.14
Na	$Na^{\cdot}$	−2.713	Pb	$Pb^{\cdot\cdot}$	−0.126
Mg	$Mg^{\cdot\cdot}$	−2.38	H_2	$H^{\cdot}$	∓0.000
Al	$Al^{\cdot\cdot\cdot}$	−1.66	Cu	$Cu^{\cdot\cdot}$	+0.34
Mn	$Mn^{\cdot\cdot}$	−1.05	Hg	$Hg_2^{\cdot\cdot}$	+0.798
Zn	$Zn^{\cdot\cdot}$	−0.763	Ag	$Ag^{\cdot}$	+0.799
Fe	$Fe^{\cdot\cdot}$	−0.44	Au	$Au^{\cdot\cdot\cdot}$	+1.42

in solutions of their salts. For this it is necessary only to find the difference of the normal potentials of the metals in question.

For the electromotive force to have a positive value, the smaller potential is always subtracted from the larger. For instance, the electromotive force of a copper-zinc cell is:

$$\text{e.m.f.} = 0.34 - (-0.763) = 1.103 \text{ volts}$$

Of course, this will be the correct value if the concentrations of $Zn^{\cdot\cdot}$-ion and $Cu^{\cdot\cdot}$-ion in the corresponding solutions equal 1 gram-ion per litre. For other concentrations the potentials of the metals, and therefore the electromotive force values, can be determined by the following formula derived by Nernst:

$$E = E_0 + \frac{0.058}{n} \log c$$

where E is the potential of the metal with the actual concentration of its ions; E_0, its normal potential; n, the valency of the metal ions; c, the concentration of these ions in the solution, in gram-ions per litre.

For instance, the potential of zinc in a 0.001 M solution of its salt equals:

$$E = -0.763 + \frac{0.058}{2} \log 10^{-3} = -0.85 \text{ volt}$$

the potential of a hydrogen electrode in a neutral solution, where $(H^{\cdot}) = 10^{-7}$, will be −0.41 volt, etc.

In constructing galvanic cells, oxidation-reduction reactions other than the displacement of metals by metals are often used, sometimes with the participation of non-metals. The normal potentials of some

of the non-metals have also been determined. But the e.m.f. series of non-metals has been established far less completely than that of metals. By way of illustration, the normal potentials of the halogens are given below:

F/F′	Cl/Cl′	Br/Br′	I/I′
+ 2.85	+1.36	+1.037	+0.54

200. Corrosion of Metals. The surface of almost any metal begins to decay more or less rapidly when it comes into contact with the gaseous or liquid medium surrounding it. This is due to chemical interaction between the metal and the gases contained in the air, or the water and the substances dissolved in it.

Any process of chemical decay of metals due to the action of the surrounding medium is called corrosion.

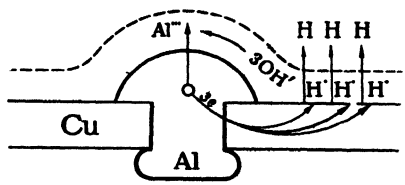


Fig. 132. Diagram of corrosion of aluminium in contact with copper

The simplest case of corrosion is that which occurs when metals come into contact with gases. The surface of the metal becomes coated with the corresponding compounds, namely, oxides, sulphides, basic carbonates, which often form a compact layer protecting the metal from further attack by the gases.

It is different when the metal is in contact with a liquid medium, say water, and the substances dissolved in it. The compounds formed in this case may dissolve, allowing corrosion to penetrate farther into the metal. Besides, water containing dissolved salts is a conductor of electric current; this promotes electrochemical processes which are one of the main causes of rapid corrosion.

In most cases pure metals are hardly attacked by corrosion. Even such a metal as iron hardly rusts at all if absolutely pure. But ordinary technical metals always contain various impurities, this promoting corrosion.

To comprehend why impurities influence the corrosion of metals, consider what happens when two different metals come into contact with one another in moist air.

Suppose, for instance, we have an aluminium rivet in a sheet of copper (Fig. 132). As all solids adsorb moisture from the air on their surfaces, the surface of the metals in question will also be coated

with a very thin film of water. But water, as we know, ionizes, albeit insignificantly, into $H^{\cdot}$ and OH'; besides, the carbon dioxide dissolved in the water forms carbonic acid, which ionizes according to the equation:

$$H_2CO_3 \rightleftarrows H^{\cdot} + HCO_3'$$

Therefore the copper and the aluminium are, in a sense, immersed in a solution containing the ions $H^{\cdot}$, OH' and HCO_3'. This is a galvanic cell, in which aluminium acts as the negative electrode and copper as the positive. Owing to the close contact between the metals, the cell is short-circuited and is thus in continuous operation: the aluminium keeps emitting ions into the solution, the excess electrons passing over to the copper on the surface of which they discharge hydrogen ions. In the solution the $Al^{\cdots}$ ions combine with the OH' ions forming $Al(OH)_3$, which separates out at the surface of the aluminium:

$$2Al - 6e^- = 2Al^{\cdots}$$
$$6H^{\cdot} + 6e^- = 3H_2$$
$$2Al^{\cdots} + 6OH' = 2Al(OH)_3$$

Thus, the aluminium corrodes quite rapidly.

The corrosion of iron in contact with some less active metal, say, also with copper, is somewhat more complicated. The iron emits bivalent $Fe^{\cdot\cdot}$ ions into solution, and these ions, combining with hydroxyl ions, turn into $Fe(OH)_2$. At the same time the electrons pass from the iron to the copper, discharging hydrogen ions at its surface.

In the presence of atmospheric oxygen and water $Fe(OH)_2$ is oxidized into ferric hydroxide $Fe(OH)_3$, forming rust:

$$4Fe(OH)_2 + 2H_2O + O_2 = 4Fe(OH)_3$$

In the above cases the aluminium and the iron corroded owing to contact with a less active metal, namely, copper. The various impurities always present in technical metals act like the copper above and promote corrosion. For instance, if ordinary steel is investigated under the microscope, it is found to consist of tiny grains of pure iron intimately intermixed with grains of iron carbide, or cementite, Fe_3C, and other impurities. Thus, an infinite number of galvanic couples are set up, the cementite grains acting as positive and the iron grains as negative electrodes. When the steel comes into contact with moist air, galvanic currents arise, causing corrosion. Impurities promote the corrosion of other metals in a similar way.

The corrosion of aluminium, zinc, iron, and, in general, metals situated above hydrogen in the e.m.f. series, reduces essentially to the displacement of hydrogen ions from solution and the passage of the

metal itself into solution as ions. The accelerating influence of contact with a less active metal in such processes can be illustrated graphically by the following experiment.

Throw a piece of chemically pure zinc into a test tube containing a dilute acid solution. Almost no hydrogen will be observed to form. The absence of any reaction is due to the fact that as the $Zn^{\cdot\cdot}$ ions begin to pass into solution, they become hydrated and form a film



Fig. 133. Dissolving of chemically pure zinc in acids in contact with copper or platinum wire

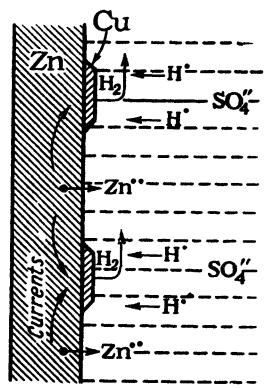


Fig. 134. Diagram of copper-plated zinc dissolving in sulphuric acid

of positively charged ions around the zinc. This film prevents the hydrogen ions from coming into contact with the zinc surface and receiving electrons from it, as a result of which the zinc stops dissolving. But if the surface of the zinc is just touched with a platinum or copper wire, a galvanic couple arises, and hydrogen immediately begins to come away vigorously from the *surface of the wire*. The electrons pass from the zinc to the platinum (or the copper) and from it to the hydrogen ions, while the zinc gradually dissolves, emitting more and more ions into the solution (Fig. 133).

The same effect is observed if a few drops of copper sulphate solution are added to the acid. The zinc displaces the copper and its surface becomes coated with a loose layer of metallic copper. The result is a galvanic zinc-copper couple which acts as in a voltaic cell. For this reason, "copper-plated" zinc displaces hydrogen vigorously from the acid, but the hydrogen is liberated at the surface of the copper, not of the zinc (Fig. 134).

Ordinary commercial zinc, containing impurities, behaves in a similar way.

Other factors besides impurities influence the rate of solution of a metal in an acid. These are the structure of the metal, its mode of treatment, the properties of the acid, etc. But in all cases the rate of dissolving can be slowed down by adding certain substances to the acid; these substances are mainly organic and are known as **inhibitors** (corrosion decelerators).

The action of inhibitors is sometimes so effective that some metals and alloys become practically insoluble in acids to which the corresponding inhibitor has been added.

While slowing down the dissolving of the metal, inhibitors do not at all influence the rate of dissolving of metal oxides, hydroxides and other substances. Therefore the addition of inhibitors makes it possible to use acids for cleaning the surface of a metal from the compounds coating it (for instance for removing rust from iron, or scale from boiler walls) without hardly affecting the metal itself.

As the elements are arranged in the e.m.f. series in order of decreasing activity, it might be expected that the higher up an element is situated in this series, the more easily it will corrode. Actually this is not always the case. For instance, aluminium, which is near the top of the series, resists atmospheric corrosion quite effectively. This stability is due to the formation on the surface of the aluminium of a thin but very dense and elastic film of aluminium oxide which severs the contact between the aluminium and the surroundings. Indeed, if this film is destroyed in any way, very rapid corrosion sets in.

Clean an aluminium plate thoroughly with emery-paper and moisten it with a solution of corrosive sublimate $HgCl_2$. The aluminium displaces the mercury and forms an alloy with it, a mercury amalgam, which prevents the formation of the protective film. Therefore, if such a plate is left in the air, it rapidly becomes coated with loose flakes of aluminium hydroxide, the corrosion product of aluminium.

In this case the contact between the aluminium and the mercury, a metal of low activity, also accelerates corrosion.

Of course, the layer of oxide or any other compound coating the surface of the metal can serve as a protective film only if it is dense and strong enough and insoluble in water. Otherwise it will not prevent corrosion. For instance, rust appearing on iron does not by any means protect it from further corrosion, because the rust layer is very loose and brittle, and adheres weakly to the surface of the metal.

Substances promoting the formation of a protective film on a metal are known as *passivizing agents*. Strong oxidants can serve as passivizing agents for most metals. A good passivizing agent for iron is also OH'-ion.

As was stated above (see p. 388), many quite active metals become passive after being treated with concentrated nitric acid, due to the formation of a very thin invisible film of oxide on the surface of the metal, preventing further oxidation. The existence of such oxide films has been proved by various methods, namely, polarization of reflected light, X-ray methods, etc.

The oxide film theory was developed in detail at the beginning of the present century by V. Kistyakovsky (1865-1952) whose works were of great importance for corrosion prevention.

Certain substances destroy or weaken the protective film of a metal and thus promote corrosion. Such substances are called *activizing agents* or *activizers*.

The most powerful activizer for most metals is Cl'-ion. The rapid destruction of the underwater metallic parts of sea vessels is due mainly to the presence of Cl'-ion in sea water. A very powerful activizer for most metals is hydrogen-ion. Oxygen dissolved in water also greatly accelerates corrosion by binding the primary reaction products (e. g., by oxidizing $Fe(OH)_2$ into $Fe(OH)_3$ in the case of the corrosion of iron) and thus eliminates the possibility of the reverse reaction.

The losses due to the corrosion of metals are tremendous. It has been calculated, for instance, that the amount of iron destroyed each year by corrosion equals about one quarter of its annual world production. That is why the study of corrosion processes and the search for the best means of its prevention attract so much attention.

Very diverse methods are used to combat corrosion. The simplest of them consists in protecting the surface of the metal from direct contact with the surroundings by coating it with oil paint, varnish, enamel or a thin layer of another metal. Of especial interest from a theoretical standpoint is the coating of one metal with another. Let us see the result it leads to.

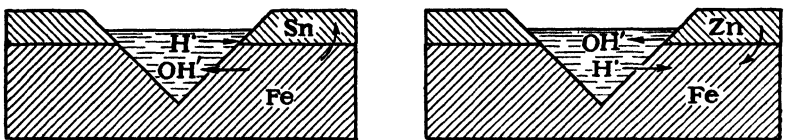
Since corrosion always begins at the surface of the metal, the object will behave as if it consisted entirely of the protecting metal as long as the protective layer on the metal is intact. But if scratches, cracks, etc., appear in the protective layer, baring the surface of the metal protected, conditions favouring corrosion arise immediately at these points. However, the course of the corrosion may vary, depending on the relative positions of the metals in question in the electrochemical series.

Let us first consider the case of what is known as a **cathode coating**, when the protecting metal is situated below that protected in the e.m.f. series. A typical example is the corrosion of *tin-plated* iron (white tin). Tin itself is very stable and protects the metal effectively as long as its coating on the iron is intact. If the protective coating, however, loses its integrity and the bared spot comes into contact with moisture, a galvanic couple arises, in which the tin serves as the positive electrode (the cathode),* and the iron as the negative

* We remind the reader that the electrode *from* which positively charged ions come away during the operation of the galvanic cell, is called the *anode*,

electrode (the anode). The electrons flow from the bared surface of the iron to the tin, where they discharge hydrogen ions, while the iron decays, sending more and more ions into solution (Fig. 135*a*). Thus tin-plated iron rusts much more rapidly where the protective coating is injured, than unplated iron.

Corrosion takes an entirely different course if the protecting metal stands higher in the e.m.f. series than the metal protected, e.g., zinc-plated iron **(anode coating)**. In this case, if the protective layer is injured, a galvanic couple also arises, but here the iron serves as the



a *b*

Fig. 135. Diagram of corrosion:
a—tin-plated iron; *b*—galvanized iron

cathode and zinc as the anode, so that electrons pass from the zinc to the iron; as a result, the zinc decays while the iron remains intact (Fig. 135b) until the entire layer of zinc has decayed, which requires quite a length of time.

It is clear from the above that to protect a metal from corrosion it is better to coat it with a more active metal than with a less active. However, other considerations often make it necessary to use coatings of less active metals as well.

In practice it is mostly necessary to take measures for the protection of iron, as a metal especially subject to corrosion. Besides zinc, one of the more active metals used sometimes for this purpose is cadmium, the action of which is similar to that of zinc. Of the less active metals, those used most frequently for coating iron are tin, copper and nickel.

Iron objects plated with nickel have a beautiful finish, which accounts for the wide use of nickel plating.

If the nickel film is injured, corrosion takes place less intensively than in the case of copper (or tin) plating, as the difference of potentials for the couple nickel-iron is much lower than for copper-iron.

Another noteworthy method of corrosion prevention is the **protactor method**, which consists in bringing the metal object to be protected

while that *towards* which positively charged ions move and where they are discharged, is called the *cathode*.

It should be noted that these names of the electrodes are in no connection with their signs; in the case of galvanic cells the anode is a negative electrode and the cathode a positive, while in electrolysis, on the contrary, the cathode is the negative electrode (as it is connected to the negative pole of the current source) and the anode is the positive electrode.

into contact with a large surface of a more active metal. For instance, zinc sheets are placed in steam boilers in contact with their walls to form galvanic cells for this purpose.

201. Extraction of Metals from Their Ores. The great majority of metals occur in nature as compounds with other elements.

Only a few metals are found in the free state, in which case they are called **native metals.** Gold and platinum are found almost exclusively, and silver and copper partly, in the native state; sometimes mercury, tin and other metals are also found native.

Gold and platinum are extracted by mechanical separation from the gangue in which they are embedded, for instance, by washing with water or by dissolving with various solvents, followed by precipitation from the solution. All other metals are extracted by chemical treatment of their natural compounds.

Minerals and rocks containing compounds of metals and suitable for the commercial extraction of those metals, are called ores. The most important ores are the oxides, sulphides and carbonates of metals.

The extraction of metals from their ores is the task of *metallurgy*, one of the most ancient branches of the chemical industry.

Reduction of Metals from Their Ores with Carbon. The most important method of extracting metals from their ores is based on the reduction of their oxides with coal or coke.

If, for instance, red copper ore Cu_2O is mixed with coke and heated strongly, the coke will reduce the copper, itself being converted to carbon dioxide, while the copper is evolved in the molten state:

$$Cu_2O + C = 2Cu + CO$$

A similar method is used to smelt pig iron from iron ores, to produce tin from tinstone, SnO_2, and to reduce other metals from their oxides.

In treating sulphide ores, the sulphides are first converted into oxides by roasting in special furnaces, after which the resulting oxides are reduced with coal. For example:

$$2ZnS + 3O_2 = 2ZnO + 2SO_2$$
$$ZnO + C = Zn + CO$$

When the ore is a carbonate it can be reduced directly with coal just as oxides are, because carbonates, when heated, decompose into the metal oxide and carbon dioxide. For example:

$$ZnCO_3 = ZnO + CO_2$$

Usually, besides the chemical compound of the metal in question, ores contain also many impurities in the form of sand, clay and limestone, which are very difficult to melt. To facilitate melting of the

metal various substances are added to the ore to form fusible compounds, known as **slags**, with the impurities. The substances added for this purpose are called **fluxes**. If the impurity consists of limestone, the flux is usually sand, which forms calcium silicate with the limestone. On the contrary, if the ore contains a large amount of sand, limestone is used as the flux.

In some ores the content of impurities (gangue) is so high that it is not economical to smelt the metals from them directly. These ores are preliminarily "concentrated," to remove part of the impurities. Especially widespread is the method of ore concentration known as **flotation**, which is based on the difference in the adsorptive properties of the pure ore and the pure gangue.

The technique of flotation is quite simple and consists essentially in the following. The ore, constituting, for instance, a metal sulphide and a silicate gangue, is finely ground and mixed with water in large tanks. A certain slightly polar organic substance, such as pine oil, is added to the water, to promote the formation of a stable froth. The water is stirred, and a small quantity of a special reagent called "collector"* is added, the latter being adsorbed readily by the surface of the mineral to be floated and making it water-repellent. Then an intense stream of air is passed through the mixture from below, promoting agitation of the ore with the water and the reagents added to it. The particles of the mineral to be floated become coated with an adsorbed film of collector molecules, adhere to the air bubbles, rise together with them to the surface and remain there entrapped in the froth; the gangue particles, on the other hand, being water-avid, remain in the pulp. The froth is collected and dewatered, the resulting concentrate containing a much higher percentage of the metal than the ore.

Reduction of Metallic Oxides with Aluminium. Lately aluminium has found wide application for the reduction of certain metals from their oxides. Its application is based on the fact that much more heat is liberated during the combustion of aluminium than during the combustion of many other metals. For example, the formation of one gram-molecule of Al_2O_3 is accompanied by the release of 393 Cal.; the formation of one gram-molecule of Fe_2O_3—by only 195 Cal. But it was stated above that the decomposition of a compound requires the expenditure of the same amount of energy as was liberated during its formation. Therefore if a mixture of iron oxide and aluminium is ignited, the iron will not only be reduced, but a large excess of heat will remain as well, this excess equalling $393 - 195 = 198$ Cal. per gram-molecule of aluminium oxide formed.

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* Various substances may be used as collectors. Some good collectors are, for instance, higher fatty acids and their salts (soaps).

The reaction involved can be expressed by the equation

$$2Al + Fe_2O_3 = 2Fe + Al_2O_3 + 198 \text{ Cal.}$$

The reaction is usually carried out in a limited space and at a very fast rate, so that the temperature of the mixture reaches 3,500° C. At this temperature the iron melts, and the aluminium oxide floats as a slag on the surface of the molten iron.

This reaction, discovered by N. Beketov, is widely used for the production of many refractory metals, such as chromium, manganese, vanadium, etc.

The reduction of metal oxides with aluminium is known as **aluminothermy.**

A mixture of magnetic iron oxide Fe_3O_4 and aluminium, known as *thermite*, is used in practice for welding iron objects, for instance, tramway rails. For this purpose, the ends of the rails to be joined are enclosed in a housing of a refractory material having the shape of the rail, and the molten iron obtained from the thermite is poured into it. At the high temperature achieved the ends of the rails soften and are welded or soldered together by the liquid iron.

Another important method of producing metals, besides reduction with coal and aluminium, is electrolysis. Some of the more active metals can be obtained only by electrolysis, all other means not being potent enough to reduce their ions.

202. Electrolysis. Electrolysis is the chemical process which takes place when an electric current is passed through a solution of electrolyte or through the molten electrolyte. When an electric current passes *through an electrolyte solution*, the positive ions move towards the cathode, and the negative towards the anode, where they are discharged. The resulting neutral atoms and atomic groups either separate out of solution or react with each other, forming what is known as *secondary electrolysis products.*

In considering the mechanism of electrolysis it must not be forgotten that besides the ions of the electrolyte all aqueous solutions contain also $H^{\cdot}$ and OH' ions from the water. These ions migrate in an electric field just like the electrolyte ions, the hydrogen ions moving towards the cathode, and the hydroxyl, towards the anode. Thus, two kinds of ions can be discharged simultaneously at the cathode, namely, the positive electrolyte ion (usually the metal ion) and the hydrogen ion from the water. Which of them will actually be discharged depends, above all, on their relative position in the e.m.f. series, then on the concentrations of the ions, and, in some cases, on the material of the electrode at which they are discharged. Generally, the more easily a metal yields its electrons, the higher its negative potential (in absolute value), the less readily its ions are discharged. Hence it follows that, other conditions being equal,

gold ions and ions of other metals of low activity should be discharged the most readily, and the ions of metals at the top of the e.m.f. series, the least readily. As the ion of any metal below hydrogen is more easily discharged than the hydrogen ion, the electrolysis of salts of copper, mercury, etc., will lead to deposition of the corresponding metals on the cathode. Ions of metals above hydrogen in the e.m.f. series are discharged less readily than hydrogen ions, and the farther away they are from it, the more difficult they are to discharge. Therefore, when the salts of the more active metals, sodium, potassium and calcium, as well as magnesium and aluminium, whose electrode potentials differ greatly from that of hydrogen, are electrolyzed, almost exclusively hydrogen ions are discharged, and gaseous hydrogen is liberated at the cathode. As more and more hydrogen ions are discharged, larger and larger quantities of water molecules ionize, as a result of which hydroxyl ions accumulate at the cathode, and the solution becomes alkaline. A different thing happens when salts of the less active metals, situated above hydrogen, such as zinc, iron, nickel, etc., are electrolyzed. Although theoretically hydrogen ions here too should have been the first to be discharged, practically, the metals are deposited at the cathode. This apparent contradiction is due to the insignificant concentration of the hydrogen ions (in comparison with that of the metal ions) and the specific influence of the substance of the electrodes, which greatly impedes the discharge of hydrogen ions.*

Now let us see what happens at the anode. The negative ions of the electrolyte and the hydroxyl ions of water move towards it. If the negative ions do not contain oxygen, as for instance Cl', Br', S'' ions, these ions, and not the hydroxyl, are discharged, as the latter give up their charge with much greater difficulty, with the result that chlorine, bromine or sulphur are liberated at the anode. If, however, the negative ions contain oxygen (SO_4'', NO_3', etc.), gaseous oxygen is liberated at the anode. In these cases the hydroxyl ions of water are evidently discharged more readily than the ions of the acid radicals.

When hydroxyl ions are discharged, they turn into neutral OH groups, which cannot exist in the free state and immediately change into water molecules and oxygen:

$$4OH' - 4e^- = 2H_2O + O_2$$

Therefore, the reason for the liberation of oxygen is the discharge of hydroxyl ions. As more and more of the latter are discharged, larger and larger quantities of water molecules ionize, and hydrogen ions accumulate at the anode.

* These problems are dealt with in greater detail in special textbooks.

Let us consider several typical cases of electrolysis.

1. *Electrolysis of* $CuCl_2$ *Solution.* The solution contains $Cu^{\cdot\cdot}$ and Cl' ions and insignificant quantities of $H^{\cdot}$ and OH' ions from the water. When current is passed through, the copper ions move towards the cathode and the chloride ions, towards the anode. Receiving two electrons each from the cathode, the $Cu^{\cdot\cdot}$ ions turn into neutral atoms which separate out of solution. The cathode gradually becomes coated with copper. At the same time, when the Cl' ions reach the anode, they yield their electrons to it and turn into chlorine atoms which combine into pairs to form Cl_2 molecules. Chlorine is liberated at the anode.

Scheme of Electrolysis of $CuCl_2$ Solution

$$\overbrace{Cu^{\cdot\cdot}\ 2Cl'}^{CuCl_2}$$

Cathode $\leftarrow Cu^{\cdot\cdot}\ 2Cl' \rightarrow$ Anode

$$Cu^{\cdot\cdot} + 2e^- = |\underline{Cu}| \qquad 2Cl' - 2e^- = 2Cl$$

$$2Cl \rightarrow |\underline{Cl_2}|$$

Reduction takes place at the cathode, and oxidation at the anode.

2. *Electrolysis of* K_2SO_4 *Solution.* The solution contains $K^{\cdot}$ and SO_4'' ions, as well as the hydrogen and hydroxyl ions of water. As the potassium ions are more difficult to discharge than the hydrogen ions and the SO_4'' ions more difficult than the OH' ions, the passage of current leads to the discharge of hydrogen ions and liberation of hydrogen at the cathode and to the discharge of hydroxyl ions and liberation of oxygen at the anode.

Scheme of Electrolysis of K_2SO_4 Solution

$$\overbrace{2K^{\cdot}\ SO_4''}^{K_2SO_4}$$

Cathode $\leftarrow 2K^{\cdot}\ SO_4'' \rightarrow$ Anode

$$2H_2O \rightleftarrows \left\{ \begin{matrix} \boxed{2K^{\cdot}} \\ \boxed{2OH'} \\ 2H^{\cdot} \end{matrix} \right. \qquad \left. \begin{matrix} \boxed{SO_4''} \\ \boxed{2H^{\cdot}} \\ 2OH' \end{matrix} \right\} \rightleftarrows 2H_2O$$

$$2H^{\cdot} + 2e^- = 2H \qquad 2OH' - 2e^- = H_2O + O$$

$$2H \rightarrow |\underline{H_2}| \qquad 2O \rightarrow |\underline{O_2}|$$

Thus, electrolysis of a K_2SO_4 solution does not lead to the discharge of either of the ions of the dissolved electrolyte, but only to the decomposition of water. At the same time, owing to the discharge of the hydrogen and hydroxyl ions of water and the continuous movement of $K^{\cdot}$ ions towards the cathode and SO_4'' ions towards the anode, a solution of alkali (KOH) forms at the cathode and a solution of acid (H_2SO_4) at the anode.

Decomposing an electrolyte requires a certain definite minimum voltage, called the *decomposition potential* of the electrolyte. For instance, if two platinum electrodes are dipped into a solution of cupric chloride $CuCl_2$ and a difference of potentials of 0.8 volt applied to them, current will at first begin to pass through the solution, but then will rapidly become weaker and will finally stop altogether. The reason for the cessation of the current is the accumulation of copper on one electrode and chlorine (adsorbed by the platinum) on the other, giving rise to a new cell, composed of copper and chlorine in a solution of their ions, which generates current in the reverse direction. This phenomenon is known as *electrode polarization*, and the electromotive force of the cell thus formed is called the polarization e.m.f. Its value for a molar solution of $CuCl_2$ can easily be found from the table of normal potentials by subtracting the potential of copper from that of chlorine: $1.36 - 0.34 = 1.02$ volts.

Obviously, to keep up electrolysis, a difference of potentials must be applied to the electrodes from the outside of not less, and even more, than 1.02 volts, in order to overcome the polarization e.m.f. This value is the decomposition potential of the electrolyte. From the above it is clear that to find it, the potential of the substance liberated at the cathode must be subtracted from the potential of the substance liberated at the anode. Thus, the decomposition potential of $CuCl_2$ in molar solution equals 1.02 volts, the decomposition potential of $ZnCl_2$ under the same conditions equals $1.36 - (-0.763) = 2.123$ volts, etc. The decomposition potentials of oxyacids and alkalis in normal solution are almost identical (about 1.67 volts), as in all these cases the same ions are discharged.

If different cations and anions are present simultaneously in the solution, electrolysis will set in when the voltage is high enough to discharge one of the types of cations and anions present. For this reason, electrolysis is often employed in analysis for separating metals from one another. For instance, at a voltage, say, of 1.2 volts only copper will be deposited from a solution containing $CuCl_2$ and $ZnCl_2$, but not zinc, as the decomposition potential of $ZnCl_2$ is much higher than 1.2 volts.

In the above examples of electrolysis the electrodes were assumed to be made of an inert material, such as graphite. When such electrodes are used, ions are discharged both at the cathode and at the anode. But if the anode consists of a metal, the process takes a different course. In this case ions will be discharged only at the cathode; at the anode, on the other hand, metal ions will pass into the solution. For instance, if a solution of nickel sulphate $NiSO_4$ is electrolyzed, using a plate of metallic nickel as the anode, nickel will be deposited, as usual, at the cathode, but at the anode hydroxyl ions will not be discharged and there will be no liberation of oxygen, nickel gradually dissolving instead. The dissolving of the nickel may be attributed to its capacity, common to all metals, for emitting ions into solution. Under ordinary conditions, when the metal is dipped into water (or a solution), the transition of its ions into the solution soon stops, owing to the appearance of a negative charge on the metal. But in this case, as a result of the work done by the current source, the free electrons are continuously "pumped away" from the nickel plate, and so nothing hinders more and more nickel ions from passing into solution.

Scheme of Electrolysis of $NiSO_4$ Solution (with Nickel Anode)

$$\overbrace{Ni^{\cdot\cdot}\ SO_4''}^{NiSO_4}$$

$$\text{Cathode} \leftarrow Ni^{\cdot\cdot}\ SO_4'' \rightarrow \text{Anode (Ni)}$$

$$Ni'' + 2e^- = \boxed{Ni}\ \qquad Ni - 2e^- = Ni^{\cdot\cdot}$$

Hence, when a nickel salt is electrolyzed with a nickel anode, nickel deposits on the cathode, while the anode gradually dissolves, the amount of nickel salt in solution remaining unchanged.

Soluble anodes are widely used for coating metals with one another by galvanic means. The object to be plated by some metal, say silver, is immersed in a solution of a silver salt, where it serves as the cathode, a piece of metallic silver being used as the anode. Current is then passed through until a layer of silver of sufficient thickness is deposited on the surface of the object.

Electrolytic methods of purification of certain metals are also based on the dissolving of anodes (see p. 560).

One of the important technical applications of electrolysis is **galvanoplastics**, a method of obtaining exact metallic replicas of relief objects by depositing a more or less thick layer of metal electrolytically on their surface. This method was discovered by the Russian Academician B. Jacobi (1801-1874) in the thirties of the last century. The first practically important use of galvanoplastics in Russia was for the production of fine clichés for printing various state papers, including paper currency.

Electrolysis can be applied not only to aqueous solutions of electrolytes, but to many substances in the molten state as well. Melting, like dissolving, breaks down the crystal lattice of the substance rendering its ions, formerly bound up in the solid crystal, capable of moving in an electric field. Electrolysis of molten aluminium oxide is employed for the preparation of aluminium, one of the most important metals of present-day engineering (see § 229). Almost all the readily oxidized metals, such as sodium, potassium, calcium, etc., are also produced by electrolysis of their molten salts or bases.

203. Laws of Electrolysis. Electrolysis was first studied quantitatively in the thirties of the last century by the English physicist Michael Faraday who established, as a result of his investigations, the following **Laws of Electrolysis:**

1. *The weight of a substance deposited by electrolysis is proportional to the quantity of electricity passing through the solution and is quite independent of any other factors.*

This law follows logically from the general conception of the mechanism of electrical conductivity of solutions and the essence of

electrolysis (see § 88). As electricity is carried through solution only by simultaneously discharged ions, it is clear that the quantity of substance liberated at the electrodes will always be proportional to the number of electrons carried through the conductors, i.e., the quantity of electricity passing through.

2. *During electrolysis equal quantities of electricity liberate equivalent quantities of substances from various chemical compounds.*

The following experiment is a graphical illustration of this law. Electric current is passed through a series of solutions containing, for instance, the following substances: HCl, $AgNO_3$, $CuSO_4$, $FeCl_3$, $SnCl_4$ (Fig. 136). The solutions are contained in vessels permitting the

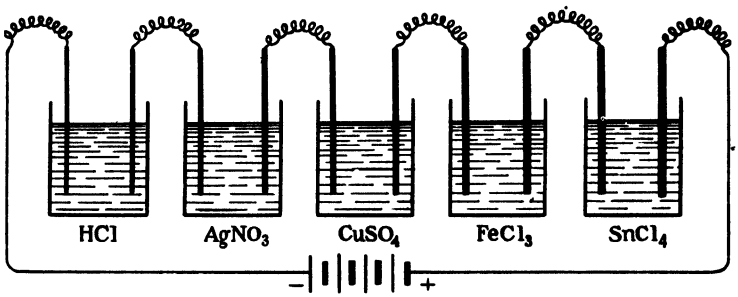


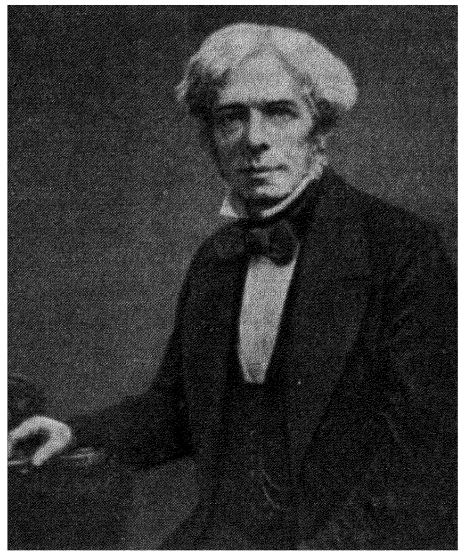
Fig. 136. Diagram of apparatus for illustrating law of electrolysis

substances liberated to be weighed after the experiment (in the figure these vessels are conventionally shown as beakers; two electrodes are immersed in each beaker). To ensure the passage of an equal quantity of electricity through all the solutions, the electrodes are connected in series. After some time, when a sufficient quantity of electrolysis products have accumulated on the electrodes, the current is switched off and the substances are weighed. It will be found that during the time it takes one gram of hydrogen (i.e., one gram-atom) to be liberated from a solution of hydrochloric acid, the following quantities of metals will be deposited from the rest of the solutions.

	Electrolyte			
	$AgNO_3$	$CuSO_4$	$FeCl_3$	$SnCl_4$
Quantity of metal deposited at the cathode, gr.	107.9	31.8	18.6	29.7
Atomic weight of metal	107.88	63.54	55.85	118.70

Comparing the quantities of metals deposited with their atomic weights, we find that the quantity of silver deposited equals 1 gram-atom, the quantity of copper, $^1/_2$ gram-atom, of iron, $^1/_3$ gram-atom,

Michael Faraday
(1791-1867)



and of tin only $^1/_4$ gram-atom. In other words, the weights of substances deposited at the cathode equal their gram-equivalents. The same result is obtained if the quantities of substances liberated at the anode are measured. Thus, in each of the first, fourth and fifth vessels one gram-equivalent of chlorine (35.5 gr.) is liberated, in the second and third vessels, one gram-equivalent of oxygen (8 gr.).

The Electrolysis Laws hold equally for the electrolysis of solutions and of fusions.

Michael Faraday was born in 1791 in Newington (England), in a very poor blacksmith's family. At the age of twelve, not having even finished elementary school, he went to work as an errand boy at a bookstore and the bookbinding shop affiliated to it. Working at this shop, Faraday got into the habit of reading scientific books, especially on the natural sciences. He also liked to attend popular lectures, and it was they that incited him with the passionate desire to devote himself to science.

In 1813 Faraday was fortunate enough, thanks to the aid of the famous English chemist Davy, to receive the position of assistant at the Royal Institute in London. Afterwards he became Davy's secretary, and in 1825 took the latter's place at the Institute.

Faraday's scientific activities were distinguished by their wide range and profoundity. Most of his numerous investigations belong to the sphere of electricity. He studied the action of current on aqueous solutions, established the two fundamental laws of electrochemistry (Laws of Electrolysis), discovered electromagnetic induction. Faraday was the first to work on the liquefaction of gases, obtained chlorine, ammonia, hydrogen chloride and other gases in the liquid form, put forth the firm conviction that all gases could be liquefied.

Other important contributions of his to chemistry were: the discovery of benzene and isobutylene, the investigation of naphthalene and the preparation of ethylsulphuric acid.

Considering the Second Law of Electrolysis from the point of view of electronic theory, it can easily be understood why substances are liberated in chemically equivalent quantities during electrolysis. Take, for instance, the electrolysis of ferric chloride. When iron is deposited from the solution each $Fe^{\cdots}$ ion receives three electrons from the cathode; at the same time three Cl' ions yield their extra electrons to the anode and become chlorine atoms. Therefore, the "transportation" of every three electrons through the solution is accompanied by the liberation of one iron atom and three chlorine atoms. No matter how many electrons pass through the solution, the number of iron atoms deposited is always three times less than the number of chlorine atoms liberated, i.e., the quantities of iron and chlorine evolved are in the same proportion as their chemical equivalents.

It has been established by measurement that the quantity of electricity liberating one gram-equivalent of substance during electrolysis equals 96,500 coulombs.* On this basis, the Second Law of Electrolysis may be formulated as follows:

> *To liberate one gram-equivalent of any substance from the solution of an electrolyte, 96,500 coulombs of electricity must be passed through the solution.*

The Second Law of Electrolysis offers a direct method of determining the equivalent weights of various elements. This law also forms the basis of all calculations involved in electrochemical industrial processes.

Example 1. Find the equivalent weight of nickel if it is known that a current of two amperes takes forty minutes to deposit 1.46 gr. of nickel from a solution of a nickel salt.

We find the quantity of electricity put through the solution by means of the following formula, given in the course of physics: $Q=I\times t$, where Q is the quantity of electricity in coulombs, I, the current intensity in amperes, t, the time in seconds.

Substituting the initial data into this formula we get:

$$Q=2\cdot 40\cdot 60=4{,}800 \text{ coulombs}$$

As 96,500 coulombs are required to liberate 1 gram-equivalent of substance, the gram-equivalent of nickel can be determined from the proportion:

$$96{,}500:4{,}800=x:1.46$$

$$x=\frac{96{,}500\cdot 1.46}{4{,}800}=29.35 \text{ gr.}$$

* More precisely 96,494 coulombs.

Therefore, the equivalent weight of nickel is 29.35.

Example 2. Electrolysis of a solution of silver nitrate resulted in the liberation of 350 ml. of oxygen at S.T.P. at the anode in 20 minutes. Find the current intensity and the amount of silver deposited at the cathode.

A gram-equivalent of oxygen (8 gr.) occupies 5.6 l. at S.T.P. The quantity of electricity passed through the solution can be found from the proportion:

$$96{,}500 : Q = 5{,}600 : 350$$

$$Q = \frac{96{,}500 \cdot 350}{5{,}600} = 6{,}031 \text{ coulombs}$$

Since this quantity of electricity passed through the solution in the course of 20 minutes, the current intensity was:

$$I = \frac{6{,}031}{20 \cdot 60} = 5.03 \text{ amperes}$$

The quantity of silver (m) deposited at the cathode is proportional to the quantity of electricity passed through the solution. A gram-equivalent of silver equals 108 gr. Hence

$$96{,}500 : 6{,}031 = 108 : m$$

$$m = \frac{6{,}031 \cdot 108}{96{,}500} = 6.75 \text{ gr.}$$

204. Alloys. Metals are insoluble in ordinary solvents, such as water, alcohol, ether, etc., but, when melted, are capable of dissolving in one another or mixing to form **alloys.**

Most molten metals are miscible in all proportions, just like alcohol and water. But some metals dissolve in one another only to a definite degree. For instance, if molten zinc and lead are mixed and left standing, the mixture separates into two layers, the lower one consisting of lead with a little zinc dissolved in it, and the upper of zinc containing some lead.

When metals are fused, either one metal simply dissolves in the other, or, more frequently, the metals form a chemical compound, and therefore alloys are usually mixtures of free metals with their chemical compounds, the formation of which is often accompanied by a considerable thermal effect. For instance, if a piece of aluminium is dropped into molten copper, so much heat is evolved that the entire mass becomes white hot.

Many metals can combine into several different compounds with each other, such as AuZn, Au_3Zn_5, $AuZn_3$, Na_4Sn, NaSn, $NaSn_2$, etc.

Solid alloys are sometimes quite homogeneous; in such cases they are either definite chemical compounds or homogeneous mixtures of indefinite composition, known as **solid solutions.** The latter form if the atoms of the metals mixed are capable of displacing one another in the crystal lattice without disturbing its structure. Such a displacement results in quite homogeneous mixed crystals containing atoms of both metals simultaneously (see § 53) and accounting for the

homogeneity of the alloy as a whole. Most alloys, however, are heterogeneous mixtures of crystals of the separate metals and their chemical compounds (if fusion of the metals gives rise to such compounds). Metals form alloys not only with each other but with some of the non-metals as well; pig iron and steel, for instance, are alloys of iron and carbon.

If the alloyed metals form neither chemical compounds nor a solid solution, one of the components, upon cooling, begins to fall out in the solid form. For instance, if a liquid alloy consisting of 10 parts of lead and 90 parts of tin by weight is cooled, crystals of pure tin will separate out first, just like pure ice from a dilute solution of sugar in water when cooled. The temperature at which the tin begins to precipitate out of the alloy, is below the freezing point of pure tin. By determining the solidification point of tin with lead dissolved in it, we can calculate the molecular weight of the latter, using the same rules as in the case of aqueous solutions. This method has been used to determine the molecular weights of many metals, which were found to be present in dilute metallic solution mostly in the form of separate atoms.

Chemical analysis methods are unsuitable for determining the composition of alloys, as in many cases the metal compounds cannot be isolated from the alloy. For this reason, physical methods of investigation are employed predominantly in the study of alloys. A prominent role in the development of these methods belongs to the Russian scientist N. Kurnakov, who founded a new scientific discipline, known as *physico-chemical analysis.*

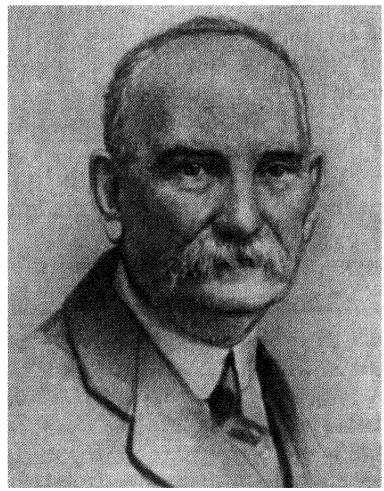
Nikolai Semyonovich Kurnakov was born in 1860, in the town of Nolinsk, Vyatka Gubernia. He studied at the Petersburg Mining Institute which he graduated in 1882. In 1893, Kurnakov submitted a thesis "On Complex Metal Bases" and was appointed professor in the chair of inorganic chemistry at the Mining Institute. In 1913 he headed the chair of general chemistry at the Petersburg Polytechnical Institute, and retained this post until 1930.

In 1913 Kurnakov was elected Member of the Russian Academy of Sciences.

During the first period of his scientific activities, Kurnakov studied the structure and properties of complex compounds and this was the theme of his Doctor's thesis. But Kurnakov's most important investigations were devoted to metal alloys, to the study of which he applied thermal analysis and other physico-chemical methods developed by himself, as well as metallography. These investigations revealed a number of very important laws, explaining the behaviour of metals when alloyed and enabling prediction of the physico-chemical and mechanical properties of alloys. Kurnakov's works were not only of great theoretical interest, but of immense practical importance as well.

Alongside his numerous investigations of alloys, Kurnakov spent a great deal of time and effort in studying natural brines. His works in this field made it possible to solve a number of very important problems concerning the utilization of the inexhaustible resources of the salt lakes of our country and of the Kara-Bogaz-Gol Bay in the Caspian Sea and led to the discovery of one of the largest deposits of potassium salts in the world, in Solikamsk District.

Nikolai Semyonovich
Kurnakov
(1860-1941)



By means of physico-chemical analysis the variation of any physical property (vapour pressure, melting point, specific gravity, viscosity, electrical conductivity, etc.) of a system, usually consisting of two substances, can be investigated quantitatively in relation to changes in the composition of the system. The results of such investigations are represented on a composition-property diagram, the composition always being plotted along the horizontal axis and expressed in per cent of one of the components of the system, while the property expressed by the numerical value of the corresponding physical constant, is plotted along the vertical axis. The shapes of these curves not only enable detection of transformations occurring in the system, but also give indications of the nature of those transformations, the composition of the resulting products, the formation of solid solutions, etc. Physico-chemical analysis methods are now widely used in the metallurgical, silicate, chemical and other branches of industry.

Kurnakov's numerous works, concerned with ascertaining the nature of metal alloys, elucidated the processes taking place during the solidification of alloys. In particular, in studying alloys he discovered chemical compounds whose composition could vary within a considerable range. Kurnakov called these compounds of variable composition **berthollides**, after Berthollet who had assumed their existence (see p. 34), and suggested that ordinary compounds of constant composition should be termed **daltonides**.

Of the various types of physico-chemical analysis, the most widely used in the study of alloys is **thermal analysis**, founded in the sixties

of the last century by the Russian metallurgist D. Chernov. Thermal analysis consists in the plotting and study of fusibility diagrams representing the dependence of the melting points of alloys on their percentage composition.

To give an idea of thermal analysis, several examples are examined below.

Figure 137 is the fusibility diagram of the system bismuth-cadmium. The horizontal axis shows the percentage composition of the alloys and the vertical axis, their melting points. Point *A* on the curve *ACB* represents the melting point of pure bismuth (271° C).

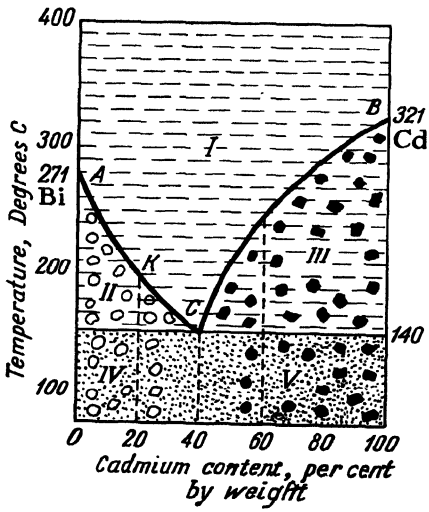


Fig. 137. Fusibility diagram of the system Bi-Cd

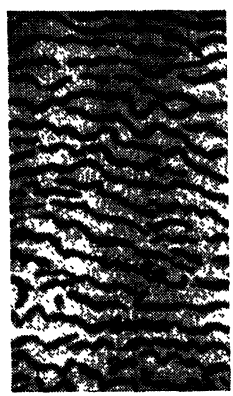


Fig. 138. Photo-micrograph of Sn-Pb eutectic alloy

As more and more cadmium is added to it, the melting point drops gradually until it reaches a certain point *C*; after this, if the cadmium content is still further increased, the melting point rises again along the curve *CB* until it reaches point *B* which is the melting point of pure cadmium (321° C). If we begin with cadmium and add bismuth gradually to the mixture, the melting point will first drop to point *C* and then rise again to point *A*.

If a liquid alloy containing, say, 20 per cent cadmium and 80 per cent bismuth is cooled, pure bismuth will begin to separate out of it at a certain temperature corresponding to point *K*, and hence, its content in the remaining liquid alloy will become smaller. As more and more bismuth crystals separate out, the temperature keeps falling and when it reaches point *C* (140° C) the entire remaining liquid alloy

will begin to solidify as a whole, at constant temperature. An analogous picture is obtained if an alloy containing 60 per cent Cd and 40 per cent Bi is cooled, with the only difference that cadmium will separate out first in this case (cf. freezing of solutions, § 82).

The temperature 140° C, the lowest possible melting point for any alloy of bismuth and cadmium, is called the eutectic temperature, while the alloy of the composition corresponding to this point is referred to as a *eutectic mixture*, or just eutectic. In the case under consideration the eutectic contains 40 per cent cadmium and 60 per cent bismuth.

As long as the alloy contains less than 40 per cent cadmium, bismuth separates out first when the alloy is cooled, thus playing the part of the solvent, while cadmium is in this case the solute. At point *C* the roles of bismuth and cadmium are reversed. From alloys containing more than 40 per cent cadmium, the latter metal crystallizes out first; here cadmium is the solvent and bismuth the solute. And only when the cadmium content in the alloys equals 40 per cent do both metals begin to separate out simultaneously as a eutectic. If the eutectic is examined under the microscope it will be found to consist of very tiny crystals of bismuth and cadmium closely intergrown with one another.* Alloys of bismuth and cadmium with other compositions contain large crystals of one of the metals included in the continuous mass of the eutectic.

In accordance with the above, five fields can be distinguished on the fusibility diagram of the system bismuth-cadmium (see Fig. 137): *I*—liquid fusion of cadmium and bismuth; *II*—mixture of the liquid fusion and bismuth crystals; *III*—mixture of the liquid fusion and cadmium crystals; *IV*—mixture of the eutectic and bismuth crystals; *V*—mixture of the eutectic and cadmium crystals.

Fusibility diagrams are usually plotted on the basis of the *cooling curves* of alloys. To obtain these curves, two pure metals are used to prepare a number of mixtures of various compositions. Each of the mixtures is fused and then cooled slowly, measuring the temperature of the alloy at definite time intervals.

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* For such investigations, constituting the subject of a special scientific discipline called metallography, a small section of the alloy is polished to a mirror-like surface.

The polished surface is etched with a solution of acid, alkali or some other reagent. Some substances are more susceptible to the action of the reagent, others less susceptible, and thus the outlines of the composite parts of the alloy are brought out on the polished surface. The resulting section is studied under the microscope in reflected light. Fig. 138 shows a microsection of a eutectic alloy of tin and lead.

The fundamentals of metallography were founded over 100 years ago by the Russian engineer P. Anosov, who was the first to begin using the above-described method of investigation at the Zlatoust plants in the Urals.

The observed data are recorded as cooling curves with the time plotted along the abscissa and the temperature, along the ordinate axis.

The left-hand curve in Fig. 139 is the cooling curve of a pure molten metal. At first the temperature decreases uniformly along *ak*. At point *k* the curve shows a break, where the solid phase begins to form, this being accompanied by the liberation of heat, so that the temperature remains constant for a certain length of time (the curve runs parallel to the abscissa axis). After the entire mass of the molten metal has solidified the temperature again proceeds to fall uniformly along *cb*.

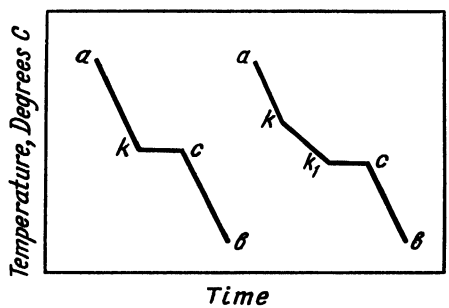


Fig. 139. Cooling curves

At times an interruption in the temperature drop may also be observed on the cooling curve of the solid metal, indicating that certain processes connected with the liberation of heat take place in the solid substance, say the transition of one allotropic modification into another.

The cooling curve of an alloy of two metals has a somewhat different shape. Such a curve is shown in the right-hand part of Fig. 139. The point *k*, as in the first curve, corresponds to the alloy beginning to solidify, to the crystals of one of the metals constituting the alloy beginning to separate out. As this takes place, the composition of the alloy remaining in the liquid state changes and its solidification temperature keeps falling continuously, as long as crystallization goes on. But the heat liberated during crystallization nevertheless retards the cooling process, so that the curve has a small break at the point *k*. Crystals continue to separate out and the temperature continues to drop uniformly until the alloy reaches the eutectic composition. Then the temperature ceases to drop (point k_1), as the eutectic separates out at a constant temperature. When the eutectic has separated out completely, the temperature again begins to decrease down the smooth curve *cb*.

The fusibility diagram of any given system can be built on the basis of a series of curves obtained in this manner for various alloys

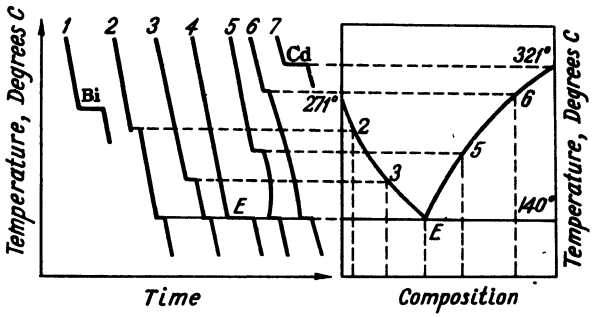


Fig. 140. Plotting fusibility diagram from cooling curves

of its two component metals. Fig. 140 shows schematically how it is built in the case of the system Bi-Cd. Curves *1* and *7* represent the solidification of the pure metals bismuth and cadmium; all the rest of the curves represent the cooling of alloys with gradually decreasing percentage of bismuth. Of these curves, *4* corresponds to the solidification of the alloy of eutectic composition (60 per cent Bi and 40 per cent Cd). Fusibility diagrams of the kind just examined result only in the simplest cases, when the alloyed metals form neither chemical compounds nor solid solutions. Examples of such alloys, besides that described, are the alloys of copper and silver (eutectic contains 28 per cent Cu and 72 per cent Ag), lead and antimony (eutectic at 13 per cent Sb and 87 per cent Pb) and many others.

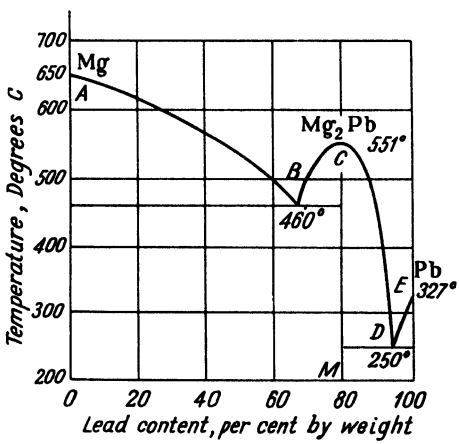


Fig. 141. Fusibility diagram of the system Mg-Pb

The fusibility diagrams are more complex when the two metals fused do not simply dissolve in one another, but form one or more chemical compounds.

Fig. 141 represents the fusibility diagram of the system magnesium-lead, i. e., of two metals forming a definite chemical compound

Mg_2Pb. Here we see two eutectic points, namely B and D, corresponding to the temperatures 460 and 250° C. The prominent maximum on the curve $ABCDE$ (point C) corresponds to the melting points of Mg_2Pb, point M on the abscissa axis indicating its composition. Magnesium separates out from the alloy upon cooling along line AB, lead, along line ED, and Mg_2Pb, along line BCD. Thus, if a liquid alloy containing, say, 40 per cent lead (60 per cent magnesium) is cooled, magnesium crystals will fall out first; as they separate out, the temperature will keep falling, and when it reaches 460° C, all the remaining liquid part of the alloy will begin to solidify at a constant temperature, forming a eutectic mixture of very minute crystals of magnesium and the chemical compound Mg_2Pb.

A similar result is obtained if a liquid alloy containing, say, 75 per cent lead is cooled, but in this case Mg_2Pb crystals will be the first to separate. This will continue until the temperature reaches 460° C, the point of formation of the eutectic.

Analogous processes with solidification of the eutectic at 250° C occur if the alloy contains over 80 per cent lead (see curve CDE in Fig. 141).

Thus, the left half of the curve, from A to C, is the fusibility curve of alloys of magnesium and Mg_2Pb, while the right half, from C to D, is the fusibility curve of alloys of lead and Mg_2Pb.

If two metals, when fused, form several chemical compounds, there will be the same number of maxima on their fusibility curve as there are compounds, each maximum defining the composition of one of the compounds.

Thus, thermal analysis makes it possible to judge both the general nature of the alloys, and the number and composition of the compounds formed by the alloyed metals, which, in the long run, determine all the properties of the alloys.

Example. Using the fusibility diagram of the system Bi-Cd, find: a) which metal will be first to separate if a liquid alloy containing 50 per cent bismuth and 50 per cent cadmium is cooled; b) how many grams of this metal will separate out of 500 gr. of the alloy before the eutectic is reached.

1. From Figure 137 on p. 538, it can be seen that the point corresponding to the temperature at which the alloy begins to solidify must lie on BC above point C. Therefore, if the alloy is cooled the first metal to crystallize will be cadmium, which will continue to separate until the remaining liquid part of the alloy reaches the eutectic.

2. As the eutectic contains 60 per cent bismuth, all the bismuth must obviously be included in the eutectic. Then the weight of cadmium included in the eutectic can be determined by the proportion

$$60:40=250:x$$

whence

$$x=\frac{40\cdot 250}{60}=166.7 \text{ gr. Cd}$$

Therefore, the amount of cadmium that will separate out before the eutectic forms will be

$$250 - 166.7 = 83.3 \text{ gr. Cd}$$

Thermal analysis has led to the discovery of the existence of an enormous number of compounds of metals with one another. These compounds bear the generic name of **intermetallic compounds.** The greatest number of such compounds, as far as we know at present, is formed by the alkali and alkaline-earth metals with the metals of the odd subgroups possessing comparatively weak metallic properties.

The composition of intermetallic compounds is usually expressed by formulas which seem to defy the laws of valency established for compounds of metals with non-metals. For instance, sodium forms the following series of compounds with tin and lead:

$$NaSn_6,\ NaSn_4,\ NaSn_3,\ NaSn_2,\ NaSn,\ Na_4Sn_2,\ Na_2Sn,\ Na_3Sn,$$
$$Na_4Sn;\ NaPb_5,\ Na_4Pb_9,\ NaPb,\ Na_2Pb,\ Na_4Pb$$

Many intermetallic compounds are very stable and do not decompose even at temperatures considerably exceeding their melting points. Intermetallic compounds are soluble in liquid ammonia, giving solutions which conduct current. When such solutions are electrolyzed, one of the metals, namely, the less electropositive, is deposited at the anode and the other at the cathode. For instance, when a solution of Na_4Pb_9 is electrolyzed, lead is liberated at the anode and sodium at the cathode.

In solution intermetallic compounds are capable of exchange reactions with various salts. For example:

$$2Ca(NO_3)_2 + K_4Pb = Ca_2Pb + 4KNO_3$$

Metals can be displaced by other metals from intermetallic compounds just as they can be from ordinary salts.

The formation of intermetallic compounds has as yet found no theoretical explanation. It has been established only that metals of very similar chemical properties usually do not form compounds with one another.

X-ray methods have found wide use of late in the study of alloys, and have made it possible to establish the internal structure of the crystals in the alloy and to determine their crystal lattices.

The properties of alloys differ in many respects from those of the alloyed metals and are not by any means their arithmetical mean, owing to the formation of various chemical compounds or solid solutions when the metals are fused.

The melting points of alloys are very often lower than that of the most fusible component in the alloy. One of the alloys with a very low melting point consists of lead (4 parts), tin (2 parts), bismuth (6 parts), and cadmium (1 part). It melts at about 75° C, i. e., even if immersed in hot water, while the melting point of the most fusible of these four metals, namely, tin, equals 232° C. On the contrary, the hardness of alloys is usually higher than that of their composite parts,

especially when it contains chemical compounds of the metals fused, these compounds being as a rule harder than the alloyed metals; but at the same time they are more brittle. Alloys containing solid solutions are especially hard.

All these properties often make alloys more valuable than the metals they consist of. That is why metals are used in industry mostly in the form of various alloys.

205. Preparation of High-Purity Metals. The development of a number of new branches of engineering during recent years has confronted industry with the task of obtaining metals of a much higher degree of purity than was tolerated previously. Thus, a nuclear reactor will operate reliably only if the content of such "dangerous" impurities as boron, cadmium, etc., in the fissile materials does not exceed millionths of one per cent. Pure zirconium is one of the best structural materials for atomic reactors, but becomes quite useless for this purpose if it contains even insignificant amounts of hafnium. Germanium for semi-conductors (see § 233) must not contain more than 1 atom of phosphorus, arsenic or antimony per 10 million atoms of the metal. Heat-resistant alloys, widely used nowadays in aircraft engineering, must not contain even infinitesimal admixtures of lead or sulphur.

Studies of metals obtained in a very pure state have shown that in several cases previous ideas of their properties have been erroneous. Many metals which have hitherto been considered brittle, non-plastic, are found to be very plastic when pure. For instance, titanium turned out to be so plastic that it can be forged, rolled into thin sheets, bands, etc. Another very plastic metal is pure chromium. Highly pure aluminium is as soft as lead; its electrical conductivity is much higher than that of ordinary aluminium.

Pure metals can be prepared by electrolysis, by reduction from various chemical compounds with hydrogen, calcium, magnesium or aluminium, and by other methods; however, the degree of purity of the metals obtained by these processes is not high enough for present-day technology. Therefore, special methods of purifying metals have been developed recently. Of these methods the most promising are: 1) purification of metals by remelting under vacuum; 2) so-called "zone" melting of metals and 3) decomposition of volatile compounds of the metals on a red-hot surface.

Purification of metals by remelting under vacuum is based on the difference between the boiling points of the metal being purified and the impurities contained in it. In this method either the impurities are driven off from the metal, or the metal is driven off from its impurities. The method is used for the preparation of very pure lithium, calcium, strontium and barium. It may also be employed for the production of chromium, manganese and beryllium.

"Zone" melting is based on the difference in solubility of the admixtures in the solid and liquid phases of the metal being purified. In the "zone" melting method a specially shaped boat or crucible containing an ingot (rod) of the metal being purified is moved very slowly (several millimetres per hour) through a furnace. As a result of this a small section (zone) of the metal, that in the furnace at the moment, is melted. As the boat (crucible) progresses, the liquid metal zone moves from one end of the ingot to the other. The impurities contained in the metal collect in the melted zone, move along together with it and when the operation is over are found at the end of the ingot. By numerous repetitions of this operation the metal can be made very pure.

"Zone" melting is used to purify germanium, silicon, tin, aluminium, bismuth and gallium.

Decomposition of volatile compounds of metals on a heated surface. Titanium, zirconium, chromium, tantalum, niobium, silicon and vanadium readily form chemical compounds which can be volatilized at comparatively low temperatures. When these compounds come in contact with a red-hot surface, they decompose, depositing a layer of very pure metal.

The preparation of pure titanium is described below by way of example. Titanium reacts readily with iodine, forming a compound which is a gas at 200 or 250° C. Thus, if a mixture of impure titanium and iodine is heated, the titanium will separate from its impurities and pass into the gaseous phase. If the gas thus formed is passed over a wire heated to 1,200-1,400° C, it will decompose into its constituent parts. The titanium deposits on the wire, while the liberated iodine comes off and can be recirculated to treat new portions of impure titanium.

CHAPTER XIX

First Group of the Periodic Table

The elements of the first group of the Periodic Table are characterized, first of all, by identical structure of the outer electron layer of their atoms, which, in all the members of this group, contains only one electron. But the structure of the second last electron layer differs in the different elements. This greatly influences their properties and accounts for the division of the group into a main and a secondary subgroup. The main subgroup includes the typical elements *lithium* and *sodium*, as well as *potassium*, *rubidium* and *caesium*, of atomic structure similar to the first two, and situated in the even series of the long periods.* Each of these elements has eight electrons in its second last layer. The secondary subgroup consists of the elements in the odd series of the long periods: *copper*, *silver* and *gold*, which have eighteen electrons in their second last layers.

ALKALI METALS

Element	Symbol	Atomic weight	Atomic number	Arrangement of electrons in layers					
Lithium . .	Li	6.940	3	2	1				
Sodium . . .	Na	22.991	11	2	8	1			
Potassium .	K	39.100	19	2	8	8	1		
Rubidium .	Rb	85.48	37	2	8	18	8	1	
Caesium . .	Cs	132.91	55	2	8	18	18	8	1

206. General Features of the Alkali Metals. The name "alkali metals," given to the elements of the main subgroup of the first group, is due to the fact that the hydroxides of the two chief representatives of this group, sodium and potassium, have long been known as "alkalis." It was from these alkalis that Davy first prepared free potassium and sodium in 1807 by electrolysis in the fused state.

* This subgroup includes also the element francium (at. no. 87), obtained artificially.

Having only one electron in their outer layer, which is a considerable distance away from the nucleus (see p. 121), the atoms of the alkali metals part with it very readily, forming positively singly-charged ions with the stable shell of the corresponding inert gas. Therefore, the alkali metals are the most typical representatives of the metals. All their metallic properties are especially pronounced. The alkali metals are absolutely incapable of gaining electrons.

Similar structure of not only the outermost, but the second last electron layer as well, accounts for the great resemblance between the alkali metals. But at the same time, the increase in nuclear charge and in the total number of electrons in the atom from lithium to caesium, gives rise to certain qualitative differences between the individual members of the group. As in other groups, these differences amount mainly to greater readiness in yielding valency electrons and to more pronounced metallic properties as the atomic number increases.

207. The Alkali Metals in Nature. Preparation and Properties of the Alkali Metals. Owing to their high oxidizability, the alkali metals occur in nature only as compounds. Sodium and potassium are among the most abundant elements on the earth: the content of sodium in the earth's crust is 2.40 per cent, and that of potassium, 2.35 per cent. Both metals are contained in various silicate type minerals and rocks. Sodium chloride is found in sea water and also forms immense deposits of rock salt at many points of the globe. The upper layers of these deposits sometimes contain quite considerable quantities of potassium, chiefly in the form of potassium chloride, and also as double salts with sodium and magnesium. However, large accumulations of potassium salts of commercial importance are scarce. The most important of them are the Solikamsk deposits in the U.S.S.R., the Stassfurt deposits in Germany and the Alsace deposits in France. Deposits of sodium nitrate have been found in Chile. Soda is contained in the waters of many lakes. Finally, enormous quantities of sodium sulphate occur in the Kara-Bogaz-Gol Bay of the Caspian Sea, where in the winter months this salt deposits in thick layers at the bottom.

The other three alkali metals, lithium, rubidium and caesium, are much less abundant than sodium and potassium. Lithium occurs more often than the others but the minerals containing it rarely form large accumulations. Traces of lithium can be detected in the waters of many mineral springs, in the soil and in the ashes of certain plants, such as beets, tobacco, hops. Rubidium and caesium are contained in small quantities in certain lithium minerals.

The alkali metals are always found in compounds as positively charged ions. As the atoms of the alkali metals are oxidized very readily, yielding electrons, their ions, on the contrary, are difficult

to reduce. Therefore, to reduce the ions of the alkali metals the most powerful reducing agent, namely electric current, must usually be resorted to. Sodium and potassium are prepared commercially by electrolysis of their fused hydroxides or chlorides; lithium is prepared by electrolysis of fused lithium chloride. Rubidium and caesium are not prepared on a commercial scale.

All the alkali metals have a bright metallic lustre, easily observed on a fresh cut. In the air the lustrous surface of the metal immediately becomes dull due to oxidation.

The characteristic features of the alkali metals are insignificant hardness, high electrical conductivity, low specific gravity and low melting and boiling points. Lithium has the lowest specific gravity, equalling 0.53; caesium has the lowest melting point, 28° C.

The chief physical constants of the alkali metals are given in Table 28.

Table 28

Chief Physical Constants of the Alkali Metals

Constants	Lithium Li	Sodium Na	Potassium K	Rubidium Rb	Caesium Cs
Specific gravity	0.53	0.97	0.86	1.53	1.9
Melting point, degrees C .	186	97.7	63	38.5	28
Boiling point, degrees C . .	1,336	880	760	700	670
Atomic radius, Å	1.57	1.92	2.36	2.53	2.74

The alkali metals dissolve in liquid ammonia, forming dark blue colloidal solutions.

If a salt of an alkali metal is introduced into the non-luminous flame of a gas burner, it decomposes, and the vapours of the liberated metal impart a characteristic colour to the flame. For instance, lithium colours it red, sodium yellow, etc. Examination of the coloured flame through a spectroscope shows the spectrum peculiar to the given metal. In this way even insignificant traces of these elements can be detected in substances.

Spectral Analysis. Numerous investigations of the spectra of various substances in the gaseous state have shown that all chemical elements, and many complex substances as well, have characteristic spectra differing from those of other substances in number and arrangement of lines. In the case of mixtures, the peculiar spectrum of each component is obtained. Thus, the presence of any definite substance in a mixture can be established by its spectrum. This is the underlying principle of a special method of investigating substances known as spectral analysis.

Spectral analysis is of immense importance for chemistry, especially when only insignificant quantities of the substance under study are present. The

sensitivity of this method by far outstrips the sensitivity of ordinary chemical reactions. For instance, the characteristic yellow line in the sodium spectrum can be detected with a spectroscope if the flame contains only a one-thousand millionth of a gram of sodium. The discovery of many rare elements occurring in small quantities, particularly rubidium and caesium, was due to spectral analysis.

Chemically the alkali metals are among the most active elements. The activities of the different alkali metals are not identical and grow perceptibly with increasing atomic weight. The rise in activity runs parallel to the increase in atomic radii, i. e., the distance between the valency electron and the nucleus (Table 28). This regularity stands to reason: the farther away the valency electron is from the nucleus, the weaker its bond with the nucleus and the more easily it can be torn away from it. And since the activity of metals depends on their readiness to yield valency electrons, it naturally increases from Li to Cs.

As has been stated above (see pp. 168-169), the strength of the electron bond in the atom is evaluated by the magnitude of the *ionization energy* or *ionization potential* of the element. The atoms of the alkali metals possess the lowest ionization potentials, characterized by the following figures in volts:

Li	Na	K	Rb	Cs
5.36	5.1	4.32	4.10	3.87

These data show that the ionization potentials decrease from lithium to caesium, and, therefore, so does the strength of the bond between their outermost electrons and nuclei.

The low ionization potential values account also for the ability of the alkali metals to yield their electrons readily under various external influences, particularly, under the action of light on the pure surface of the metal. This phenomenon is the fundamental principle of *photoelectric cells*, devices for transforming luminous energy directly into electrical. Caesium is especially sensitive to the action of light.

A photoelectric cell is shown diagrammatically in Fig. 142. Half the surface of a glass bulb is coated on the inside with a thin layer of an alkali metal. Above the metallic layer is a ring or grid of platinum wire. The bulb is filled with neon or some other inert gas at a very low pressure. The grid and the metal layer are connected to the outer circuit, which includes a dry cell battery and a galvanometer. In the absence of light the circuit remains open and no current will flow through the photoelectric cell. But if the surface of the metal is illuminated, electrons begin to tear away from it and fly towards the grid, thus completing the circuit and giving rise to a direct current in it.

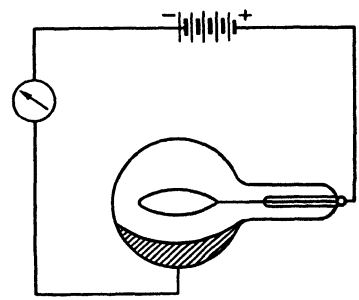


Fig. 142. Diagram of photoelectric cell

Photoelectric cells are widely used in practice for transmitting images over distances (for instance, television), in various signalling devices, for automatic control of mechanisms, in sound pictures, etc.

All the alkali metals combine vigorously with oxygen. Rubidium and caesium even ignite spontaneously in the air; lithium, sodium and potassium burst into flame if gently heated. It is very characteristic that only lithium forms the normal oxide Li_2O when burnt, the rest of the alkali metals being converted into peroxides of the following compositions:

$$Na_2O_2;\ K_2O_4;\ Rb_2O_4;\ Cs_2O_4$$

The exact structure of peroxides of the M_2O_4 type, where M stands for an alkali metal, is not known as yet.

The alkali metals react with the halogens no less vigorously than with oxygen, especially with chlorine and fluorine.

As the alkali metals are far above hydrogen in the electrochemical series, they displace hydrogen not only from acids, but also from water (in which the H^+-ion concentration is very low), forming strong bases:

$$2K + 2HOH = 2KOH + H_2$$

Parting readily with their valency electrons during chemical reactions, *the alkali metals are the most powerful reducing agents.*

The reducing ability of the alkali metals is so strong that they are capable even of reducing hydrogen atoms, converting them into negatively charged H' ions with the electron configuration of the inert gas helium. Thus, if the alkali metals are heated in a stream of hydrogen, solid crystalline substances of the type MH, called **hydrides**, result, these compounds containing negatively charged hydrogen.

$$2Na + H_2 = 2Na^+H^-$$

Hydrides react with water to form hydrogen and alkalis.

In chemical nature the hydrides are somewhat similar to the salts of the hydrohalic acids. The hydrides of the alkali metals are soluble in liquid ammonia, with which they form electrically conductive solutions. If such solutions are electrolyzed the metal is liberated at the cathode and hydrogen at the anode; therefore the latter is present in solution in the form of the anions H':

$$MH \rightleftarrows M^+ + H'$$

The alkali metals form a large number of salts. With the exception of a few salts of lithium (LiF, Li_2CO_3, Li_3PO_4), almost all the salts of the alkali metals are readily soluble in water. Therefore, whenever an anion is required to accomplish any desired reaction, it is almost always added as a salt of an alkali metal. Solutions of their salts with weak acids react strongly alkaline owing to hydrolysis.

The two alkali metals sodium and potassium are of great practical importance.

208. Sodium (Natrium); at. wt. 22.991. It has already been stated that metallic sodium is prepared by the electrolysis of fused sodium hydroxide with about 12 per cent soda added, or by the electrolysis of sodium chloride.

The diagram of an apparatus for the preparation of sodium from sodium hydroxide is shown in Fig. 143. An iron vessel *1*, holding up to 200 kg. of NaOH and cemented into a furnace, is heated from without by hot gases to keep the sodium hydroxide in a molten state. The

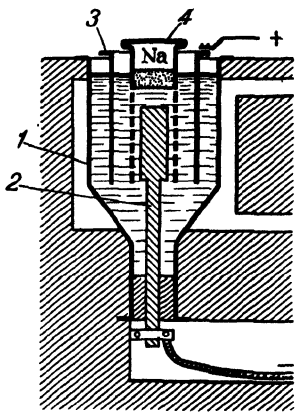


Fig. 143. Diagram of apparatus for preparation of metallic sodium from NaOH:
1—reaction vessel; *2*—cathode; *3*—anode; *4*—iron cylinder with gauze and cap

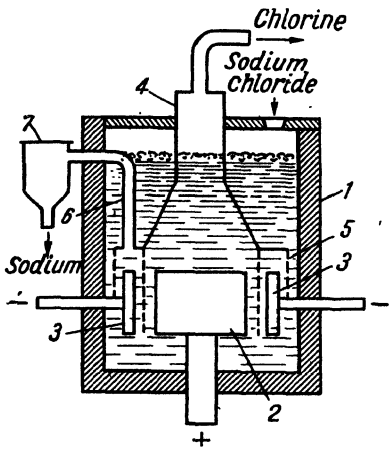


Fig. 144. Diagram of apparatus for preparation of metallic sodium from NaCl:
1—iron body; *2*—anode; *3*—cathode; *4*—bell; *5*—perforated partition; *6*—pipe; *7*—collector

cathode is a thick nickel or copper rod *2* passing through the bottom of the vessel, and the anode is a nickel cylinder *3*. The cathode is surrounded by an iron wire gauze fastened at the top to a capped iron cylinder *4*. The purpose of the gauze is to prevent the sodium liberated from passing through to the anode.

As the electrolysis proceeds, the molten sodium accumulates within the iron cylinder from which it is removed periodically and poured into moulds.

Owing to the hydroxyl ions being discharged at the anode, oxygen is liberated there:

$$4OH' - 4e^- = 2H_2O + O_2$$

The water formed evaporates almost entirely, but some of it, nevertheless, is decomposed by the current, so that a little hydrogen is liberated at the cathode together with the sodium.

Of great interest is the preparation of sodium from molten sodium chloride, as in this case sodium hydroxide is replaced by common salt which is a much cheaper material.

The bath for the electrolysis of NaCl (Fig. 144) consists of an iron body *1*, lined on the inside with fire-brick. The graphite anode *2* is surrounded by a nickel cathode *3*, the outer walls of which are coated with an insulating material. Under the bell *4* is a perforated partition *5* surrounding the cathode. The metallic sodium collects in the annular cathode space and passes through pipe *6* into the collector *7*. Sodium chloride is introduced through an opening in the bath cover.

The disadvantage of this method is the necessity of carrying on the process at a comparatively high temperature (610-650° C) which complicates the apparatus.

In the free state sodium is a silvery-white metal with a specific gravity of 0.97, and a melting point of 97.7° C. Sodium is so soft that it can easily be cut with a knife. It is readily oxidized in the air, and for that reason is usually kept under kerosene.

Metallic sodium is quite widely used. It serves as a raw material for the preparation of sodium peroxide and sodium amide and is employed also for the synthesis of many organic compounds. In the laboratory sodium is often used to remove the last traces of moisture from certain organic solvents.

With mercury sodium forms a solid alloy, sodium amalgam, which is sometimes used as a reductant instead of the pure metal.

Sodium forms two compounds with oxygen, sodium oxide Na_2O and sodium peroxide Na_2O_2.

Sodium oxide Na_2O can be prepared by passing a moderate quantity of oxygen over sodium heated to not over 180°, or by heating sodium peroxide with metallic sodium:

$$Na_2O_2 + 2Na = 2Na_2O$$

Sodium oxide reacts violently with water, giving sodium hydroxide and releasing a large amount of heat:

$$Na_2O + H_2O = 2NaOH$$

Sodium peroxide Na_2O_2 results when sodium is burnt in the air or in oxygen. In industry sodium peroxide is prepared by heating metallic sodium in flat aluminium dishes inside an iron tube through which a stream of air freed from carbon dioxide is passed. The resulting product is a yellow powder and contains about 93 per cent Na_2O_2.

Sodium peroxide is a very powerful oxidant. Many organic substances burst into flame when brought into contact with it.

If sodium peroxide is carefully dissolved in cold water the resulting solution will contain sodium hydroxide and hydrogen peroxide. The

reader will recall that all peroxides are now regarded as salts of hydrogen peroxide, a very weak acid. Therefore, the reaction between sodium peroxide and water is essentially the hydrolysis of the salt of a weak acid and a strong base:

$$Na_2O_2 + 2H_2O \rightleftarrows H_2O_2 + 2NaOH$$
$$O_2'' + 2H_2O \rightleftarrows H_2O_2 + 2OH'$$

If this solution is heated, oxygen will be liberated due to decomposition of the hydrogen peroxide.

Dilute acids also react with sodium peroxide to give hydrogen peroxide:

$$Na_2O_2 + H_2SO_4 = Na_2SO_4 + H_2O_2$$
$$O_2'' + 2H^{\cdot} = H_2O_2$$

Owing to the formation of hydrogen peroxide when Na_2O_2 is dissolved in water or in dilute acids, sodium peroxide is widely used for bleaching fabrics, wool, silk, straw, feathers, bones, etc.

Of great importance is the reaction between sodium peroxide and carbon dioxide:

$$2Na_2O_2 + 2CO_2 = 2Na_2CO_3 + O_2$$
$$\left|\begin{array}{l} O_2^{2-} + 2e^- = 2O^{--} \\ O_2^{2-} - 2e^- = O_2 \end{array}\right.$$

This reaction forms the basis for the use of sodium peroxide in oxygen breathing (or self-contained) gas masks, as well as in submarines for absorbing the carbon dioxide exhaled by people and at the same time supplementing the supply of oxygen in the air.

Sodium hydroxide NaOH is a white solid, very hygroscopic, melting at 328° C. Owing to its strong corrosive effect on fabrics, skin, paper and other organic substances it is also called caustic soda.

Sodium hydroxide dissolves in water, liberating a large amount of heat owing to the formation of various hydrates. Sodium hydroxide must be kept in well-stoppered vessels, as it readily absorbs carbon dioxide from the air, turning gradually into sodium carbonate.

The chief method of preparation of caustic soda is by the electrolysis of aqueous solutions of common salt. When current is passed through, hydrogen ions are discharged at the cathode, leaving hydroxyl-ion in solution, which accumulates (cf. p. 529) and forms sodium hydroxide; chlorine is liberated at the anode. It is very important to keep the electrolysis products from mixing, for if they do, the sodium hydroxide will react with the chlorine to form NaCl and NaClO:

$$Cl_2 + 2NaOH = NaCl + NaClO + H_2O$$

There are several ways of preventing the chlorine from penetrating into the sodium hydroxide solution. The most commonly used is

the **diaphragm method**, in which the anode and cathode chambers are separated by means of an asbestos partition. In electrolytic baths used for the manufacture of sodium hydroxide according to this method (Fig. 145) a vertical diaphragm *1*, fitting tightly against the perforated iron cathode *2*, separates the anode chamber *3* from the cathode chamber *4*. The anodes *5* are graphite rods. As electrolysis proceeds a NaCl solution flows continuously into the anode chamber and a solution containing a mixture of NaCl and NaOH keeps flowing out of the cathode chamber. NaCl is then crystallized out by evaporation, leaving an almost pure solution of alkali. The latter is decanted from the NaCl and evaporated to remove all the water. The resulting NaOH is melted and poured into moulds. The by-products in the manufacture of sodium hydroxide are chlorine and hydrogen.

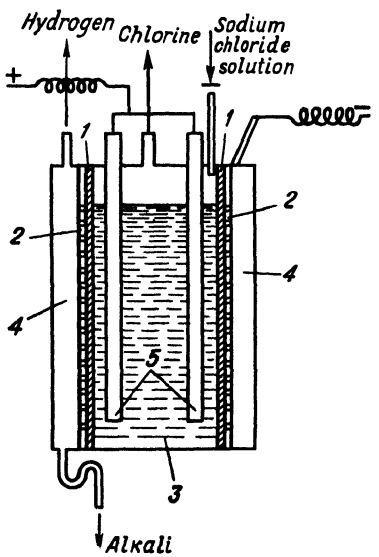


Fig. 145. Diagram of electrolytic bath with vertical diaphragm: *1*—diaphragm; *2*—cathode; *3*—anode chamber; *4*—cathode chamber; *5*—anodes

Electrolysis of the NaCl solution proceeds somewhat differently if metallic mercury is used as the cathode. In this case sodium ions are discharged at the cathode instead of hydrogen ions. The sodium liberated dissolves in the mercury, forming a liquid alloy, called sodium amalgam.* The amalgam is easily decomposed by hot water into sodium hydroxide, hydrogen and mercury. Thus, with mercury as the cathode, absolutely pure sodium hydroxide can be obtained, containing no admixtures of undecomposed sodium chloride.

Fig. 146 shows the diagram of an arrangement for the preparation of sodium hydroxide by the mercury method. The apparatus consists of two vessels, namely, the electrolyzer *1*, in which the sodium amalgam is formed, and the decomposer *2*, in which sodium hydroxide is obtained and hydrogen liberated. The bottom of the electrolyzer is covered with a layer of mercury. A saturated solution of sodium chloride enters the electrolyzer continuously at one side, and an impoverished solution containing less NaCl is discharged at the other. The chlorine liberated is discharged at the top, while the sodium amalgam keeps flowing continuously into the decomposer *2*, where it is broken

* Containing less sodium than the solid amalgam mentioned on p. 552.

down by the hot water entering it. The resulting alkali solution flows out through a special outlet, while the hydrogen is discharged through a pipe at the top of the decomposer. The regenerated mercury is returned to the electrolyzer *1* by means of a mercury elevator.

Besides the electrolytic method for the manufacture of caustic soda, another, older, method is sometimes employed, consisting in boiling a solution of soda with slaked lime

$$Na_2CO_3 + Ca(OH)_2 \rightarrow \downarrow CaCO_3 + 2NaOH$$

When the reaction is over, the solution is decanted from the calcium carbonate precipitate and the water evaporated, after which the resulting sodium hydroxide is fused.

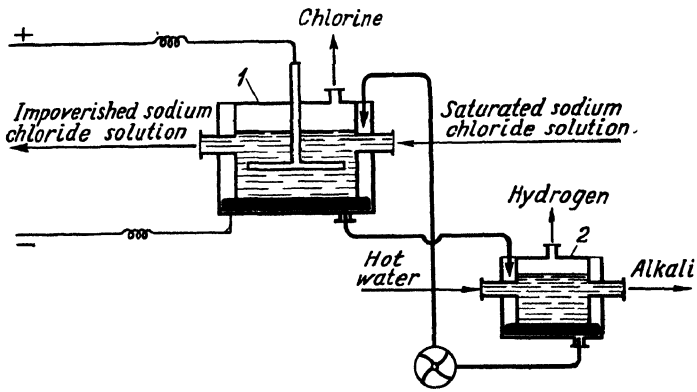


Fig. 146. Diagram of apparatus for preparation of caustic soda by the mercury method

Sodium hydroxide is one of the most important products of the basic chemical industry. The yearly world output (not counting the U.S.S.R.) exceeds 6.5 million tons. It is usually known in commerce as caustic soda. Enormous quantities of caustic soda are consumed by the oil industry, where NaOH is employed for the purification of refined oil products, in the soap industry, in the manufacture of paper, textiles, artificial silk and in a number of other processes.

Sodium Salts. Sodium forms salts with all the known acids.

As the most important salts of sodium and their uses have been described already when discussing the corresponding acids, they are only enumerated below.

NaCl—sodium chloride or common (table) salt (p. 314).

Na_2S—sodium sulphide (p. 349).

$Na_2SO_4 \cdot 10H_2O$—decahydrous sodium sulphate, or Glauber's salt (p. 356).

$NaNO_3$—sodium nitrate or Chile saltpetre (p. 394).
$Na_2CO_3 \cdot 10H_2O$—sodium carbonate or soda (p. 425).
Na_2SiO_3—sodium silicate, water glass (p. 481).
$Na_2S_2O_3 \cdot 5H_2O$—sodium thiosulphate or "hypo" (p. 352).

Very many sodium salts form crystal hydrates containing considerable quantities of crystallization water.

All sodium salts will colour a gas flame yellow. This reaction makes it possible to detect the presence of very insignificant quantities of sodium in any substance.

209. Potassium (Kalium); at. wt. 39.100. In external appearance as well as in physical and chemical properties potassium is very similar to sodium, but is even more active. Like sodium it is silvery white in colour, melts at a low temperature, oxidizes rapidly in the air and reacts violently with water liberating hydrogen.



Fig. 147. Influence of potassium salt content in soil on development of oats

Potassium hydroxide, or *caustic potash* is prepared analogously to caustic soda, by the electrolysis of potassium chloride solutions.

Although its action is the same as that of sodium hydroxide, it is used much more rarely than NaOH, owing to its higher cost. The chief consumer of potassium hydroxide is the soap industry, where KOH is used for the preparation of liquid green soap.

Potassium salts greatly resemble sodium salts. They usually crystallize out of solution without any water of hydration, while many sodium salts contain crystallization water.

If introduced into a gas flame potassium salts give a characteristic reddish-violet colour. If the salt has even an insignificant admixture of sodium, this colour is easily masked by the yellow colouring characteristic of the latter metal. However, the colouring due to the potassium becomes quite visible if the flame is observed through a blue glass which absorbs yellow rays.

Potassium salts play an important part in agriculture. Potassium is one of the indispensable elements for plant nutrition. The importance of potassium salts for plants has been established by many experiments and observations. Fig. 147, for instance, illustrates the influence of potassium on the development of oats. The oats were

planted in two pots, one of which (the left in the figure) was filled with soil devoid of potassium salts, while the soil in the other pot contained them. The results of the experiment are self-explanatory.

Although the soil contains quite considerable quantities of potassium, the latter is removed from it also in large quantities by certain cultivated plants. An especially large amount of potassium is consumed by flax, hemp and tobacco.

Potassium deposits chiefly in the stems of plants, and therefore, fertilizing the soil with manure mixed with straw supplements the potassium deficiency to a certain extent. But as the stalks of the above-mentioned plants are used for industrial purposes, a large part of the potassium is, in the long run, removed from the soil, and to supplement it potassium fertilizers have to be added.

The sources of raw materials for the production of potassium fertilizers are natural deposits of potassium salts.

Such deposits have been found in the U.S.S.R. at Solikamsk. Layers of salt, consisting mainly of the minerals carnallite $KCl \cdot MgCl_2 \cdot 6H_2O$ and sylvinite $KCl \cdot NaCl$ occur over a large area between the upper reaches of the Kama and the Ural foothills.

The Solikamsk deposits were discovered in the twenties of this century. In 1933 an immense potassium mine equipped with up-to-date machinery was built and put into operation. Since then the extraction of potassium salts has been increasing from year to year.

The explored reserves of the Solikamsk deposits are well above the reserves of potassium salts in all the rest of the world and ensure a quite sufficient supply of potassium fertilizers for U.S.S.R. agriculture.

COPPER SUBGROUP

Element	Symbol	Atomic weight	Atomic number	Arrangement of electrons in layers					
Copper . . .	Cu	63.54	29	2	8	18	1		
Silver . . .	Ag	107.880	47	2	8	18	18	1	
Gold	Au	197.0	79	2	8	18	32	18	1

210. General Features of the Copper Subgroup. The copper subgroup includes three elements, *copper*, *silver* and *gold*, which begin the odd series of the long periods in the Mendeleyev Table. Like the alkali metals, all three elements have one electron each in the outermost layer of their atoms; their second last electron layer, however, has

a different structure, consisting of eighteen electrons, whereas in the atoms of the alkali metals, except lithium, this layer has only eight electrons.

The difference in structure of the second last layer accounts for the rather pronounced difference in the properties of the elements of these subgroups, depending, apparently, on the relative sizes of their atoms. In Table 29 the atomic radii and ionization potentials of the elements of the copper subgroup are compared with those of the alkali metals located in the same periods.

Table 29

Atomic Radii and Ionization Potentials of the Copper Subgroup and the Alkali Metals

Element	Atomic radius, Å	Ionization potential, V	Element	Atomic radius, Å	Ionization potential, V
Copper	1.27	7.72	Potassium . . .	2.36	4.32
Silver	1.44	7.51	Rubidium . . .	2.53	4.10
Gold	1.44	9.22	Caesium	2.74	3.87

The data given in this table show that in the atoms of copper, silver and gold the outer electron is much closer to the nucleus and must therefore be attracted by it more strongly than in the atoms of the corresponding alkali metals. Accordingly, the ionization potential, i. e., the energy that has to be expended to tear the electron away from the atom, is much higher in the copper subgroup elements than in the alkali metals. Indeed, the alkali metals part with their outer electron very readily, whereas the elements of the copper subgroup hold on to it rather tenaciously. That is why they are much more difficult to oxidize, and their ions, on the other hand, more easy to reduce; they do not decompose water, their hydroxides are comparatively weak bases, etc. At the same time, the 18-electron layer, stable in other elements, is not quite so in these elements, and is capable of yielding some of its electrons. Thus, besides its univalent cations, copper also forms bivalent cations, which are even more characteristic of this metal. Likewise, the most characteristic compounds of gold are those in which it is trivalent. Silver is usually univalent in its compounds, but may sometimes be bi- or trivalent.

211. Copper (Cuprum); at. wt. 63.54. Copper occurs occasionally in the native state, but is found mainly as compounds. The most important copper ores are *chalcopyrite* (or copper pyrite) $CuFeS_2$, *chalcocite* (copper glance) Cu_2S, *cuprite* (red copper ore) Cu_2O and *malachite* $CuCO_3 \cdot Cu(OH)_2$. The total content of copper in the earth's crust is comparatively low; it does not exceed 0.01 per cent.

High-grade copper deposits have been found in the Urals, in Kazakhstan, in the Armenian and Uzbek S.S.R. In 1928 one of the largest copper deposits in the world, the Kounrad deposit, was discovered near Lake Balkhash in Kazakhstan. During the years of the Second and Third Five-Year plans the Balkhash Copper Works arose there, a huge copper plant, unequalled in Europe. Large copper plants have been built also in the Urals and in the Caucasus.

Copper ores often contain so many impurities, that direct extraction of copper from them is uneconomical. Therefore, an especially important item in copper metallurgy is the flotation process for ore concentration, which makes possible the utilization of very low-grade copper ores.

Copper is reduced from its oxide ores by fusing the latter with sulphur-containing materials (sulphide copper ore or pyrite). Treatment of sulphide ores, however, especially when they contain iron, is much more complex. In this case the ore is first roasted to drive off part of the sulphur as SO_2 and to convert the iron sulphide in the ore into ferrous oxide FeO. The sulphur dioxide obtained in this way is usually utilized for the manufacture of sulphuric acid or for the production of sulphur.

After roasting, the ore is melted with suitable fluxes in shaft or reverberatory furnaces. During this process the greater part of the iron passes into the slag as $FeSiO_3$, while the copper is converted to the sulphide Cu_2S which forms *matte* with the remaining iron sulphide, and accumulates at the bottom of the furnace under a layer of slag.

The matte is then treated in converters, operating on the same general principles as those used for the production of steel (p. 655), to burn the remaining iron out of it. For this purpose air is blown through the molten matte in the converter after adding a precalculated amount of sand.

The chemical processes taking place in the converter are rather complex. The iron sulphide contained in the matte is converted into ferrous oxide and removed as a silicate slag

$$2FeS + 3O_2 = 2FeO + 2SO_2$$
$$2FeO + 2SiO_2 = 2FeSiO_3$$

The copper is reduced to the metal, probably, as a result of the following reactions:

$$2Cu_2S + 3O_2 = 2Cu_2O + 2SO_2$$
$$2Cu_2O + Cu_2S = 6Cu + SO_2$$

The heat released during this reaction maintains a temperature of 1,100 to 1,200° C in the converter, making the use of fuel unnecessary.

Air is blown through until all the copper is reduced, the end point being determined by the appearance of the flame coming out of the converter. The molten copper is poured out of the converter into steel moulds, in which it solidifies as thick slabs.

The raw or *blister* copper smelted from the ore still contains between 2 and 3 per cent of various impurities (zinc, nickel, iron, lead, silver, gold, etc.) and requires further purification, or refining, which is

carried out by the so-called dry, or furnace, method, usually followed by electrolysis.

Furnace refining of blister copper consists in melting it in a stream of air. Part of the copper is oxidized to Cu_2O, which dissolves in the molten copper and yields its oxygen for the oxidation of the base metal impurities. The excess of Cu_2O formed is reduced by introducing green wood or reducing gases into the molten mass. The result is refined copper containing only about 0.5 per cent impurities and suitable for the preparation of bronzes, brasses and other alloys.

For most purposes, and chiefly for the manufacture of electric wires, the copper must be very pure, as even insignificant impurities greatly decrease its electrical conductivity, resulting in power losses when electricity is transmitted through the wires. Very pure copper is obtained from furnace refined copper by electrolysis.

For electrolytic refining the furnace refined copper is cast into thick anode plates which are hung in a bath containing copper sulphate solution and connected with the anode of a current source. The cathodes are thin plates of pure copper inserted in the gaps between the anode plates and covered with graphite to facilitate removal of the copper deposited during electrolysis. Electrolysis is carried out at a very low voltage, not over 0.4 volt. Under such conditions only copper ions and ions of the metals above copper in the electrochemical series (zinc, iron, nickel, etc.) pass into solution from the anode. All the other impurities contained in the blister copper sink to the bottom of the bath as a precipitate, known as anode slime. Owing to the low voltage, only copper ions are discharged at the cathode, and thus the latter becomes coated with pure copper. Silver, gold, selenium and other valuable elements are extracted from the anode slime. The value of these substances is often high enough to cover all the costs of production, and therefore copper containing noble and rare elements is always refined electrolytically.

Pure copper is a ductile tough metal of a light red colour readily rolled into thin sheets. The specific gravity of copper is 8.9 and its melting point is 1,083.2° C. Copper is an excellent conductor of heat and electricity, second only to silver in this respect. In dry air copper hardly undergoes any change, as the very thin oxide film which forms on its surface (and darkens the copper) protects it effectively from further oxidation; but in the presence of moisture and carbon dioxide, the surface of copper becomes coated with a greenish deposit of basic copper carbonate $Cu_2(OH)_2CO_3$. If heated in air copper turns into black cupric oxide which decomposes at a higher temperature, losing oxygen and passing into cuprous oxide Cu_2O.

Owing to its high thermal and electrical conductivity, malleability, good casting properties, high tensile strength and resistance to

corrosion, copper is widely used in industry, being second in extensiveness of application only to iron. In 1954 the copper extracted in the capitalist countries amounted to 2.5 million tons.

Immense quantities of pure electrolytic copper (about 40 per cent of the entire copper output) are used for making electric wires and cables. More or less pure copper is employed to manufacture various industrial apparatuses, such as boilers, evaporation tanks, stills, etc. Various alloys, containing copper in combination with other metals, are widely used in machine-building, as well as electrical engineering and other branches of industry. The most important of these alloys are *brasses* (alloys of copper and zinc), *bronzes* (alloys of copper and tin), *nickel silver* (65 per cent copper, 20 per cent zinc and 15 per cent nickel) and *German silver* (80 per cent copper and 20 per cent nickel) which resemble silver in appearance, *constantan* (60 per cent copper and 40 per cent nickel), used for resistance boxes and thermocouples, and many others.

As to chemical properties, copper is a metal of low activity, although it will unite directly with oxygen, sulphur, the halogens and several other elements.

Situated below hydrogen in the electrochemical series, copper does not displace it from acids. For this reason hydrochloric and dilute sulphuric acids by themselves will not attack copper. However, in the presence of atmospheric oxygen, copper dissolves in them giving the corresponding salts:

$$2Cu + 4HCl + O_2 = 2CuCl_2 + 2H_2O$$

This reaction may be thought of as proceeding in two steps: first, the oxygen oxidizes copper into cupric oxide, then cupric oxide, like any other basic oxide, reacts with hydrochloric acid to form a salt and water. Under such conditions even the weakest acids are capable of gradually dissolving copper. Copper dissolves readily in nitric acid and in concentrated sulphuric acid if heated.

All volatile copper compounds colour the non-luminous flame of a gas burner blue or green.

Copper forms two series of compounds, derivatives, respectively, of its two oxides, cuprous oxide Cu_2O and cupric oxide CuO. In the first series of compounds copper is univalent, in the second, bivalent. The compounds of univalent copper are as a rule less stable than those of bivalent copper and are of little practical importance.

Compounds of Univalent Copper. Cuprous oxide Cu_2O occurs in nature as cuprite, or red copper ore. It can be prepared by heating a solution of any cupric salt with an alkali and some strong reducing agent, say formalin or grape sugar. At first a yellow precipitate appears, with respect to which it has not yet been established whether it is cuprous hydroxide CuOH or an amorphous gel of cuprous oxide. When heated more intensely the precipitate passes into red cuprous oxide.

Cuprous oxide can be prepared also by calcining copper in the air. The black cupric oxide formed at first decomposes at about 800° C into red cuprous oxide.

Hydrochloric acid converts cuprous oxide into a colourless solution of cuprous chloride CuCl. If this solution is poured into water the cuprous chloride precipitates out as white insoluble curds. Cuprous chloride can be obtained also by boiling a solution of $CuCl_2$ with hydrochloric acid and copper turnings:

$$CuCl_2 + Cu = 2CuCl$$

One more stable compound of univalent copper should be mentioned. This is cuprous sulphide Cu_2S, resulting when copper combines directly with sulphur.

Compounds of Bivalent Copper. Cupric oxide CuO is a black substance, usually prepared by heating copper cuttings, filings or turnings in the air to redness. It can easily be obtained also by calcining certain copper salts, such as basic copper carbonate (II) $Cu_2(OH)_2CO_3$ or copper nitrate (II) $Cu(NO_3)_2$.* Cupric oxide is a rather active oxidant. When heated with various organic substances cupric oxide oxidizes them, converting the carbon into carbon dioxide and the hydrogen into water, itself being reduced to metallic copper. This reaction is widely used for the so-called elementary analysis of organic substances for determining their carbon and hydrogen content.

Cupric hydroxide $Cu(OH)_2$ precipitates out of solutions of cupric salts, when treated with alkalis, as a light blue jelly-like mass. If even gently heated and even under water it decomposes into black cupric oxide.

Cupric hydroxide is a very weak base. Therefore, solutions of bivalent copper salts mostly react acid, and with weak acids copper forms basic salts.

The most important salts of bivalent copper are the following:

1. *Copper sulphate* (II) or *cupric sulphate* $CuSO_4$ is a white powder in the anhydrous state but turns blue upon absorbing water, and is for that reason often used to detect traces of moisture in various organic liquids. Aqueous solutions of copper sulphate possess a light blue colour, characteristic of hydrated $[Cu(H_2O)_4]^{\cdot\cdot}$-ion. That is why all dilute solutions of bivalent copper salts have the same colour, unless they contain coloured anions. Copper sulphate crystallizes out of aqueous solutions with five molecules of water, as transparent blue crystals in the triclinic system. In this form it is known as *blue vitriol.*

Blue vitriol is prepared by dissolving copper scrap either in hot concentrated sulphuric acid or in warm dilute sulphuric acid with free

* A Roman numeral in parentheses after the name of the salt is used to denote the valency of the metal (cations) contained in it, when the metal possesses variable valency, and the name of the salt does not indicate which valency is meant. For instance: CuCl is copper chloride (I) or cuprous chloride; $CuCl_2$ is copper chloride (II) or cupric chloride; $Fe_2(SO_4)_3$ is iron sulphate (III) or ferric sulphate, etc.

access of oxygen. Blue vitriol is used for copper plating, for the manufacture of certain mineral paints, as a pesticide for plants in agriculture.

2. *Copper chloride* (II) or *cupric chloride* $CuCl_2 \cdot 2H_2O$ forms dark green crystals, readily soluble in water. Is usually prepared by dissolving basic copper carbonate in hydrochloric acid. Very concentrated solutions of $CuCl_2$ are green in colour, but dilute solutions are blue, as usual. Copper chloride (II) colours a non-luminous gas flame intense green.

3. *Copper nitrate* (II) or *cupric nitrate* $Cu(NO_3)_2 \cdot 3H_2O$ is prepared by dissolving copper in nitric acid. If heated, the blue crystals of copper nitrate first lose water, and then decompose readily, liberating oxygen and brown nitrogen oxide and passing into black cupric oxide. Is used for the preparation of cupric oxide as well as for the manufacture of certain paints.

4. *Basic copper carbonate* (II) $Cu_2(OH)_2CO_3$ is found in nature as the mineral malachite which has a beautiful emerald green colour. Can be synthesized by treating solutions of bivalent copper salts with soda:

$$2CuSO_4 + 2Na_2CO_3 + H_2O = \downarrow Cu_2(OH)_2CO_3 + 2Na_2SO_4 + CO_2$$

Is used for the preparation of cupric chloride, for the manufacture of blue and green mineral paints and in pyrotechnics.

5. *Copper (cupric) acetate* $Cu(CH_3COO)_2 \cdot H_2O$ is prepared by the action of acetic acid on metallic copper or cupric oxide. The commercial product is usually a mixture of basic salts of varying composition and colour (green and bluish green). Is used under the name of *neutral verdigris* for the preparation of oil colours.

The double acetate-arsenite of copper (known as "Paris green") $Cu(CH_3COO)_2 \cdot Cu_3(AsO_3)_2$ is used to destroy agricultural pests.

Copper salts are employed for the manufacture of a large number of mineral paints of various colours: green, blue, brown, violet, and black.

All copper salts are poisonous, and that is why copper pots are tinned on the inside to prevent the formation of copper salts.

Complex Compounds of Copper. A very characteristic property of bivalent copper ions is their ability to combine with ammonia molecules to form what are known as **complex** ions.

If ammonia solution is added to a solution of copper sulphate, the result is a blue precipitate of the basic salt, which dissolves readily in an excess of ammonia, colouring the liquid an intense blue. Addition of an alkali to this solution brings down no $Cu(OH)_2$ precipitate; therefore it must be concluded that the solution contains no $Cu^{\cdot\cdot}$-ion, or contains so little of it, that the solubility product of $Cu(OH)_2$ is not reached even with a high concentration of hydroxyl-ion. Hence, it

follows that the cupric ions react with the ammonia added to form new ions of some kind which give no insoluble compound with OH' ion. At the same time the SO_4'' ions remain unchanged, as can be proved experimentally by adding barium chloride to the ammonia solution, this immediately bringing down a precipitate of $BaSO_4$ (test for SO_4''-ion).

It has been established by investigation that the dark blue colouring of the ammonia solution is due to the presence in it of the complex ions $[Cu(NH_3)_4]^{\cdot\cdot}$, a result of the addition of four ammonia molecules to each cupric ion. If the water is evaporated, the $[Cu(NH_3)_4]^{\cdot\cdot}$ ions combine with the SO_4'' ions, and dark blue crystals separate out of the solution, their composition being represented by the formula $[Cu(NH_3)_4]SO_4 \cdot H_2O$.

Thus, when copper sulphate (II) is treated with ammonia, the following reaction takes place:

$$CuSO_4 + 4NH_3 = [Cu(NH_3)_4]SO_4$$

The ionic equivalent of this reaction is

$$Cu^{\cdot\cdot} + 4NH_3 = [Cu(NH_3)_4]^{\cdot\cdot}$$

Ions which, like $[Cu(NH_3)_4]^{\cdot\cdot}$, *are formed by the addition of neutral molecules or other ions capable of existing independently in solution to the ion in question, are called complex ions.* Salts containing such ions are referred to as **complex salts.** Complex acids and complex bases are also known, these compounds ionizing in solution into complex ions.

In writing the formulas of complex compounds the complex ion is usually enclosed in square brackets. This indicates that when the compound in question is dissolved in water, the complex ion remains in solution without breaking down into its composite parts.

Other salts of bivalent copper react with ammonia in a manner similar to copper sulphate (II). In all such cases the result is a dark blue solution containing the complex ions $[Cu(NH_3)_4]^{\cdot\cdot}$.

Univalent copper combines with ammonia to give colourless complex ions of the composition $[Cu(NH_3)_2]^{\cdot}$.

Cupric hydroxide also dissolves in ammonia, forming a dark blue solution which contains $[Cu(NH_3)_4]^{\cdot\cdot}$-ion and hydroxyl-ion:

$$Cu(OH)_2 + 4NH_3 = [Cu(NH_3)_4]^{\cdot\cdot} + 2OH'$$

The resulting solution is capable of dissolving cellulose (cotton wool, filter paper, etc.). If the cellulose solution is forced through very fine apertures into dilute sulphuric acid, the cellulose separates out again in the form of fine shiny threads. That is how one of the types of artificial silk is made.

Cupric hydroxide dissolves also in very concentrated alkali solutions, forming bluish-violet solutions of cuprites, salts containing the complex ion $[Cu(OH)_4]''$:

$$Cu(OH)_2 + 2NaOH \rightleftarrows Na_2[Cu(OH)_4]$$

or in the ionic form

$$Cu(OH)_2 + 2OH' \rightleftarrows [Cu(OH)_4]''$$

Unlike the copper-ammonia complexes, the $Cu^{\cdot\cdot}$ ions do not add electrically neutral molecules in this case, but four negative OH' ions, forming **complex anions** instead of cations.

Cuprites are very unstable, and if their alkaline solutions are diluted with water they decompose, releasing cupric hydroxide again as a precipitate. Thus, although cupric hydroxide does manifest some acidic properties by dissolving in alkalis, these properties are but slightly pronounced.

Of the other complex anions of bivalent copper, mention should be made of the ions $[CuCl_4]''$, which form in concentrated solutions of cupric chloride and account for their green colouring:

$$CuCl_2 + 2Cl' \rightleftarrows [CuCl_4]''$$

When the solutions are diluted with water, the $[CuCl_4]''$ ions turn into ordinary hydrated cupric ions $[Cu(H_2O)_4]^{\cdot\cdot}$, changing the colour of the solutions from green to blue:

$$[CuCl_4]'' + 4H_2O = [Cu(H_2O)_4]^{\cdot\cdot} + 4Cl'$$

212. Silver (Argentum); at. wt. 107.880. Silver is much less abundant in nature than copper; its content in the earth's crust is only 4×10^{-6} per cent. In some places (for instance in Canada) silver is found in the native state, but most silver is obtained from its compounds. The most important silver ore is *silver glance* (argentite) Ag_2S, followed by *horn silver* (cerargyrite) AgCl. Silver is present in greater or smaller amounts as an isomorphic admixture in almost all copper, and especially lead, ores. In the U.S.S.R. silver is extracted from silver-lead ores, deposits of which have been found in the Urals, the Altai, the Northern Caucasus, Kazakhstan and some other places.

The world production of silver in 1953 amounted to 5,900 tons (not counting the U.S.S.R.).

When treating copper and lead ores containing silver, the latter is extracte in the free state together with the chief metals. It is usually separated from the copper in the process of electrolytic refining (see p. 560). To extract silver from its alloys with lead one of the following two methods is employed.

The first method consists in melting the lead containing the silver and then allowing it to cool slowly. As the alloy cools, crystals of pure lead appear on its surface and are ladled out. After the residue has thus become enriched in silver,

it is oxidized by passing a powerful blast of air through it. The lead is then oxidized into lead oxide, while the silver remains unoxidized.

The second method is based on the fact that molten zinc does not mix with molten lead, while silver dissolves much better in molten zinc than in lead.

When zinc is added to molten lead containing silver, the latter passes almost entirely into the zinc, which is then ladled out and distilled. The silver left after the zinc has been distilled off is purified from a minor admixture of lead in the same way as in the first method.

Pure silver is a very soft, ductile metal having a specific gravity of 10.49 and a melting point of 960.8° C. It is the best conductor of heat and electricity among the metals.

Silver is not used in the pure form for practical purposes due to its softness. It is usually alloyed with a greater or smaller amount of copper. Silver alloys are used to make domestic utensils, jewellery and silver coins. The content of silver in alloys is indicated by its **standard**. The standard shows how many parts of pure silver are contained in 1,000 parts of the alloy. In the U.S.S.R. silver wares are made of silver of the 875 standard, i. e., containing 87.5 per cent silver and 12.5 per cent copper. A considerable part of the silver mined is used for plating other metals, which is accomplished at present only galvanically.

Silver is one of the least active metals and is situated almost at the bottom of the electrochemical series. It is not oxidized in the air at ordinary temperatures or even when heated. The blackening of silver objects frequently observed, is due to the formation of black silver sulphide Ag_2S under the influence of hydrogen sulphide contained in the air and also due to contact with food products containing sulphur compounds.

Hydrochloric and dilute sulphuric acids do not attack silver. It is usually dissolved in nitric acid.

Silver forms only one series of salts, the solutions of which contain colourless Ag^+ cations.

Silver oxide Ag_2O. When solutions of silver salts are treated with alkalis one would expect to obtain silver hydroxide AgOH, but instead, a brown precipitate of silver oxide is thrown down:

$$2AgNO_3 + 2NaOH = 2NaNO_3 + Ag_2O + H_2O$$

Silver oxide dissolves perceptibly in a large quantity of water imparting alkaline properties to the solution. Such a solution will colour litmus blue and, like alkalis, precipitates the hydroxide of many metals from solutions of their salts. Obviously, the solution contains some amount of silver hydroxide AgOH, which is quite a strong base. This is confirmed also by the fact that silver salts are not hydrolyzed.

Another oxide of silver is *silver peroxide* Ag_2O_2 which forms under the action of ozone.

The most important silver salts are the following:

1. *Silver nitrate* $AgNO_3$, known also as *lunar caustic*, forms colourless crystals, readily soluble in water. It is prepared by dissolving silver in nitric acid and is employed in medicine for cauterization, as silver-ion oxidizes organic substances, itself being reduced to metallic silver. It serves as a raw material for the preparation of other silver compounds, is used in the photographic industry, in the manufacture of mirrors and in galvanoplastics.

2. *Silver chloride* AgCl forms as a white curdy precipitate, insoluble in water and acids, whenever $Ag^{\cdot}$-ion encounters Cl'-ion. In the light, silver chloride gradually darkens, due to decomposition, during which metallic silver is liberated. Silver bromide and iodide possess similar properties, but, unlike silver chloride, these two compounds are yellowish in colour. On the contrary, silver fluoride AgF is soluble in water.

Complex Compounds of Silver. Like copper, silver possesses a pronounced tendency to form complex compounds.

Many silver compounds, such as Ag_2O, AgCl and others, though insoluble in water, dissolve readily in ammonia solution. The reason for their dissolving is the formation of complex ammonia-silver ions $[Ag(NH_3)_2]^{\cdot}$ when ammonia molecules encounter silver ions.

In the case, say, of silver chloride, the reaction can be represented as follows:

$$\underset{\text{precipitate}}{AgCl} \rightleftarrows \underset{\text{solution}}{Ag^{\cdot} + Cl'}$$
$$+$$
$$2NH_3$$
$$\downarrow$$
$$[Ag^{\cdot}(NH_3)_2]^{\cdot}$$

A certain quantity of $Ag^{\cdot}$ ions passes into solution from the silver chloride, and a dynamic equilibrium is established between them and the precipitate. When ammonia is added, its molecules combine with the silver ions into complex $[Ag(NH_3)_2]^{\cdot}$ ions, and the equilibrium begins to shift continuously to the right until the entire precipitate dissolves. Thus, in ammonia solution silver exists as the complex cations $[Ag(NH_3)_2]^{\cdot}$. But together with them, there is always a certain, albeit insignificant, amount of $Ag^{\cdot}$-ion left in the solution due to ionization of the complex ion according to the equation

$$[Ag(NH_3)_2]^{\cdot} \rightleftarrows Ag^{\cdot} + 2NH_3$$

If the solution is treated with an alkali, no precipitate will result, though solutions of ordinary silver salts, as we have seen above, immediately give a precipitate of Ag_2O. Evidently, the concentration

of silver-ion in the ammonia solution is too small for the solubility product value of AgOH ($SP_{AgOH}=2\times10^{-8}$) to be reached, even if an excess of hydroxyl-ion is introduced. However, if potassium iodide is added, a precipitate of silver iodide will be thrown down. This shows that $Ag^{\cdot}$-ion is present in solution. No matter how small its concentration, it proves to be high enough to form this precipitate, as the solubility product of AgI is only 1×10^{-16}, i. e., much smaller than that of AgOH. Likewise, hydrogen sulphide gives a precipitate of Ag_2S, as the solubility product of the latter equals 1×10^{-49}.

According to the above equation, the ionization of $[Ag(NH_3)_2]^{\cdot}$ ions, like the ionization of any other weak electrolyte, obeys the Law of Mass Action and can be characterized by a corresponding constant referred to as the **instability constant** of the complex ion:

$$K_{inst.}=\frac{[Ag^{\cdot}]\cdot[NH_3]^2}{[Ag(NH_3)_2^{\cdot}]}=6.8\times10^{-8}$$

The instability constants of various complex ions differ greatly and may serve as a measure of the stability of the complex.

Especially stable complex anions result when $Ag^{\cdot}$ ions unite with CN' ions.

If potassium cyanide is added to an $AgNO_3$ solution, a white precipitate of silver cyanide results:

$$Ag^{\cdot}+CN'=\downarrow AgCN$$

In an excess of potassium cyanide the precipitate dissolves readily, passing into the complex salt $K[Ag(CN)_2]$ which exists in solution in the form of the ions $K^{\cdot}$ and $[Ag(CN)_2]'$:

$$AgCN+KCN=K[Ag(CN)_2]$$

or its ionic equivalent

$$AgCN+CN'=[Ag(CN)_2]'$$

If the solution is evaporated, $K[Ag(CN)_2]$ crystallizes out in the solid state.

$[Ag(CN)_2]'$-ion is very stable; its instability constant is 1×10^{-21}. Therefore, even the addition of potassium iodide to a solution of $K[Ag(CN)_2]$ will not cause AgI to precipitate out. But if acted on with hydrogen sulphide, a precipitate of Ag_2S separates, owing to the exceedingly low solubility product of silver sulphide.

Complex argenticyanide compounds are used for galvanic silver plating, as solutions of ordinary silver salts, when electrolyzed, do not give dense adherent layers. When current is passed through the argenticyanide solution, silver deposits on the cathode at the expense of the insignificant quantity of $Ag^{\cdot}$-ion formed due to ionization of

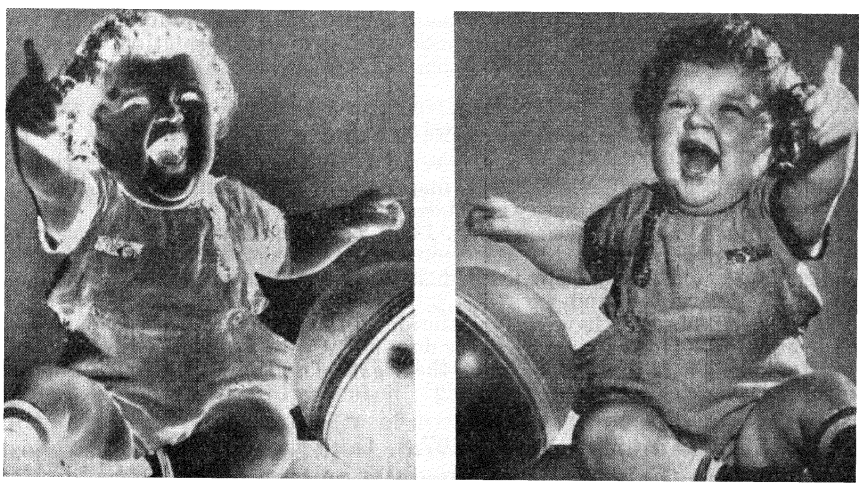
the complex anion:

$$[Ag(CN)_2]' \rightleftarrows Ag^{\bullet} + 2CN$$

All silver compounds are readily reducible, liberating metallic silver.

If a little glucose or formalin is added as a reducing agent to an ammonia solution of silver oxide in a glass vessel, metallic silver is deposited as a dense shiny mirror-like layer on the surface of the glass. This method is now employed for the manufacture of mirrors as well as for silver plating the interiors of the glass vessels used in thermos bottles to decrease heat losses due to radiation.

Photography. Silver salts, especially the chloride and the bromide, owing to their ability to decompose under the action of light with the liberation of metallic silver, are widely used in photography for the preparation of sensitized plates, films and papers.



a *b*

Fig. 148. Negative (*a*) and positive (*b*)

Photographic plates and films are prepared as follows. A certain amount of gelatine is added to a warm solution of silver nitrate, which is then mixed with a solution of KBr. Silver bromide and potassium nitrate form according to the equation:

$$AgNO_3 + KBr = AgBr + KNO_3$$

Owing to the protective action of the gelatine, the silver bromide does not precipitate, but remains suspended in a very finely divided state. The resulting turbid liquid is referred to as "silver bromide emulsion" (though it would be more correct to call it a suspension). As AgBr is not sensitive enough when very finely

divided, the emulsion is left standing for a time in a warm place until it becomes *ripe*, i. e., until the degree of dispersity of the silver bromide decreases and larger particles are formed; this increases the sensitivity of the AgBr by hundreds of times.

After ripening, the emulsion is cooled, and the resulting gelatine jelly is crushed and washed with water to remove the KNO_3. Then it is melted and applied to glass plates or celluloid films. All these processes are carried out in red light which does not act on silver bromide.

If a photographic plate is exposed to light it darkens very slowly. However, this process can be greatly accelerated by the action on the plate of various substances called *developers*. It is remarkable that a developer is capable of decomposing (reducing) silver bromide only after the latter has been exposed to light for at least a very short time (fractions of a second).

To obtain an image of any subject on a photographic plate, the latter is placed in a camera and is exposed for a very short time to the rays admitted by the lens (rather, by a system of converging lenses) of the camera, which throw an image of the subject onto the plate. If the plate is then immersed in a developer solution (this being done in a dark room by red light) the exposed parts of the plate darken rapidly, and the image of the subject photographed appears on the plate. This process is called *developing*. After the image has been developed, it is fixed by immersing the plate in a solution of sodium thiosulphate (hypo) $Na_2S_2O_3$. The undecomposed silver bromide dissolves in this solution, the silver and thiosulphate ions combining into complex ions, probably of the composition $[Ag(S_2O_3)]'$:

$$Ag^{\cdot} + S_2O_3'' = [Ag\,(S_2O_3)]'$$

This gives the *negative*, a reversed image, on which the light parts of the subject appear dark and vice versa (Fig. 148*a*).

The normal image or *positive* (Fig. 148*b*) can be printed from the negative on sensitized paper, prepared in the same manner as the plate. For this purpose the negative is placed on the paper and exposed to light for a short time, then the paper is developed and fixed.

Some types of paper have silver chloride in their sensitized layer instead of silver bromide. Printing on such paper does not require subsequent developing, the paper being held in the light under the negative until a visible image appears on it, after which the print is fixed.

213. Gold (Aurum); at. wt. 197.0. Gold occurs in nature almost exclusively in the native state, mainly, as tiny grains embedded in quartz or mixed with quartz sand. The only natural compound of gold is *gold telluride* $AuTe_2$. Minor amounts of gold are contained in iron, lead and copper sulphide ores. Traces of gold have been detected in sea water. The total gold content in the earth's crust is estimated at 5×10^{-7} per cent.

The U.S.S.R. has gold deposits in Siberia and the Urals. Major gold deposits have been discovered in South Africa, Alaska, Canada and Australia.

The gold is separated from the sand or ground quartz rock either by washing with water, which carries off the sand particles as the lighter fraction, or by treating the sand with various liquids capable of dissolving gold. The most commonly used liquid is a solution of

sodium cyanide NaCN, which dissolves gold in the presence of oxygen, converting it into the complex anion $[Au(CN)_2]'$:

$$4Au + 8CN' + O_2 + 2H_2O = 4[Au(CN)_2]' + 4OH'$$

Gold is usually extracted from the resulting solution by means of zinc filings:

$$2[Au(CN)_2]' + Zn = [Zn(CN)_4]'' + 2Au$$

The precipitated gold is treated with dilute sulphuric acid to separate it from the zinc; then it is washed, dried and freed from impurities (mainly silver) by treatment with not concentrated sulphuric acid or by electrolysis.

The method of extracting gold from its ores by dissolving in potassium or sodium cyanide solutions (known as the cyanide method) was discovered in 1843 by the Russian engineer P. Bagration. This method is now the most widely used in gold metallurgy.

The world gold output in 1953 (not counting the U.S.S.R.) totalled 752 tons.

Pure gold is a bright yellow lustrous metal with a specific gravity of 19.3 and a melting point of 1,063° C. Gold is very malleable and ductile; it can be rolled into leaves less than 0.0002 mm. thick, and one gram of gold can be drawn out into a thread 3.420 metres long. Gold is an excellent conductor of heat and electricity, being inferior in this respect only to silver and copper.

Owing to its softness gold is used only in alloys, usually with silver or copper. Gold wares usually contain about 58 per cent gold, and coins about 90 per cent.

Chemically gold is an inactive metal. In the air it does not change at all even if strongly heated. The acids taken separately do not attack gold, but a mixture of hydrochloric and nitric acids (aqua regia) dissolves it readily, converting it into $AuCl_3$ (rather, into $H[AuCl_4]$). Gold dissolves just as readily in chlorine water and in the solutions of the alkali cyanides. Mercury also dissolves gold, forming an amalgam, which is a solid if the gold content exceeds 15 per cent.

Gold forms two oxides, *aurous oxide* Au_2O and *auric oxide* Au_2O_3, and two corresponding series of compounds. The most important and stable compounds are those of trivalent gold (the auric series).

When dissolved in aqua regia gold passes into chloroauric acid $H[AuCl_4]$, a complex compound crystallizing into yellow needle-like prisms with four molecules of water (the usual commercial gold preparation). This acid gives distinctly crystalline salts, such as $Na[AuCl_4]$, the solutions of which contain gold as the complex anion $[AuCl_4]'$.

If $H[AuCl_4]$ is gently heated, HCl is driven off and *gold chloride* (III) or *auric chloride* $AuCl_3$ drops out as reddish-brown crystals.

Alkalis react with solutions of chloroauric acid, precipitating brown *auric hydroxide* $Au(OH)_3$, known also as *auric acid*, as it possesses weak acidic properties and forms salts. At 100° C $Au(OH)_3$ loses water and passes into brown auric oxide Au_2O_3.

If gold chloride (III) is heated in a stream of carbon dioxide to 180° C, *gold chloride* (I) or *aurous chloride* AuCl results, this being a white substance, slightly soluble in water. From solutions of AuCl alkalis precipitate violet aurous oxide Au_2O.

All gold compounds decompose readily when heated, liberating metallic gold.

CHAPTER XX

Theory of Formation of Complex Compounds

214. Structure of Complex Compounds. In discussing the elements of the copper subgroup we saw that the ions of these elements are capable of combining with other ions or neutral molecules (such as NH_3) to form more elaborate "complex" ions. If water is evaporated from solutions containing complex ions, the latter combine with the ions of the opposite sign present in the solution, producing various "complex compounds."

The formation of complex compounds cannot be explained from the standpoint of the conventional theory of valency. Their composition is far from conforming with the valency number employed in deriving the formulas of the simpler "binary" compounds, i.e., compounds consisting of only two elements. For this reason fruitful study of complex compounds became possible only after certain new conceptions of valency bonds had been introduced into chemistry. These conceptions form the basis of the theory of complex compounds suggested in 1893 by Alfred Werner (1866-1919), a professor of the Zürich University. This theory is now known as the **Coordination Theory.**

According to the coordination theory one of the ions in the molecule of any complex compound (usually possessing a positive charge) occupies a central position and is called the **complex former** or central ion. In the direct vicinity around it are arranged, or as we say **coordinated**, a certain number of ions with charges opposite to that of the central ion or electrically neutral molecules, called addends and forming the **inner coordination sphere** of the compound. The rest of the ions, not contained in the inner sphere, are farther away from the central ion and constitute the **outer coordination sphere.**

Fig. 149 shows diagrammatically the structure of the complex salt $K_2[PtCl_6]$. The complex former in this case is the Pt^{4+} ion and the addends are the Cl^- ions. The outer coordination sphere contains K^+ ions.

To distinguish between the inner and outer spheres in formulas of complex compounds, the addends are enclosed in square brackets together with the complex former.

When a complex compound dissolves in water the outer sphere ions split off. For this reason their bond with the central ion is called **ionogenous**. On the other hand, the ions or molecules coordinated in the inner sphere (the addends) remain bound to the central ion, forming a stable, non-dissociating (or almost so) complex ion. For instance, $K_2[PtCl_6]$ ionizes according to the equation:

$$K_2[PtCl_6] = 2K^+ + [PtCl_6]''$$

In most cases complex compounds result from reactions between substances in aqueous solutions. But sometimes the complex compound may form under other conditions. For instance, anhydrous

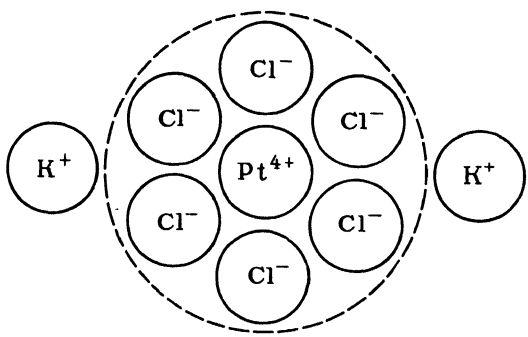


Fig. 149. Structure of $K_2(PtCl_6)$

calcium chloride combines directly with ammonia into the complex salt $[Ca(NH_3)_8]Cl_2$.

The question as to which of the ions contained in the complex compound belong to the inner sphere and which to the outer, is solved by studying the properties of the compound. Consider, for instance, the structure of the following complex compounds of platinum as explained by the coordination theory:

$$PtCl_4 \cdot 6NH_3; \quad PtCl_4 \cdot 4NH_3; \quad PtCl_4 \cdot 2NH_3; \quad PtCl_4 \cdot 2KCl$$

The first of these compounds, $PtCl_4 \cdot 6NH_3$, is an electrolyte, ionized in solution. If treated with silver nitrate, all the chlorine contained in it is precipitated as silver chloride. Apparently, all four chloride ions are in the outer sphere of the compound, as they are easily split off in solution; therefore, the inner sphere consists only of ammonia molecules. The structure attributed to this compound is therefore $[Pt(NH_3)_6]Cl_4$.

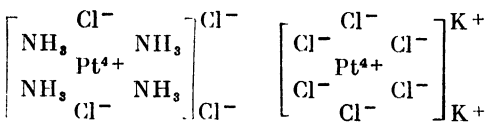
The second compound, $PtCl_4 \cdot 4NH_3$, is also an electrolyte, but the electrical conductivity of its solution is lower than that of the first compound in solution; hence, it forms less ions. Silver nitrate

will precipitate only half the chlorine (i.e., two ions of the four). The structure of this compound should therefore be represented as $[Pt(NH_3)_4Cl_2]Cl_2$. As there are only two chloride ions in the outer sphere, only they can split off in solution and be precipitated by silver nitrate. The other two chloride ions are included together with the four ammonia molecules in the composition of the inner sphere and remain linked to the platinum ion in solution.

The third compound, $PtCl_4 \cdot 2NH_3$, is a non-electrolyte. Its solution practically does not conduct current and gives no precipitate with silver nitrate; hence it must be concluded that all four chloride ions are part of the inner sphere, together with the two ammonia molecules. The structure of this compound is expressed by the formula $[Pt(NH_3)_2Cl_4]$. As the outer sphere does not contain a single ion, this compound will not split off any ions when dissolved.

Finally, the last compound indicated, $PtCl_4 \cdot 2KCl$, though an electrolyte, gives no silver chloride precipitate when its solutions are treated with silver nitrate. It can be established by exchange reactions that the solution contains potassium ions. On these grounds, the structure of this compound should be represented by the formula $K_2[PtCl_6]$. In this case all six chloride ions are in the inner sphere, whereas the outer sphere consists only of two potassium ions.

To give a more graphic idea of the structure of complex compounds they are often represented by elaborated structural formulas, such as:



$[Pt(NH_3)_4Cl_2]\,Cl_2$ $\qquad$ $K_2\,[PtCl_6]$

The total number of neutral molecules and ions linked to the central ion in the complex compound is called the **coordination number** of the complex former. For instance, in the platinum compounds shown above, the coordination number of the complex former, which in this case is the Pt^{4+} ion, equals six. The coordination number plays a no less important part in the chemistry of complex compounds than the valency numbers of atoms (ions), and is just as fundamental a property of the latter as valency. The coordination number depends mainly on the size, charge and electron shell structure of the complex former. The most common coordination number is 6; it is found, for instance, in iron, chromium, zinc, nickel, cobalt, tetravalent platinum; a coordination number of 4 is characteristic of bivalent copper, trivalent gold, bivalent mercury and cadmium. Other coordinations are sometimes also encountered, but much less frequently (for instance 2 in the case of silver and univalent copper).

Like valency, which does not always manifest itself in full in the compounds of an element, the coordination number of a complex former may also at times be smaller than usual. Compounds in which the maximum coordination number characteristic of the given ion is not attained, are termed **coordinationally unsaturated.** Such compounds are comparatively scarce among typical complex compounds.

The charge on a complex ion equals the algebraic sum of the charges on its constituent simple ions. For example:

$$Ag^{\cdot} + 2CN' = [Ag(CN)_2]' \ (+1-2=-1)$$
$$Pt^{\cdot\cdot\cdot\cdot} + 6Cl' = [PtCl_6]'' \ (+4-6=-2)$$

The electrically neutral molecules contained in a complex ion, such as NH_3, NO, etc., do not influence its charge. Therefore, in determining the charge of a complex ion these molecules need not be taken into account. If the entire inner coordination sphere consists of neutral molecules only, the charge on the complex ion equals that on the complex former, for example:

$$Cu^{\cdot\cdot} + 4NH_3 = [Cu(NH_3)_4]^{\cdot\cdot}$$

The charge on a complex ion can be judged also by the charges on the ions contained in the outer coordination sphere. For instance, in the compound $K_4[Fe(CN)_6]$ the charge on the complex ion $[Fe(CN)_6]''''$ equals -4, as the outer sphere contains four positive singly charged potassium ions, whereas the molecule as a whole is electrically neutral. Hence, the charge on the complex former is, in its turn, also easy to determine, if we know the charges on the rest of the ions contained in the complex compound.

Neutral molecules contained in the inner coordination sphere of a complex compound can be successively displaced by other molecules or negative ions. For example, substituting the ammonia molecules in the complex cobalt salt $[Co(NH_3)_6]Cl_3$ by NO_2' ions, the following compounds can be obtained:

$$[Co(NH_3)_5NO_2]\,Cl_2;\quad [Co(NH_3)_4(NO_2)_2]\,Cl;\quad [Co(NH_3)_3(NO_2)_3]$$
$$[Co(NH_3)_2(NO_2)_4]\,K;\quad [Co(NH_3)(NO_2)_5]\,K_2;\quad [Co(NO_2)_6]\,K_3$$

It is clear that this displacement is accompanied by a gradual change in the charge on the complex ion, which decreases from $+3$ on the $[Co(NH_3)_6]^{\cdot\cdot\cdot}$ ion to -3 on the $[Co(NO_2)_6]'''$ ion.

The platinum compounds described above, viz., $[Pt(NH_3)_4Cl_2]Cl_2$, $[Pt(NH_3)_2Cl_4]$ and $K_2[PtCl_6]$, may also be regarded as products of successive replacement of the ammonia molecules in $[Pt(NH_3)_6]Cl_4$ by two, four and six chloride ions respectively.

215. Crystal Hydrates and Double Salts as Complex Compounds. Of especial interest is the possibility of ammonia molecules being displaced in a complex by water molecules. In the case of chromium, for instance, the following series of complex compounds is known:

$$[Cr(NH_3)_6]\,Cl_3;\quad [Cr(NH_3)_5H_2O]\,Cl_3;\quad [Cr(NH_3)_4(H_2O)_2]\,Cl_3;$$
$$[Cr(NH_3)_3(H_2O)_3]\,Cl_3;\quad [Cr(NH_3)_2(H_2O)_4]\,Cl_3;\quad [Cr(H_2O)_6]\,Cl_3$$

The last compound of this series is nothing but the ordinary crystal hydrate of chromium chloride $CrCl_3 \cdot 6H_2O$. Therefore, the crystal hydrate of chromium chloride is essentially a complex compound, which in solution splits off the ions $[Cr(H_2O)_6]^{\cdots}$.

Crystal hydrates containing six molecules of water are encountered very often; for instance, the crystal hydrates of $FeCl_3$, $NiCl_2$, $AlCl_3$, etc. According to the coordination theory the structure of all of them is analogous to that of the crystal hydrate of chromium chloride, viz.:

$$[Fe(H_2O)_6]\,Cl_3;\quad [Ni(H_2O)_6]\,Cl_2;\quad [Al(H_2O)_6]\,Cl_3$$

Likewise, other crystal hydrates should also be regarded as complex salts, although part of their water of crystallization may be contained in the outer sphere. For instance, the structure of the crystal hydrate $CuSO_4 \cdot 5H_2O$ is probably:

$$[Cu(H_2O)_4]\begin{matrix}SO_4\\H_2O\end{matrix}$$

Very close in nature to complex salts are the so-called **double salts**, for instance, ordinary alum:

$$KAl(SO_4)_2 \cdot 12H_2O \text{ or } K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$$

Like double salts, complex salts are often formed from two simple salts and can be represented by formulas analogous to those of double salts. For example:

$$AgCN + KCN = K[Ag(CN)_2] \text{ or } AgCN \cdot KCN$$

The chief difference between double and complex salts is that upon ionization the former yield all the ions found in solutions of the simple salts they consist of:

$$KAl(SO_4)_2 = K^{\cdot} + Al^{\cdots} + 2SO_4^{''}$$

the latter, on the other hand, ionize into complex ions:

$$K[Ag(CN)_2] = K^{\cdot} + [Ag(CN)_2]'$$

However, no sharp dividing line can be drawn between the two types. As we have already seen in the case of silver salts, complex ions are themselves capable of ionizing. Depending on the degree of ionization compex ions may be divided into more stable and less

stable ions. For instance, a solution of the complex salt $K_4[Fe(CN)_6]$ does not respond to a single test for $Fe^{\cdot\cdot}$ or CN' ions; therefore the $[Fe(CN)_6]''''$ ion ionizes according to the equation

$$[Fe(CN)_6]'''' \rightleftarrows Fe^{\cdot\cdot} + 6CN'$$

so insignificantly, that it can practically be considered unionized. But the presence of silver ions in a solution of $[Ag(NH_3)_2]Cl$ can be detected with certain reagents (see § 212), showing that the $[Ag(NH_3)_2]$ ion is somewhat more ionized than the $[Fe(CN)_6]''''$ ion. Finally, a solution of the salt $K[MgCl_3]$ responds to all tests for magnesium- and chloride-ion, viz., alkalis precipitate $Mg(OH)_2$, silver nitrate throws down AgCl, etc. Obviously, the ionization equilibrium

$$[MgCl_2]' \rightleftarrows Mg^{\cdot\cdot} + 3Cl'$$

favours the left-to-right reaction. On these grounds $K[MgCl_3]$ is usually regarded as a double salt and its formula is written $KCl \times \times MgCl_2$.

Thus, double salts are the same as complex salts with the difference that their inner coordination sphere is rather unstable. A greater or smaller amount of complex ions are always present in a solution of any double salt.

216. Spatial Arrangement of Coordinated Groups in a Complex Compound. It was stated above that each complex former is characterized by a definite coordination number, for instance, the coordination number of Pt^{4+} ion is 6,

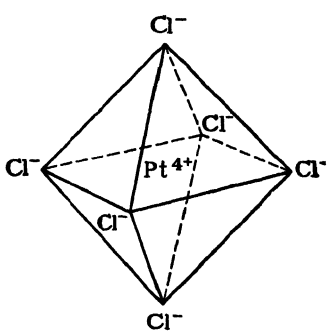


Fig. 150. Constitution of the complex ion $[PtCl_6]^{2-}$

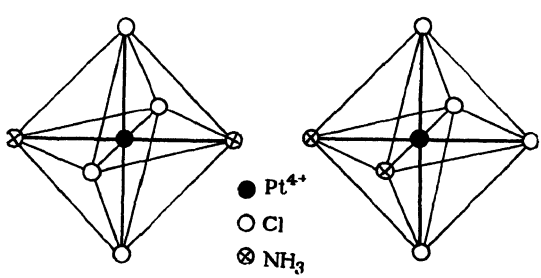


Fig. 151. Trans-isomer (left) and cis-isomer (right)

that of the Cu^{2+} ion is 4, etc. The fact that different ions have different coordination numbers is closely connected with the conception of the spatial arrangement of the coordinated groups (molecules and ions) around the central ion. Studying the isomerism of complex compounds, Werner came to the conclusion that when the coordination number equals 6, the coordinated groups should be arranged symmetrically around the central ion, forming a regular octahedron

(Fig. 150). If all the coordinated groups are identical, as shown in the figure, their permutations will not, of course, cause any change in the structure of the complex compound. But if the groups are not identical various arrangements are possible, resulting in different isomers. And indeed, experiment shows that, say, the compound $[Pt(NH_3)_2Cl_4]$, in which the coordination number of platinum is 6, can exist in two isomeric forms differing both in colour and in other properties. The structures of these isomers, according to Werner, are shown diagrammatically in Fig. 151. In one case the NH_3 molecules are located at opposite corners of the octahedron (the trans-isomer), while in the other they are situated at adjacent peaks (the cis-isomer). Spatial isomerism of this kind is observed also in a number of other complex compounds with six groups in their inner spheres.

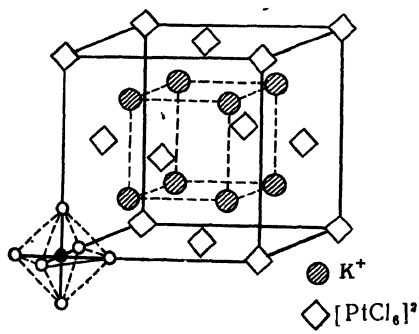


Fig. 152. Crystal lattice of $K_2[PtCl_6]$

Werner's assumptions concerning the octahedral structure of 6-coordination complex compounds were brilliantly confirmed when the crystals of the corresponding compounds were investigated by X-rays. Fig. 152 shows the crystal lattice of the complex salt $K_2[PtCl_6]$. In it the complex ions $[PtCl_6]^{--}$ are situated at the corners and face centres of a cube, the chloride ions within the complex ion being located at the corners of a regular octahedron. Thus, the $[PtCl_6]^{--}$ ion is not only retained in solution but is also an independent structural unit in the crystal lattice.

In 4-coordination complex compounds the coordinated groups are either situated at the corners of a square, the centre of which is occupied by the complex former, or the complex former is at the centre of a tetrahedron and the coordinated groups at its peaks.

217. Nature of the Forces Causing Complex Formation. Now that we have become acquainted with the structure of complex compounds, we may pass over to the nature of the forces causing the chemical bond in their complex parts.

In explaining the formation of complex compounds, reference is now made to the two general theories of formation of chemical compounds discussed earlier, namely, the electrostatic theory and the theory of covalent bonds. According to the first of these, the bonds between the central atom or ion and its addends is due to electrostatic attraction between the particles and is of a nature analogous to ionic bonds.

The second theory explains complex formation proceeding from the conception of electron pairs binding the addends with the complex former, just as in ordinary atomic compounds.

Let us see, for instance, how the electrostatic theory explains the formation of the typical complex salt $K_2[PtCl_6]$, a product of the combination of platinum chloride $PtCl_4$ and potassium chloride. When platinum reacts with chlorine each platinum atom yields four electrons to chlorine atoms, and turns into a Pt^{4+} ion.

The Pt^{4+} ions unite with the resulting chloride ions to give the salt $PtCl_4$:

$$\overset{4e^-}{\overbrace{}}\\ Pt + 2Cl_2 = PtCl_4$$

But the presence of four Cl^- ions by no means deprives the Pt^{4+} ion of the ability of influencing other chloride ions. Therefore, if there happen to be any in the vicinity, the Pt^{4+} ion immediately begins to attract them. However, approaching the Pt^{4+} ion, each Cl^- ion is at the same time repelled by the four chloride ions already there. If the attractive force of the Pt^{4+} ion is greater than the force of repulsion, more chloride ions will be added. As they accumulate the repulsive force increases, and when it finally exceeds the force of attraction, the addition of new ions will cease. In our case, this moment arrives when the platinum ion is linked with six chloride ions (the four initially combined and two new ones). The resulting group, consisting of one Pt^{4+} ion and six Cl^- ions and containing two excess negative charges, is the complex ion $[PtCl_6]^{--}$. Adding two positive K^+ ions which form its outer sphere, the ion turns into the complex salt $K_2[PtCl_6]$.

The addition of neutral molecules to the complex former is just as simple to explain. It must only be taken into account that usually the molecules taking part in the formation of complex ions are those with pronounced dipoles (such as H_2O, NH_3). Attracted by the electric field of the complex former, these dipoles become orientated in a definite manner with respect to it and approach it with their oppositely charged poles, forming the complex ion. Inasmuch as the mutual repulsion of polar molecules is much weaker than that of ions, such complex ions are usually very stable.

Thus, according to the electrostatic theory, the formation of complex ions in complex compounds is due to the same electrostatic forces that account for simpler binary compounds. The difference is only in the mechanisms of these processes. In simple binary compounds the valency bond appears as a result of the transition of electrons from one set of atoms to another, after which the ions formed are linked by mutual attraction of the unlike charges. In complex compounds, on the other hand, ready-made ions (or polar

molecules) are the participants. There is no transition of electrons in this case, the ions or ions and molecules being "pulled together" electrostatically. The nature of the valency bonds is obviously the same in both cases.

The other theory of formation of chemical compounds, the theory of covalent bonds, has been applied above to explain the formation of the complex ammonium ion from a hydrogen ion and an ammonia molecule (§ 136).

$$H^+ + :\underset{\cdot\cdot}{\overset{H}{\overset{\cdot\cdot}{N}}}:H = \left[H:\underset{\cdot\cdot}{\overset{H}{\overset{\cdot\cdot}{N}}}:H \right]^+$$

A second example is the formation of the complex anion $[BF_4]^-$ from F^- ions and BF molecules:

$$\left[:\underset{\cdot\cdot}{F}: \right]^- + \underset{\cdot\cdot}{\overset{F}{\overset{\cdot\cdot}{B}}}:F = \left[F:\underset{\cdot\cdot}{\overset{F}{\overset{\cdot\cdot}{B}}}:F \right]^-$$

In the boron trifluoride molecule the boron atom is linked to the fluorine atoms by six electrons, the number of which increases to eight when the $[BF_4]^-$ anion is formed, at the expense of the electron pair of the fluoride ion.

The covalent bonds in the complex ions $[NH_4]^+$ and $[BF_4]^-$ differ only in origin from ordinary covalent bonds due to pairs of common electrons. While in ordinary covalent bonds each of the combining atoms submits one electron for the pair, in complex compounds the bond is due to a pair of electrons which belonged previously to only one of the combining atoms. Bonds of this kind are otherwise called **coordination** or **donor-acceptor** bonds.

The atom or ion submitting the electron pair for the bond is called the **donor**, while that which accepts the pair is known as the **acceptor**. In the first of the above examples the donor is the nitrogen of the ammonia molecule; in the second, it is the fluoride ion. A similar role may be played by the oxygen atom in the hydroxyl ion $[:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:H]^-$ or in the water molecule $H:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:H$, the chloride ion $[:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:]^-$, and, generally, any atom or ion possessing "unoccupied" electron pairs.

The acceptors in the ions $[NH_4]^+$ and $[BF_4]^-$ were, respectively, the H^+ ion, and the boron atom of the BF_3 molecule, which possess incomplete electron shells. Generally, acceptors are always atoms or ions with incomplete electron shells, i.e., possessing possible orbits in their outer electron layer, not occupied by electrons.



Lev Alexandrovich
Chugayev
(1873-1922)

In concluding, it should be indicated that the anions of ordinary oxyacids may also be regarded as complex ions. For instance, the structure of the sulphuric and perchloric acid anions, $[SO_4]^{--}$ and $[ClO_4]^-$, may be represented as follows:



Complex compounds are exceedingly numerous and diverse. They are important not only from a theoretical, but also from a practical standpoint. In particular, they play a very significant part in the development of qualitative and quantitative analysis methods and in the production of the chemically pure platinum group metals.

The necessity of systematic studies of complex compounds was constantly stressed by D. Mendeleyev. Important studies in this connection were carried out as early as the end of last century by Academician Kurnakov, but of especially great significance in the investigation of complex compounds were the works of L. Chugayev.

Lev Alexandrovich Chugayev was born in 1873, in Moscow. He received an education at the University of Moscow.

Chugayev's first studies were devoted to questions of organic chemistry. In 1903 he published a major work entitled "Investigations in the Field of Terpenes

and Camphors", which gained him his Master's degree. Soon after Chugayev was entrusted with the chair of chemistry at the Higher Technical School of Moscow, which gave him the opportunity to considerably extend his research. However, here he turned his scientific activities chiefly to the study of complex compounds of copper, nickel, cobalt, iron, silver, platinum and palladium.

Studying the interaction between various organic substances and inorganic compounds, Chugayev discovered many new complex compounds of major theoretical importance for proving the coordination theory; at the same time they were of great practical interest. Thus, he obtained compounds of nickel and palladium with the organic substance dimethylglyoxime which has been used ever since in laboratories all over the world for qualitative and quantitative determinations of these elements.

In 1907 Chugayev became head of the chair of inorganic chemistry at the Petersburg University, where he continued his investigations mainly in the field of the platinum group metals. Chugayev's classical works on the metals of the platinum group not only enriched science with new facts and new compounds, but also outlined the trend of subsequent investigations in this field.

Another point to Chugayev's credit was the organization in 1918 of the Platinum Institute, the works of which have played an important part in the development of the Soviet platinum industry.

CHAPTER XXI

Second Group of the Periodic Table

The second group of the Periodic Table includes elements containing two electrons in the outermost layer of their atoms and capable of yielding only these two electrons. The typical elements of the second group are *beryllium* and *magnesium*. They are followed by *calcium*, *strontium*, *barium* and *radium*, elements situated in the even series of the long periods and having octets in their second last layers.

The six elements named constitute the *main subgroup of the second group*. The secondary subgroup includes the metals *zinc*, *cadmium* and *mercury*, situated in the odd series of the long periods and having eighteen electrons in the second last electron layers of their atoms.

MAIN SUBGROUP OF THE SECOND GROUP

Element	Symbol	Atomic weight	Atomic number	Arrangement of electrons in layers						
Beryllium . . .	Be	9.013	4	2	2					
Magnesium . .	Mg	24.32	12	2	8	2				
Calcium	Ca	40.08	20	2	8	8	2			
Strontium . . .	Sr	87.63	38	2	8	18	8	2		
Barium	Ba	137.36	56	2	8	18	18	8	2	
Radium	Ra	226.05	88	2	8	18	32	18	8	2

218. General Features of the Main Subgroup of the Second Group. All the elements in the main subgroup of the second group, except beryllium, possess distinct metallic properties. In the free state they are silvery-white substances, harder than the alkali metals and having rather high melting and boiling points. In specific gravity all of them, except radium, are light metals. Their chief physical constants are given in Table 30.

The two electrons in their outer layer being at a considerable distance from the nucleus, the atoms of the main subgroup elements

part with them easily, turning into positively charged ions. Therefore, in chemical activity these elements are but little inferior to the alkali metals. Like the latter, they oxidize quite rapidly in the air and are capable of displacing hydrogen from water at ordinary temperatures. But beryllium and magnesium react with water very slowly, as the hydroxides, resulting from these reactions, are very sparingly soluble in water; coating the surface of the metal, the hydroxides retard the further progress of the reaction. The other four metals react with water more vigorously, as their hydroxides are more soluble.

Table 30

Chief Physical Constants of the Elements of the Main Subgroup of the Second Group

Constants	Beryllium Be	Magnesium Mg	Calcium Ca	Strontium Sr	Barium Ba	Radium Ra
Specific gravity . . .	1.82	1.74	1.54	2.6	3.5	5.0
Melting point, degrees C	1,285	651	851	770	704	960
Boiling point, degrees C	2,970	1,107	1,440	1,370	1,540	1,140
Atomic radius, Å . .	1.13	1.60	1.97	2.16	2.25	—

Calcium, strontium and barium of the main subgroup have long been known as the alkaline-earth metals. The origin of this name is connected with the fact that calcium, strontium and barium hydroxides, like sodium and potassium hydroxides, have long been known as "alkalis" and have alkaline properties; on the other hand, their oxides resemble aluminium oxide and the oxides of the heavy metals somewhat in refractoriness, the latter oxides having been known formerly as **earths**.

Combustion of the alkaline-earth metals always results in normal oxides of the type MO. The peroxides, if they form at all, are much less stable than those of the alkali metals.

Calcium, strontium and barium oxides combine directly with water to form hydroxides. The solubility of the latter increases rapidly in the order Ca, Sr, Ba, reaching 38 gr. per litre in the case of barium hydroxide. The basicity of the hydroxides increases in the same order.

Like the alkali metals, the alkaline-earth metals are capable of combining with hydrogen to form hydrides (for instance, CaH_2).

A remarkable tendency of the alkaline-earth metals is that of combining with nitrogen, this tendency increasing with their atomic weight. The alkaline-earth metals combine slowly with nitrogen even at ordinary temperatures to form nitrides.

Unlike the salts of the alkali metals, many of the salts of the alkaline-earth metals are but sparingly soluble in water. These include the carbonates, sulphates, phosphates and some other salts.

The alkaline-earth metals are only bivalent in all their compounds.

219. Beryllium; at. wt. 9.013. Beryllium occurs rarely in nature (its content in the earth's crust is 0.0004 per cent by weight). It is contained in several minerals, the most common of which is *beryl* $Be_3Al_2(SiO_3)_6$.

Some varieties of beryl, variously coloured due to traces of admixtures, are precious stones. Such, for instance, are green emeralds, bluish-green aquamarines, etc.

Metallic beryllium is prepared by electrolysis of its fused salts. It is a very hard, white, light metal with a specific gravity of 1.82, stable in the air owing to the formation of a protective oxide film on its surface. Beryllium is hardly attacked at all by water, but it dissolves readily in acids, liberating hydrogen.

A very characteristic feature of beryllium is that alkalis will also dissolve it to give salts known as **beryllates**, in which beryllium plays the part of a non-metal:

$$\underset{\text{sodium beryllate}}{Be + 2NaOH = Na_2BeO_2} + H_2$$

Metallic beryllium possesses many remarkable properties. Thin beryllium plates are good transmitters of X-rays and are therefore unequalled for the preparation of the parts of X-ray tubes through which the rays are to pass. Alloys of beryllium with magnesium and aluminium are very light and strong, which accounts for the growing use of beryllium in aircraft engineering despite its high cost. Alloyed with copper, beryllium gives a very hard bronze, suitable for the manufacture of excellent springs.

Highly pure beryllium is used in nuclear reactors. The metal used for this purpose must not contain more than 1 gr. of boron per ton of beryllium.

Owing to the valuable properties of beryllium, its production keeps rising rapidly. In 1935 only 5 tons of beryllium ore were mined; in 1953 the world production (not counting the U.S.S.R.) was over 8,600 tons.

Beryllium oxide BeO is a white, very refractory substance which combines with water into beryllium hydroxide.

Beryllium hydroxide $Be(OH)_2$ is pronouncedly amphoteric, which distinguishes it sharply from the hydroxides of the typical alkaline-earth metals. It is practically insoluble in water, but dissolves readily both in acids and in alkalis, forming beryllates in the latter case:

$$Be(OH)_2 + 2NaOH = Na_2BeO_2 + 2H_2O$$

As the acidic properties of $Be(OH)_2$ are very feeble, beryllates are completely hydrolyzed in aqueous solution.

The majority of beryllium salts, including the sulphate, dissolve readily in water, while the sulphates of the typical alkaline-earth metals are practically insoluble in water.

220. Magnesium; at. wt. 24.32. Magnesium is rather widespread in nature. It is found in large quantities as magnesium carbonate in the minerals *magnesite* $MgCO_3$ and *dolomite* $MgCO_3 \cdot CaCO_3$. Magnesium sulphate and chloride are contained in the potassium minerals, *kainite* $KCl \cdot MgSO_4 \cdot 3H_2O$ and *carnallite* $KCl \cdot MgCl_2 \times \times 6H_2O$, and are contained also in sea water, accounting for its bitter taste. The total content of magnesium in the earth's crust is about 2.35 per cent by weight.

Magnesium is prepared by electrolysis of fused magnesium chloride, or more often by electrolysis of fused carnallite.

Magnesium is a silver-white, very light metal with a specific gravity of 1.74. It changes little in the air as it rapidly becomes coated with a thin film of the oxide, which protects it from further oxidation.

Although magnesium is far above hydrogen in the e.m.f. series, it decomposes water very slowly, as stated above, owing to the formation of sparingly soluble magnesium hydroxide. Magnesium dissolves readily in acids, liberating hydrogen. Alkalis do not act on magnesium. When heated, magnesium bursts into flame and burns, forming magnesium oxide and a minor quantity of magnesium nitride Mg_3N_2. The light emitted by burning magnesium is very bright and very rich in ultra-violet rays. For this reason, magnesium is sometimes used for illumination in photography. Magnesium is used also in pyrotechnics.

The chief field of application of metallic magnesium is for the preparation of various light alloys. The addition of small amounts of other metals to magnesium sharply changes its mechanical properties, imparting to the alloy considerable hardness, strength and resistance to corrosion. Especially valuable properties are possessed by the alloy *electron* (about 90 per cent magnesium, the rest being aluminium, zinc, manganese) which, owing to its low specific gravity (1.8) and considerable strength, has found wide use in aircraft engineering.

The world production of magnesium, which amounted to but several hundred tons in 1915, reached 23.8 thousand tons in 1938 (not counting the U.S.S.R.) and 380,000 in 1944 (not counting the U.S.S.R.). The present output of magnesium has grown still more in connection with the wide use of its alloys in industry.

The first metallic magnesium plant in the U.S.S.R. was started up in 1935. Magnesium was obtained here by electrolysis of magnesium

chloride. Later on, Soviet magnesium plants began to work almost exclusively on carnallite. The development of the magnesium industry in the U.S.S.R. was greatly aided by the investigations of Prof. Fedotyev (1874-1934), the founder of the Soviet school of electrochemists. In the course of many years P. Fedotyev carried on a systematic study of the conditions of electrolysis of magnesium salts, and as early as 1915-17 organized the first production of magnesium at a pilot plant in Petrograd. He participated directly in the mastering of the industrial method for the preparation of magnesium.

Magnesium oxide MgO is usually prepared by calcining natural magnesite $MgCO_3$. It is a white loose powder, known more commonly as *magnesia*. Owing to its high melting point (about 3,000° C) technical magnesium oxide is used for the manufacture of refractory crucibles, pipes and bricks.

Magnesium hydroxide $Mg(OH)_2$ is thrown down as a white precipitate when soluble magnesium salts are treated with alkalis. Unlike $Be(OH)_2$, it possesses only basic properties, being a base of moderate strength. Magnesium hydroxide is slightly soluble in water and makes it react alkaline.

The most widely used salts of magnesium are:

Magnesium sulphate $MgSO_4 \cdot 7H_2O$, or *Epsom salts* (see p. 357), unlike the sulphates of the alkaline-earth metals, dissolves readily in water. The solubility of this salt and its crystalline structure make magnesium similar to zinc.

Magnesium chloride $MgCl_2 \cdot 6H_2O$ forms colourless, readily soluble, deliquescent crystals. The hygroscopicity of unpurified table salt is due to insignificant admixtures of $MgCl_2$.

Magnesium carbonate $MgCO_3$ is found in nature as the mineral magnesite. If soluble magnesium salts are treated with soda, the result will not be the normal carbonate, but a mixture of different basic carbonates. This mixture is used in medicine under the name of *white magnesia*.

Of great industrial importance is the basic salt MgOHCl which forms owing to hydrolysis when a magnesium chloride solution is evaporated:

$$MgCl_2 + H_2O \rightleftarrows MgOHCl + HCl$$

The technical product is prepared by mixing magnesium oxide with a concentrated aqueous solution of magnesium chloride and is called *magnesia cement*. This mixture hardens after some time, turning into a compact, white, readily polishable mass.

Hardening of the mixture is due to the formation of the basic salt according to the equation:

$$MgO + MgCl_2 + H_2O = 2MgOHCl$$

Magnesia cement is used as a binding material in the manufacture of millstones, whetstones, various plates, etc. A mixture of magnesia cement and sawdust is used under the name of *xylolite* for flooring.

Other widely used compounds are the natural silicates of magnesium: *talc* $3MgO \cdot 4SiO_2 \cdot H_2O$ and especially *asbestos* $CaO \cdot 3MgO \times \times 4SiO_2$. The latter, owing to its non-flammability, low thermal conductivity and fibrous structure, is an excellent heat insulating material.

Magnesium salts are contained in small quantities in all soils and are necessary for plant nutrition, as magnesium is one of the constituents of chlorophyll.

221. Calcium; at. wt. 40.08. Calcium is very widespread in nature as a great variety of compounds. We have already mentioned the immense deposits of limestone, chalk and marble, which are the natural forms of calcium carbonate $CaCO_3$. Other natural compounds found in large quantities are gypsum $CaSO_4 \cdot 2H_2O$, phosphorite $Ca_3(PO_4)_2$ and various calcium-containing silicates. The total content of calcium in the earth's crust is 3.25 per cent by weight.

Metallic calcium is prepared by the electrolysis of molten calcium chloride. It is a malleable, rather hard, white metal, melting at 851° C. In the air calcium rapidly becomes coated with an oxide film, and if heated, burns with a bright reddish flame. Calcium reacts with cold water rather slowly, but displaces hydrogen rapidly from hot water, forming calcium hydroxide.

Calcium is a very active metal, combining readily with the halogens, sulphur, nitrogen, and reducing almost all the metals from their oxides when heated with them.

Metallic calcium is added in small quantities to certain bearing alloys.

If heated in a stream of hydrogen, metallic calcium combines with the hydrogen to form a hydride.

Calcium hydride CaH_2 is a crystalline solid which reacts violently with water, liberating hydrogen:

$$\left.\begin{array}{l} CaH_2 + 2H_2O = Ca(OH)_2 + 2H_2 \\ 2H' \text{ (from the hydride)} - 2e^- = H_2 \\ 2H^{\cdot} \text{ (from water)} + 2e^- = H_2 \end{array}\right|$$

Owing to its ability to liberate a large quantity of hydrogen (44.8 litres for every gram-molecule of CaH_2, weighing 42 grams), calcium hydride is used under the name of "hydrolyte" for the preparation of hydrogen to fill observation balloons in the field.

Calcium oxide CaO is a white, very fire-resistant substance, which can be melted only in an electric furnace at a temperature of about 3,000° C. In engineering calcium oxide is usually called *quicklime* or *burnt lime*. The latter name indicates its method of preparation,

namely, by calcining or "roasting" calcium carbonate (limestone or chalk).

Limestone is roasted in tall vertical *lime kilns.* The kiln is charged with alternate layers of fuel and limestone and is fired from below. When calcined, the calcium carbonate dissociates into carbon dioxide and lime:

$$CaCO_3 \rightleftarrows CO_2 + CaO - 34.6 \text{ Cal.}$$

Applying the Law of Mass Action to this equation and keeping in mind that the concentration of the solids is not included in the expression for the equilibrium constant (p. 193), we find:

$$[CO_2] = K$$

As the concentration of a gas can be represented by its partial pressure, the resultant expression means that equilibrium is attained in the reaction in question at a certain definite partial pressure of carbon dioxide. The value of this "equilibrium" pressure for various temperatures is as follows:

Temperature, degrees C . .	500	600	700	800	900	1,000
Pressure, mm. Hg	0.11	2.35	25.3	168	773	2,710

To shift the established equilibrium towards the formation of fresh portions of CaO, either the temperature must be raised, or part of the CO_2 formed must be removed, to lower its partial pressure. If at any definite temperature the partial pressure of the carbon dioxide is kept lower than the equilibrium pressure, the decomposition of $CaCO_3$ will proceed continuously. Therefore, a very important factor in roasting limestone is good ventilation of the kiln, promoting removal of the carbon dioxide and enabling the reaction to be carried out at lower temperatures.

If quicklime is treated with water, the latter is first absorbed by the porous lumps of lime and then reacts with it, liberating a considerable amount of heat. Part of the water turns into steam and the lumps of lime fall apart into a loose mass of calcium hydroxide:

$$CaO + H_2O = Ca(OH)_2 + 15 \text{ Cal.}$$

This operation is called "quenching" the lime, and the resulting product is known in practice as *slaked lime.*

Calcium hydroxide $Ca(OH)_2$ is a strong base, sparingly soluble in water; one litre of water at 20° C will dissolve only 1.56 gr. of $Ca(OH)_2$. The saturated solution is called *lime water* and reacts alkaline. In the air lime water soon grows turbid, due to the absorption of carbon dioxide and the formation of insoluble calcium carbonate.

Slaked lime is widely used in the building industry. A mixture of slaked lime with sand and water is called *mortar* and is used to bind bricks in bricklaying, as well as for plastering. Lime hardens at first due to evaporation of the water in it, and then as a result of the slaked lime absorbing carbon dioxide from the air and turning into calcium carbonate

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$

Owing to the low content of carbon dioxide in the air, the mortar hardens very slowly, and, as it evolves water in doing so, structures built with the use of mortar remain damp for a long time.

The most important salts of calcium are: calcium chloride $CaCl_2$ (p. 317), calcium sulphate $CaSO_4$ (p. 357), calcium carbonate $CaCO_3$ (p. 424), calcium nitrate $Ca(NO_3)_2$ (p. 394), calcium phosphates (p. 403), calcium acid sulphite $Ca(HSO_3)_2$ (p. 352) and calcium hypochlorite $Ca(ClO)_2$ (p. 322).

Owing to the great abundance of calcium in nature, its salts are almost always contained in natural waters. Of the natural salts of calcium, only gypsum is slightly soluble in water; however, if the water contains carbon dioxide, calcium carbonate can also pass into solution in the form of the acid carbonate $Ca(HCO_3)_2$.

Natural water containing a large amount of calcium salts in solution in the form of the acid carbonate and the sulphate, as well as the corresponding salts of magnesium, is referred to as **hard water** in contradistinction to **soft water** containing but small quantities of calcium salts or not containing them at all.

Hardness of water caused mainly by $Ca(HCO_3)_2$ is called **temporary** or **removable** hardness, as boiling will cause this salt to decompose into calcium carbonate which precipitates out, so that the water becomes soft. If the water contains $CaSO_4$ or $MgSO_4$, its hardness is **permanent**, and can be eliminated only by distillation or by chemical means. In the U.S.S.R. the hardness of water is expressed as the total number of milligram-equivalents of calcium and magnesium ions per litre of water. One milligram-equivalent of hardness corresponds to a content of 20.04 mg. per 1. of $Ca^{\cdot\cdot}$ or 12.16 mg. per 1. of $Mg^{\cdot\cdot}$. Prior to 1952 the hardness of water used to be measured in **degrees of hardness**, showing the number of grams of calcium oxide present in 100 litres of water. The magnesium content and that of other bivalent metals was recalculated for an equivalent amount of CaO. In terms of the now accepted units of measurement, one degree of hardness equals 0.35663 mg.-equiv. of calcium- or magnesium-ion.

An exemplary computation of the hardness of water is given below.

Example. Calculate the total hardness of water if it took 10.6 grams of soda to remove all the $Ca^{\cdot\cdot}$-ion from 50 litres of it.

From the equations

$$Ca(HCO_3)_2 + Na_2CO_3 = \downarrow CaCO_3 + 2NaHCO_3$$
$$CaSO_4 + Na_2CO_3 = \downarrow CaCO_3 + Na_2SO_4$$

we find that one gram-molecule of soda is required for each gr.-ion of calcium, making one mg.-equiv. of soda for each mg.-equiv. of $Ca^{\cdot\cdot}$-ion.

The molecular weight of soda is 106, therefore, one mg.-equiv. weighs 106 : 2=53 mg.

To precipitate the $Ca^{\cdot\cdot}$-ion contained in 50 litres of water, 10.6 grams or 10,600 milligrams of soda were required, which makes 10,600 : 53=200 mg.-equiv.

Obviously, 50 litres of water contain the same number of mg.-equiv. of $Ca^{\cdot\cdot}$-ion. Hence the hardness of the water is 200 : 50=4 mg.-equiv.

The presence of a considerable amount of calcium or magnesium salts in water renders it quite unsuitable for many technical purposes.

For instance, if steam boilers are fed for any length of time with hard water their walls gradually become coated with a compact crust of scale. If only 1 mm. thick, this crust greatly reduces the heat transfer through the walls of the boiler, and therefore increases the fuel consumption. Besides, it may lead to swellings and cracks in the boiler tubes and on the boiler walls. Breaking the scale off by mechanical means may injure the boiler.

Hard water does not froth with soap, as the soluble sodium salts of palmitic and stearic acids, contained in the soap, pass into insoluble calcium salts of the same acids:

$$\underset{\text{sodium stearate}}{2C_{17}H_{35}COONa} + CaSO_4 = \downarrow \underset{\text{calcium stearate}}{(C_{17}H_{35}COO)_2Ca} + Na_2SO_4$$

This continues until all the calcium-ions are removed from the solution. That is why the use of hard water in washing clothes leads to an excessive expenditure of soap.

Hard water cannot be used for certain technological processes, for instance, in dyeing.

The above examples illustrate the necessity of carefully purifying water intended for technical purposes from calcium and magnesium salts.

Water may be purified by various methods, the most important of which are the chemical ones, consisting essentially in the precipitation of the calcium and magnesium as insoluble salts. The reagents most commonly used for chemical purification, are slaked lime and soda. Lime converts the acid carbonates of calcium and magnesium into the insoluble carbonates:

$$Ca(HCO_3)_2 + Ca(OH)_2 = \downarrow 2CaCO_3 + 2H_2O$$

soda also precipitates calcium and magnesium as carbonates:

$$CaSO_4 + Na_2CO_3 = \downarrow CaCO_3 + Na_2SO_4$$

In laundries hard water is sometimes softened by means of spirits of ammonia, the action of which is similar to that of lime, or by means of borax, which precipitates the calcium as calcium borate.

A method of softening water which has found wide application in industry is by ionic exchange (cationite, permutite or zeolite method). This method is based on the ability of certain alumosilicates of the type $Na_2Al_2Si_2O_8 \cdot nH_2O$ to exchange the sodium ions contained in them for the calcium and magnesium ions present in water, thus removing the latter from solution. Such alumosilicates are known as *zeolites*.

If passed through a layer of finely divided zeolite hard water is completely freed of $Ca^{\cdot\cdot}$- and $Mg^{\cdot\cdot}$-ion. The reactions which take place can be represented schematically by the following equations:

$$Na_2R + Ca(HCO_3)_2 \rightleftarrows CaR + 2NaHCO_3$$
$$Na_2R + CaSO_4 \rightleftarrows CaR + Na_2SO_4$$

where R stands for the complex alumosilicate anion $(Al_2Si_2O_8 \times \times nH_2O)^{\prime\prime}$.

When all the sodium in the zeolite is replaced by calcium (or magnesium), the zeolite loses its ability to soften water, but can easily be regenerated by the action of a concentrated solution of NaCl. This causes the reverse reaction to take place, the calcium being replaced by sodium. Thus, in this method of softening water only sodium chloride, a comparatively cheap product, is consumed.

Various artificial resins, high molecular organic substances containing acidic or basic functional groups, can also be employed for abstracting the ions of dissolved substances from water. Resins which can be used as cationites contain carboxyl groups COOH, sulpho groups SO_3H, and others, capable of exchanging their hydrogen ions for metal ions. Such cationites are called H-*cationites*. Denoting the molecular radical combined with the functional group by R, the reaction of an H-cationite with metal ions, say, with the ions of sodium and calcium, can be represented by the following equations:

$$RCOOH + Na^{\cdot} \rightleftarrows RCOONa + H^{\cdot}$$
$$2RCOOH + Ca^{\cdot\cdot} \rightleftarrows (RCOO)_2Ca + 2H^{\cdot}$$

As a result of these reactions any solution containing salts (say NaCl, $CaSO_4$, etc.) is converted into a solution of the corresponding acids (HCl, H_2SO_4).

To remove the acids the solution is passed through an *anionite*, a resin containing amino groups. The acids are then bound as a result of the formation of insoluble salts. Denoting the anionite by the formula RNH_2, the reaction taking place in the case of a solution of hydrogen chloride, for example, can be represented by the equation:

$$RNH_2 + HCl = [RNH_3]Cl$$

This method gives practically pure water without the trouble of distillation.

Used up H-cationites and anionites can be regenerated, the first by treatment with concentrated sulphuric acid, and the second by treatment with concentrated sodium hydroxide solution:

$$2RCOONa + H_2SO_4 = 2RCOOH + Na_2SO_4$$
$$[RNH_3]Cl + NaOH = RNH_2 + NaCl + H_2O$$

222. Strontium; at. wt. 87.63. Barium; at. wt. 137.36. Strontium and barium are found in nature chiefly as the sulphates and carbonates. They form the minerals: *celestite* $SrSO_4$, *strontianite* $SrCO_3$, *barite* $BaSO_4$ and *witherite* $BaCO_3$. The content of strontium and barium in the earth's crust is much smaller than that of calcium, and equals, respectively, 0.035 and 0.05 per cent by weight.

Metallic strontium and barium are prepared in the same manner as calcium, by electrolysis of their fused chlorides. These metals are very active, oxidize rapidly in the air, react quite vigorously with water (especially barium) and combine directly with many elements.

Strontium and *barium oxides*, SrO and BaO, resemble lime. Both metals also form peroxides. *Barium peroxide* BaO_2 is prepared by heating barium oxide in air to approximately 500° C. At a higher temperature it will decompose back into the oxide and oxygen. This was the basis of one of the methods of obtaining oxygen from air, which has, however, at present, become obsolete. Barium peroxide is used, like sodium peroxide, for bleaching various materials.

Strontium and *barium hydroxides*, $Sr(OH)_2$ and $Ba(OH)_2$, are strong bases, more soluble in water than calcium hydroxide: one litre of water at 20° C will dissolve 8 gr. of $Sr(OH)_2$ and 38 gr. of $Ba(OH)_2$, while the solubility of $Ca(OH)_2$ at the same temperature is only 1.56 gr. per litre. A saturated solution of $Ba(OH)_2$ is known as *baryta water*, and is often used in the laboratory as a reagent. If a solution of barium hydroxide is evaporated, crystals of $Ba(OH)_2 \cdot 3H_2O$ separate out.

Strontium and *barium salts* bear a great resemblance to those of calcium. The carbonates and sulphates, $SrCO_3$, $BaCO_3$, $SrSO_4$, and $BaSO_4$, are insoluble in water and fall out of solution as precipitates when $Sr^{\cdot\cdot}$-ion and $Ba^{\cdot\cdot}$-ion encounter $CO_3^{''}$- and $SO_4^{''}$-ion. The insolubility of these salts is utilized in analysis for separating strontium and barium from other metals.

A characteristic feature distinguishing the three metals from one another is the colour imparted by their volatile salts to a non-luminous flame. Calcium salts colour the flame brick-red, those of strontium, scarlet-red and barium salts, yellowish-green. Strontium and barium salts are used in pyrotechnics for preparing red and green Bengal lights.

ZINC SUBGROUP

Element	Symbol	Atomic weight	Atomic number	Arrangement of electrons in layers					
Zinc . . .	Zn	65.38	30	2	8	18	2		
Cadmium .	Cd	112.41	48	2	8	18	18	2	
Mercury .	Hg	200.61	80	2	8	18	32	18	2

The elements of this subgroup, *zinc*, *cadmium* and *mercury*, are characterized by the presence of two electrons in the outer layer of their atoms and 18 in the second last layer. Although they are not capable of gaining electrons, their metallic properties are much less pronounced than those of the alkaline-earth metals of the even subgroup. They are less active, oxidize with greater difficulty, do not react with water at ordinary temperatures. Their hydroxides are insoluble in water and are weaker bases than the hydroxides of the alkaline-earth metals, zinc hydroxide being even amphoteric.

All the elements of the zinc subgroup are bivalent; mercury, besides, forms a series of compounds in which it is formally univalent.

223. Zinc (Zincum); at. wt. 65.38. The most important natural compounds of zinc, from which it is extracted, are the minerals *smithsonite* or *dry bone* $ZnCO_3$ and *sphalerite* or *zinc blende* ZnS. The total content of zinc in the earth's crust is 0.02 per cent by weight.

Most zinc ores contain but little zinc and require concentration. Zinc is extracted from the resulting zinc concentrate either by distillation or by electrolysis.

The first method depends on the fact that zinc volatilizes and is driven off as a vapour when zinc ore is roasted and then reduced with coal at 1,300 to 1,400° C. The zinc vapour condenses in earthenware receivers. Part of the zinc deposits on the walls of the receiver as metallic dust mixed with zinc oxide ("zinc dust"); but most of the zinc accumulates as a liquid at the bottom of the receiver, from which it is tapped into moulds.

The second method consists in depositing the zinc electrolytically from its sulphate. The latter is obtained by treating roasted zinc ores or concentrates with sulphuric acid. The electrolytic method yields a purer product and is more economical than the distillation method.

The electrolytic method of extracting zinc from its ores consists of the following operations: a) roasting the ore, b) preparing the zinc sulphate solution, c) electrolysis of this solution. The ore is roasted under conditions calculated to convert as much of the zinc sulphide as possible into the sulphate. Part of the sulphide inevitably turns into the oxide, and is converted to the sulphate by the action of sulphuric acid. The resulting zinc sulphate solution is treated with zinc dust to remove impurities of the more noble metals, situated below zinc in the e.m.f. series (cadmium, cobalt, nickel, lead, etc.). Then the solution is electrolyzed. The zinc is evolved on an aluminium cathode as a deposit containing 99.5 per cent zinc, while sulphuric acid forms at the lead anode, owing to accumulation of hydrogen-ion and SO_4''-ion, in quantities quite sufficient to dissolve the subsequent portions of ore.

Zinc deposits have been found in the U.S.S.R. in Kazakhstan, in the Urals, in the North Caucasus, in Siberia and in the Far East.

Zinc is a bluish-white metal having a specific gravity of 7.14. It melts at 419.5° C and vapourizes at 907° C. At ordinary temperatures zinc is rather brittle. But at 100 or 110° C it becomes quite flexible and can be rolled into sheets. In the air zinc becomes coated with a thin film of the oxide or the basic carbonate, which protects it from further oxidation. Water hardly attacks zinc, although it is well above hydrogen in the e.m.f. series. This is due to the fact that the hydroxide forming on the surface of the zinc when it reacts with water is practically insoluble and checks the further progress of the reaction. But in dilute acids zinc dissolves readily, giving the corresponding salts. Besides, zinc, like beryllium and other metals with amphoteric hydroxides, is soluble in alkalis. If zinc is heated in air to the boiling point, its vapour bursts into flame and burns with a greenish-white flame forming zinc oxide.

The uses of zinc are very diverse. More than half the zinc produced is used for coating iron to keep it from rusting (galvanized iron). Large quantities are employed in the manufacture of galvanic cells and for the preparation of numerous alloys (for instance, brasses).

The world output of zinc (not counting the U.S.S.R.) amounted to 2.1 million tons in 1954. Up to the beginning of the First Five-Year Plan zinc was produced in but insignificant quantities in the U.S.S.R. (a few thousand tons per year). During the years of the pre-war five-year plans the zinc output increased greatly and grew especially during the post-war period.

In 1955 zinc production increased twofold compared with 1950. This was achieved both by starting up new plants and by considerably intensifying the work of earlier installed equipment. During the Sixth Five-Year Plan a further 77 per cent increase of the zinc output has been envisaged. A very important factor for the successful fulfilment of this task is the use of the fluidized roasting process for zinc concentrates.

"Fluidized bed" roasting. The so-called "fluidized bed" roasting process for finely divided solids has lately found wide application in various branches of industry. This method consists in the following. A stream of air (or some other gas) is blown upwards through a layer of powdered material on a grating, at a high enough rate for the stream to penetrate the material and agitate it intensively, so that it appears to be boiling. This condition of the solid material is often called "fluosolid," as only substances in the fluid state can boil.

Owing to the intimate contact attained between the solid material and the gas, chemical reactions in the "fluosolid" state proceed at a very high rate. "Fluidized bed" roasting increases the output of roasting ovens at zinc plants three- to fourfold, and results in more complete recovery of the zinc from its concentrates.

This method is very effective for roasting sulphide ores and concentrates, for sublimation of low-boiling metals, for calcining, cooling, drying and chlorination of various substances.

Zinc oxide ZnO is a loose white powder which turns yellow if heated, but becomes white again when cooled. Zinc oxide is used for the preparation of white oil paint (zinc white); in medicine and cosmetics; for the preparation of various ointments; a considerable part of the zinc oxide produced is consumed by the rubber industry as a rubber filler.

Zinc hydroxide $Zn(OH)_2$ is thrown down as white precipitate when solutions of zinc salts are treated with alkalis:

$$Zn^{\cdot\cdot} + 2OH' = \downarrow Zn(OH)_2$$

The precipitate dissolves readily in acids to form zinc salts (for example, $ZnCl_2$), but will dissolve also in alkalis, forming **zincates**, salts of zincic acid. Hence, zinc hydroxide is amphoteric.

Formerly zincates were considered to have a composition corresponding to the formula Na_2ZnO_2. At present they are regarded as salts containing the complex ion $[Zn(OH)_3]'$. Salts of this kind are known as **hydroxysalts** in contradistinction to salts containing such anions as SO_4'', CO_3'', NO_3', etc., referred to as **oxysalts**. Hydroxysalts are obtained by the action of an excess of alkali on the corresponding hydroxides, resulting in complex compounds:

$$Zn(OH)_2 + OH' = [Zn(OH)_3]'$$

or in the molecular form

$$Zn(OH)_2 + NaOH = Na\,[Zn(OH)_3]$$

Analogous hydroxysalts are formed when certain other amphoteric hydroxides are treated with alkalis.

Dissolving metallic zinc in alkalis also gives zincates. This reaction is usually represented by the equation

$$Zn + 2NaOH = Na_2ZnO_2 + H_2$$

However, actually the course of the reaction is probably somewhat different. As has been stated already, metallic zinc does not practically react with water, owing to the formation of a $Zn(OH)_2$ film on its surface, checking the further progress of the reaction. But alkalis dissolve zinc hydroxide, converting it into the complex anion $[Zn(OH)_3]'$, and the zinc, in accordance with its position in the e.m.f. series, begins to displace hydrogen from the water. Thus, the liberation of hydrogen during the action of an alkali solution on zinc is due to the reaction between the zinc and the hydrogen ion of the water, and not the hydroxyl ion of the alkali; the role of the

latter consists in dissolving the resulting zinc hydroxide:

$$\begin{gathered} Zn + 2H_2O = Zn(OH)_2 + H_2 \\ Zn(OH)_2 + OH' = [Zn(OH)_3]' \\ \hline Zn + 2H_2O + OH' = [Zn(OH)_3]' + H_2 \end{gathered}$$

or in the molecular form:

$$Zn + 2H_2O + NaOH = Na\,[Zn(OH)_3] + H_2$$

Zinc hydroxide is soluble also in ammonia solution, due to the formation of the complex ion $[Zn(NH_3)_4]^{\cdot\cdot}$:

$$Zn(OH)_2 + 4NH_3 = [Zn(NH_3)_4]^{\cdot\cdot} + 2OH'$$

The most common zinc salts are:

1. *Zinc sulphate* $ZnSO_4$ crystallizes out of aqueous solution as a crystal hydrate of the composition $ZnSO_4 \cdot 7H_2O$, in which form it is known as *white vitriol*. Is used in dyeing and cotton printing, for the preparation of metallic zinc by electrolysis and in medicine as an astringent. It is also an initial material for the preparation of other zinc compounds.

2. *Zinc chloride* $ZnCl_2$. Solutions of this salt are used for impregnating railway ties to protect them from rotting. Zinc chloride is used also in soldering. It cleanses the surfaces to be soldered from oxides and prevents oxidation of the metal at the moment of soldering.

Some zinc chloride is employed in the manufacture of vegetable parchment paper. The unglued paper is treated with a concentrated solution of zinc chloride which partially decomposes the surface layers of the cellulose, filling the pores of the paper with the decomposition products. Then the paper is thoroughly washed and treated with a solution of glycerine to make it soft and flexible.

3. *Zinc sulphide* ZnS. This compound is one of the few metal sulphides having a white colour.

Zinc sulphide results as a white precipitate when zinc salts are treated with alkali sulphides:

$$Zn^{\cdot\cdot} + S'' = \downarrow ZnS$$

A mixture of zinc sulphide and barium sulphate is used as a white paint, known as *lithopone*.

224. Cadmium; at. wt. 112.41. Cadmium resembles zinc greatly in properties and is constantly associated with it in its natural compounds.

Cadmium is much less abundant than zinc; its content in the earth's crust amounts to only 5×10^{-4} per cent by weight.

Cadmium is extracted as a by-product in the production of zinc. As cadmium (b.p. 767° C) is more volatile than zinc (b.p. 907° C)

and cadmium oxide is more easily reduced than zinc oxide, cadmium distills off first when zinc ores are reduced and can thus be separated from zinc.

In the free state cadmium is a white metal with a specific gravity of 8.65 and a melting point of 320.9° C. Cadmium stands below zinc in the e.m.f. series, but above hydrogen, and therefore displaces the latter from acids.

Metallic cadmium is used in electrical engineering for the manufacture of copper wires subject to friction against sliding contacts (for instance, tram and trolleybus wires).

Admixtures of cadmium improve the mechanical properties of copper, prolonging the lifetime of the wires and at the same time scarcely decreasing the electrical conductivity of the copper. Cadmium is also a composite part of fusible alloys used, for instance, in automatic fire extinguishers. It is added to type alloys to increase their lifetime and to lead-tin solders. Lately , cadmium has been employed quite extensively for coating iron (cadmium plating). Cadmium is used also in alkaline storage batteries (see § 256) as a substitute for nickel.

As cadmium has a great affinity for neutrons, cadmium rods are used in nuclear reactors (see § 267) to regulate the rate of the chain reaction.

If strongly heated, cadmium will burn, turning into brown *cadmium oxide* CdO.

Cadmium hydroxide $Cd(OH)_2$, unlike zinc hydroxide, is insoluble in alkalis, showing that it is basic in nature.

An especially important cadmium compound is *cadmium sulphide* CdS, which separates out as a yellow precipitate when hydrogen sulphide is passed through solutions of cadmium salts. Cadmium sulphide is an excellent yellow paint.

The production of cadmium in the capitalist countries in 1953 totalled 6,800 tons.

225. Mercury (Hydrargyrum); at. wt. 200.61. Mercury is not abundant in nature; its content in the earth's crust is only 5×10^{-6} per cent by weight. Mercury occurs rarely in the native state, embedded in rocks, but is mainly found in nature as the sulphide HgS, known as *cinnabar*. This mineral is bright red and is used as a red paint.

The richest deposits of cinnabar have been discovered in Spain (Almadén) which hold about 80 per cent of the world's resources of mercury. The output of mercury in the capitalist countries in 1952 totalled 5,000 tons, of which Spain and Italy accounted for more than two-thirds. In the U.S.S.R. mercury ores have been found in the Donets Basin, where they have been mined for a long time.

Metallic mercury is extracted from cinnabar by simple roasting in special furnaces. The sulphur burns to form sulphur dioxide and the mercury comes off as vapours and is condensed in a cooled receiver:

$$HgS + O_2 = Hg + SO_2$$

Mercury is the only liquid metal at ordinary temperatures. It freezes at −38.87° C and boils at 356.9°; its specific gravity is 13.55.

Metallic mercury has a variety of applications. It is used to fill various physical instruments, such as barometers, thermometers, etc. Owing to its very high specific gravity, mercury is quite indispensable in many experiments involving gases. Large quantities of mercury are consumed in the preparation of mercury fulminate, used to make the so-called "initiating" explosives for filling detonating fuses, including ordinary percussion primers. Mercury is employed also for separating native gold from its non-metallic admixtures.

Mercury is capable of dissolving many metals to form liquid or solid alloys called **amalgams**. This often results also in the formation of various chemical compounds of mercury with the metals.

Sodium amalgam is widely used as a reducing agent. Tin and silver amalgams are used in dentistry for filling teeth.

Gold amalgamates with especial readiness, and therefore gold objects should never be allowed to come into contact with mercury. Iron does not form amalgams, and so mercury may be transported in iron vessels.

The mercury of commerce usually contains metallic impurities, most of which can be removed by shaking with a solution of mercury nitrate; this causes all the metals above mercury in the e.m.f. series (that is, most of the metals) to pass into solution, displacing an equivalent quantity of mercury from it. Mercury can be completely purified by distillation, best of all at low pressure.

Mercury vapours are very toxic and may cause serious poisoning. Even the insignificant quantity of vapours formed at ordinary temperatures is enough for this. Therefore, when working with mercury, great care must be taken not to drop it on the floor.

Mercury is the least active metal of the zinc subgroup, and parts with its electrons with greater difficulty than the others. Neither dilute sulphuric and hydrochloric acids, nor alkalis, attack mercury. Mercury dissolves readily in nitric acid. Concentrated sulphuric acid will dissolve mercury if heated.

Mercury will not oxidize in the air at ordinary temperatures. If heated for a long time to a temperature close to the boiling point, mercury combines with the oxygen of the air forming red *mercuric oxide* HgO, which, if heated still more strongly, decomposes again into mercury and oxygen. Mercury forms another compound with oxygen, known as *mercurous oxide* Hg_2O, which is black in colour.

Thus, mercury may be bivalent or univalent and, accordingly, forms two series of salts. Salts in which mercury is bivalent are known as **mercuric salts**, and those where it is univalent as **mercurous salts.**

Although in mercurous compounds (such as Hg_2O) mercury is ostensibly a univalent metal, it may now be considered established that the mercury atoms in all such compounds are linked into bivalent groups: $—Hg_2—$ or $—Hg—Hg—$. Hence, mercury is bivalent in its mercurous compounds. But one of the valency bonds of each mercury atom is used to link it to the other mercury atom. This linkage persists in solutions of mercurous salts, which contain $Hg_2^{\cdot\cdot}$-ion, and not $Hg^{\cdot}$-ion.

Thus, the composition of mercurous salts containing univalent acid radicals (represented by R) should be expressed by the empiric formula Hg_2R_2 and not by the formula HgR (for instance, Hg_2Cl_2, not HgCl).

One of the peculiarities of mercury is that no hydroxides of this metal are known. Whenever their formation might be expected, the anhydrous oxides result instead. Thus, when alkalis are added to solutions of mercurous salts, brownish-black mercurous oxide precipitates:

$$Hg_2^{\cdot\cdot} + 2OH' = \downarrow Hg_2O + H_2O$$

Alkalis likewise precipitate mercuric oxide, and not mercuric hydroxide, from solutions of mercuric salts:

$$Hg^{\cdot\cdot} + 2OH' = \downarrow HgO + H_2O$$

The resulting precipitate is yellow in colour, but if heated changes to red mercuric oxide.

The most important mercury salts are:

1. *Mercury nitrate* (I) or *mercurous nitrate* $Hg_2(NO_3)_2$, one of the few soluble salts of "univalent" mercury. It is obtained by the action of dilute cold nitric acid on an excess of mercury:

$$\overset{0}{6Hg} + 8\overset{+V}{H}\overset{+V}{N}O_3 = 3\overset{+I}{Hg}_2(NO_3)_2 + 2\overset{+II}{N}O + 4H_2O$$

2. *Mercury chloride* (I) or *mercurous chloride* Hg_2Cl_2, known also as *calomel*, is a white insoluble powder. It is prepared by heating a mixture of corrosive sublimate with mercury:

$$HgCl_2 + Hg = Hg_2Cl_2$$

Calomel can be produced also by the action of hydrochloric acid or common salt on soluble mercurous salts:

$$Hg_2^{\cdot\cdot} + 2Cl' = \downarrow Hg_2Cl_2$$

Calomel is used in medicine as a laxative.

3. *Mercury nitrate* (II) or *mercuric nitrate* $Hg(NO_3)_2$ is obtained by the action of an excess of hot nitric acid on mercury. Dissolves well in water. Hydrolyzes readily in dilute solutions in the absence of free acid to form a white precipitate of the basic salt $HgO \cdot Hg(NO_3)_2$. When heated with a large quantity of water, the basic salt also decomposes, resulting in mercuric oxide.

4. *Mercury chloride* (II), *mercuric chloride* $HgCl_2$, or *corrosive sublimate*, can be prepared by the direct union of mercury and chlorine. It is a colourless substance, rather sparingly soluble in cold water. Corrosive sublimate crystallizes out of solution in long, lustrous prisms. It is usually produced by heating mercury sulphate (II) with common salt:

$$HgSO_4 + 2NaCl = Na_2SO_4 + HgCl_2$$

The corrosive sublimate thus formed volatilizes, or sublimes; hence its name.

An aqueous solution of corrosive sublimate practically does not conduct electricity. Thus, corrosive sublimate is one of the few salts which *hardly ionizes* in solution.

Corrosive sublimate, like all soluble mercury salts, is a strong poison. Very dilute solutions of corrosive sublimate (1:1,000) are used in medicine as disinfectant.

5. *Mercury iodide* (II) or *mercuric iodide* HgI_2 can be brought down as a beautiful orange-red precipitate by adding a solution of potassium iodide to any salt of bivalent mercury:

$$Hg^{\cdot\cdot} + 2I' = HgI_2$$

The precipitate dissolves readily in an excess of potassium iodide, forming a colourless solution of the complex salt $K_2[HgI_4]$

$$HgI_2 + 2KI = K_2[HgI_4]$$

6. *Mercury sulphide* (II) or *mercuric sulphide* HgS, as mentioned above, occurs in nature (cinnabar). Mercury sulphide (II) can be prepared artificially as a black amorphous substance, either by the direct union of sulphur and mercury or by the action of hydrogen sulphide on solutions of mercuric salts:

$$Hg^{\cdot\cdot} + S'' = \downarrow HgS$$

If heated without access of air black mercury sulphide (II) turns into the red crystalline modification, cinnabar.

CHAPTER XXII

Third Group of the Periodic Table

The third group of the Periodic Table embraces a large number of chemical elements, as it includes, besides the usual eight or nine members, the rare-earth elements (lanthanides), all of which are crowded into one box in the Table.

The typical elements of the third group are *boron* and *aluminium*, whose atoms contain three electrons each in their outer layer. *Gallium*, *indium* and *thallium* possess a similar electronic structure, though they are not complete analogues in this respect to the typical elements (like, for instance, calcium, etc., in the second group). They have three valency electrons, but the cations formed by removing these electrons have an 18-electron outer shell.

Owing to this similarity they are often placed together with the typical elements in the *main subgroup of the third group*.

The secondary subgroup of the third group constitutes the even series elements of the long periods: *scandium*, *yttrium*, *lanthanum* and *actinium*. This subgroup includes also the rare-earth elements (lanthanides).

MAIN SUBGROUP OF THE THIRD GROUP

Element	Symbol	Atomic weight	Atomic number	Arrangement of electrons in layers					
Boron . . .	B	10.82	5	2	3				
Aluminium	Al	26.98	13	2	8	3			
Gallium . .	Ga	69.72	31	2	8	18	3		
Indium . .	In	114.76	49	2	8	18	18	3	
Thallium . .	Tl	204.39	81	2	8	18	32	18	3

226. General Features of the Main Subgroup of the Third Group. As stated above, the elements of this subgroup are distinguished by the presence of three electrons in the outer layer of their atoms.

Therefore, the metallic properties of these elements are much less pronounced than in the corresponding elements of the second, and especially the first group, while boron, having a small atomic radius, possesses predominantly non-metallic properties.

All the elements in question are positively trivalent in their most typical compounds. With the exception of boron, they can all exist in aqueous solution as hydrated positive trivalent ions.

The metallic properties of the elements under consideration become more and more pronounced with increasing atomic number, as was the case in the other main subgroups we have examined. Thus, whereas boron is an acid-forming element, the oxides and hydroxides of the next three elements, aluminium, gallium and indium, are amphoteric, with increasingly basic properties, while the oxide of trivalent thallium is exclusively basic in character.

The most important elements of the third group, practically, are boron and aluminium. The rest of them are rare elements and of no significant use.

227. Boron (Borum); at. wt. 10.82. Boron is comparatively scarce in nature; it is found almost exclusively as oxycompounds. Its total content in the earth's crust is 0.005 per cent by weight.

The chief natural compounds of boron are boric acid H_3BO_3 and various boric acid salts, the most common of which is borax $Na_2B_4O_7 \cdot 10H_2O$. Boric acid is contained in the waters of certain hot springs. In Italy boric acid is emitted together with steam from cracks in the earth's crust in volcanic districts.

Large deposits of high-grade boron ores were discovered in the U.S.S.R. in 1934 in the Inder District of the Kazakh S.S.R. Besides, rather large deposits of the mineral *datolite* $CaHBSiO_5$ have been found in the Caucasus. Boron compounds are contained in small quantities also in the volcanic muds of the Taman and Kerch peninsulas.

Although boron belongs to the third group of the Periodic Table, it resembles silicon, located in the fourth group, more than the other members of the third group. The resemblance between boron and silicon is manifested also in their compounds.

Like silicon, free boron is prepared by the reduction of boric anhydride B_2O_3 with sodium or magnesium. Boron is thus evolved as a brown amorphous powder with a specific gravity of 2.3 and a melting point of 2.075° C.

Crystalline boron can be prepared by crystallization from molten aluminium; it contains a minor amount of aluminium and is almost as hard as diamond. Boron is used in metallurgy as a component of certain alloys.

At ordinary temperatures boron is very inert, does not oxidize in air and will not combine with other elements.

If amorphous boron is heated to 700° C it bursts into flame and burns with a reddish flame, turning into boric anhydride and releasing a large amount of heat:

$$4B + 3O_2 = 2B_2O_3 + 564 \text{ Cal.}$$

At a high temperature boron combines with many metals to form **borides**, such as magnesium boride Mg_3B_2. Boron combines just as readily with the halogens if heated. With carbon it forms a very hard carbide B_4C. Water does not attack boron, but concentrated sulphuric and nitric acids oxidize it to boric acid. For instance:

$$\overset{3e^-}{\overset{\longrightarrow}{B}} + 3HNO_3 = H_3BO_3 + 3NO_2$$

Like silicon, boron dissolves in concentrated alkalis, liberating hydrogen:

$$2B + 2KOH + 2H_2O = 2KBO_2 + 3H_2$$

228. **Boron Compounds.** In most of its compounds boron is positively trivalent. Exceptions are the hydrogen borides and their derivatives, in which boron is formally tetravalent.

Hydrogen borides (boranes). When treated with hydrochloric acid magnesium boride Mg_3B_2 gives a complex mixture of different hydrogen borides, analogous to the hydrogen compounds of carbon and silicon. The following most important hydrogen borides have been isolated in the pure form from this mixture:

$$\underset{\text{gaseous}}{B_2H_6};\ \underbrace{B_4H_{10};\ B_5H_9;\ B_5H_{11};\ B_6H_{10}}_{\text{liquid}};\ \underset{\text{solid}}{B_{10}H_{14}}$$

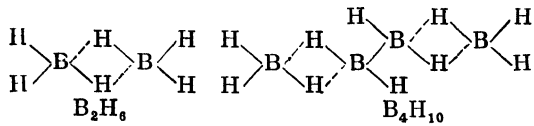
The chief product of the reaction between magnesium boride and hydrochloric acid is *borobutane* B_4H_{10}, a volatile liquid (b.p. 18° C) with a disgusting odour, its vapours igniting spontaneously in the air. Upon standing borobutane gradually decomposes, forming the simplest of the hydrogen borides obtained so far, namely, boroethane B_2H_6. The latter is a gas which condenses into a liquid at —92.5° C; it does not burst into flame in the air but is immediately decomposed, like the other hydrogen borides, by water, during which reaction hydrogen is split off and *boric acid* H_3BO_3 formed:

$$B_2H_6 + 6H_2O = 2H_3BO_3 + 6H_2$$

An examination of the above formulas of the boron hydrides suggests that in them boron is tetravalent. However, the fact that boron has only three outer electrons precludes this assumption.

The contradiction disappears if the molecules of the boron hydrides are regarded as a result of linkage of saturated valency structures

through the agency of hydrogen bonds (p. 214):



B_2H_6 B_4H_{10}

Practically the most important compounds of boron are its oxygen compounds.

Boric anhydride or *boron oxide* B_2O_3 can be prepared either by the direct combination of boron and oxygen or by calcining boric acid. It is a colourless, brittle vitreous mass, melting at about $+600°$ C. Boric anhydride is very refractory and is not reduced by coal even if heated to whiteness. It dissolves in water forming boric acid and releasing a large quantity of heat:

$$B_2O_3 + 3H_2O = 2H_3BO_3 + 16.8 \text{ Cal.}$$

Boric or *boracic acid* H_3BO_3 is a white crystalline solid, the shiny scales of which dissolve readily in hot water. Boric acid can be prepared by the action of sulphuric acid on a hot solution of borax:

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O = Na_2SO_4 + 4H_3BO_3$$

When the solution is cooled the boric acid crystallizes out, as it is but sparingly soluble in cold water.

If a solution of boric acid is boiled some of the boric acid will come away together with the water vapour. This accounts for its presence in the steam escaping from cracks in the earth's crust in volcanic regions.

Boric acid is a very weak acid ($K = 6.4 \times 10^{-10}$).

If heated boric acid loses water, passing first into *metaboric acid* HBO_2, then into *tetraboric acid* $H_2B_4O_7$ and finally into *boric anhydride* B_2O_3. When dissolved in water both acids, as well as boric anhydride, pass back into boric acid. Boric acid is used as an antiseptic in the canning industry as well as in the tanning of leather and in the preparation of certain paints and enamels.

The salts of boric acid, known as **borates**, are mostly derivatives not of the normal acid (orthoboric) H_3BO_3, but of tetraboric acid $H_2B_4O_7$ and other acids containing still less water, most of which are unknown in the free state.

Borax $Na_2B_4O_7 \cdot 10H_2O$ is the sodium salt of tetraboric acid (*sodium tetraborate*). It forms large colourless crystals which effloresce in dry air. It is prepared by the reaction between boric acid and sodium hydroxide:

$$4H_3BO_3 + 2NaOH = Na_2B_4O_7 + 7H_2O$$

Aqueous solutions of borax react strongly alkaline due to hydrolysis.

When heated, borax loses its water of crystallization and then melts into a transparent vitreous mass. Molten borax dissolves the oxides of various metals forming double salts of metaboric acid, many of which possess characteristic colours. For instance:

$$Na_2B_4O_7 + CuO = Cu(BO_2)_2 \cdot 2NaBO_2$$

This property of borax is utilized in analytical chemistry for the detection of certain metals. The determination is carried out by fusing the borax in a loop of platinum wire together with the substance studied, resulting in characteristically coloured spheres known as borax "beads."

Borax is widely used to produce fusible glazes for majolica and porcelain wares and especially for iron pots (enamel); besides, it is used for the manufacture of special brands of glass (see p. 485).

The ability of borax to dissolve metallic oxides is the underlying principle of its use in the soldering of metals. As only pure metallic surfaces can be soldered, the joints are first sprinkled with borax to remove the oxides, then the solder is added and they are heated. The borax dissolves the oxides, making the solder adhere well to the surface of the metal.

Boron plays an important part in the life of plants. The presence of small quantities of boron compounds in the soil is necessary to promote normal growth of many agricultural crops, such as cotton, tobacco, sugar beet, etc. That is why boron fertilizers are finding wider and wider application in agriculture.

229. Aluminium; at. wt. 26.98. Aluminium is the most widespread metal in nature. It is a composite part of clays, feldspars, micas and many other minerals. The total content of aluminium in the earth's crust is 7.45 per cent by weight. The chief raw material for the production of aluminium is bauxite. Bauxite is a complex mineral containing alumina Al_2O_3. Other important aluminium ores are *alunite* $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 2Al_2O_3 \cdot 6H_2O$ and *nephelite* $Na_2O \times \times Al_2O_3 \cdot 2SiO_2$.

The U.S.S.R. possesses immense reserves of aluminium ores. Besides bauxites, of which the Soviet Union has large deposits in the Urals, in the Bashkir A.S.S.R., in Kazakhstan and elsewhere, a very rich source of aluminium has been found in the form of the mineral nephelite, occurring together with apatite in the Khibiny Mountains.

Despite its great abundance in nature, aluminium was classed as a rare metal up to the end of the last century. It was first obtained by Wohler in 1827 by the action of metallic potassium on aluminium chloride. Then, up to the eighties of the last century aluminium

was prepared by displacement with metallic sodium from the molten double salt $AlCl_3 \cdot NaCl$, which was, of course, very expensive. In the fifties of the last century one kg. of aluminium still cost about 500 rubles.

After the discovery in 1886 and industrial realization of the electrolytic process for the manufacture of aluminium the price of aluminium went down very rapidly: before World War I (1914-18) 1 kg. of aluminium already cost about 1 ruble. At present aluminium is produced in immense quantities by the electrolysis of aluminium oxide dissolved in molten cryolite.

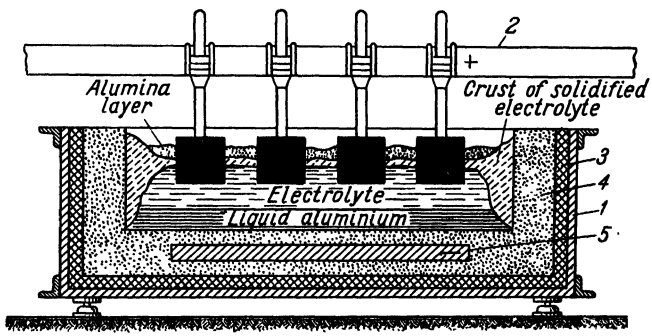


Fig. 153. Cross-section of an aluminium furnace:
1—box; *2*—anode bus; *3*—heat insulation; *4*—graphite lining; *5*—cathode bus

A furnace for the production of aluminium is shown diagrammatically in Fig. 153. It consists of an iron box (bath) lined on the inside with graphite or plates of pressed charcoal, which act as the cathode during electrolysis. The anodes are a number of graphite plates connected to a common bus. The bath is filled with a mixture of pure aluminium oxide and cryolite. The cryolite is added to lower the melting point of aluminium oxide, which is very refractory. When the current is switched on the cryolite melts and dissolves the aluminium oxide, which undergoes electrolysis. The process is carried out at a temperature of about +1,000° C with a current of 35,000 amperes and an average voltage of 4 or 5 volts. Aluminium is deposited at the cathode and oxygen is liberated at the anode. The aluminium collects at the bottom of the bath and is tapped periodically. As the aluminium is evolved, new batches of aluminium oxide are added to the fusion.

Deposits of cryolite, this very important mineral for the aluminium industry, are very scarce. Large quantities have been found only in Greenland. For this reason cryolite is usually prepared artificially by the reaction between aluminium hydroxide and hydrofluoric acid, the resulting acid solution being subsequently neutralized with soda.

Pure aluminium oxide is obtained by treating natural bauxite. The necessity of using pure aluminium oxide is due to the difficulty of purifying aluminium metal; therefore, to obtain the pure metal it is preferred to purify the raw materials.

The rate of growth of the aluminium industry is interesting to trace. The world production of aluminium, which amounted to only 8,000 tons in 1900, had reached 567,000 tons by 1938, and during World War II about 1 million tons of aluminium were put out yearly by the capitalist countries alone. Recently a very rare metal, aluminium has now become one of the most widely produced and extensively used metals. In 1954 the output of aluminium in the capitalist countries amounted to 2.4 million tons.

The first aluminium plant in the U.S.S.R. was started up in 1932. Two years later a second plant was put into operation, and as early as 1935 the Soviet Union already occupied the third place in the world in aluminium production. In the subsequent years the aluminium industry continued to develop very rapidly. During the period 1956-60 the aluminium output increased more than twofold in comparison with the Fifth Five-Year Plan period.

During the first years following the discovery of the electrolytic method for the manufacture of aluminium, its production was based exclusively on practical data. The scientific principles of the process were laid down only at the beginning of the second decade of this century. Of great importance in the development of the theory of the electrometallurgy of aluminium were the works of P. Fedotyev and his pupils.

Aluminium is a silvery-white light metal, its specific gravity being 2.7 and its melting point 660.1° C. It is very ductile and has a high tensile strength, can easily be drawn into wire and rolled into thin sheets.

At ordinary temperatures aluminium does not change in the air. But this is due only to the fact that it very rapidly becomes coated with a thin, dense oxide film, which protects the metal from further oxidation. If this film is broken down, say by amalgamating the aluminium, the metal begins to oxidize rapidly, becoming quite hot (see p. 522).

The normal potential of aluminium equals —1.66 volts. In spite of this, aluminium does not displace hydrogen from water (cf. zinc, § 223), owing to the formation of a dense, very slightly soluble film of aluminium hydroxide on its surface. Amalgamated aluminium reacts vigorously with water, liberating hydrogen.

Dilute hydrochloric and sulphuric acids dissolve aluminium readily, especially when hot. Aluminium dissolves just as readily in alkalis, forming aluminates, compounds analogous to zincates and containing the anion $[Al(OH)_4]^-$ (see p. 611). On the contrary, cold

nitric acid not only fails to dissolve aluminium, but even makes it "passive," so that after treatment with nitric acid it will not dissolve in dilute sulphuric or hydrochloric acids either. The reason for the passivity of aluminium was indicated in § 142.

If aluminium powder (or thin aluminium foil) is heated strongly it bursts into flame and burns with a blinding white flame, forming aluminium oxide. The combustion takes place very rapidly; for instance, a thin sheet of aluminium will burn up in 0.01 second.

Due to its lightness and comparative resistance to corrosion aluminium has found very wide application. Its chief consumers are the aircraft and automobile industries, where aluminium is used as various light alloys. Admixtures of small quantities of other metals greatly increase its strength without changing its weight to any considerable degree.

The most important aluminium alloys are *duralumin*, which contains about 95 per cent aluminium, 4 per cent copper, 0.5 per cent magnesium and 0.5 per cent manganese. Other widely used alloys are *magnalium* (an alloy containing up to 12 per cent magnesium) and *silumin* (an alloy of aluminium and silicon). Aluminium is gradually forcing copper out of electrical engineering as a material for wires. Although the electrical conductivity of aluminium is only about 60 per cent that of copper, this is made up for by the lightness of aluminium, which enables aluminium wires to be made thicker: an aluminium wire weighs only half as much as a copper wire of equal electrical conductivity.

A very important use of aluminium is for **calorization**, i. e., saturation of the surface of steel or iron parts with aluminium to protect the main material from oxidation when strongly heated.

Calorization is carried out either by immersing the part in molten aluminium, or more often by heating it in a mixture of powdered aluminium and aluminium oxide. When heated the aluminium penetrates into the surface layer of the part, forming a solid solution with the iron. Calorized steel parts can withstand heating in the air to a temperature of 900° C without becoming oxidized.

One more application of aluminium worth mentioning is for the manufacture of the simplest types of a. c. rectifiers. The rectifier consists of an aluminium and an iron (or lead) electrode dipped into a solution of soda. An apparatus of this kind will allow current to pass only in one direction, namely, in that which makes the aluminium the cathode. If an aluminium rectifier is wired into an a. c. circuit, pulsing current of a constant direction will result.

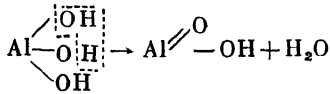
Finely powdered aluminium is used as a paint for coating iron to protect it from corrosion, as a lithographic colour and for making up certain explosive mixtures of the ammonal type (see p. 393). Large-grained aluminium powder is employed for the reduction of

many metals (see p. 526), for illuminating rockets and for the preparation of thermite. Thin aluminium foil is used for packing chocolate, candies and other confectionery goods. Finally, the wide use of aluminium for the manufacture of various kitchen utensils, such as pots, spoons, etc., is well known to everybody.

Aluminium forms only one oxide, namely Al_2O_3, and is trivalent in all its compounds.

Aluminium oxide Al_2O_3, called also *alumina*, occurs in nature in the crystalline form as the mineral *corundum*. Corundum is second in hardness only to diamond. Transparent red or blue corundum crystals are precious stones known as *ruby* and *sapphire*. Rubies are now obtained artificially by fusing alumina in an electric furnace. They are used not so much for decoration as for technical purposes, such as for the manufacture of precision instrument parts, for the jewels in watches, etc. Non-transparent corundum crystals containing considerable impurities are commonly known as *emery*.

Aluminium hydroxide $Al(OH)_3$ separates out as a jelly-like precipitate when solutions of aluminium salts are acted on by an alkali, and passes readily into the colloidal state. When heated, $Al(OH)_3$ loses water gradually, forming hydrates containing less water, for instance:



Aluminium hydroxide is a typical amphoteric hydroxide. With acids it forms salts containing the hydrated aluminium ion $[Al(H_2O)_6]^{\cdot\cdot\cdot}$, and with alkalis it forms salts containing the anion $[Al(OH)_4]'$ and called **aluminates** (for instance, $Na[Al(OH)_4]$. The latter were formerly regarded as salts of *metaluminic acid* $HAlO_2$:

$$Na\,[Al(OH)_4] = NaAlO_2 \cdot 2H_2O$$

The reaction of formation of an aluminate may be recorded as follows:

$$Al(OH)_3 + NaOH = Na\,[Al(OH)_4]$$

or

$$Al(OH)_3 + OH' = [Al(OH)_4]'$$

Aluminates can be prepared also by dissolving metallic aluminium in alkalis:

$$2Al + 2NaOH + 6H_2O = 2Na\,[Al(OH)_4] + 3H_2$$

The reaction proceeds analogously to the dissolving of zinc in alkalis (see p. 597).

Salts containing $Al^{\cdot\cdot\cdot}$-ion are greatly hydrolyzed in aqueous solution and react acid:

$$AlCl_3 + H_2O \rightleftarrows AlOHCl_2 + HCl$$

or

$$Al^{\cdot\cdot\cdot} + H_2O \rightleftarrows AlOH^{\cdot\cdot} + H^{\cdot}$$

Dialysis of a solution of an aluminium salt will lead to complete decomposition of the salt due to the gradual removal of the acid. The aluminium hydroxide formed passes into the colloidal state.

With weak acids aluminium hydroxide forms either basic salts or none at all. For instance, if a solution of an aluminium salt is treated with soda, aluminium hydroxide results instead of the carbonate:

$$2Al^{\cdot\cdot\cdot} + 3CO_3'' + 3H_2O = \downarrow 2Al(OH)_3 + 3CO_2$$

The course of the reaction may be pictured as follows. Hydrolysis of aluminium salts in aqueous solution leads to the equilibrium:

$$2Al^{\cdot\cdot\cdot} + 6H_2O \rightleftarrows 2Al(OH)_3 + 6H^{\cdot}$$

Owing to the same process, in a solution of soda the following equilibrium is set up:

$$3CO_3'' + 3H_2O \rightleftarrows 3HCO_3' + 3OH'$$

When the solutions are mixed $H^{\cdot}$-ion combines with OH'-ion and HCO_3'-ion forming molecular H_2O and H_2CO_3, the latter then decomposing into water and carbon dioxide. As a result, both equilibria shift continuously to the right, until, at length, all the aluminium precipitates out as $Al(OH)_3$.

Of the salts of aluminium the following are noteworthy:

1. *Aluminium chloride* $AlCl_3$. Anhydrous aluminium chloride can be prepared by the direct action of chlorine on aluminium. It is widely used as a catalyst for various organic syntheses. Aluminium chloride dissolves in water, releasing a great amount of heat. If the solution is evaporated hydrolysis sets in, hydrogen chloride is evolved and aluminium hydroxide precipitates out. If evaporated in an excess of hydrochloric acid it gives crystals of the composition $AlCl_3 \cdot 6H_2O$.

2. *Aluminium sulphate* $Al_2(SO_4)_3 \cdot 18H_2O$ is prepared by the action of hot sulphuric acid on alumina or pure clay (kaolin). It is used for sizing in the manufacture of writing paper and for the purification of water (see p. 500).

3. *Aluminium alum* $KAl(SO_4)_2 \cdot 12H_2O$ is the most important technical aluminium salt. Is used in great quantities for tanning leather and as a mordant in dyeing cotton fabrics. In the latter case

its action is based on the fact that the $Al(OH)_3$ formed due to hydrolysis deposits on the fibres of the fabric in a very finely divided state, adsorbs the dye and retains it well on the fibre.

4. *Ultramarine* is a well-known blue dye used as a powder for "bluing" clothes. In chemical composition it is the product of the addition of Na_2S_3 to the alumosilicate $Na_2Al_2Si_2O_3$. It is prepared by heating a mixture of kaolin, sulphur and soda with a small quantity of sugar.

230. Gallium Subgroup. The elements belonging to this subgroup, *gallium*, *indium* and *thallium*, contain three electrons each in the outermost orbit of their atoms and eighteen in the second last. Like aluminium, they display rather weak metallic properties which become somewhat more pronounced with increasing atomic number. They are all rare elements and do not occur in any considerable quantities. Their content in the earth's crust is respectively 1×10^{-4}, 1×10^{-5} and 1×10^{-5} per cent by weight.

In the free state gallium, indium, and thallium are silvery-white soft metals with low melting points. (Gallium melts at as low a temperature as 29.8° C, indium at 156.2° C and thallium at 303° C.) They are quite stable in the air, do not decompose water but dissolve readily in acids, gallium and indium dissolving in alkalis as well. Besides their maximum valency of three, they are capable also of showing lower valency. In particular, thallium has characteristic compounds in which it is univalent.

The oxides and hydroxides of trivalent gallium and indium are amphoteric; thallium hydroxide $Tl(OH)_3$, however, possesses only basic properties.

Of great interest are the compounds of univalent thallium, resembling compounds of alkali metals on the one hand, and silver compounds on the other. For instance, thallium oxide Tl_2O combines vigorously with water to form the hydroxide TlOH, which is a strong base, quite soluble in water.

Most of the salts of univalent thallium dissolve readily in water, but its halides are almost insoluble and, like silver salts, are sensitive to light.

The practical applications of the gallium subgroup elements are limited.

Metallic gallium has recently been used to fill quartz thermometers for measuring high temperatures. As gallium melts at 29.8° and boils only at 2,000°, such thermometers make it possible to measure temperatures as high as 1,000°C and higher, for which ordinary thermometers cannot be employed. Admixtures of gallium in aluminium give alloys which can readily be worked hot; alloys of gallium and gold are used in jewellery making and for false teeth.

Indium is used instead of silver to coat reflectors. Since reflectors coated with indium do not tarnish in time, their coefficient of reflection remains constant. Indium is employed also to coat bearing inserts and as one of the ingredients of the alloy used for making fuses.

Thallium compounds have found application in photography and medicine, as well as in the manufacture of high-refracting optical glasses.

SCANDIUM SUBGROUP

Element	Symbol	Atomic weight	Atomic number	Arrangement of electrons in layers						
Scandium . .	Sc	44.96	21	2	8	9	2			
Yttrium . . .	Y	88.92	39	2	8	18	9	2		
Lanthanum . .	La	138.92	57	2	8	18	18	9	2	
Actinium . . .	Ac	227	89	2	8	18	32	18	9	2

231. General Features of the Scandium Subgroup. The scandium subgroup includes, besides those indicated above, the elements with atomic numbers from 58 to 71, known as the rare-earth elements or lanthanides.

All the elements of the scandium subgroup, including the lanthanides (see Table 10, p. 163), contain two electrons in the outermost layer of their atoms. In their second last layer scandium, yttrium, lanthanum and actinium, as well as the lanthanides, gadolinium and lutetium, contain nine electrons, all the rest of the lanthanides containing eight.

The maximum valency of the scandium subgroup elements, as a rule, equals three. However, cerium also forms a number of derivatives in which it is tetravalent. Oxides of tetravalent praseodymium and terbium are also known, but they are rather unstable.

In nature these elements occur usually in intimate association with one another and with the elements of the fourth group, zirconium, hafnium and thorium. One of the main sources for their preparation is the mineral *monazite*, which is a mixture of phosphates of cerium, lanthanum, etc. The isolation of the separate elements from monazite is a very complex problem owing to the great resemblance in their properties. The lanthanides are especially difficult to separate. To date only very few of them have been obtained in the pure form (lanthanum, cerium), while some of them are very little known in general.

In the free state the elements of the scandium subgroup are metals with high melting points (with the exception of terbium which melts at 310° C). Their metallic properties are much more pronounced than those of the elements of the gallium subgroup. They decompose water at ordinary temperature or if heated, and dissolve readily in dilute acids. With hydrogen some of them form hydrides (such as LaH_3).

The oxides and hydroxides of the elements of this subgroup possess only basic properties. Their salts hydrolyze but very slightly.

All the elements of the scandium subgroup give characteristic line spectra, which are the only way of precisely establishing the individuality of each.

The rare-earth elements and their salts find more and more applications in technology from year to year. The oxides of lanthanum, neodymium, and cerium are used as admixtures in the manufacture of special brands of glass. For instance, optical glass for the manufacture of photographic lenses and glasses for protective goggles contain lanthanum or neodymium. Glasses containing cerium do not darken under the action of radioactive irradiation.

Cerium nitrate is used in the manufacture of incandescent gas mantles, which contain about 2 per cent cerium oxide and 98 per cent thorium oxide. Cerium salts are sometimes used to colour glass and porcelain. An alloy consisting of 30 per cent iron and 70 per cent cerium (together with other rare-earth elements) is used to make "flints" for cigarette lighters, as when rubbed on a rough steel surface they give sparks which will light a wick moistened with gasoline. Metallic cerium is used as an admixture in aluminium and magnesium alloys.

CHAPTER XXIII

Metals of the Fourth and Fifth Groups of the Periodic Table

GERMANIUM SUBGROUP

Element	Symbol	Atomic weight	Atomic number	Arrangement of electrons in layers					
Germanium	Ge	72.60	32	2	8	18	4		
Tin	Sn	118.70	50	2	8	18	18	4	
Lead . . .	Pb	207.21	82	2	8	18	32	18	4

232. General Features of the Germanium Subgroup. The elements *germanium*, *tin* and *lead* are the closest analogues of the typical elements of the fourth group, namely, *carbon* and *silicon*, which have been considered above, and form together with them the *main subgroup of the fourth* or *carbon group*. All the five elements of the carbon group have four electrons in the outermost layer of their atoms. They are, therefore, capable not only of yielding, but also of gaining electrons in sufficient number to make up an octet, with the formation of covalent bonds, this being generally characteristic of non-metals. However, the tendency of the germanium subgroup elements to gain electrons is very weakly pronounced, owing to the presence of eighteen electrons in the second last layer of their atoms and to their rather large atomic radii. Although, like carbon and silicon, they also form gaseous hydrogen compounds, the latter are very unstable. On the other hand, they yield electrons rather readily and the more so, the higher their atomic number. That is why the non-metallic and metallic properties of germanium are almost equally pronounced, whereas in tin and lead the latter are clearly predominant. Tin and lead are typical metals in physical properties, their non-metallic nature being manifested only in chemical combination.

As was stated above in Chapter XVII, all the elements of the carbon group show a valency of +2, besides their maximum positive valency of +4. But while the compounds of bivalent carbon and silicon (CO and SiO) are not characteristic and quite unstable, the tendency of the germanium subgroup elements to manifest bival-

ency is much stronger: the bi- and tetravalent states of tin are almost equally stable, whereas lead is bivalent in most of its compounds.

233. Germanium; at. wt. 72.60. Germanium is one of the most dispersed elements. Minerals containing germanium in any considerable quantities are extremely rare. The most important of these minerals are *argyrodite* $4Ag_2S \cdot GeS_2$ and *germanite* $6CuS \cdot GeS_2$. At the same time, germanium compounds are found in very small quantities in many ores. The total content of germanium in the earth's crust amounts to 4×10^{-4} per cent by weight. The usual source for the preparation of germanium is the ashes of bituminous and brown coals and zinc metallurgy wastes.

Not so long ago germanium had hardly any practical application, but in recent years it has acquired exceptional importance in electrical and radio engineering, where it is used as a semi-conductor.

Semi-Conductors. Semi-conductors are substances whose electrical conductivity is intermediate between conductors and insulators. A characteristic feature of semi-conductors is that under ordinary conditions they do not conduct electricity, but acquire the ability to do so under the action of heat, light and other factors. Semi-conductors of a definite type, when brought into contact, possess the property of conducting current only in one direction.

Owing to the qualitative difference of semi-conductors from metals and insulators, they have been employed by modern electrical and radio engineering to solve a number of technical problems of immense practical importance.

For instance, the comparatively large, breakable vacuum valves used in radio-engineering can be replaced by tiny, long-lived crystalline germanium diodes and triodes; the volume of some of them does not exceed 0.01 cu. cm. This makes it possible to considerably diminish the size of radio and television sets, computing machines, radar units and other apparatuses and to improve their performance essentially, at the same time greatly decreasing their power consumption. Germanium amplifiers are very durable, operate without vacuum and require no power or time for heating filaments, as ordinary valves do. Their lifetime is very long.

Semi-conductors are widely used in various instruments for automatic control of many industrial processes. The power industry employs germanium rectifiers for converting high-power alternating current into direct current. By means of semi-conductors thermal and luminous energy can be changed directly into electrical, with an efficiency, at present, of 8 to 10 per cent. Semi-conductors can be used to convert the energy of radioactive radiations into electric current.

Other semi-conductors, besides germanium, are silicon, grey tin, certain chemical compounds and alloys.

The germanium used in semi-conductor apparatuses must be very pure, as even one atom of impurities per 10 million atoms of germanium increases its conductivity. Such pure germanium is prepared by "zone" melting (see p. 545).

Germanium is a silvery-white, very brittle metal, having a specific gravity of 5.36 and melting at 959° C. In the compact state it changes neither in dry, nor in moist air, even if heated. Powdered

germanium passes into the dioxide GeO_2 even if only moderately heated.

Hydrochloric and dilute sulphuric acids do not attack germanium, but nitric and concentrated sulphuric acids oxidize it to the dioxide. Germanium dissolves slowly in alkalis. At about 200 or 250° C germanium reacts actively with the halogens and sulphur.

Germanium is bi- and tetravalent in its compounds. *Compounds of bivalent germanium* are comparatively unstable; they oxidize easily, passing into compounds of tetravalent germanium; hence, they are active reducing agents.

Germanium oxide GeO is a black crystalline powder. It is very unstable. It is prepared by carefully reducing germanium dioxide with magnesium or metallic germanium. It reacts with the hydrohalic acids, forming dihalides.

Germanium hydroxide $Ge(OH)_2$ can be precipitated by alkalis or ammonia from a solution of germanium chloride:

$$GeCl_2 + 2NaOH = Ge(OH)_2 + 2NaCl$$

It is amphoteric in properties and dissolves perceptibly in water, its aqueous solution reacting acid.

Compounds of tetravalent germanium are the most characteristic of this element. They are more stable, better known, and greater in number, than the derivatives of bivalent germanium.

Germanium dioxide GeO_2 is a white crystalline substance of specific gravity 4.703; it is perceptibly soluble in water, the solution conducting electricity. It can be prepared by several methods. In particular, it can be obtained by heating germanium in oxygen or by oxidizing it with concentrated nitric acid.

Germanium dioxide is an amphoteric oxide with strongly predominating acidic properties, as a result of which it is readily soluble in alkalis, giving salts of germanic acid. These salts are, as a rule, colourless. The potassium and sodium salts of germanic acid are quite soluble.

Germanium dioxide is employed in technology for the manufacture of optical glass with a very high index of refraction.

Germanium tetrachloride $GeCl_4$ is prepared by heating germanium in a stream of chlorine or by passing hydrogen chloride through a heated suspension of germanium dioxide in concentrated hydrochloric acid:

$$GeO_2 + 4HCl \rightleftarrows GeCl_4 + 2H_2O$$

The reaction is reversible and goes from right to left in an excess of water.

Germanium tetrachloride is a colourless mobile liquid with a specific gravity of 1.874 and a boiling point of 83° C. In properties it resembles silicon tetrachloride.

Germanium disulphide GeS_2 is known to occur in two modifications—amorphous and crystalline. The moisture of the air decomposes GeS_2, liberating hydrogen sulphide:

$$GeS_2 + 2H_2O = GeO_2 + 2H_2S$$

Germanium disulphide readily forms stable thiosalts.

Germanium hydrides. Treatment of germanium chloride with sodium amalgam in a stream of hydrogen, or decomposition of a germanium-magnesium alloy by acids results in germanium tetrahydride GeH_4. It is a colourless gas which, like arsenic hydride, decomposes when heated to form a metallic mirror. The melting point of germanium tetrahydride is —166° C and its boiling point —88° C.

During the preparation of the simplest germanium hydride, small quantities of its homologues, Ge_2H_6 and Ge_2H_8, are also formed.

234. Tin (Stannum); at. wt. 118.70. Tin cannot be regarded as a widespread metal (its content in the earth's crust has been estimated at 8×10^{-3} per cent by weight). But it is easily extracted from its ores and for that reason became known to man in ancient times; man used tin in the form of its alloy with copper (bronze) as far back as the very dawn of his civilized life (the Bronze Age). Tin is sometimes found in nature in the native state, but usually occurs as its compound with oxygen SnO_2, called *cassiterite* or *tinstone*, from which it is reduced by coal.

The largest deposits of tin ores have been found in Malaya, Viet-Nam, Bolivia and Indonesia. In the U.S.S.R. tin ores of commercial importance have been discovered in Eastern Siberia and in the Yakut A.S.S.R.

In 1954 the output of tin in the capitalist countries was 178,000 tons.

In the free state tin is a silvery-white soft metal with a specific gravity of 7.30 and a melting point of 231.9° C. It has a decidedly crystalline structure. When a stick of tin is bent it emits a characteristic crackling noise, probably due to friction between the individual crystals. Tin is soft and ductile and is readily rolled into thin sheets known as tin foil or just *foil*.

Besides ordinary *white tin*, crystallizing in the tetragonal system, tin has another modification, a grey crystalline powder with a specific gravity of 5.7. It has long been known that grey spots sometimes appear on tin objects kept for a long time in a strong frost. This phenomenon has been referred to as *tin plague*. It was subsequently established that ordinary tin is stable only at temperatures above 13.2° C; below this temperature it may turn into *grey tin*. The lower the temperature, the more rapidly this transformation takes

place. When heated, grey tin passes back into the white modification.

If tin is heated above 161° C it passes into a third (rhombic) modification. In this form it is very brittle, can be ground readily into a powder and breaks into small fragments if dropped from a small height.

Tin does not become oxidized in the air at ordinary temperatures. But if heated above the melting point it gradually changes into tin dioxide SnO_2. Tin is indifferent to water. Dilute acids dissolve it very slowly due to the insignificant difference between the normal potentials of tin and hydrogen (see Table 27, p. 518). Tin dissolves best of all in concentrated hydrochloric acid.

Tin also reacts vigorously with concentrated nitric acid, which changes it into a white powder, insoluble in water, called β-stannic acid.

Owing to the resistance of tin to the action of air and water, it is used to coat other metals, such as copper and iron (this process being known as "tinning"). About half the tin produced is used for the manufacture of tin plate or *tin*, i.e., tin-coated sheet iron. Of great importance are also many tin alloys, such as bronze, babbits, etc. Finally, tin is widely used both in the pure form and as alloys with lead for soldering.

Tin forms two oxides, namely, *stannous oxide* SnO and tin dioxide or *stannic oxide* SnO_2. And, accordingly, two series of tin compounds are known. In the first tin is bivalent and behaves mainly like a metal, whereas in the second it is tetravalent and is more like a non-metal in properties.

Compounds of Bivalent Tin. Stannous oxide SnO is a dark brown powder which results when tin is heated in a limited supply of air, as well as from the decomposition of stannous hydroxide $Sn(OH)_2$ in an atmosphere of carbon dioxide.

Stannous hydroxide $Sn(OH)_2$ is obtained as a white precipitate when bivalent tin salts are treated with alkalis:

$$Sn^{\cdot\cdot} + 2OH' = \downarrow Sn(OH)_2$$

Stannous hydroxide is amphoteric, dissolving readily both in acids and in alkalis, in the latter case to form hydroxysalts, known as *stannites*, analogous to zincates (see p. 597):

$$Sn(OH)_2 + NaOH = Na[Sn(OH)_3]$$

Tin chloride (II) or *stannous chloride* $SnCl_2 \cdot 2H_2O$ is prepared by dissolving tin in hydrochloric acid; it forms colourless crystals containing two molecules of crystallization water. When heated or greatly diluted with water, aqueous solutions of $SnCl_2$ hydrolize

partly, giving a precipitate of the basic salt:

$$SnCl_2 + H_2O \rightleftarrows \downarrow SnOHCl + HCl$$

Stannous chloride is a powerful reducing agent. For instance, it reduces ferric chloride $FeCl_3$ to ferrous chloride $FeCl_2$:

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$$

If stannous chloride is added to a solution of corrosive sublimate, a white precipitate of calomel separates. In an excess of $SnCl_2$ the corrosive sublimate is further reduced to metallic mercury:

$$2HgCl_2 + SnCl_2 = \downarrow Hg_2Cl_2 + SnCl_4$$
$$Hg_2Cl_2 + SnCl_2 = 2Hg + SnCl_4$$

Compounds of Tetravalent Tin. Stannic oxide or *tin dioxide* SnO_2 is found in nature as the mineral tinstone or cassiterite, the most important tin ore. It can be produced artificially by burning the metal in air or by oxidizing it with nitric acid and then calcining the resulting product. It is used for the preparation of various white glazes and enamels.

Stannic acids. The hydrates of stannic oxide are known as stannic acids and exist in two modifications: as α-stannic acid, and β-stannic acid. *α-stannic acid* H_2SnO_3 can be prepared by the action of an aqueous ammonia solution on a solution of stannic chloride $SnCl_4$.

The formation of the white precipitate which separates out is usually represented by the equation

$$SnCl_4 + 4NH_4OH = \downarrow H_2SnO_3 + 4NH_4Cl + H_2O$$

As the precipitate is dried it gradually loses water until pure stannic oxide remains. Thus, no acid of any definite composition is obtained. Therefore, the above formula for α-stannic acid is but the simplest of its possible formulas. It would be more correct to represent the composition of this acid by the formula $mSnO_2 \cdot nH_2O$.

α-stannic acid dissolves readily in alkalis, forming salts which contain the complex anion $[Sn(OH)_6]^{--}$ and are called **stannates**:

$$H_2SnO_3 + 2NaOH + H_2O = Na_2[Sn(OH)_6]$$

Sodium stannate separates out of solution as crystals of a composition which may also be expressed by the formula $Na_2SnO_3 \cdot 3H_2O$. This salt is used as a mordant in dyeing and as a filler for silk. Silk fabrics treated before dyeing with solutions of tin compounds sometimes contain as much as 50 per cent of their total weight in tin.

Acids also dissolve α-stannic acid to form salts of tetravalent tin. For example:

$$H_2SnO_3 + 4HCl \rightleftarrows SnCl_4 + 3H_2O$$

In an excess of hydrochloric acid $SnCl_4$ adds two HCl molecules to form complex chlorostannic acid $H_2[SnCl_6]$. The ammonium salt of this acid $NH_4[SnCl_6]$ is used for the same purposes as sodium stannate.

β-*stannic acid* is obtained as a white powder by the action of concentrated nitric acid on tin. Its composition is just as indefinite as that of α-stannic acid. Contrary to α-stannic acid, it dissolves neither in acids nor in alkalis. But it can be transferred into solution as a stannite by fusion with alkalis. If kept in contact with the solution from which it was precipitated α-stannic acid also gradually passes into β-stannic acid.

Tin chloride (IV) or *stannic chloride* $SnCl_4$ is a liquid with a boiling point of +114° C, fuming strongly in the air. It is prepared by the action of chlorine on metallic tin or on stannous chloride. Is produced in industry mainly by treating tin waste (old cans) with chlorine.

Though stannic chloride is similar in some of its properties to the chlorides of non-metals, it dissolves in water without decomposing perceptibly, and can be evolved from solution as various crystal hydrates, such as $SnCl_4 \cdot 5H_2O$.

In dilute aqueous solutions $SnCl_4$ hydrolyzes to a large degree according to the equation:

$$Sn^{\cdots\cdot} + 3H_2O \rightleftarrows H_2SnO_3 + 4H^{\cdot}$$

The resulting stannic acid passes into colloidal solution.

Tin Sulphides. If a solution of $SnCl_2$ is treated with hydrogen sulphide a brown precipitate of *tin sulphide* (II) SnS results. A solution of $SnCl_4$ treated in the same manner yields a yellow precipitate of *tin disulphide* SnS_2. The latter compound can be prepared also by a dry method, for instance, by heating tin filings with sulphur and ammonium chloride. Prepared in this way, the disulphide has the form of golden-yellow scales and is used for gilding wood under the name of "mosaic gold".

Tin disulphide dissolves in the alkali sulphides and in ammonium sulphide solution, giving readily soluble salts of *thiostannic acid* H_2SnS_3:

$$SnS_2 + (NH_4)_2S = (NH_4)_2SnS_3$$

Thiostannic acid (like the corresponding thioacids of arsenic and antimony) is unknown in the free state. Its salts are decomposed by acids into hydrogen sulphide and tin disulphide:

$$(NH_4)_2SnS_3 + 2HCl = \downarrow SnS_2 + H_2S + 2NH_4Cl$$

Stannous sulphide is insoluble in the alkali sulphides, as there are no thiosalts corresponding to bivalent tin. But the alkali polysulphides dissolve it to form salts of thiostannic acid:

$$SnS + (NH_4)_2S_2 = (NH_4)_2SnS_3$$

$$\begin{vmatrix} \overset{+II}{Sn} - 2e^- = \overset{+IV}{Sn} \\ S_2^{--} + 2e^- = 2\overset{-II}{S} \end{vmatrix}$$

Tin hydride or *stannane* SnH_4 was first obtained in 1919 as an impurity in hydrogen by treating an alloy of magnesium and tin with hydrochloric acid. It is a colourless, very poisonous gas which condenses into a liquid at —52° C and decomposes slowly, but spontaneously, at ordinary temperatures into tin and hydrogen.

235. Lead (Plumbum); at. wt. 207.21. Lead is found in nature as various compounds. The most important ore used for the extraction of lead is *glance* or *galena* PbS.

Large deposits of lead ores have been found in Australia, the U.S.A., Canada, Mexico and Germany. Lead deposits have been discovered in the U.S.S.R.—in Kazakhstan, Eastern Siberia, Northern Ossetia, the Altai Mountains and elsewhere.

Lead can be extracted from galena in the ordinary way, by roasting the ore to convert it into lead oxide and then reducing the resulting lead oxide with coke.

Another method of reducing lead from its ores without the use of coke consists in incomplete roasting of the ore by heating it moderately in special furnaces in the presence of air, so that only part of the PbS is oxidized. This involves the following reactions:

$$2PbS + 3O_2 = 2PbO + 2SO_2$$
$$PbS + 2O_2 = PbSO_4$$

Then the air is cut off, but the heating is continued. The unaltered lead sulphide reacts with the lead oxide and sulphate giving metallic lead:

$$PbS + 2PbO = 3Pb + SO_2$$
$$PbS + PbSO_4 = 2Pb + 2SO_2$$

The abundance of lead in the earth's crust is represented by a value of the same order as that of tin (1.6×10^{-3} per cent by weight).

Lead is a bluish-white heavy metal with a specific gravity of 11.34. It is very soft, being easily cut with a knife. The melting point of lead is 327.4° C. In the air lead rapidly becomes coated with a thin oxide film which protects it from further oxidation. In the e.m.f. series lead stands just above hydrogen. Its normal potential equals —0.126 volt.

Water itself does not attack lead, but in the presence of air lead is gradually destroyed by water, which converts it into lead hydroxide:

$$2Pb + O_2 + 2H_2O = 2Pb(OH)_2$$

However, in contact with hard water lead becomes coated with a protective film of insoluble salts (mainly lead sulphate and lead basic carbonate), which impedes the further action of the water and the formation of $Pb(OH)_2$. As all soluble lead compounds are

poisonous, lead pipes may be used safely for the delivery of drinking water only if the latter is hard.

Dilute hydrochloric and sulphuric acids hardly attack lead owing to the low solubility of the corresponding lead salts. Lead dissolves readily in nitric acid. Organic acids, especially acetic, also dissolve lead in the presence of the oxygen of the air. The process takes place analogously to the dissolving of copper (see p. 561).

Lead dissolves also in alkalis, which convert it into *plumbites.*

The applications of lead are diverse. The chief consumers of lead are the cable and storage battery industries, where it is used to manufacture cable sheaths and storage battery plates. At sulphuric acid plants lead is used to make the housings of towers, the coils of coolers and other responsible parts of the equipment. Considerable quantities of lead are used for the manufacture of ammunition, e. g., rifle and shrapnel bullets, as well as shot. Lead is a component part of many alloys, such as bearing alloys (babbits), type metal, solder, etc. Lead is a good absorber of gamma rays and is widely used for protection against gamma radiations in working with radioactive substances.

The production of lead in the capitalist countries totalled 1.6 million tons in 1954.

In its compounds lead is mainly positively bivalent. However, like the other elements of the germanium subgroup, it may be also positively tetravalent. The compounds of tetravalent lead are much less stable than those in which it is bivalent.

It has been shown possible to prepare a volatile compound of lead and hydrogen PbH_4, which is still less stable than SnH_4.

Lead forms two simple oxides PbO and PbO_2, corresponding to its bi- and tetravalent states, and two mixed oxides Pb_2O_3 and Pb_3O_4, in which both degrees of valency of lead are manifested simultaneously. Plumbous oxide Pb_2O, another compound of lead and oxygen, is very unstable.

Compounds of Bivalent Lead. Plumbic oxide PbO is a yellow powder which results when molten lead is heated in air. If strongly calcined it acquires a reddish-yellow colour and in this form is known as *litharge.* Plumbic oxide has a variety of applications: it is used to prepare other lead compounds, serves for filling the cells of storage battery plates, for the manufacture of certain types of glass, etc.

Plumbic hydroxide $Pb(OH)_2$ precipitates out when soluble bivalent lead salts are treated with alkalis. It is amphoteric in nature, dissolving in acids to form salts of bivalent lead and in alkalis, giving salts known as **plumbites:**

$$Pb(OH)_2 + 2NaOH = Na_2PbO_2 + 2H_2O$$

sodium plumbite

However, it is more probable that when dissolved in alkalis plumbic hydroxide forms hydroxysalts, according to the equation:

$$Pb(OH)_2 + NaOH = Na[Pb(OH)_3]$$

Of the salts of bivalent lead the following are noteworthy:

1. *Lead chloride* (II) or *plumbous chloride* $PbCl_2$ is obtained as a white precipitate when solutions of lead salts are treated with hydrochloric acid or soluble chlorides. It is very slightly soluble in cold water but dissolves considerably in hot water.

2. *Lead iodide* (II) or *plumbous iodide* PbI_2 separates as a yellow precipitate from solutions of lead salts when iodide-ion is added to them. It is practically insoluble in cold water but dissolves rather well in hot, giving a colourless solution. When the latter is cooled, the lead iodide falls out as lustrous golden-yellow crystals.

3. *Lead acetate* (II) or *plumbous acetate* $Pb(CH_3COO_2)_2$ is one of the few readily soluble lead salts and is widely used in laboratory practice. Owing to its strong sweet taste lead acetate is also called *lead sugar*. It is employed to colour fabrics and to obtain other lead compounds.

4. *Lead sulphate* (II) or *plumbous sulphate* $PbSO_4$ drops out as a white powder-like precipitate when sulphuric acid is added to solutions of lead salts. Lead sulphate is almost insoluble in water and in dilute acids, but dissolves quite well in concentrated alkali solutions to form plumbites. Concentrated sulphuric acid also dissolves lead sulphate, converting it into the acid salt $Pb(HSO_4)_2$.

5. *Lead sulphide* (II) or *plumbous sulphide* PbS separates as a black precipitate upon the action of hydrogen sulphide on lead salts. For this reason, a piece of filter paper moistened with a solution of any lead salt darkens rapidly if hydrogen sulphide is present in the air even in insignificant quantities, this often being used as a test for hydrogen sulphide. PbS occurs in large quantities in nature as *galena*.

6. *Basic lead carbonate* (II) $Pb_3(OH)_2(CO_3)_2$ precipitates out of solutions of lead salts under the action of soda. Was formerly widely used for the preparation of a white oil paint of excellent covering power, known as *lead white*. Under the action of hydrogen sulphide this paint darkens owing to the formation of dark lead sulphide (II) PbS (this being the reason for the darkening of old pictures painted with oil colours).

As lead is very difficult to oxidize from its bivalent to its tetravalent state, bivalent lead salts, in contradistinction to tin salts, practically do not possess reducing properties.

Compounds of Tetravalent Lead. Lead dioxide PbO_2 is a dark brown powder formed by the action of strong oxidizers on lead oxide and salts of bivalent lead. Chemically lead dioxide resembles tin dioxide,

being amphoteric with predominating acid properties. Corresponding to lead dioxide are *ortho-* and *meta*plumbic acids H_4PbO_4 and H_2PbO_3, which do not exist in the free state but form rather stable salts. For instance, if lead dioxide is fused with potassium hydroxide, the result is the potassium salt of *meta*plumbic acid K_2PbO_3.

The basic properties of lead dioxide are manifested in the formation of very unstable salts of tetravalent lead. For instance, when lead dioxide is treated with hydrochloric acid, *lead chloride* (IV) $PbCl_4$ is first formed, but it very readily splits off chlorine and passes into $PbCl_2$:

$$PbO_2 + 4HCl \rightleftarrows PbCl_4 + 2H_2O$$
$$PbCl_4 \rightleftarrows PbCl_2 + Cl_2$$

Both reactions are reversible. If a suspension of $PbCl_2$ in hydrochloric acid is acted on with chlorine, lead tetrachloride will be obtained as an oily liquid, solidifying at $-15°$ C into a crystalline mass. Water decomposes it completely into lead dioxide and hydrochloric acid.

$$PbCl_4 + 2H_2O = PbO_2 + 4HCl$$

Another salt of tetravalent lead is the sulphate $Pb(SO_4)_2$, which is decomposed by water similarly to $PbCl_4$.

Red lead or *minium* Pb_3O_4 is a bright red substance, used to prepare ordinary red oil paint. Red lead is obtained by prolonged heating of lead oxide in air. It may be regarded as a lead salt of *ortho*-plumbic acid $\overset{+II}{Pb_2}\overset{+IV}{PbO_4}$.

When heated with dilute nitric acid red lead decomposes into brown lead dioxide:

$$Pb_2PbO_4 + 4HNO_3 = 2Pb(NO_3)_2 + PbO_2 + 2H_2O$$

The other mixed oxide of lead Pb_2O_3 may be regarded as the lead salt of *meta*plumbic acid $\overset{+II}{Pb}\overset{+IV}{PbO_3}$.

Lead dioxide and all the compounds of tetravalent lead are powerful oxidizing agents, owing to their instability.

236. The Lead Storage Battery. The oxidizing properties of tetravalent lead and its transition into the more stable bivalent state are the basis of the design and operation of widely used *lead storage batteries.*

Electric storage batteries are devices for accumulating electric power for use at some future moment. Power is accumulated by passing electric current through the battery, thus giving rise to a chemical process during which electrical energy is transformed into chemical; the storage battery is then said *to be charged.* The charged battery may subsequently be used as a galvanic cell, whereupon the reaction by which it was charged proceeds in the opposite direction,

and the chemical energy accumulated in the storage battery is converted back into electrical; as this energy is used up, the battery is said to be *discharged.*

In the simplest case a lead storage cell* consists of two lead grids, the spaces of which are filled with a putty of lead oxide and water. The plates are immersed in a rectangular glass vessel containing dilute sulphuric acid of specific gravity between 1.15 and 1.20 (22 to 28 per cent H_2SO_4).

Owing to the reaction

$$PbO + H_2SO_4 = PbSO_4 + H_2O$$

the lead oxide is presently converted into lead sulphate. If direct current is now passed through the device by connecting one plate to the negative and the other to the positive pole of a current source, the battery will be charged, the following processes taking place at the electrodes:

cathode

$$\overset{+II}{PbSO_4} + 2e^- = \overset{0}{Pb} + SO_4''$$

anode

$$\overset{+II}{PbSO_4} - 2e^- + 2H_2O = \overset{+IV}{PbO_2} + 4H^{\cdot} + SO_4''$$

Adding up these equations we get the summary equation of the reation of charging a storage battery:

$$2PbSO_4 + 2H_2O = Pb + PbO_2 + 4H^{\cdot} + 2SO_4''$$

Thus, as the current is passed through, the lead sulphate at the cathode turns into a spongy mass of metallic lead and that at the anode, into dark brown lead dioxide.

When this process is complete, the storage battery is fully charged. Completion of charging is indicated by the water beginning to decompose vigorously, liberating hydrogen at the cathode and oxygen at the anode (the accumulator is said to "boil").

If the plates of a charged storage battery are connected by means of a conductor, current arises in the latter, the electrons moving from the lead plate to the lead dioxide plate. The appearance of current is due to the following. Some $Pb^{\cdot\cdot}$ ions pass into solution from the lead plate charging the latter negatively. The electrons liberated at the lead plate pass over to the PbO_2 and reduce the tetravalent lead into bivalent. As a result $Pb^{\cdot\cdot}$ ions form at both plates and combine with the SO_4'' ions in solution into insoluble lead sulphate, discharging the battery.

* A storage battery usually consists of several storage cells connected in parallel and/or in series.

The processes taking place during the discharge of a storage battery can be represented by the following scheme:

Negative Electrode

$$\overset{0}{Pb} + 2e^- + SO_4'' = \overset{+II}{PbSO_4}$$

Positive Electrode

$$\overset{+IV}{PbO_2} + 2e^- + 4H^+ + SO_4'' = \overset{+II}{PbSO_4} + 2H_2O$$

Addition of the above equations makes it obvious that the reaction taking place during discharge of the battery is the reverse of the charge reaction. Therefore both processes may be expressed by a single equation:

$$2PbSO_4 + 2H_2O \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} Pb + PbO_2 + 4H^+ + 2SO_4''$$

When a storage battery is discharged the concentration of the sulphuric acid gradually decreases, owing to the consumption of H^+-ion and SO_4''-ion and the formation of water. Therefore, the degree of discharge of a storage battery can be judged by the specific gravity of the acid, measured by means of a densimeter.

The e.m.f. of a lead storage battery equals two volts and under normal load remains almost unaltered throughout its entire period of operation. If the voltage begins to fall, the storage battery must be recharged.

TITANIUM SUBGROUP

Element	Symbol	Atomic weight	Atomic number	Arrangement of electrons in layers					
Titanium .	Ti	47.90	22	2	8	10	2		
Zirconium .	Zr	91.22	40	2	8	18	10	2	
Hafnium . .	Hf	178.6	72	2	8	18	32	10	2

237. General Features of the Titanium Subgroup. The titanium subgroup includes the fourth group elements of the Periodic Table, *titanium*, *zirconium* and *hafnium* situated in the even series of the long periods. Formerly this subgroup also included the element thorium which is now, however, usually included in the actinide group (see § 266). As thorium resembles the elements of the titanium subgroup in chemical properties, we shall describe it together with these elements. Unlike the elements of the odd subgroup, the atoms

of the titanium subgroup elements contain only two electrons in their outermost layer and are incapable of gaining electrons. Therefore, no compounds are known in which they are negatively valent. At the same time, the maximum positive valency of the elements equals 4, as besides the two outermost electrons they are capable of yielding two more electrons from their incomplete second last layer, which consists of ten electrons.

Owing to the presence of only two electrons in the outermost electron layer of their atoms, the metallic properties of the titanium subgroup elements are much more pronounced than in the case with the elements of the germanium subgroup and become stronger with increasing atomic number. For instance, titanium hydroxide $Ti(OH)_4$ is amphoteric, zirconium and hafnium hydroxides are predominantly basic, while thorium hydroxide is exclusively basic.

In the free state all four elements are typical metals, resembling steel. They all have rather high melting points. At ordinary temperatures the elements of the titanium subgroup are stable both against water and air, and, with the exception of titanium, are quite resistant to the action of acids; but at high temperatures they become very active, combining readily with the halogens, oxygen, sulphur, as well as with nitrogen and carbon.

With the exception of titanium, which can be reduced quite readily to its lower valency state, the rest of the elements of this subgroup are almost always tetravalent in their compounds.

The most important of them, from a practical standpoint, are titanium and zirconium.

238. Titanium; at. wt. 47.90. Titanium is very abundant in nature; it constitutes 0.61 per cent of the earth's crust by weight.

The most important titanium minerals are the *titanomagnetites* $FeTiO_3 \cdot nFe_3O_4$, *ilmenite* $FeTiO_3$, *sphene* or *titanate* $CaTiSiO_5$ and *rutile* TiO_2. The most important of them as a raw material for the production of titanium are the titanomagnetites.

The largest deposits of titanium ores in the U.S.S.R. are in the Urals.

Metallic titanium has a specific gravity of 4.54 and melts at 1,725° C. It is prepared in the free state from its dioxide by aluminothermy. Reduction of ferrotitanic ores results in an alloy of titanium and iron known as ferrotitanium and used in metallurgy for steel production. The addition of about 0.1 per cent titanium to steel greatly improves its quality. The action of titanium is based partly on its ability to combine with the nitrogen contained in molten steel and thus to prevent the separation of the latter as bubbles when the steel solidifies; as a result, castings made of this steel are homogeneous and contain no cavities.

Under ordinary conditions titanium is not very active but at a high temperature it combines readily with the halogens, oxygen, sulphur, nitrogen and other elements.

However, the significance of titanium as a very valuable structural material became known comparatively recently, after the development of commercial methods of preparing the metal in its pure form.

Pure titanium is obtained by reducing its chloride with metallic sodium or magnesium in an atmosphere of hydrogen, or by decomposing titanium iodide on a red-hot surface (see p. 545).

Titanium can be obtained also by the reduction of its dioxide TiO_2 with metallic magnesium. However, the titanium produced by this method is not so pure.

Pure titanium is readily amenable to mechanical treatment. It forges well and can be rolled into sheets and bands and even into foil. Titanium is just a little heavier than aluminium, but it is three times as strong. This promises great opportunities for its application in aircraft engineering. The resistance of titanium to sea water makes it a good plating for ships not requiring anti-corrosive coatings. Titanium can be employed as a material for responsible parts in chemical engineering and in turbine manufacture. The use of titanium or titanium alloy parts in internal combustion engines decreases the weight of the latter by about 20 per cent.

The extensive use of titanium in engineering led to a rapid rise in its output. It will suffice to mention that while only 75 tons of titanium were produced in the U.S.A. in 1950, this figure had risen to 1,000 tons by 1952 and was about 20,000 tons in 1955.

The U.S.S.R. possesses large reserves of titanium ores, enabling extensive production of metallic titanium.

At a high temperature titanium combines readily with the halogens, oxygen, sulphur, nitrogen and other elements. Titanium combines with carbon to form a carbide. Carbides of titanium and tungsten with admixtures of cobalt give alloys almost as hard as diamond.

Titanium dioxide TiO_2 can be prepared by calcining titanium in air or in an atmosphere of oxygen, as a white refractory substance insoluble in water and dilute acids. Titanium dioxide is amphoteric in nature, but both its basic and its acidic properties are manifested very weakly.

Titanium dioxide is used for the manufacture of a white oil paint of very high covering power (*titanium white*) and also for the manufacture of refractory glass, glazes, enamels and heat-resistant laboratory glassware.

239. Zirconium (Zirkonium); at. wt. 91.22. Thorium; at. wt. 232.05. *Zirconium* is rather abundant in the earth's crust, but it is highly dispersed and occurs rarely in considerable accumulations.

In the U.S.S.R. deposits of zirconium ores have been found in the Donets Basin.

In the elemental state zirconium is a hard lustrous metal; its specific gravity is 6.5 and melting point 1,860° C. It is used in metallurgy as an admixture to pig iron, raising the quality of the cast metal. Steels containing zirconium are suitable for the manufacture of armour, armour-piercing shells, etc.

For a long time extensive application of zirconium was impeded by the difficulty of its preparation. However, lately the extraction of zirconium from its ores has greatly increased owing to the fact that the pure metal possesses a number of very valuable properties.

Its high melting point, sufficient strength and great resistance to corrosion, in combination with its almost complete inability to capture thermal neutrons, make pure zirconium a good structural material for atomic reactors.

Admixtures of zirconium in copper greatly enhance the strength of the latter without hardly decreasing its conductivity. A magnesium alloy containing 4 or 5 per cent zinc and 0.6 to 0.7 per cent zirconium is twice as strong as pure magnesium and does not lose its strength even at 200° C. In 1953, 56.5 per cent of the magnesium alloys manufactured in Great Britain contained zirconium as one of their admixtures. The quality of aluminium alloys can also be considerably improved by adding zirconium to them.

Zirconium dioxide ZrO_2 is an excellent refractory owing to its high melting point (about 2,700° C), its very low coefficient of expansion and its stability against chemical action. It is used for the manufacture of various refractory wares, such as crucibles. In the glass industry zirconium dioxide is used to manufacture refractory glasses, and in the ceramic industry for the production of enamels and glazes.

Zirconium carbide ZrC is employed, owing to its great hardness, as a grinding material and as a substitute for diamonds in cutting glass. Wide application of zirconium is impeded as yet by the difficulty of extracting it from its ores.

Thorium is a radioactive element, its content in the earth's crust being 1×10^{-3} per cent by weight. Minerals rich in thorium (such as *thorite* $ThSiO_4$) occur very rarely, and therefore thorium is usually referred to as a rare element. The main source for the extraction of thorium is the mineral *monazite*, which contains, besides thorium, various rare-earth elements. The largest deposits of thorium ores have been found in India.

In the free state thorium is a metal having a specific gravity of 11.5, melting at 1,800° C and resembling platinum in appearance.

The practical importance of thorium is connected with the production of subatomic energy. Of some importance is *thorium nitrate*

(IV) $Th(NO_3)_4$, used for the preparation of incandescent gas mantles. The latter contain about 92 per cent ThO_2 and 2 per cent CeO_2 and emit a bright white light when strongly heated.

VANADIUM SUBGROUP

Element	Symbol	Atomic weight	Atomic number	Arrangement of electrons in layers					
Vanadium .	V	50.95	23	2	8	11	2		
Niobium . .	Nb	92.91	41	2	8	18	12	1	
Tantalum .	Ta	180.95	73	2	8	18	32	11	2

240. General Features of the Vanadium Subgroup. The vanadium subgroup includes the three elements, *vanadium*, *niobium* and *tantalum*, of the fifth group of the Periodic Table, located in the even series of the long periods. Formerly this subgroup included also protactinium, which is now usually included in the actinide group (see § 266). Having two or even only one electron in the outermost layer of their atoms, the elements of the vanadium subgroup differ from the elements of the main subgroup (nitrogen, phosphorus, etc.) in the predominance of metallic properties and in the absence of hydrogen compounds. But the highest valency derivatives of the elements of both subgroups resemble each other in many respects.

The most typical compounds of vanadium and its analogues are those in which they are pentavalent. Their highest oxides are of the nature of anhydrides, forming respectively vanadic, niobic and tantalic acids, each of which has a number of corresponding salts. The lower oxides possess basic properties only.

In the free state vanadium, niobium and tantalum are greyish-white metals, very indifferent to all kinds of chemical action and with high melting points. The most important practically is vanadium.

241. Vanadium; at. wt. 50.95. Vanadium compounds are rather abundant in nature but they are very dispersed and do not form considerable accumulations. For this reason vanadium is considered a rare element, although its total content in the earth's crust is estimated at 0.02 per cent and is a little higher than that of copper.

The richest deposits of vanadium ores are in South America, in Peru. The world output of vanadium (not counting the U.S.S.R.) amounts to several thousand tons per year and falls mainly on Peru, the U.S.A., South-Western Africa and Northern Rhodesia.

The main sources of vanadium in the U.S.S.R. are iron and polymetallic ores, which contain small quantities of vanadium. Usually

either an alloy of vanadium and iron, known as *ferrovanadium*, or salts of vanadic acid, are produced from the ores.

Pure vanadium is a very hard, light metal, its specific gravity being 5.8 and its melting point 1,735° C. It does not oxidize in the air and is indifferent to hydrochloric and sulphuric acids, but dissolves in hydrofluoric acid and in acids which are strong oxidants (nitric acid and aqua regia).

Vanadium forms four oxides: VO, V_2O_3, VO_2 and V_2O_5. The highest oxide of vanadium, vanadic anhydride V_2O_5, is pronouncedly acidic in nature; vanadium dioxide VO_2 is amphoteric; both lower oxides possess only basic properties. The most important is V_2O_5 and its derivatives.

Vanadic anhydride V_2O_5 is an orange substance, readily soluble in alkalis, with which it forms salts of metavanadic acid HVO_3, an acid which has never been obtained in the free state. The salts of this acid are known as **vanadates.** One of them, the usual commercial preparation of vanadium, is *ammonium metavanadate* NH_4VO_3.

The principal field of application of metallic vanadium is steel manufacture. Steel containing only 0.1 to 0.3 per cent vanadium is very strong, resilient, has a high tensile strength and is insensitive to jars and jolts, this being especially important, for instance, for automobile axles, which are subject to shocks. In the chemical industry vanadic anhydride and vanadates are used as catalysts in the contact process for the manufacture of sulphuric acid instead of platinum, which is more expensive. Vanadium compounds are used also in the glass industry, in medicine and in photography.

242. Niobium; at. wt. 92.91. Tantalum; at. wt. 180.95. Both elements resemble vanadium in many respects. In the free state they are refractory, hard, but not brittle and easy to machine. The specific gravity of niobium is 8.6 and that of tantalum 16.6; niobium melts at 2,415° C and tantalum at 3,000° C.

Niobium and tantalum are much less abundant in nature than vanadium; the content of niobium in the earth's crust is 3.2×10^{-5}, and that of tantalum 2.4×10^{-5} per cent by weight.

In spite of the fact that niobium and tantalum belong to the rare elements they are produced in considerable quantities. In 1953 a total of 5,000 tons of ores containing niobium and tantalum was mined in the capitalist countries. Three quarters of this amount was mined in Nigeria and the Belgian Congo.

Their exceedingly high resistance to corrosion makes niobium and tantalum similar to the noble metals; in some cases they are even superior to platinum.

The high resistance of niobium and tantalum to chemical reagents renders these metals especially useful for the manufacture of chemical apparatuses and various parts of industrial chemical equipment.

Cheaper and stronger than platinum, niobium and tantalum are gradually forcing it out of many spheres of application.

Niobium is employed mainly as an admixture to steel, greatly improving the mechanical qualities of the latter and its resistance to corrosion. Steels containing from 1 to 4 per cent of niobium are very heat-resistant and are used for the manufacture of high-pressure boilers and parts of jet motors working under high temperatures.

Steel with an admixture of niobium is an excellent material for the electric welding of steel structures, ensuring very high weld strengths.

Recently *tantalum* has been employed in surgery for joining broken limbs. Its advantage over the materials used formerly for this purpose is that it does not irritate live tissue, and thus does not impair the vital activities of the organism.

Tantalum and niobium carbides are very hard and are used in the metal-working industry for the manufacture of various types of cutting tools.

CHAPTER XXIV

Metals of the Sixth and Seventh Groups of the Periodic Table

CHROMIUM SUBGROUP

Element	Symbol	Atomic weight	Atomic number	Arrangement of electrons in layers					
Chromium	Cr	52.01	24	2	8	13	1		
Molybdenum . . .	Mo	95.95	42	2	8	18	13	1	
Tungsten	W	183.92	74	2	8	18	32	12	2

The metallic elements of the sixth group of the Periodic Table are *chromium*, *molybdenum* and *tungsten*, located in the even series of the long periods and constituting the secondary subgroup of the sixth group, otherwise known as the *chromium subgroup*. This subgroup formerly included the element uranium, which is now regarded as one of the actinides (see § 266). As the chemical properties of uranium resemble those of the other elements of the chromium subgroup, we shall consider it together with these elements.

The outermost electron layer of the atoms of the chromium subgroup elements contains one or two electrons, which accounts for the metallic nature of these elements and their difference from the elements of the main subgroup. At the same time, their maximum positive valency equals 6, as, besides the outer electrons, a corresponding number of electrons from the incomplete second last layer can also take part in the formation of bonds.

Chromium and its analogues do not form hydrides. Their most typical compounds are their derivatives of highest valency, which in many respects resemble the corresponding compounds of sulphur.

The most important element of the subgroup under consideration is chromium, which has found diverse applications both in the free state and as compounds. The analogues of chromium, molybdenum and tungsten, are classed as rare elements; like chromium, they are of great practical importance.

243. Chromium; at. wt. 52.01. The content of chromium in the earth's crust amounts to 0.03 per cent by weight. It occurs in nature chiefly as *chromite* $FeO \cdot Cr_2O_3$, rich deposits of which in the U.S.S.R.

have been found in Kazakhstan and in the Urals. Outside the U.S.S.R. the largest deposits of high-grade chromium ores have been found in the Union of South Africa, Turkey, Southern Rhodesia, Philippines and in Yugoslavia. In 1953 the production of chromium ores in the capitalist countries amounted to 2.9 million tons, or, recalculated for metallic chromium, to 1.4 million tons.

If chromite is reduced with carbon in an electric or regenerative furnace, the result is an alloy of chromium and iron known as *ferrochrome*, which is used directly in the metallurgical industry for the production of chrome steels. Pure chromium is obtained by first preparing chromic oxide and then reducing it by aluminothermy.

Chromium is a hard, white lustrous metal with a specific gravity of 7.14 and a melting point of 1,800° C. At ordinary temperatures chromium is quite indifferent to air and water. Dilute sulphuric and hydrochloric acids dissolve chromium, liberating hydrogen. But chromium is, like aluminium, insoluble in cold nitric acid, and after treatment with nitric acid becomes passive.

Metallic chromium is employed mainly in the steel industry. Steels containing 1 or 2 per cent chromium are very hard and strong and are used to manufacture tools, rifle, and cannon barrels, armour plates and various machine parts. Steel containing about 12 per cent chromium is commonly known as "stainless steel." *Chrome plating*, i. e., coating other metals with chromium to protect them from corrosion, has lately found wide application, especially in the automobile industry. Chrome plating is carried out by the electrolytic method, which gives a very hard, adherent, lustrous film of metal.

Chromium forms three oxides: *chromous oxide* CrO with basic properties; *chromic oxide* Cr_2O_3 with amphoteric properties and *chromic anhydride* CrO_3, a real acidic oxide. In accordance with these three oxides chromium has three series of compounds.

Compounds of Bivalent Chromium. When chromium dissolves in hydrochloric acid, the result is a blue solution containing a salt of bivalent chromium, *chromous chloride* $CrCl_2$. If an alkali is added to this solution a yellow precipitate of *chromous hydroxide* $Cr(OH)_2$ falls out. If dissolved in sulphuric acid the precipitate is converted into $CrSO_4$, etc.

Bivalent chromium compounds are very unstable and are oxidized by the oxygen of the air into compounds of trivalent chromium.

Compounds of trivalent chromium. Chromic oxide Cr_2O_3 is a green refractory substance, widely used under the name of *green crown* for the preparation of distemper and oil paint. When fused with silicates chromic oxide colours them green and is therefore used to colour glass and porcelain.

Chromic hydroxide $Cr(OH)_3$ separates out as a bluish-grey precipitate when salts of trivalent chromium are treated with alkalis:

$$Cr^{\cdots} + 3OH' = \downarrow Cr(OH)_3$$

Like aluminium, zinc and other hydroxides, it is amphoteric, dissolving in acids to form salts of trivalent chromium, and in alkalis to form emerald green solutions of *chromites*, salts of chromous acid $HCrO_2$:

$$Cr(OH)_3 + NaOH = NaCrO_2 + 2H_2O$$

However, in such solutions chromium is probably present not as CrO_2'-ion, but as the complex anion $[Cr(OH)_4]'$ (cf. aluminates, p. 611) which forms according to the reaction:

$$Cr(OH)_3 + OH' = [Cr(OH)_4]'$$

or

$$Cr(OH)_3 + NaOH = Na\,[Cr(OH)_4]$$

Complex salts possessing this structure have been obtained in crystalline form.

On the other hand, chromites obtained by dry methods (for instance by fusing Cr_2O_3 with oxides of other metals) and known mainly for the bivalent metals, have a composition corresponding to the formula $Me(CrO_2)_2$. These include also natural chromite $Fe(CrO_2)_2$.

The most widespread salt of trivalent chromium is the double salt of chromium and potassium, *chrome alum* $KCr(SO_4)_2 \cdot 12H_2O$, which forms bluish-violet crystals isomorphous with the crystals of aluminium alum. It is usually prepared by reducing potassium dichromate $K_2Cr_2O_7$ with sulphur dioxide (see p. 640). Chrome alum is used in the leather industry for chrome tanning of leather and in the textile industry as a mordant in dyeing.

Trivalent chromium salts greatly resemble those of aluminium. In aqueous solution they are greatly hydrolized and pass easily into basic salts. Like aluminium, trivalent chromium does not form salts at all with weak acids.

Solutions of trivalent chromium salts possess a very interesting property: ordinarily bluish-violet in colour, they turn green when heated, but regain their original colour some time after cooling. This change in colour is due to the formation of isomeric hydrates of the salts which, according to the Werner theory, are complex compounds in which all or part of the water molecules are coordinationally bound up in the inner sphere. In some cases such hydrates have been isolated in the solid form. For instance, the crystal hydrate of *chromic chloride* $CrCl_3 \cdot 6H_2O$ is known to exist in three isomeric forms: as blue-violet, dark green and light green crystals of exactly the same composition. The nature of the isomery of chromic chloride hydrates becomes evident from the different attitude of the isomers in freshly prepared solution to silver nitrate. Under the action of the latter a solution of the blue-violet hydrate precipitates all the chlorine contained in it, that of the dark green hydrate $^2/_3$ of its chlorine and the light green hydrate only $^1/_3$ of its chlorine. If this, as well as the 6-coordination number of chlorine, is taken into account, the crystal hydrates in question may be considered to have the following structures:

$[Cr(H_2O_6)]\,Cl_3$	$[Cr(H_2O)_5\,Cl]\,Cl_2 \cdot H_2O$	$[Cr\,(H_2O)_4\,Cl_2]\,Cl \cdot 2H_2O$
blue-violet	dark green	light green

Thus, the isomery of chromic chloride hydrates is due to different arrangements of the same groups (H_2O and Cl') in the inner and outer spheres.

Compounds of Hexavalent Chromium. The chief compounds of hexavalent chromium are: *chromic anhydride* CrO_3 and the salts of its corresponding acids, namely *chromic* H_2CrO_4 and *dichromic* $H_2Cr_2O_7$. Both acids exist only in aqueous solution and on attempts to isolate them from solution decompose immediately into chromic anhydride and water. But their salts are quite stable. Salts of chromic acid are called **chromates** and those of dichromic acid—**dichromates**.

The chromates of the alkali metals, which are soluble in water, are obtained by oxidizing trivalent chromium compounds in the presence of an alkali. For instance, if a solution of potassium chromite is treated with bromine, the following reaction ensues, resulting in potassium chromate:

$$2KCrO_2 + 3Br_2 + 8KOH = 2K_2CrO_4 + 6KBr + 4H_2O$$

or

$$2K[Cr(OH)_4] + 3Br_2 + 8KOH = 2K_2CrO_4 + 6KBr + 8H_2O$$

$$\begin{array}{r|l} 2 & \overset{+III}{Cr} - 3e^- = \overset{+IV}{Cr} \\ 3 & Br_2 + 2e^- = 2Br^- \end{array}$$

The fact that oxidation is taking place can be judged by the emerald green chromite solution turning bright yellow, the colour of CrO_4''-ion.

Chromates can be produced also by dry methods, namely, by fusing Cr_2O_3 with an alkali in the presence of an oxidant, such as potassium chlorate:

$$Cr_2O_3 + 4KOH + KClO_3 = 2K_2CrO_4 + KCl + 2H_2O$$

Chromates are usually prepared from natural chromite $Fe(CrO_2)_2$; if the latter is heated strongly with soda in the presence of the oxygen of the air the resulting fusion will contain sodium chromate which can be extracted by water:

$$4Fe(CrO_2)_2 + 8Na_2CO_3 + 7O_2 = 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

$$\begin{array}{r|l} 4 & \left\{ \begin{array}{l} \overset{+II}{Fe} - e^- = \overset{+III}{Fe} \\ \overset{+III}{2Cr} - 6e^- = \overset{+IV}{2Cr} \end{array} \right. \\ 7 & O_2 + 4e^- = \overset{-II}{2O} \end{array}$$

Potassium chromate K_2CrO_4 can be obtained analogously by taking potash instead of soda.

Almost all the chromates are yellow in colour. Some of them are used as paints. For instance, insoluble *lead chromate* $PbCrO_4$ is

employed for the preparation of a yellow oil colour, called *yellow crown.*

If a solution of any chromate, say K_2CrO_4, is acidified, the pure yellow colour of the solution changes to orange due to the transition of CrO_4''-ion into Cr_2O_7''-ion. From the resulting solution a salt of dichromic acid, potassium dichromate $K_2Cr_2O_7$, can be isolated as orange-red crystals. The reaction of transformation of chromate into dichromate is represented by the equation

$$2CrO_4'' + 2H^+ \rightleftarrows Cr_2O_7'' + H_2O$$

The arrows show that the reaction is reversible. This means that when dichromate is dissolved in water a certain, albeit insignificant, quantity of H^+-and CrO_4''- ion is formed owing to the interaction between Cr_2O_7''- ion and water (the solution reacts acid). If an alkali is added to such a solution the hydroxyl-ion will bind the hydrogen-ion in solution, the equilibrium will shift to the left and, as a result, dichromate will be converted back into chromate. Thus, in an excess of hydroxyl-ion practically only CrO_4'', i. e., chromate-ion, exists in solution, and in an excess of hydrogen-ion—only dichromate-ion.

Chromates and dichromates are very powerful oxidants. That is why they are used constantly in chemical practice for the oxidation of various substances. Oxidation is carried out in acid solution. Acting as an oxidant, Cr_2O_7''-ion, which contains hexavalent chromium, gains electrons and passes into trivalent chromic-ion. Oxidation is usually accompanied by a sharp change in colour (solutions of dichromates are orange, while trivalent chromium salts are green or greenish-violet).

Given below are several examples of oxidation-reduction reactions involving dichromates.

1. If hydrogen sulphide is passed through a dichromate solution acidified with sulphuric acid, the orange solution turns green and at the same time the liquid becomes turbid due to the liberation of sulphur:

$$K_2Cr_2O_7 + 3H_2S + 4H_2SO_4 = Cr_2(SO_4)_3 + 3S + K_2SO_4 + 7H_2O$$

$$\begin{array}{r|l} 1 & \overset{+VI}{2Cr} + 6e^- = \overset{+III}{2Cr} \\ 3 & \overset{-II}{S} + 2e^- = \overset{0}{S} \end{array}$$

2. Concentrated hydrochloric acid reacts with potassium dichromate, liberating chlorine and resulting in a green solution, containing a trivalent chromium salt:

$$K_2Cr_2O_7 + 14HCl = 2CrCl_3 + 3Cl_2 + 2KCl + 7H_2O$$

3. If sulphur dioxide is passed through a concentrated solution of potassium dichromate, containing a sufficient amount of sulphuric acid, equimolecular quantities of potassium sulphate and chromic sulphate are formed:

$$K_2Cr_2O_7 + 3SO_2 + H_2SO_4 = Cr_2(SO_4)_3 + K_2SO_4 + H_2O$$

If the resulting solution is evaporated chrome alum, $KCr(SO_4)_2 \cdot 12H_2O$, crystallizes out. This reaction is employed for the industrial preparation of chrome alum.

The most important dichromates are: *potassium dichromate* $K_2Cr_2O_7$, which forms large orange-red crystals, and *sodium dichromate* $Na_2Cr_2O_7 \cdot 2H_2O$, which crystallizes with two molecules of water. Both salts are widely used under the name of **dichromates** as oxidants in the manufacture of many organic compounds, in the leather industry for tanning leather, in the match and textile industries, etc.

A mixture of concentrated sulphuric acid and an aqueous solution of potassium or sodium dichromate, known as "chromic acid mixture," is often used for vigorous oxidation.

All chromic acid salts are poisonous.

Chromic anhydride CrO_3 separates out as dark red needle-like crystals when a saturated solution of potassium or sodium dichromate is treated with concentrated sulphuric acid:

$$K_2Cr_2O_7 + H_2SO_4 = \downarrow 2CrO_3 + K_2SO_4 + H_2O$$

Chromic anhydride is one of the most powerful oxidizing agents. Some organic substances, such as alcohol, even burst into flame when brought into contact with it. In oxidizing other substances, chromic anhydride is itself converted into Cr_2O_3.

Chromic anhydride dissolves readily in water, forming chromic and dichromic acids.

244. Molybdenum (Molibdenium); at. wt. 95.95. The chief natural compound of molybdenum is the mineral *molybdenite* MoS_2, very similar in appearance to graphite and long considered such. In 1778 Scheele showed that the action of nitric acid on molybdenite results in a white residue possessing the properties of an acid. Scheele called this residue molybdic acid and drew the absolutely correct conclusion that the mineral itself was the sulphide of a new element. Five years later the element was obtained in the free state by calcining molybdic acid with charcoal.

The total content of molybdenum in the earth's crust is 0.001 per cent by weight. The largest deposits of molybdenum ores have been found in the U.S.A. in the State of Colorado. Deposits of these ores have been found also in the U.S.S.R., Mexico, Norway, Morocco

and Peru. Large quantities of molybdenum are contained in sulphide copper ores.

The world production of molybdenum ore in 1953 exceeded 30,000 tons (not counting the U.S.S.R.).

To prepare metallic molybdenum from molybdenite the latter is roasted to convert it into molybdic anhydride, which is reduced to the metal with hydrogen or by aluminothermy. If reduced with hydrogen the molybdenum is obtained as a powder, owing to its very high melting point.

The powder thus obtained is moulded into rods and then heated with a strong alternating current almost to incipient melting, after which the caked mass is forged or rolled at a high temperature.

The method of preparing a compact metal by compressing a metal powder and heating the resulting ware to a temperature not high enough to melt the metal completely, is known as *powder metallurgy*, or *metalloceramics*. Powder metallurgy is an advanced method of manufacturing various wares from metals, especially refractory ones (tungsten, molybdenum, etc.). Powder metallurgy methods are used to make tungsten and molybdenum wire, hard alloys on the basis of tungsten and titanium carbides, etc.

Molybdenum is a silvery-white metal with a specific gravity of 10.2 and a melting point of 2,622° C. At ordinary temperatures it does not change in the air but burns when strongly heated, turning into white molybdic anhydride MoO_3. Molybdenum is not attacked by hydrochloric or dilute sulphuric acid; it dissolves only in nitric acid or hot concentrated sulphuric acid.

About 90 per cent of all the molybdenum produced is used for the production of various special brands of steel. The introduction of molybdenum into steel increases its resilience, makes the steel stronger, refractory and resistant to corrosion. Molybdenum steels are quite indispensable in the aircraft and automobile industries. They are used also for the manufacture of rifle and cannon barrels, armour plates, shafts, etc.

Molybdenum may be hexa-, penta-, tetra-, tri- and bivalent in its compounds. The most stable compounds are those of hexavalent molybdenum. The most important of them are the salts of molybdic acid H_2MoO_4, known as **molybdates**, and often of a very complex composition.

Ammonium molybdate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ is used in analysis for the detection and quantitative determination of phosphoric acid with which it forms a characteristic yellow precipitate of the composition $(NH_4)_3PO_4 \cdot 12MoO_3 \cdot 6H_2O$.

If an acidified solution of molybdic acid is reduced with zinc, a dark blue liquid results, this being a colloidal solution, known as *molybdenum blue*, of the composition Mo_5O_{14} (a mixture of various molybdenum oxides). Molybdenum blue is readily adsorbed by

vegetable and animal fibres and is used for colouring feathers, hair, furs, silk, etc.

245. Tungsten (Wolfram); at. wt. 183.92. The natural compounds of tungsten are in most cases salts of tungstic acid H_2WO_4. The most important tungsten ore, *wolframite*, is an isomorphic mixture of iron and manganese tungstates (Fe, Mn) WO_4.

Another frequently occurring mineral is *scheelite* $CaWO_4$, so named in honour of Scheele who in 1781 first obtained tungstic acid from it.

Tungsten is less abundant in the earth's crust (0.007 per cent by weight) than chromium but somewhat more so than molybdenum. Large deposits of tungsten have been discovered in China, Burma, Bolivia, on the Malay Islands and in Portugal. In 1953 the world production of tungsten ore (not counting the U.S.S.R.), recalculated for WO_3, exceeded 42,000 tons.

To extract tungsten from wolframite the latter is fused with soda in the presence of air. The tungsten passes into sodium tungstate Na_2WO_4, which is leached out of the resulting fusion with water, while the iron and manganese are converted into the insoluble compounds Fe_2O_3 and Mn_3O_4 (cf. production of chromates from chromite).

Free tungstic acid can be isolated as an amorphous yellow precipitate from the resulting aqueous solution by the action of hydrochloric acid:

$$Na_2WO_4 + 2HCl = \downarrow H_2WO_4 + 2NaCl$$

If tungstic acid is calcined it passes into tungstic anhydride WO_3. The metallic tungsten powder obtained by reducing the anhydride with carbon or hydrogen is then subjected to the same treatment as molybdenum powder to convert it into the compact metal.

Metallic tungsten is a heavy white metal with a specific gravity of 19.3. Its melting point (3,380° C) is higher than that of any other metal. Tungsten can be welded and drawn into fibres as thin as 0.2 mm. in diameter.

Tungsten oxidizes in air only at red heat. It is very indifferent to acids, even to aqua regia, but dissolves in a mixture of nitric and hydrofluoric acids.

Most of the tungsten extracted is employed in metallurgy for the preparation of special steels and alloys. High-speed tool steel contains up to 18 or 22 per cent of tungsten and is capable of self-hardening. Such a steel does not lose its hardness even if heated to redness. That is why the use of cutting tools made of tungsten steel makes it possible considerably to increase the metal cutting speeds.

Another branch of industry which makes wide use of tungsten is the manufacture of electric incandescent light bulbs, for which tungsten is indispensable owing to its high melting point. As is known, the quantity of light emitted by a hot body depends on the temperature of the body. The higher the temperature, the higher the relative amount of thermal or electric energy converted into luminous

energy. The carbon filaments used in the first electric light bulbs could not be heated above the temperature of emission of yellow light, as the carbon would begin to evaporate at higher temperatures; tungsten, on the other hand, does not evaporate practically even at white heat. The use of tungsten filaments in incandescent lamps made it possible to convert a larger portion of the electrical energy into luminous energy than with the use of carbon filaments. That is why electric light bulb filaments are now made almost exclusively of tungsten.

Tungsten compounds greatly resemble those of molybdenum. The most important are tungstic acid H_2WO_4 and its salts, known as **tungstates**. Some tungstates are used as oil colours.

The tungsten carbides WC and W_2C are almost as hard as diamond. They are composite parts of the so-called superhard carbide alloys, widely used in the national economy. For instance, the alloy "pobedit" manufactured by Soviet plants consists of tungsten carbides with a 10 per cent admixture of metallic cobalt. The use of superhard carbide alloys in the metal-working industry has made it possible considerably to increase machine output.

246. Uranium; at. wt. 238.07. Uranium is less abundant in nature than the metals of the chromium subgroup. Its content in the earth's crust amounts to 0.0004 per cent by weight. The most important uranium ore, *pitch-blende*, is a mineral of very complex composition, containing about 80 per cent of the oxide U_3O_8. Rich deposits of this ore have been found in Central Africa (Belgian Congo). Supplies of uranium ores have been discovered also in Canada, the U.S.A., Norway, Australia and other countries.

Uranium is a white metal having a specific gravity of 18.3 and a melting point of 1,133° C. Unlike molybdenum and tungsten, uranium is very active: if even gently heated it bursts into flame in the air, combines readily with the halogens and sulphur, displaces hydrogen from dilute acids, forming salts in which it behaves like a tetravalent metal. In very finely divided form it will displace hydrogen even from warm water.

Uranium forms a rather large number of compounds. The most characteristic of them are those in which it is hexavalent.

Uranium trioxide or *uranic anhydride* UO_3 is produced as an orange powder by the decomposition of certain more complex uranium compounds. It has the character of an amphoteric oxide, forming salts with both acids and bases. When dissolved in acids, uranium trioxide forms salts in which the part of the metal is played by the positive doubly charged ion UO_2^{++}, known as *uranyl* (for instance, UO_2Cl_2, etc.).

Uranyl salts are usually yellowish-green and dissolve readily in water. Uranyl nitrate $UO_2(NO_3)_2$ is used in photography.

Under the action of alkalis, solutions of uranium salts give salts of *uranic acid* H_2UO_4, called uranates and diuranates, such as Na_2UO_4 and $Na_2U_2O_7$. Many other uranates can be obtained by heating UO_3 with various basic oxides. Sodium diuranate $Na_2U_2O_7$ is used to colour porcelain and for the manufacture of uranium glass, which fluoresces with a yellowish-green colour.

If uranium or its compounds are calcined in the air the result is always the mixed oxide U_3O_8 (or $UO_2 \cdot 2UO_3$), the most stable of all the uranium oxides.

As to the use of uranium for the production of atomic energy see § 267.

MANGANESE SUBGROUP

Element	Symbol	Atomic weight	Atomic number	Arrangement of electrons in layers					
Manganese .	Mn	54.94	25	2	8	13	2		
Technetium	Tc	99 *	43	2	8	18	13	2	
Rhenium . .	Re	186.31	75	2	8	18	32	13	2

* Stablest isotope.

The secondary subgroup of the seventh group includes the elements of the even series of the long periods *manganese*, *technetium* and *rhenium*. The relation between these elements and those of the main subgroup of the seventh group, i.e., the halogens, is about the same as between the elements of the main and secondary subgroups of the sixth group. Having only two electrons in the outermost layer of their atoms, manganese and its analogues are incapable of gaining electrons, and, contrary to the halogens, do not form hydrides. However, the highest oxygen compounds of these elements have some resemblance to the corresponding compounds of the halogens, as seven electrons can participate in the formation of bonds with oxygen just as is the case with the halogens. Therefore, their highest positive valency equals 7.

Of the elements of the manganese subgroup, the most important is manganese itself. Rhenium, discovered in 1925, is a very rare element, but, owing to a number of valuable properties, has already found certain practical applications. Technetium does not occur in nature. It was produced artificially in 1937 by bombarding molybdenum nuclei with deuterons, heavy hydrogen nuclei, accelerated by means of a cyclotron (see § 261). Technetium was the first element

obtained artificially, "technically", which accounts for its name. The chief raw materials for the preparation of technetium are the products formed during the operation of nuclear reactors (see § 267).

247. Manganese (Manganum); at. wt. 54.94. Manganese is one of the more abundant elements, constituting 0.1 per cent of the weight of the earth's crust. The most frequently occurring natural compound containing manganese is the mineral *pyrolusite*, manganese dioxide MnO_2. Of great importance are also the minerals *hausmannite* Mn_3O_4 and *brownite* Mn_2O_3. Deposits of high grade manganese ores have been found in South Africa, India and Brazil.

The production of manganese ore (recalculated for metallic manganese) amounted to 2.36 million tons in 1953 in the capitalist countries alone. The U.S.S.R. possesses especially large reserves of manganese. Very rich deposits of pyrolusite have been found in the Transcaucasia (Chiatura deposits) and in the Ukraine, in the Nikopol District; considerable reserves of manganese ores have been found also in the Urals and in Western Siberia. The U.S.S.R. possesses the largest reserves of high-grade manganese ores in the world.

Metallic manganese is prepared by reduction of its oxides with aluminium. It is a hard lustrous metal with a specific gravity of 7.4, resembling iron in appearance and melting at 1,250° C. In the air manganese becomes coated with a thin oxide film. In the e.m.f. series manganese stands between aluminium and zinc; it dissolves readily in dilute acids, liberating hydrogen and forming $Mn^{\cdot\cdot}$-ion.

The most important application of manganese is in the metallurgical industry. The addition of manganese to pig iron when the latter is being converted into steel helps to remove the sulphur contained in the iron by forcing it into the slag; in the absence of manganese the sulphur remains in the steel and greatly inhibits its mechanical properties. Manganese is not used in the pure form in steel smelting, but in the form of its alloys with iron, known as *spiegel* and *ferromanganese*. Spiegel or specular iron is obtained by reducing a mixture of iron and manganese ores with coke in a blast furnace, and contains 10 to 25 per cent manganese; ferromanganese, which contains up to 80 per cent manganese, is prepared from pyrolusite and iron ores in electric furnaces. Steel containing 12 to 15 per cent manganese is very hard and highly resistant to shocks and wear. It is used for the manufacture of crushing machines, railway rails, etc. *Alloy steels* (i.e., alloys of steel and other metals), containing, besides manganese, admixtures of chromium and vanadium, are widely used in engineering. A very important alloy for electrical engineering is *manganin* (83 per cent copper, 13 per cent manganese and 4 per cent nickel); manganin wire is used to make resistance coils, as its electrical conductivity is almost independent of the temperature.

Manganese forms five simple oxides, namely, MnO, Mn_2O_3, MnO_2, MnO_3, Mn_2O_7 and a mixed oxide Mn_3O_4 (or $MnO \cdot Mn_2O_3$). The first two oxides are basic in character, manganese dioxide MnO_2 is amphoteric and the higher oxides MnO_3 and Mn_2O_7 are acid anhydrides. Thus, the character of the oxide gradates with increasing valency in the same manner as in the chromium subgroup.

The most important practically are the derivatives of bivalent manganese, manganese dioxide and the salts of permanganic acid, known as permanganates, in which manganese is heptavalent.

Compounds of Bivalent Manganese. Bivalent manganese salts are obtained by dissolving manganese in dilute acids or by the action of acids on various natural manganese compounds. For instance, *manganous chloride* $MnCl_2$ can be evolved as light pink crystals from the solution left after the preparation of chlorine by the action of hydrochloric acid on manganese dioxide. In the solid form manganous salts are usually pink; their solutions are almost colourless.

The addition of alkalis to solutions of bivalent manganese salts throws down a white precipitate of *manganous hydroxide* $Mn(OH)_2$. The precipitate dissolves readily in acids, but is insoluble in alkalis, as manganous hydroxide possesses only basic properties. In the air the precipitate darkens rapidly, being oxidized into brown hydrated manganese dioxide $Mn(OH)_4$.

Manganous oxide MnO can be produced as a green powder by reducing manganese oxides with hydrogen.

Compounds of Tetravalent Manganese. The most stable compound of manganese is *manganese dioxide* MnO_2; it is formed readily both by oxidation of the lower compounds of manganese and by reduction of its higher compounds. Manganese dioxide is amphoteric in character. However, both its acidic and basic properties are but weakly pronounced.

Manganese dioxide is a rather powerful oxidizing agent. It is used as such, for instance, in the preparation of chlorine from hydrochloric acid, in dry galvanic cells, in glass manufacture, in the match industry, etc. Tetravalent manganese salts, for instance $MnCl_4$, $Mn(SO_4)_2$, are very unstable.

Compounds of Hexa- and Heptavalent Manganese. If manganese dioxide is fused with potash and saltpetre (as an oxidant) the result is a green fusion which dissolves in water to give a beautiful green solution. From the latter dark green crystals of *potassium manganate* K_2MnO_4 can be isolated. This salt is very unstable even in *manganic acid* (H_2MnO_4) solution.

Potassium manganate forms according to the following equation:

$$\overset{+IV}{MnO_2} + K_2CO_3 + \overset{+V}{KNO_3} = \overset{+VI}{K_2MnO_4} + \overset{+III}{KNO_2} + CO_2$$

If a green manganate solution is left standing in the air, its colour gradually changes, passing from green to blue and finally to violet. The change in colour is due to the fact that in aqueous solution manganates change spontaneously into permanganates, salts of permanganic acid $HMnO_4$, and manganese dioxide.

The reaction that takes place may be represented by the equation

$$\underset{\text{manganate}}{3K_2MnO_4} + 2H_2O \rightleftarrows \underset{\text{permanganate}}{2KMnO_4} + MnO_2 + 4KOH$$

or its ionic equivalent

$$3MnO_4'' + 2H_2O \rightleftarrows 2MnO_4' + MnO_2 + 4OH'$$

$$\begin{array}{r|l} & {}^{+VI} \qquad {}^{+VII} \\ 2 & Mn - e^- = Mn \\ & {}^{+VI} \qquad {}^{+IV} \\ 1 & Mn + 2e^- = Mn \end{array}$$

In this reaction a MnO_4'' ion oxidizes two similar ions into MnO_4' ions, and is itself reduced to manganese dioxide MnO_2.

The transformation of manganate into permanganate is a reversible reaction. Therefore, in the presence of an excess of hydroxyl-ion a green solution of manganate can keep for a long time without changing. However, if an acid is added, binding the hydroxyl-ion, the green colour changes almost instantaneously to dark red.

If a manganate solution is treated with a powerful oxidizing agent, such as chlorine, all the manganese passes from the hexavalent into heptavalent state, and thus the manganate is converted completely into permanganate:

$$2K_2MnO_4 + Cl_2 = 2KMnO_4 + 2KCl$$

Potassium permanganate $KMnO_4$ is practically the most important salt of permanganic acid. It crystallizes in beautiful dark violet, almost black, prisms, moderately soluble in water. Solutions of potassium permanganate are dark red and at higher concentrations violet, which is the characteristic colour of MnO_4'-ion. Like all compounds of heptavalent manganese, potassium permanganate is a powerful oxidant. It readily oxidizes many organic substances, converts ferrous salts into ferric, oxidizes sulphurous acid into sulphuric, displaces chlorine from hydrochloric acid, etc.

In oxidation reactions involving potassium permanganate heptavalent manganese is reduced either to the tetravalent state, in which case the product is manganese dioxide, or to the bivalent state, forming salts of manganous oxide. The nature of the oxidation reaction depends on the medium in which it is carried out. In acid solution heptavalent manganese is reduced to bivalent, in neutral or alkaline solution—to tetravalent. Both cases may be illustrated graphically by the reactions between potassium permanganate and soluble sulphites in acid and neutral solution.

If potassium sulphite K_2SO_3 is added to a red-violet solution of potassium permanganate acidified with sulphuric acid, the liquid turns almost colourless, as the bivalent manganese salt formed is of a light pink colour. The reaction that takes place can be expressed by the equation

$$2KMnO_4 + 5K_2SO_3 + 3H_2SO_4 = 2MnSO_4 + 6K_2SO_4 + 3H_2O$$

or in the ionic form

$$2MnO_4^{\prime} + 5SO_3^{\prime\prime} + 6H^{\cdot} = 2Mn^{\cdot\cdot} + 5SO_4^{\prime\prime} + 3H_2O$$

$$\begin{array}{r|l} 2 & \overset{+VII}{Mn} + 5e^- = \overset{+II}{Mn} \\ 5 & \overset{+IV}{S} - 2e^- = \overset{+VI}{S} \end{array}$$

The addition of K_2SO_3 to a neutral solution of potassium permanganate also decolourizes the solution, but a brown precipitate of manganese dioxide falls out besides, and the liquid becomes alkaline:

$$2KMnO_4 + 3K_2SO_3 + H_2O = \downarrow 2MnO_2 + 3K_2SO_4 + 2KOH$$

or in the ionic form

$$2MnO_4^{\prime} + 3SO_3^{\prime\prime} + H_2O = \downarrow 2MnO_2 + 3SO_4^{\prime\prime} + 2OH^{\prime}$$

$$\begin{array}{r|l} 2 & \overset{+VII}{Mn} + 3e^- = \overset{+IV}{Mn} \\ 3 & \overset{+IV}{S} - 2e^- = \overset{+VI}{S} \end{array}$$

In alkaline solution the reaction usually follows the same course as in neutral. In exceptional cases, with very high concentrations of alkali and small quantities of reductant, manganate-ion may result instead of MnO_2, according to the equation

$$2MnO_4^{\prime} + SO_3^{\prime\prime} + 2OH^{\prime} = 2MnO_4^{\prime\prime} + SO_4^{\prime\prime} + H_2O$$

$$\begin{array}{r|l} 2 & \overset{+VII}{Mn} + e^- = \overset{+VI}{Mn} \\ 1 & \overset{+IV}{S} - 2e^- = \overset{+VI}{S} \end{array}$$

Potassium permanganate is widely used as a powerful oxidant in chemical practice and is also an excellent disinfectant.

If heated dry potassium permanganate decomposes at as low a temperature as 200° C, according to the equation

$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2$$

This reaction is sometimes employed in the laboratory for the generation of oxygen.

Free *permanganic acid* $HMnO_4$, corresponding to the permanganates, has not been obtained in the anhydrous state and is known only

in solution. The concentration of its solution may be increased as high as 20 per cent. It is a very strong acid, completely ionized in aqueous solution; its apparent degree of ionization in 0.1N solution equals 93 per cent.

Manganic anhydride Mn_2O_7 can be obtained by the action of concentrated sulphuric acid on potassium permanganate:

$$2KMnO_4 + H_2SO_4 = Mn_2O_7 + K_2SO_4 + H_2O$$

It is a greenish-brown oily liquid, very unstable, decomposing eruptively into manganese dioxide and oxygen when heated or brought into contact with combustible substances.

248. Rhenium; at. wt. 186.31. The existence of rhenium in nature was predicted as far back as 1871 by D. Mendeleyev, who called it eka-manganese. Rhenium is one of the most dispersed elements and does not form individual minerals. It is contained in insignificant quantities in certain molybdenum ores and other rare minerals.

In the free state rhenium is a white metal resembling platinum in appearance; its specific gravity is 20.9 and its melting point 3,170° C. Dilute hydrochloric and sulphuric acids do not attack rhenium. Nitric acid dissolves it readily, oxidizing it to perrhenic acid $HReO_4$.

Rhenium forms several oxides, of which the most stable and characteristic is rhenic anhydride Re_2O_7, a yellow solid. Rhenic anhydride reacts with water to give a colourless solution of *perrhenic acid* $HReO_4$ which forms a series of salts known as **perrhenates.** Unlike permanganic acid and its salts, perrhenic acid and the perrhenates do not, as a rule, possess oxidizing properties.

Owing to its refractoriness, metallic rhenium is of great interest in electrical engineering: admixtures of rhenium raise the resistance of tungsten filaments used in electric light bulbs and increase their lifetime. Rhenium is used as an alloy with platinum for the manufacture of high precision thermocouples suitable for measuring temperatures up to 1,900° C. Rhenium alloys are used to manufacture the tips of steel fountain-pen nibs, bearing pin points for compass needles, and other parts requiring great hardness and high resistance to wear and corrosion. Rhenium is used also as a catalyst in various chemical processes.

CHAPTER XXV

Eighth Group of the Periodic Table

The eighth group of the Periodic Table consists of the three triads of elements located in the middle of the long periods. The first triad comprises the elements *iron*, *cobalt* and *nickel* (atomic numbers 26 to 28), the second triad includes *ruthenium*, *rhodium* and *palladium* (atomic numbers 44 to 46) and the third triad—*osmium*, *iridium* and *platinum* (atomic numbers 76 to 78).

Most of the elements of the eighth group have two electrons in the outermost electron layer of their atoms, so that their properties are predominantly metallic. Besides the outer electrons, they are capable of yielding electrons from their incomplete second last layer, manifesting a valency of +3, +4, etc. However, valency exceeding 4 is manifested very rarely.

A comparison of the physical and chemical properties of the elements of the eighth group shows that iron, cobalt and nickel, situated in the first long period, resemble each other very closely but differ pronouncedly from the elements of the two other triads. For that reason they are usually united into a separate **iron subgroup.** The other six elements of the eighth group are united under the generic name of **platinum metals.**

IRON SUBGROUP

Element	Symbol	Atomic weight	Atomic number	Arrangement of electrons in layers			
Iron	Fe	55.85	26	2	8	14	2
Cobalt	Co	58.94	27	2	8	15	2
Nickel	Ni	58.69	28	2	8	16	2

249. Iron in Nature. Iron (ferrum), at. wt. 55.85, is the most abundant metal on the globe, after aluminium, constituting 4.2 per cent of the weight of the earth's crust. Iron occurs only in the form of various compounds: oxides, sulphides, silicates. It is found in the free state only in meteorites that fall on the earth.

The most important iron ores are: *magnetic iron ore* or *magnetite* Fe_3O_4, *red iron ore* or *hematite* Fe_2O_3, *brown hematite* or *limonite* $2Fe_2O_3 \cdot 3H_2O$ and *spathic iron* or *siderite* $FeCO_3$. *Iron pyrites* or just *pyrite* FeS_2 is rarely used in metallurgy, as the iron obtained from it is of very low quality, due to high sulphur content. Being of little interest for metallurgy, pyrite has nevertheless found an important application as a raw material for the manufacture of sulphuric acid.

In the Soviet Union deposits of iron ores have been found in the Urals, in the form of hills (e.g., Magnitnaya, Kachkanar, Vysokaya, etc.) made up of magnetic iron ore of excellent quality. No less rich deposits have been found in the Krivorozhye District and on the Kerch Peninsula. The Krivorozhye ores, which feed the Ukrainian metallurgical industry, consist of hematite and the Kerch ores, of limonite. Large deposits of iron ore have been discovered near Kursk in the region of the so-called *Kursk Magnetic Anomaly*. Immense reserves of iron ore have been detected also in the depths of Kola Peninsula, in Western and Eastern Siberia and in the Far East. The total reserves of iron ore in the U.S.S.R. constitute more than half the world's reserves of iron.

Of all the metals extracted by man, iron is the most important in our life. All modern engineering is connected with the use of iron and its alloys. To illustrate the importance of iron it will suffice to mention that the amount of iron produced exceeds the total output of all the other metals taken together about twentyfold.

The extraction of iron grew especially rapidly during the past century. As late as the beginning of the XIX century the world production of pig iron was only 0.8 million tons per year, but by the end of the XIX century it had already reached 66 million tons per year. In 1929 the world production of steel attained 115.7 million tons, after which it fell sharply during the crisis years (to a low of 44.8 million tons in 1932); and then increased again. By 1939 it had reached 117.2 million tons, and in 1954 amounted to 171 million tons (not counting the U.S.S.R.).

250. Smelting of Pig Iron. The method used for the production of iron from its ores is fundamentally very simple and consists essentially in the reduction of iron oxide with coke. However, as molten iron dissolves carbon, this operation does not result in pure iron, but in an alloy known as *pig iron*, containing up to 5 per cent carbon, as well as certain other impurities.

Pig iron is smelted in large blast furnaces, built of refractory brick, up to 80 feet high and about 20 feet in inside diameter.

Fig. 154 shows diagrammatically a vertical section of a blast furnace. Its upper half is called the *shaft*, at the top of which is the *throat*, sealed by means of the *bell locker*, consisting of two cone-shaped

valves. Just below the widest part of the blast furnace is the *bosh*, and below that, the *hearth*. Hot air is blown into the furnace through *tuyères*, special holes at the bottom.

The blast furnace is charged first with coke and then alternately with a mixture of ore, coke and flux and with pure coke. Combustion and the temperature needed to smelt the pig iron are sustained by blowing preheated air into the hearth. The latter enters a main encircling the furnace just below its widest part and thence passes through bent pipes and the tuyères into the hearth. In the hearth

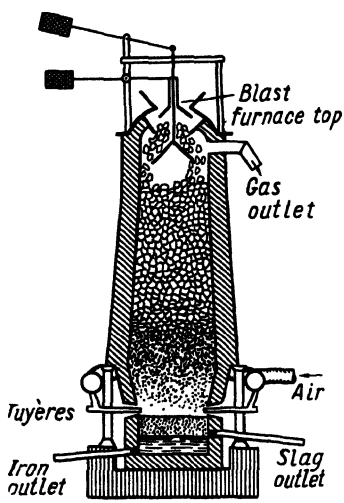


Fig. 154. Cross-section of blast furnace

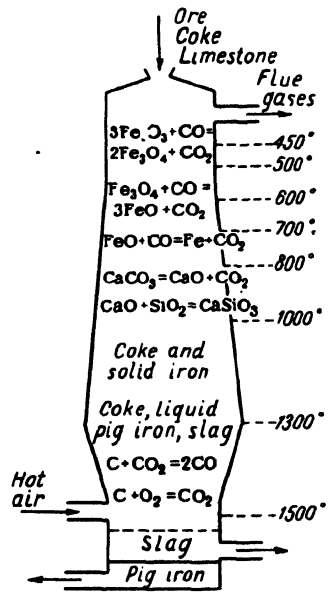


Fig. 155. Blast furnace process

the coke is converted into carbon dioxide, which is reduced to carbon monoxide as it rises through the layer of red-hot coke above it. The carbon monoxide, in its turn, reduces most of the ore and passes back into carbon dioxide.

The ore is reduced mainly in the upper part of the shaft, the summary equation of this reaction being as follows:

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2$$

The individual steps of this process are shown as equations in Fig. 155.

The gangue contained in the ore reacts with the flux to form slag.

The reduced iron settles, still solid, into the top of the bosh, which is the widest and hottest part of the blast furnace, and here, at a temperature of 1,200° C, is melted in contact with the coke, partially dissolving it and turning into pig iron.* The molten pig iron trickles down to the bottom of the hearth, the liquid slag accumulating on its surface and protecting it from oxidation. The pig iron and slag are discharged periodically as they accumulate, through special tap-holes which at other times are plugged up with clay.

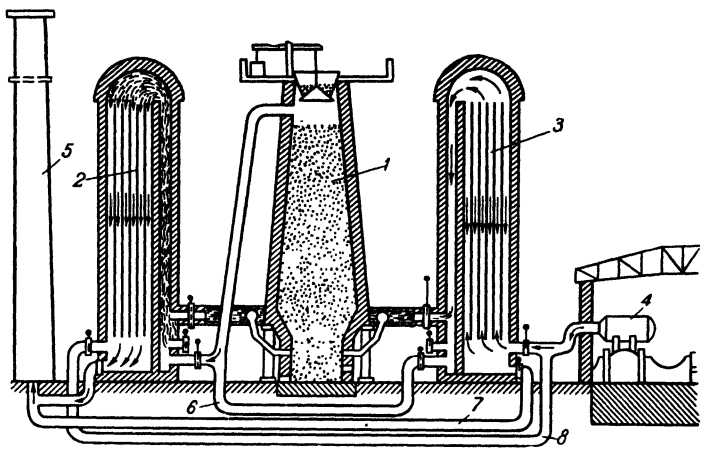


Fig. 156. Operation of blast furnace together with Cowper stoves: *1*—blast furnace; *2*—Cowper stove being heated; *3*—Cowper stove heating air; *4*—blower; *5*—chimney stack; *6*—gas channel; *7*—smoke valve; *8*—air pipe

The carbon dioxide formed during the reduction of the ore rises to the top of the shaft, where it is partly reconverted into carbon monoxide. For this reason the gases discharged from the throat of the blast furnace contain up to 25 per cent carbon monoxide. They are burnt in special *Cowper stoves* for preheating the blast of air blown into the furnace.

Cowper stoves are tall, cylindrical towers built of brick and having vertical channels inside (Fig. 156). The blast furnace gases enter the stove and burn in it, heating the walls of the channels to redness. At the same time the air being blown into the blast furnace passes through the other stove which has already been heated in a similar manner. After some time the air blast is switched to the first stove, and the second stove is heated with the blast furnace gases, etc.

* The addition of carbon to iron greatly lowers its melting point. Pure iron melts at 1,535° C, while a eutectic alloy of iron and carbon, containing 4.3 per cent carbon, melts at 1,150° C.

Blast furnaces operate continuously. As the upper layers of ore and coke sink downwards, fresh portions of ore-flux-coke mixture are added. This mixture, known as the *charge*, is hauled up a steep track in skip cars to the platform at the top of the furnace, and is dumped into an iron hopper closed at the bottom by the bell locker. When the bell is depressed the charge drops into the furnace. The furnace operates day and night for several years until it requires a general overhaul.

Blast furnace performance is appraised by the "useful-blast-furnace-volume-to-daily-production" ratio obtained by dividing the furnace volume in cubic metres by the daily output of the furnace in tons. For instance, if the volume of the furnace is 900 cu. m., and the output 500 tons per 24 hours, the "useful-blast-furnace-volume-to-daily-production" ratio will be 900/500 = 1.8. Thus, the smaller this ratio, the higher the output of the furnace.

Before the Revolution the useful-volume-to-daily-production ratio of blast furnaces in the south of Russia was about 2.30. Soviet metallurgy has greatly increased the efficiency of the blast furnace process by extensive development of progressive working methods and has brought the useful-volume-to-daily-production ratio down to an average of 0.80.

The use of oxygen offers great opportunities for accelerating the process of pig iron smelting in blast furnaces. If air enriched with oxygen is blown into the blast furnace, it need not be preheated, eliminating the necessity of using complex and clumsy Cowper stoves, and greatly simplifying the entire metallurgical process. At the same time, the productivity of the blast furnace increases sharply and the fuel consumption decreases. A blast furnace operating on oxygen blast yields one and a half times more metal and consumes 25 per cent less coke than with an ordinary air blast.

The pig iron produced by blast furnaces averages about 93 per cent iron, up to 5 per cent carbon and contains minor quantities of silicon, manganese, phosphorus and sulphur.

When the pig iron solidifies, the carbon in it may crystallize out as graphite, or combine with the iron to form iron carbide Fe_3C, known also as *cementite*. Unlike graphite, the softest component of pig iron, cementite is its hardest component. Upon prolonged heating up to 900° C or more, cementite decomposes into iron and graphite, this taking place especially readily in the presence of silicon. That is why pig iron containing considerable quantities of silicon (from 2 to 3.5 per cent) is grey in colour, due to the liberated graphite. Such pig iron is known as grey pig iron; it is not very hard, can be cast readily into various shapes, but is brittle and fractures easily when struck. Grey pig iron is used for casting machine frames, flywheels, drainage pipes, plates, etc.

Pig iron containing almost all its carbon in the form of cementite is harder and whiter than grey pig iron and for this reason is known as *white cast iron*; it is distinguished by an insignificant silicon content (under 1 per cent) and a high manganese content (1 to 1.5 per cent). White cast iron is not used as such but is re-treated to make steel and iron, which differ from pig iron in their lower carbon content and absence of other impurities (silicon, phosphorus, manganese). A product containing from 0.3 to 2 per cent carbon is called *hard steel*, and if it contains less than 0.3 per cent carbon it is known as *mild steel* or *iron*.

251. Production of Iron and Steel from Pig Iron. Two principal methods are used at present for the production of steel and iron from pig iron. They are both based on the oxidation of the impurities in the pig iron.

The *Bessemer process* consists in blowing a strong blast of air through the molten pig iron.

The Bessemer process is accomplished in large pear-shaped iron vessels called *converters* (Fig. 157), lined on the inside with silica brick and holding up to 40 or 50 tons of pig iron at a time. The converter is mounted on horizontal trunnions, around which it can be tilted by means of gears. The bottom of the converter has a large number of small openings and an air chamber fastened to it for the blast. The converter is filled with molten pig iron and air is blown into the air chamber. Passing through the openings in the bottom of the converter, the air penetrates through the entire mass of the pig iron and oxidizes its impurities. The first to burn out, passing into the slag, are silicon and manganese, which are followed by carbon. The entire Bessemer process lasts about 10 to 20 minutes, after which the converter may be emptied by tilting.

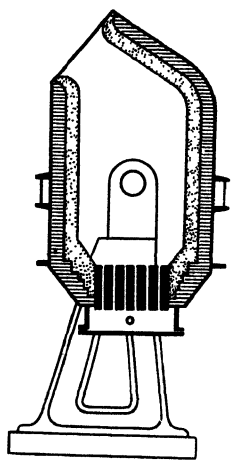


Fig. 157. Diagrammatic section of converter

The Bessemer process produces iron containing less than 0.3 per cent carbon. If it is desired to obtain steel, the air blast is either shut off before all the carbon has burnt out, or a definite amount of pig iron rich in carbon is added to the iron produced in the converter, after which air is again blown through for a short period to mix the ingredients.

If the pig iron contains phosphorus, the latter cannot be eliminated with the usual converter lining. At the same time, phosphorus must be removed, as its presence makes the iron short (or brittle). In such cases on the suggestion of the English inventor Thomas, the lining

of the converter is made of a mixture of magnesium and calcium oxides obtained by roasting the mineral dolomite $MgCO_3 \cdot CaCO_3$, and 10 to 15 per cent lime is added besides to the pig iron. The P_2O_5 resulting from the combustion of the phosphorus combines with the lime, giving slags which can be used as fertilizers and are known as *Thomas slags.*

The Bessemer process has a number of shortcomings. Owing to the intensive oxidation that takes place when air is blown through the mass of molten pig iron, a considerable amount of metal is burnt out, and the yield of steel averages about 90 per cent of the weight of the pig iron. The production of low-carbon steels leads to even higher losses of iron. Besides, due to the strong blast of air some of the slag gets entangled in the iron and remains in it when it is cooled, spoiling its quality.

A more perfect method is the *open-hearth process*, by which the pig iron is treated in regenerative furnaces (p. 438). In these furnaces the pig iron is melted together with scrap iron and a small quantity of ore. The admixtures are burnt out partly at the expense of the oxygen of the air entering the furnace together with the combustible gases and partly at the expense of the oxygen in the ore added.

Regenerative furnaces may have either an acid silica lining or a basic lime lining. By adding scrap iron and ore to the pig iron in definite proportions the steel can be produced with any desired content of carbon and is higher in quality than Bessemer steel.

The productivity of open-hearth furnaces is characterized by the amount of steel produced per 24-hour day per sq. m. of hearth area. It was formerly considered that four tons per sq. m. per day was the upper limit of furnace output. However, the experience of foremost workers and engineers at Soviet plants has shown that much higher outputs can be obtained from open-hearth furnaces. At present the daily output of steel per sq. m. of hearth area constitutes 6.55 tons.

Lately *electric furnaces* have found wide use for steel production. The source of heat in these furnaces is electric power, which greatly simplifies the process and creates favourable conditions for controlling the melting conditions. The most widespread furnaces are the electric arc type which easily give a temperature of 2,000° C and higher. The very process of steel smelting in electric furnaces hardly differs from the open-hearth process, but owing to the possibility of regulating the furnace temperature and therefore the course of the process, the quality of the steel produced is higher. This method is used for the production of tool steel and various special types of steel.

Especially important brands of steel for responsible parts and tools are made by the so-called *crucible processes.* A mixture of various

types of steel and special admixtures is placed in crucibles, which are covered and placed on the hearth of a reverberatory furnace of the open-hearth type where the mixture is melted and yields steel of a definite grade.

Scientific and engineering thought is now occupied also with the problem of obtaining iron by direct reduction from its ores at moderate temperatures. To produce iron according to this method, the ground iron ore is reduced with coke or gas at 800 to 1,000° C; then part of the gangue and the ash of the reducing agent is eliminated by means of a magnetic separator and the resulting spongy iron is re-treated in open-hearth or electric furnaces to produce steel. Any solid or gaseous fuel may be used as the reductant. Steel obtained from reduced iron has high mechanical properties. However, present-day plants for the direct production of iron from its ores are still rather clumsy and far from perfection, which limits the use of the method.

252. Heat Treatment of Steel. The mechanical properties of steel depend largely on its structure. To impart the desired structure to steel, it is subjected to heat treatment, i.e., to heating and cooling under definite conditions. The most important types of heat treatment are hardening and tempering.

Hardening of steel consists in heating it to a high temperature and then cooling it suddenly. This process makes the steel very hard, but at the same time brittle. If hardened steel is reheated to a definite temperature (lower than before) and then cooled slowly, it is said to be "tempered," i.e., it becomes softer and loses its brittleness. The steel may thus be given the desired degree of hardness, depending on the temperature to which it is reheated.

The phenomenon of hardening is explained as follows: when molten steel solidifies the carbon contained in it as cementite may form a solid solution with the iron, referred to as *austenite* and distinguished by very great hardness. Austenite is quite stable only at high temperatures, but it can be retained more or less completely at low temperatures as well, by cooling the heated steel suddenly. If the steel is cooled slowly, the austenite gradually decomposes into cementite and iron, and the steel becomes soft.

Very often quite different requirements are set for the surface layers of steel objects (shafts, gears, etc.) and for their bulk. For instance, an automobile axle must have a hard surface, highly resistant to wear, but at the same time must not be brittle, i.e., should be resilient enough to withstand shocks. To give the part the required properties, it is made of soft, tough, low-carbon steel, the surface of which is subsequently saturated with carbon. This is done by heating the finished part in an atmosphere of carbon monoxide or in boxes filled with charcoal.

The process of saturating steel surfaces with carbon is called "case-hardening." Case-hardening results in a very hard and strong surface layer, 0.5 to 2 mm. thick, leaving the bulk of the steel tough and resilient.

Analogous results can be achieved by *nitriding steel*, i.e., saturating its surface with nitrogen. For this purpose the steel is heated for a long time in an atmosphere of ammonia at 500 to 600° C. Nitrided steel is still harder than case-hardened steel owing to the formation of iron nitrides in its surface layer. It can withstand heating to 500° C without losing its hardness.

The father of the branch of science concerned with the changes in structure of steels was the Russian metallurgist Dmitry Konstantinovich Chernov (1839-1921). Investigating the properties of steel after heating to various temperatures, Chernov first established that at definite temperatures steel undergoes certain changes altering its structure and properties. These "critical temperatures" characterized by internal changes in the steel are now known all over the world as the "Chernov points." One of these points, called by Chernov point *a*, is notable for the fact that steel heated below this point (about 700° C) cannot be hardened no matter how rapidly it is cooled. Another point, *b*, is characterized by the fact that as soon as the temperature of the steel reaches it (800 to 850° C), the steel rapidly passes from the coarse crystalline into the fine crystalline state, in which it possesses the best mechanical properties. If the temperature is raised still further, the metal crystals begin to increase again in size, and the higher the temperature, the more rapidly they grow.

The discovery of the critical points of steel was of very great importance for metallurgical theory and practice. Explaining the phenomena of tempering and hardening of steel and the structural changes taking place in steel when heated, it enabled accurate determination of the hardening temperatures and selection of favourable conditions of forging and other types of steel treatment, promoting improvement of its mechanical properties.

253. Development of Iron and Steel Metallurgy in the U.S.S.R. The production of ferrous metals (pig iron, steel, iron) occupies one of the first places in the national economy of the U.S.S.R. The progress of almost all branches of the national economy depends largely on the amount of metal produced in the country.

Tsarist Russia was far behind the foremost industrial countries in iron and steel output. The Russian metallurgical industry produced only 4.2 million tons of pig iron and an equal amount of steel in 1913. World War I and the civil war were a heavy blow to all the branches of the national economy, especially metallurgy. In 1920 the output of pig iron had fallen to an unprecedented low level and

amounted to only 2.7 per cent of the 1913 figure. The reconstruction of iron and steel metallurgy accomplished under exceptionally difficult conditions required immense effort and a long time: the steel output regained its 1913 level only in 1929.

Soviet metallurgy began to progress rapidly during the years of the pre-war five-year plan periods. Not only was the southern metallurgy completely reconstructed, but a new coal and metallurgy base was created as well in the eastern regions of the country. Huge metallurgical enterprises were built, such as the Magnitogorsk, Kuznetsk mills and others. By the end of the First Five-Year Plan the pig iron output had already reached 147 per cent of the 1913 level.

Under conditions of planned socialist economy Soviet metallurgy soon outstripped the capitalist countries in rate of development. Having recovered the pre-revolutionary level of pig iron output by 1929, Soviet metallurgy increased its pig iron production almost three and a half-fold in the course of the next eight years. It took the U.S.A. twenty years, and Germany twenty-three years, to effect an equal increase in metallurgical output.

In 1957, 37 million tons of pig iron and 51 million tons of steel were smelted in the Soviet Union, while in 1959 the output of pig iron totalled 43 million tons and that of steel—59.9 million tons. The control figures for the economic development of the U.S.S.R. in 1959 to 1965 provide for a further considerable growth of the iron and steel industry of the country. It is planned to raise the yearly pig iron production to 65-70 million tons and that of steel to 86-91 million tons in 1965. The iron ore production will be increased approximately twofold, new iron ore deposits being developed in Kazakhstan, Siberia and the Kursk Magnetic Anomaly district. To attain the planned level of iron and steel production wide use will be made in the iron and steel industry of new highly effective technologies based on the use of natural gas and oxygen, which will make it possible to increase the capacities of blast and open-hearth furnaces. The production of special-purpose steels and alloys will be increased by considerably extending electrometallurgical practices and the ferro-alloy industry.

254. Properties of Iron. Iron Compounds. Pure iron can be prepared by reducing iron oxide with hydrogen or by electrolysis of certain iron salts. It is a silvery-white, lustrous, tough metal, greatly resembling platinum in appearance. The specific gravity of iron is 7.87 and its melting point 1,539° C. Pure iron is magnetized and demagnetized very easily and is therefore used to make the cores of dynamos and electric motors.

Ordinary iron does not change in dry air but rusts rapidly in damp, becoming covered with a brown deposit of ferric hydroxide which, being loose, does not protect the iron from further oxidation. It was

long thought that the property of rusting was an undesirable, but inseparable property of iron. But lately it has been proved that chemically pure iron produced by electrolysis is hardly attacked by corrosion and is quite acid-resistant. The reasons for the corrosion of ordinary iron were discussed in § 200.

If calcined in air iron burns, turning into ferrosoferric oxide Fe_3O_4 (or $FeO \cdot Fe_2O_3$). The same substance forms when red-hot iron is forged ("iron scale").

The normal potential of iron equals —0.441 volt. Therefore, iron dissolves readily in dilute acids, displacing hydrogen from them and forming $Fe^{\cdot\cdot}$-ion. Cold concentrated sulphuric acid does not attack iron. The action of concentrated nitric acid on iron is the same as on aluminium and chromium, i.e., it renders it "passive." Alkalis do not act on iron.

Iron forms two series of compounds corresponding to its two oxides: *ferrous oxide* FeO and *ferric oxide* Fe_2O_3. In the first, iron is bivalent, in the second, trivalent. Besides these, salts of *ferric acid*, H_2FeO_4, are known, in which iron behaves like a hexavalent non-metal.

Compounds of Bivalent Iron. Salts of bivalent iron (ferrous salts) are obtained by dissolving iron in dilute acids. The most important of them is *ferrous sulphate* (II) or *green vitriol* $FeSO_4 \cdot 7H_2O$, which forms eight green crystals, readily soluble in water. In the air ferrous sulphate gradually effloresces and at the same time oxidizes at its surface, passing into a yellowish-brown basic salt of trivalent iron.

Green vitriol is prepared by dissolving iron trimmings in 20 to 30 per cent sulphuric acid:

$$Fe + H_2SO_4 = FeSO_4 + H_2$$

and is obtained also as a waste product when iron is "etched" with sulphuric acid prior to zinc plating.

Ferrous sulphate is used in agriculture as a pesticide and in the production of certain mineral paints, for dyeing fabrics, etc.

When ferrous sulphate is heated, water is first given off, leaving a white mass of the anhydrous salt $FeSO_4$. If heated more strongly, the salt decomposes, liberating sulphur dioxide and sulphur trioxide, which in moist air forms dense white fumes of sulphuric acid:

$$2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$$

Addition of an alkali to ferrous sulphate solution results in a white precipitate of ferrous hydroxide $Fe(OH)_2$ which oxidizes rapidly in the air, turning first green and then brown as it passes into ferric hydroxide $Fe(OH)_3$:

$$4Fe(OH)_2 + 2H_2O + O_2 = 4Fe(OH)_3$$

Ferrous hydroxide is almost exclusively basic in nature and does not dissolve in alkalis.

Anhydrous *ferrous oxide* FeO can be prepared by reducing ferric oxide with carbon monoxide at 500° C, and is a black, easily oxidized powder:

$$Fe_2O_3 + CO = 2FeO + CO_2$$

Alkali carbonates will precipitate white *ferrous carbonate* (II) $FeCO_3$ from solutions of bivalent iron salts. Under the action of water, containing carbon dioxide, ferrous carbonate, like calcium carbonate, passes partly into the more soluble acid salt $Fe(HCO_3)_2$. Iron is contained in the form of this salt in ferruginous mineral waters.

Salts of bivalent iron can easily be converted into trivalent iron salts by the action of various oxidants: nitric acid, potassium permanganate, chlorine, etc.; for example:

1) $6FeSO_4 + 2HNO_3 + 3H_2SO_4 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O$
2) $10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$

Owing to their ready oxidizability bivalent iron salts are often used as reducing agents.

Compounds of Trivalent Iron. Of the salts of trivalent iron (ferric salts) the most commonly used is *ferric chloride* $FeCl_3$. The anhydrous salt is obtained as dark green scales when chlorine is passed over heated iron. Ordinary ferric chloride is a dark yellow crystalline deliquescent substance having the composition $FeCl_3 \cdot 6H_2O$.

Ferric sulphate (III) $Fe_2(SO_4)_3$ is prepared by oxidizing $FeSO_4$ with nitric acid in sulphuric acid solution. With ammonium sulphate it forms *ferric ammonium alum* $NH_4Fe(SO_4)_2 \cdot 12H_2O$, which crystallizes as beautiful light violet crystals, isomorphous with the crystals of aluminium and chrome alums.

Under the action of ammonia or alkalis, solutions of trivalent iron salts evolve a reddish-brown precipitate of *ferric hydroxide* $Fe(OH)_3$, insoluble in an excess of alkali.

Ferric hydroxide is a weaker base than ferrous hydroxide; this is manifested by the fact that the salts of ferric hydroxide are greatly hydrolyzed, and that $Fe(OH)_3$ does not form salts at all with weak acids (for instance, with carbonic or hydrosulphuric). Hydrolysis also accounts for the colour of solutions of trivalent iron salts. In spite of the fact that $Fe^{\cdot\cdot\cdot}$-ion is almost colourless, its solutions have a yellow-brown colour owing to the presence of basic salts or $Fe(OH)_3$, formed as a result of hydrolysis:

$$Fe^{\cdot\cdot\cdot} + H_2O \rightleftarrows Fe(OH)^{\cdot\cdot} + H^{\cdot}$$
$$Fe^{\cdot\cdot\cdot} + 2H_2O \rightleftarrows Fe(OH)_2^{\cdot} + 2H^{\cdot}$$
$$Fe^{\cdot\cdot\cdot} + 3H_2O \rightleftarrows Fe(OH)_3 + 3H^{\cdot}$$

The colour of the solutions darkens when they are heated, and they become lighter if acids are added, owing to the reverse direction of the reaction.

If calcined, ferric hydroxide loses water and passes into *ferric oxide* Fe_2O_3. Ferric oxide occurs in nature as red iron ore and is used as a brown paint known as Indian red or colcothar.

Alongside its purely basic properties, ferric oxide and hydroxide manifest also certain, albeit feeble, acid properties. For instance, if ferric oxide is fused with soda or potash, the result is one of the salts known as **ferrites**, analogous to chromites or aluminates, these salts being derivatives of metaferrous acid $HFeO_2$:

$$Fe_2O_3 + Na_2CO_3 = 2NaFeO_2 + CO_2$$

Hot water completely hydrolyzes ferrites into ferric oxide and the corresponding alkalis:

$$2NaFeO_2 + H_2O = 2NaOH + Fe_2O_3$$

One of the technical methods of preparing sodium hydroxide from soda is based on the formation of sodium ferrite and its subsequent decomposition by water.

A characteristic reaction distinguishing ferric salts from ferrous is the action of potassium thiocyanate KCNS or ammonium thiocyanate NH_4CNS on iron salts. Potassium thiocyanate contains colourless CNS'-ion in solution, which combines with $Fe^{\cdot\cdot\cdot}$-ion to form ferric thiocyanate $Fe(CNS)_3$, a blood-red, slightly ionized compound. Ferrous-ion does not give this reaction.

Cyanide Compounds of Iron. If potassium cyanide is added to the solution of a ferrous salt, a white precipitate of ferrous cyanide results:

$$Fe^{\cdot\cdot} + 2CN' = \downarrow Fe(CN)_2$$

The precipitate dissolves in an excess of potassium cyanide owing to the formation of the complex salt $K_4[Fe(CN)_6]$, known as potassium ferrocyanide:

$$Fe(CN)_2 + 4KCN = K_4[Fe(CN)_6]$$

or

$$Fe(CN)_2 + 4CN' = [Fe(CN)_6]''''$$

Potassium ferrocyanide $K_4[Fe(CN)_6] \cdot 3H_2O$ crystallizes in the form of large light yellow prisms.

This salt is known also as *yellow prussiate of potash*, as it was prepared formerly by calcining dried blood with potash and iron. When dissolved in water the salt ionizes into $K^{\cdot}$-ion and the exceedingly stable complex ion $[Fe(CN)_6]''''$. The solution contains practically no $Fe^{\cdot\cdot}$-ion and does not respond to a single characteristic test for bivalent iron.

Potassium ferrocyanide corresponds to *ferrocyanic acid* $H_4[Fe(CN)_6]$, a white solid forming many other salts besides the potassium salt.

It is noteworthy that despite the fact that potassium ferrocyanide contains iron, it can serve as a sensitive test for *trivalent iron*, as $[Fe(CN)_6]''''$-ion combines with $Fe^{\cdots}$-ion, when they encounter each other in solution, to form the iron salt of ferrocyanic acid, ferric ferrocyanide $Fe_4[Fe(CN)_6]_3$, which is insoluble in water and has a characteristic blue colour; this salt is called *Prussian blue*:

$$4Fe^{\cdots} + 3[Fe(CN)_6]'''' = \downarrow Fe_4[Fe(CN)_6]_3$$

Prussian blue is used as a paint. Alkalis decompose it into ferric hydroxide, liberating $[Fe(CN)_6]''''$-ion:

$$Fe_4[Fe(CN)_6]_3 + 12OH' = \downarrow 4Fe(OH)_3 + 3[Fe(CN)_6]''''$$

Under the action of chlorine or bromine the anion in potassium ferrocyanide solution is oxidized, passing from the tetravalent to the trivalent state:

$$2[\overset{\overset{2e^-}{\longrightarrow}}{Fe(CN)_6}]'''' + Cl_2 = 2[Fe(CN)_6]''' + 2Cl'$$

The potassium salt corresponding to this anion, $K_3[Fe(CN)_6]$, is called potassium ferricyanide or red prussiate of potash. It crystallizes as dark red anhydrous crystals. Its solution contains the anions $[Fe(CN)_6]'''$ of the same composition as the ferrocyanide anions, but having three instead of four negative charges and therefore possessing other properties than $[Fe(CN)_6]''''$ ions.

If a solution containing bivalent iron is treated with potassium ferricyanide, the result is a blue precipitate known as *Turnbull's blue*, very much like Prussian blue in appearance, but of a different composition:

$$3Fe^{\cdot\cdot} + 2[Fe(CN)_6]''' = \downarrow Fe_3[Fe(CN)_6]_2$$

With salts of trivalent iron $K_3[Fe(CN)_6]$ gives a brown solution.

The reaction of formation of Turnbull's blue is used extensively for printing copies of drawings made on tracing paper (blue-prints). This process is based on the fact that certain salts of trivalent iron and organic acids are reduced under the action of light into salts of bivalent iron. The paper used for printing is usually coated with a mixture of $K_3[Fe(CN)_6]$ with ferric ammonium citrate. If a drawing made on tracing paper is laid on such paper and intensely illuminated, the trivalent iron is reduced to bivalent everywhere except the places protected by the lines of the drawing. After this the paper is washed with water. Turnbull's blue precipitates in the pores of the paper in all the areas illuminated, while the places protected

from the light, remain white. The result is a white drawing on a blue background.

Compounds of Hexavalent Iron. If iron filings or ferric oxide are heated with potassium nitrate and potassium hydroxide the resulting fusion contains the potassium salt of *ferric acid* H_2FeO_4, called *potassium ferrate* K_2FeO_4:

$$Fe_2O_3 + 4KOH + 3KNO_3 = 2K_2FeO_4 + 3KNO_2 + 2H_2O$$

$$\begin{array}{r|l} 1 & \overset{+III}{2Fe} - 6e^- = \overset{+VI}{2Fe} \\ 3 & \overset{+V}{N} + 2e^- = \overset{+III}{N} \end{array}$$

If the fusion is dissolved in water a red-violet solution results, from which insoluble *barium ferrate* $BaFeO_4$ can be precipitated by adding $BaCl_2$.

All ferrates are very powerful oxidants, even stronger than permanganates. Neither ferric acid H_2FeO_4, corresponding to the ferrates, nor its anhydride FeO_3 have been obtained in the free state.

Iron Carbonyls. Iron forms quite singular volatile compounds with carbon monoxide, called iron carbonyls. *Iron pentacarbonyl* $Fe(CO)_5$ is a pale yellow liquid with a specific gravity of 1.5, a high index of refraction and a boiling point of 100° C. It is prepared by passing carbon monoxide over finely divided iron under pressure and at an elevated temperature. Iron pentacarbonyl is insoluble in water but dissolves in many organic solvents. At 250° C it decomposes into carbon monoxide and absolutely pure iron.

255. Cobalt (Cobaltum); at. wt. 58.94. Cobalt is not very abundant in nature; its content in the earth's crust amounts to 0.002 per cent by weight. Cobalt usually occurs in compounds with arsenic; the most important minerals containing this element are *smaltite* $CoAs_2$ and *cobaltite* or *cobalt glance* CoAsS. In 1954 the world production of cobalt amounted to about 13,000 tons (not counting the U.S.S.R.).

Cobalt is a hard, ductile lustrous metal, resembling iron, with a specific gravity of 8.9, melting at 1,492° C. Like iron, cobalt possesses magnetic properties. Water and air do not attack cobalt. It dissolves in dilute acids much less readily than iron and its normal potential equals —0.28 volt.

Cobalt forms two simple oxides: *cobaltous oxide* CoO and *cobaltic oxide* Co_2O_3, with their corresponding hydroxides $Co(OH)_2$ and $Co(OH)_3$, both of which are basic in character. Both hydroxides give salts, but those of trivalent cobalt are unstable and decompose readily, passing into bivalent cobalt salts. Besides the two above oxides, another mixed oxide of cobalt is known, having the formula Co_3O_4 (or $CoO \cdot Co_2O_3$) and called *cobalto-cobaltic oxide.*

Bivalent cobalt salts are usually blue in the anhydrous state and reddish-pink in solution or as hydrated crystals. By way of example mention may be made of *cobaltous chloride*, which forms bright pink crystals of the composition $CoCl_2 \cdot 6H_2O$. A piece of filter paper impregnated with a solution of this salt and dried can serve as a

rough hygroscope, as it changes colour from blue to pink, depending on the humidity of the air.

Cobaltous hydroxide $Co(OH)_2$ is prepared by the action of alkalis on solutions of bivalent cobalt salts, resulting in a precipitate of the blue basic salt, which, when the liquid is boiled, passes into the pink hydroxide $Co(OH)_2$. The latter, if calcined, is converted into greyish-green cobaltous oxide CoO.

In the air cobaltous hydroxide oxidizes slowly into dark brown *cobaltic hydroxide* $Co(OH)_3$. This process proceeds very rapidly under the action of strong oxidants, such as NaClO:

$$2Co(OH)_2 + NaClO + H_2O = 2Co(OH)_3 + NaCl$$

When treated with acids cobaltic hydroxide does not give trivalent cobalt salts, but liberates oxygen, leaving a bivalent cobalt salt; for example:

$$4Co(OH)_3 + 4H_2SO_4 = 4CoSO_4 + 10H_2O + O_2$$

$$4 \left| \overset{+III}{Co} + e^- = \overset{+II}{Co} \right.$$

$$2 \left| \overset{-II}{O} - 2e^- = O \right.$$

Cobaltic hydroxide displaces chlorine from hydrochloric acid:

$$2Co(OH)_3 + 6HCl = 2CoCl_2 + Cl_2 + 6H_2O$$

In general $Co(OH)_3$ and Co_2O_3 act as oxidants, like MnO_2 and PbO_2, which also form unstable salts.

A very characteristic feature of cobalt is its capacity for forming various complex compounds, and it is noteworthy that in such compounds it is almost always trivalent. Though complex compounds of bivalent cobalt can be obtained, they are very unstable; on the other hand, in the case of the simple compounds the bivalent cobalt compounds are the more stable ones. In complex salts cobalt may form part of the cation or of the anion, for instance $[Co(NH_3)_6]Cl_3$ and $K_3[Co(NO_2)_6]$. The coordination number of cobalt is 6.

The practical applications of cobalt are rather limited. Cobalt is a component of certain alloys, its tendency being to increase their hardness. An alloy of cobalt with chromium and tungsten, known as *stellite*, is employed for the manufacture of high-speed cutting tools. The Soviet superhard carbide alloy, "pobedit" (see p. 643), contains 10 per cent cobalt. Cobalt compounds added to glass impart to it a dark blue colour (owing to the formation of cobalt silicate). Ground to a fine powder, such glass is used as a blue paint known as "smalt" or "cobalt".

256. Nickel (Niccolum); at. wt. 58.69. Like cobalt, nickel occurs in nature as arsenides or sulphides; such, for instance, are the

minerals *niccolite* or *arsenic nickel* NiAs, *hersdorfite* NiAsS, and others.

Nickel is more abundant than cobalt (0.02 per cent by weight of the earth's crust). The largest deposits of nickel occur in Canada, the second place being occupied by the Soviet Union, which has high-grade nickel deposits in the Urals, in Kazakhstan, and on the Taimyr and Kola peninsulas.

The Ural nickel deposits were known long before the Revolution, but tsarist Russia had no nickel industry and imported all its nickel from abroad. This branch of industry was built up only in Soviet times. The first nickel plant was started in the Urals in 1934.

The world production of nickel (not counting the U.S.S.R.) was about 160,000 tons in 1953.

Metallic nickel is yellowish-white, very hard, takes a good polish and is attracted by a magnet. Its specific gravity is 8.9 and its melting point 1,453° C. Nickel does not oxidize in the air and is dissolved readily only by nitric acid. The normal potential of nickel is —0.23 volt.

Nickel has a number of important practical applications. Nickel is consumed in minor quantities for plating other metals (nickel-plating). Most of the nickel, however, goes for the manufacture of various alloys with iron, copper, zinc and other metals. The addition of nickel to steel increases its toughness and mechanical strength, makes it refractory and resistant to corrosion. Alloy steels containing nickel and other metals, for instance, chrome-nickel steel, with 1 to 4 per cent nickel and 0.5 to 2 per cent chromium, are used extensively for the manufacture of cannon, armour of all kinds, armour-piercing shells, bullet jackets, etc.

Alloys of nickel and copper, high in nickel, practically do not corrode and are widely used in the chemical industry, in shipbuilding, and aircraft engineering. Alloys containing less nickel are used for coinage (nickel bronze).

Of the other nickel alloys of great practical importance, the following are noteworthy: 1) *invar*, a steel containing 35 to 37 per cent nickel and having a very low coefficient of expansion; it is used to make rods for watch pendulums, scales for various measuring instruments; 2) *platinite*, a steel containing 0.15 per cent carbon and 44 per cent nickel; it has the same coefficient of expansion as glass and can therefore be fused into the latter; is used in the manufacture of electric light bulbs; 3) *nichrome*, an alloy of nickel and chromium characterized by high electrical resistance; is used in the manufacture of rheostats and various heating apparatuses; 4) *nickeline*, an alloy of copper, nickel and zinc, also having a considerable electrical resistance and changing very little under elevated temperatures.

Finely divided nickel is a very important catalyst widely used in many chemical processes. Pure nickel is employed to make crucibles for laboratory use.

Nickel compounds greatly resemble cobalt compounds. Like cobalt, nickel forms two principal oxides: *nickel monoxide* NiO and *nickel sesquioxide* Ni_2O_3, and the corresponding hydroxides, but only one series of salts, in which nickel is bivalent.

Nickelous hydroxide $Ni(OH)_2$ separates out as a light green precipitate when solutions of bivalent nickel salts are treated with alkalis. It loses water if heated, passing into greyish-green nickel monoxide NiO.

Nickel salts are mostly green both in the solid state and in solution. The most widely used of them is *nickel sulphate* $NiSO_4 \cdot 7H_2O$ or *nickel vitriol* which forms beautiful emerald-green crystals.

Nickelic hydroxide $Ni(OH)_3$ is blackish-brown in colour. It is obtained by the action of powerful oxidants on nickelous hydroxide. Its properties are similar to those of cobaltic hydroxide $Co(OH)_3$.

Nickel forms many complex salts but unlike cobalt it is always bivalent in them.

With carbon monoxide nickel gives a liquid volatile compound, known as *nickel tetracarbonyl* $Ni(CO)_4$, which decomposes when heated, liberating nickel. One of the methods of extracting nickel from its ores is based on the formation of $Ni(CO)_4$.

One of the practically important nickel compounds is nickel sesquioxide, used in the manufacture of alkaline iron-nickel storage batteries.

One of the plates in a charged iron-nickel storage cell consists of pressed powdered iron, and the other, of hydrated nickel sesquioxide with nickel filings added to improve its conductivity. The electrolyte is a 30 per cent solution of potassium hydroxide.

The action of the iron-nickel storage battery is analogous to that of the lead storage battery, the iron playing the part of the lead and the nickel sesquioxide, the part of the lead dioxide. When discharged the iron atoms lose two electrons each, being converted into $Fe^{\cdot\cdot}$ ions, which combine with hydroxyl ions to form $Fe(OH)_2$. The electrons yielded by the iron pass through the outer circuit to the nickel sesquioxide, where they reduce Ni_2O_3, forming $Ni(OH)_2$.

Negative electrode	Positive electrode
$Fe - 2e^- + 2OH' = Fe(OH)_2$	$Ni_2O_3 + 2e^- + 3H_2O = 2Ni(OH)_2 + 2OH'$

Adding up these two equations we get the summary equation of the reaction taking place when the storage battery is discharged:

$$Fe + Ni_2O_3 + 3H_2O = Fe(OH)_2 + 2Ni(OH)_2$$

When the battery is charged the same reaction proceeds in the reverse direction: at the cathode $Fe(OH)_2$ gains electrons to form metallic iron, while at the anode $Ni(OH)_2$ yields electrons and forms Ni_2O_3 again. For this reason both processes, those of charging and of discharging the battery, can be expressed

by a single equation.

$$Fe(OH)_2 + 2Ni(OH)_2 \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} Fe + Ni_2O_3 + 3H_2O$$

The electromotive force of an iron-nickel storage battery equals 1.4 volts. Although its electromotive force is lower than that of the lead storage battery, it is simpler to handle and gives longer service.

PLATINUM METALS

Element	Symbol	Atomic weight	Atomic number	Arrangement of electrons in layers					
Ruthenium .	Ru	101.1	44	2	8	18	15	1	
Rhodium . .	Rh	102.91	45	2	8	18	16	1	
Palladium . .	Pd	106.7	46	2	8	18	18	0	
Osmium . .	Os	190.2	76	2	8	18	32	14	2
Iridium. . .	Ir	192.2	77	2	8	18	32	15	2
Platinum . .	Pt	195.23	78	2	8	18	32	17	1

The elements of the second and third triads of the eighth group in the Periodic Table, *ruthenium*, *rhodium*, *palladium*, *osmium*, *iridium* and *platinum*, are combined under the generic name of *platinum metals.*

257. General Features of the Platinum Metals. The platinum metals form a group of rather scarce metals, but they are so similar to one another in properties that it is very difficult to separate them. On the other hand, they resemble the elements of the iron group very little.

The platinum metals occur in nature almost exclusively in the native state, usually all together, but are never found in iron ores.

Being greatly disseminated through various rocks, the platinum metals became known to mankind comparatively recently. The existence of platinum was established earlier than that of the others, in 1750. Then, in the early XIX century, palladium, rhodium, osmium and iridium were discovered. The last platinum metal, ruthenium, was discovered only in 1844 by Prof. Klaus of the Kazan University who named it in honour of Russia (Ruthenia—Russia).

The most important constants of the platinum metals are given in Table 31.

The platinum metals belong to the less active chemical elements and are very stable against various kinds of chemical action. Some of them fail to dissolve not only in acids but even in aqua regia.

Although the platinum metals may manifest various degrees of valency in their compounds, their typical compounds are those in which they are tetravalent.

The most important of the platinum metals from a practical standpoint is platinum itself.

Table 31

Chief Physical Constants of the Platinum Metals

Constant	Ruthenium Ru	Rhodium Rh	Palladium Pd	Osmium Os	Iridium Ir	Platinum Pt
Atomic weight . .	101.1	102.91	106.7	190.2	192.2	195.23
Nuclear charge . .	44	45	46	76	76	78
Atomic radius, Å	1.32	1.34	1.37	1.34	1.35	1.38
Specific gravity . .	12.2	12.44	11.9	22.46	22.5	21.45
Melting point, degrees C	2,450	1,960	1,552	2,700	2,443	1,769

258. Platinum; at. wt. 195.23. In nature platinum, like gold, occurs in placer deposits as grains, always with admixtures of the other platinum metals. The richest deposits of platinum have been found in the U.S.S.R., in the Urals. The world production of platinum in 1953 amounted to 16 tons (not counting the U.S.S.R.).

Platinum is a white lustrous malleable metal with a specific gravity of 21.45, melting at 1,769° C. In the air platinum does not change even if heated very intensively. It is not attacked by the separate acids. Platinum will dissolve only in aqua regia, but much less readily than gold. Platinum is extracted from its ores with the aid of aqua regia.

Owing to its refractoriness and resistance to chemical action platinum is widely used in scientific and technical laboratories; in analytical work use is made of platinum crucibles, evaporating dishes, electrodes, etc.

Platinum is employed as a catalyst for accelerating many chemical processes. Finely divided platinum is capable of adsorbing considerable quantities of hydrogen and oxygen (as many as 100 volumes per volume of platinum). In the adsorbed state the hydrogen and oxygen become very active; this forms the basis for the use of platinum as a carrier of hydrogen and oxygen.

In its compounds platinum is predominantly bi- and tetravalent. It is capable of forming complex compounds in both states; the tetravalent compounds of platinum are the more important.

When platinum is dissolved in aqua regia the result is *chloroplatinic acid* $H_2[PtCl_6]$, which separates out when the solution is

evaporated as reddish-brown crystals of the composition $H_2[PtCl_6] \cdot 6H_2O$. This is the usual commercial preparation of platinum. The potassium salt of this acid is one of the least soluble salts of potassium, and its formation is employed in chemical analysis for the detection of potassium.

If heated in a stream of chlorine at 360° C, $H_2[PtCl_6]$ decomposes, giving off HCl and leaving *platinum chloride* (IV) or *platinic chloride* $PtCl_4$.

If an alkali is added to a solution of chloroplatinic acid a brown precipitate of $Pt(OH)_4$ falls out. This substance is called *platinic hydroxide*, and forms salts when dissolved in an excess of alkali. Another compound of tetravalent platinum is *platinic oxide* or *platinum dioxide* PtO_2.

Platinum chloride (II) or *platinous chloride* $PtCl_2$ is prepared by passing chlorine over finely divided platinum. Platinous chloride has a greenish colour and is insoluble in water.

Bivalent platinum forms many complex salts. The most important of them are the salts of *cyanoplatinic acid* $H_2[Pt(CN)_4]$. The barium salt of this acid, $Ba[Pt(CN)_4]$, fluoresces brightly under the action of ultra-violet and X-rays and is used in röntgenoscopy for coating fluorescent screens.

259. Palladium; at. wt. 106.7. Iridium; at. wt. 192.2. *Palladium* is a silvery-white metal having a specific gravity of 11.9 and melting at 1,552° C. It is the lightest of the platinum metals, the softest and most malleable. It is remarkable for its capacity for absorbing immense quantities of hydrogen (up to 900 volumes per volume of metal). Absorbing hydrogen, palladium retains its metallic appearance but increases considerably in volume, becomes brittle and cracks easily. The hydrogen absorbed by the palladium is probably in a state approaching that of monatomic hydrogen and is therefore very active. A palladium plate saturated with hydrogen will convert chlorine, bromine and iodine into the hydrogen halides, reduce salts of trivalent iron into bivalent iron salts, corrosive sublimate into calomel, sulphur dioxide into hydrogen sulphide, etc.

Owing to its attractive external appearance palladium is used to manufacture various kinds of jewellery.

Chemically palladium differs from the other platinum metals, being considerably more active. If heated to redness it will combine with oxygen to form the oxide PdO; it dissolves in nitric acid, hot concentrated sulphuric acid and aqua regia.

Like platinum, palladium may be bi- or tetravalent, but its bivalent compounds are more stable. Most palladium salts are soluble in water and are greatly hydrolyzed in solution. *Palladium chloride* $PdCl_2$ is reduced very readily in solution to the metal by certain

gaseous reductants, particularly, carbon monoxide, this being the basis of its use as a test for CO in gaseous mixtures.

Iridium differs from platinum in its very high melting point (2,443° C) and even greater resistance to chemical action. Iridium is attacked neither by the separate acids nor by aqua regia. Besides, iridium is much harder than platinum.

Pure iridium is used for the manufacture of various kinds of scientific instruments. An alloy containing 90 per cent platinum and 10 per cent iridium is used for the same purpose. Particularly, the international standard metre and standard kilogram are made of this alloy.

260. Compounds of the Octavalent Elements of the Platinum Group. Of the platinum group metals only osmium and ruthenium are octavalent in their compounds. The most important of them are: *osmium tetroxide*, *ruthenium tetroxide* and *osmium octofluoride*.

Osmium tetroxide OsO_4 is the stablest oxide of this element and forms slowly even if osmium is just kept in contact with air. It is a fusible crystalline substance (melting point 40° C), pale yellow in colour. Its vapours have a pungent odour and are very poisonous.

Osmium tetroxide dissolves rather well in water, its solution not reacting acid with litmus. However, as was first established by L. Chugayev (1918), osmium tetroxide is capable of forming unstable complex compounds with strong alkalis.

Possessing pronounced oxidative properties, osmium tetroxide reacts very vigorously with organic substances, being itself reduced to black osmium dioxide OsO_2. This forms the basis for the use of OsO_4 for staining microscope preparations.

Ruthenium tetroxide RuO_4 resembles osmium tetroxide in physical properties. It is a crystalline solid of a golden-yellow colour, melting at 25°C and soluble in water. Ruthenium tetroxide is much less stable than osmium tetroxide, and decomposes eruptively at a temperature of about 108° C, below its boiling point, into Ru_2O and oxygen.

Osmium octofluoride OsF_8 is prepared by the direct combination of osmium and fluorine at 250° C as colourless vapours, which condense, when cooled, into lemon-yellow crystals with a melting point of 38°C.

Osmium octofluoride possesses pronounced oxidative properties. It is gradually decomposed by water into osmium tetroxide and hydrofluoric acid:

$$OsF_8 + 4H_2O = OsO_4 + 8HF$$

CHAPTER XXVI

Atomic Nucleus

The theory of atomic structure gave the key to an understanding of the nature of chemical reactions and the mechanism of formation of chemical compounds. The changes which atoms undergo during chemical transformations are related only to the outer shell of the atom, the atomic nucleus remaining quite unaltered. However, there are processes of another kind taking place in nature, such as radioactive transformations, artificial production of new elements, etc. These processes involve changes occurring inside the nuclei, and depend wholly on their structure. Therefore, our study of general chemistry would be incomplete without at least a brief acquaintance with the data at the disposal of modern science on the structure of the atomic nucleus. It must be noted, however, that despite the considerable progress made lately in this field, our knowledge of the structure of the atomic nucleus is still far from complete.

261. Complexity of Atomic Nuclei and Their Artificial Disintegration. The complexity of atomic nuclei first became evident due to radioactive phenomena. All radioactive changes bore witness to the fact that the nuclei of the heavier atoms are complex formations which decay spontaneously, evolving helium nuclei and electrons. It was natural to suppose, therefore, that the nuclei of the non-radioactive elements were also complex in structure. The most radical method of verifying this assumption would have been to cause artificial disintegration of the nucleus and to study the new particles formed thereupon. But the nuclei of the non-radioactive elements proved to be very stable and unresponsive to any of the then known means of action.

The situation seemed hopeless. Very soon, however, thanks to a clever idea suggested by Rutherford, great progress was made in this field. To break down nuclei Rutherford resorted to the colossal kinetic energy of flying alpha particles or, as they are now called, **helions.** His paper communicating the results of experiments with nitrogen appeared in 1919. By bombarding nitrogen atoms with the helions emitted by radium-C, Rutherford succeeded in breaking down nitrogen nuclei, knocking hydrogen nuclei out of them. He called the latter, the simplest of all atomic nuclei, **protons.** Thus, artificial

decomposition of the atom, as it was called at that time, had been accomplished; more precisely, this was the first indication to the effect that nuclei contained protons.

Subsequent experiments by Rutherford and other investigators established that protons could be knocked out of the nuclei of all the light elements, up to iodine. It could, therefore, be expected that the detection of protons in the atomic nuclei of all the rest of the chemical elements was only a question of time.

However, when nuclei are bombarded with helions they do not break down completely. When a helion strikes a nucleus only one proton appears to be knocked out of it, the remainder of the nucleus combining with the helion to form a new nucleus. For instance, a study of the collision of helions with nitrogen nuclei showed that this led to the formation of two new particles, namely, a proton and a nucleus with a mass number of 17 (oxygen isotope), including the helion. Schematically this process may be represented by the following equation*:

$$_{7}N^{14} + {}_{2}He^{4} = {}_{1}H^{1} + {}_{8}O^{17}$$

In other words, knocking one proton out of the nitrogen nucleus, whose mass number is 14, the helion is absorbed by the remainder of the nucleus, which, as a result, changes into the nucleus of an oxygen isotope with the mass number 17. Similar nuclear transformations were observed for other elements.

Rutherford's works and a study of the disintegration products of the radioactive elements led to the assumption that atomic nuclei contain helions, i.e., helium nuclei, protons, and electrons. But as the helium nucleus in its turn can be pictured as consisting of four protons, there followed the involuntary conclusion that atomic nuclei are made up of protons and electrons.

Such was the first (subsequently altered) conception of the structure of atomic nuclei, which arose as a result of experiments on the artificial disintegration of nuclei.

At first nuclei were disintegrated only by bombardment with helions emitted by radioactive substances. Taking into account the minute quantity of the substances at the disposal of investigators and the insignificant percentage of hits made by the helions, it can easily be understood that the efficiency of such bombardments was extremely low. Further investigations in the field of nuclear reactions required the construction of special apparatuses which would make it possible to obtain powerful streams of charged particles.

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* According to the accepted system, the superscript at the upper right-hand corner of the symbol of the element indicates the mass of the nucleus and the subscript at the lower left-hand corner its atomic number, i.e., nuclear charge.

The first units for this purpose were built in the early thirties of this century. In them helions were substituted by a powerful stream of protons, obtained from ordinary hydrogen in a vacuum discharge tube under the action of a high voltage, amounting to several million volts. The substances to be bombarded were placed at the end of the tube. Under such conditions the protons acquired a very high velocity and were able to disintegrate the nuclei of many elements.

The first element bombarded was lithium. Fission of the lithium nucleus resulted in the release of an immense quantity of energy, greatly exceeding that of a flying proton, and in the transformation of the nucleus, together with the proton captured by it, into two helium nuclei:

$$_3Li^7 + {}_1H^1 = {}_2He^4 + {}_2He^4$$

It was found that in most other cases nuclear disintegration also led to the emission of helium nuclei.

This new method of bombarding atomic nuclei with fast protons offered great opportunities for a study of the structure of the atomic nucleus. Its great advantage was the possibility of regulating the velocity of the protons, of gathering them into a narrow beam and directing them at any spot desired.

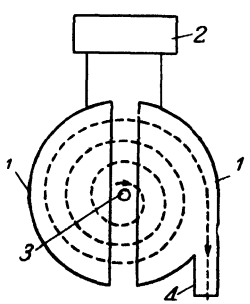


Fig. 158. Diagram of cyclotron

The use of electrostatic apparatuses was a considerable step forward in comparison with the use of radioactive sources; however, it entailed a number of difficulties and inconveniences. Soon afterwards, therefore, new apparatuses—**cyclotrons**—came into use for the production of streams of fast particles. Cyclotrons were based on repeated acceleration of the particles by means of an alternating electric field.

The principal parts of a cyclotron (Fig. 158) are two halves of a hollow disk *1*, *1*, placed at a certain distance from one another and called *dees*. Both dees are located in a magnetic field of a direction perpendicular to their plane, and are connected with an a. c. generator *2*. The combined action of the magnetic and electric fields makes the stream of charged particles travel through the apparatus in a single plane along an evolutive spiral.

The charged particles pass from the auxiliary apparatus *3* into the clearance between the dees and under the influence of the electric field begin to travel with growing velocity from one dee to the other in the direction indicated on the figure by arrows. Entering the dee, where there is no electric field, the particles move uniformly, retaining the velocity they have acquired, until, having described a semicircle, they return to the other side of the clearance between the dees. The generator is adjusted to change the direction of the electric field at this moment, so that the particles are again accelerated in the clearance and then continue their circular motion through the second dee. Upon passing from the second dee back into the first, the velocity of the particles is again

stopped up, etc. After several hundred revolutions the stream of particles is discharged from the apparatus through the opening *4*.

In this way the final velocity of the particles, and therefore their kinetic energy, can be raised to a very high magnitude. For instance, if the particles do 100 half-revolutions in an electric field with a voltage of 5,000 volts, their energy on discharge will be equal to $100 \times 5{,}000 = 500{,}000$ electron-volts.*

The energy acquired by particles in the cyclotron may be as high as several tens of millions of electron-volts.

Cyclotrons are very large apparatuses. For instance, the weight of the magnet in one of the cyclotrons is 4,000 tons. Still, they are considerably smaller than electrostatic units.

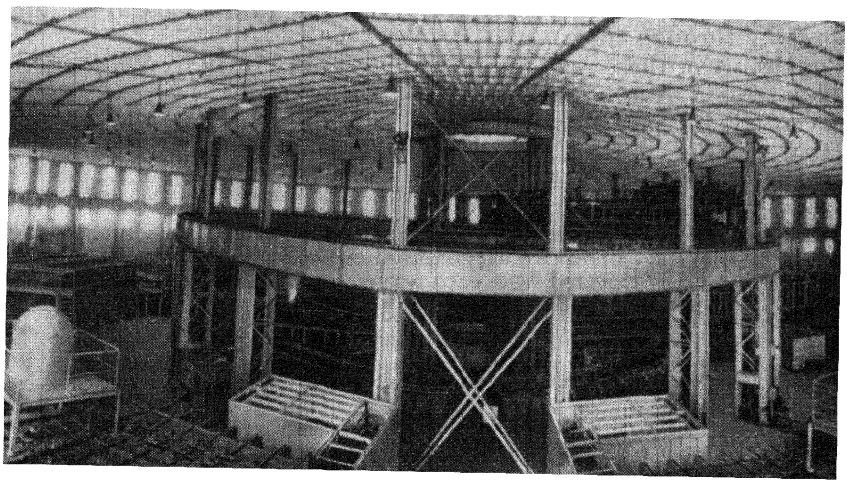


Fig. 159. General view of synchrophasotron

The further progress of atomic physics required the erection of even more powerful particle accelerators than the cyclotron, the possibilities of which had proved to be exhausted. Accordingly, a number of new types of "super-accelerators" have been constructed in the U.S.S.R. and abroad.

These include the **synchrophasotron** (Fig. 159) installed recently in the U.S.S.R., at the Institute for Nuclear Research, and calculated to impart energies as high as 10,000 million electron-volts to particles.

* One electron-volt (ev) is the energy acquired by an electron in traversing a potential difference of one volt:

$$1 \text{ ev} = 1.59 \cdot 10^{-12} \text{ erg} = 3.82 \cdot 10^{-20} \text{ Cal.}$$

It is customary in nuclear physics to express energy in terms of electron-volts.

262. Discovery of Neutrons and Positrons. The conception of atomic nuclei consisting of protons and electrons persisted in science for over ten years, although it contained a number of essential contradictions. But subsequently new discoveries were made, which brought a radical change in this conception. In 1930 Bothe and Becker noticed that when beryllium atoms were bombarded with helions new rays were emitted, having a tremendous penetrating power: a layer of lead three centimetres thick could absorb only half of them. The appearance of these rays was observed also by Irène Curie* and her husband Frédéric Joliot-Curie, who observed also that the rays discovered by Bothe and Becker knock very fast protons out of substances containing hydrogen (water, paraffin, etc.) in passing through them.

The nature of these rays was established only in 1932. They proved to be a stream of new electrically neutral particles, emitted at enormous speeds by beryllium nuclei and possessing a mass almost equal to that of the proton. These particles have become known as **neutrons** and are now designated by the letter *n*.

The process leading to the emission of neutrons by beryllium atoms consists in the absorption of helions by beryllium nuclei (isotope 9) with the simultaneous emission of one neutron from each nucleus, as a result of which the latter changes into a carbon nucleus:

$$_4Be^9 + _2He^4 = _0n^1 + _6C^{12}$$

Further investigations showed that neutrons form also when lithium, boron, fluorine, aluminium and other atoms are bombarded with helions.

The immense penetrating power of neutrons is due to the fact that they carry no charge. Therefore, they do not interact with the nuclei of the atoms they pass through, so that their motion is not retarded unless they collide directly with the nuclei.

The neutron was first considered a complex particle consisting of a proton and an electron linked intimately with one another. Afterwards, however, an entirely different conception was also found possible.

Almost simultaneously with neutrons another type of particles was discovered having the same mass as the electron, but carrying a positive electric charge. These particles were called **positrons.**

The existence of positrons was first observed in the study of cosmic rays, which were discovered as far back as 1911. These rays enter the earth's atmosphere from universal space and possess tremendous energies, and therefore a very high penetrating power. The nature of cosmic rays has not been established exactly to this day. They are

* The daughter of Marie Curie-Sklodowska, who discovered radium.

apparently electromagnetic waves of a nature similar to the gamma rays emitted by radioactive substances, but at the same time contain fast particles.

In 1929 the Soviet Academician D. Skobeltsyn, in experimenting with the Wilson chamber, noticed in it the appearance of traces left by charged particles of some kind, though no radiations had been let into the chamber from the outside. The appearance of these particles could be explained only by the action of cosmic rays on the chamber. A similar phenomenon was observed in 1932 by the American physicist Anderson who studied the deflection of the particles in a magnetic field and came to the conclusion that most of them were electrons, but that positively charged particles of a mass equal to that of electrons were also present. It was soon established that positrons appear also due to the action of gamma rays on many heavy metals and may be emitted by certain light metals when bombarded with helions. The positron is designated by the symbol e^+.

The distinguishing feature of the positron is its very short lifetime, averaging 10^{-7} second. A positron cannot exist for any length of time in a material medium, as upon colliding with an electron (in the shell of some atom), it immediately combines with it to form two photons of gamma rays:

$$e^+ + e^- = 2h\nu$$

The transformation of the positron-electron pair into photons is often very inappropriately called "annihilation" (from the Latin *nihil*—nothing). This term is apt to lead to the idea that the collision between a positron and an electron results in the disappearance of matter. Actually, of course, nothing of the kind happens, as a definite amount of photons appear instead of the positron and electron, these photons having a mass equal to that of the positron and electron that have "disappeared." Thus annihilation is but a transition of matter from one of its forms (positron and electron) into another (photon).

The reverse process, i.e., the "birth" of the positron-electron pair, is also known, being observed in the Wilson chamber when very hard gamma rays are passed into it.

263. Theory of the Atomic Nucleus. As soon as the existence of neutrons became evident, there arose an entirely new conception of nuclear structure, first put forth and grounded by the Soviet physicist D. Ivanenko in 1932. According to this conception the *nucleus consists only of protons and neutrons*, and contains no electrons at all. The ratio between the number of protons and neutrons in the nucleus is expressed very simply. The nuclear mass equals the sum of the mass of protons and neutrons. The whole number expressing (approximately) the mass of the nucleus in conventional atomic weight

units, is called the **mass number of the atom** (nucleus). As both the proton and the neutron have a mass very close to unity, the mass number indicates the total number of protons and neutrons in the nucleus. But the number of protons obviously equals the number of positive charges on the nucleus, i.e., the atomic number of the element; therefore, the number of neutrons equals the difference between the mass number and the atomic number of the element.

Denoting the mass number of an atom by A, the charge on its nucleus by Z and the number of neutrons by N, we get the equation:

$$A=Z+N$$

the number of protons equals Z and the number of neutrons $A-Z$.

Isotopes, obviously, possess equal numbers of protons, but different numbers of neutrons.

Two types of forces act between the particles constituting the nucleus, namely, ordinary Coulomb forces of repulsion between the positively charged protons, on the one hand, and special attractive forces between all the particles, effective only at very short distances, on the other. The latter forces are referred to as nuclear forces. The existence of these forces is confirmed by experiments on the scattering of a neutron beam in hydrogen, which show that at very short distances of nuclear order a strong attraction arises between protons and protons, neutrons and neutrons, and between protons and neutrons. The attractive nuclear forces are considerably more powerful than the repulsive forces due to like charges, and account both for the stability and for the very possibility of existence of proton-neutron nuclei.

However, not all combinations of protons and neutrons are stable. The atomic nuclei of the lighter elements are stable as long as the number of neutrons is approximately equal to the number of protons. As the nuclear mass increases, however, the relative number of neutrons needed to render it stable grows and, in the latter series of the Periodic Table, considerably exceeds the number of protons. Thus, bismuth (at. wt. 209) contains 126 neutrons for its 83 protons, while the nuclei of the heavier elements are generally unstable.

At present the proton-neutron theory of the nucleus is universally recognized, the proton and the neutron being regarded now as two independent **elementary** particles (i.e., not consisting of smaller particles) or, more precisely, as two states of one and the same particle; therefore, under certain conditions they are capable of changing into one another, at the same time "giving birth" to a positron or an electron:

$$\text{proton} \rightarrow \text{neutron} + \text{positron}$$

$$\text{neutron} \rightarrow \text{proton} + \text{electron}$$

In particular, such electron "birth" takes place during radioactive β-decay. The emission of electrons by radioactive elements may be attributed to the fact that one of the neutrons contained in the nucleus is transformed into a proton; the electron thus formed is emitted, and the charge of the nucleus increases by one unit. Owing to the mutual convertibility of protons and neutrons, they are often combined under the common name of "nuclons".

264. Binding Energy of Atomic Nuclei. Mass Defect. Above, in discussing the numbers of protons and neutrons in the nucleus, we found that the mass of an atomic nucleus equals the total mass of all its protons and neutrons. We then proceeded from the assumption that the mass of the nucleus is always represented by a whole number and that the masses of the proton and the neutron equals unity. Actually this is only approximately true. As far back as 1932, when Aston began to work with his new improved mass spectrograph, he found that the masses of individual isotopes in most cases deviate somewhat from whole numbers. Besides, the mass of the proton and neutron were also found not to equal unity exactly. When the masses of various nuclei were calculated using the exact values for the mass of the proton and the neutron, it was found that the calculated values differed slightly from the values found experimentally.

Let us, for instance, calculate the mass of the helium nucleus, which consists of two protons and two neutrons. According to the most accurate modern determinations, the mass of a neutron equals 1.0089, and that of a proton 1.0076 oxygen units. The total mass of the protons and neutrons in the helium nucleus equals

$$2 \cdot 1.0076 + 2 \cdot 1.0089 = 4.033$$

while actually the mass of the helium nucleus is 4.003, i.e., 0.03 oxygen unit less.

Similar results were obtained when the masses of the other nuclei were calculated. It was found that the mass of the nucleus is always less than the total mass of the particles constituting the nucleus, i.e., of all the protons and neutrons taken separately. This phenomenon is known as the **mass defect.**

How is the loss of mass in the formation of atomic nuclei to be accounted for? Modern physics gives the following answer to this question. According to the theory of relativity, founded by one of the most prominent scientists of the XX century Albert Einstein (1879-1955), there exists a definite relation between mass and energy, expressed by the equation

$$E = mc^2$$

where E is the energy in ergs; m, the mass in grams; c, the velocity of light in cm. per sec. (3×10^{10}).

It follows, therefore, that any change of mass must be accompanied by a corresponding change in energy. If there is an appreciable change of mass when atomic nuclei are formed, this means that at the same time an enormous amount of energy has been released.

The mass defect involved in the formation of the helium nucleus amounts to 0.03 oxygen unit, and in the formation of 1 gram-atom of helium—0.03 gr. According to the above equation this corresponds to a release of $0.03 \times (3 \times 10^{10})^2 = 2.7 \times 10^{19}$ ergs, or 6.5×10^8 Cal. of energy. To give an idea of this tremendous quantity of energy it will suffice to mention that it is approximately equal to that produced in one hour by an electric power station of about 700,000 kw. capacity.

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

The binding energy of the helium nucleus equals 28 million electron-volts.

If the binding energy of the nucleus is calculated and divided by the total number of particles (protons and neutrons) in it, we find the energy referred to one particle in the nucleus.

Such calculations carried out for all the nuclei reveal a remarkable fact: the binding energy referred to one particle in the nucleus is approximately the same in all nuclei and equals 7 to 8 million electron-volts. Thus, each particle increases the binding energy of the nucleus by the same value. Hence, the proton and the neutron bonds in the nucleus are equally strong, i.e., nuclear forces are manifested identically with respect to the proton and the neutron.

265. Artificial Radioactivity. In 1933 Irène Curie and Frédéric Joliot-Curie discovered that certain light elements, boron, magnesium and aluminium, emit positrons when bombarded with helions. The next year they found that when the source of helions was removed the emission of positrons did not cease immediately, but continued for some length of time. This meant that helion bombardment had resulted in the formation of certain radioactive atoms with a definite lifetime, but which emitted positrons instead of helions or electrons. Thus was discovered *artificial radioactivity*, which proved to be of quite a specific nature, the nuclear decay in this case leading to the emission of positrons.

Irène Curie and Frédéric Joliot-Curie attributed these phenomena to the formation of very unstable nuclei under the influence of helion bombardment, which then disintegrated, emitting positrons. For example, in the case of aluminium the process takes place in two steps:

$$_{13}Al^{27} + {}_2He^4 = {}_{15}P^{30} + {}_0n^1.$$

where ${}_{15}P^{30}$ is an artificial phosphorus isotope, called "radiophosphorus." As ordinary phosphorus does not contain this isotope, the latter is obviously unstable and disintegrates into a stable nucleus:

$$ {}_{15}P^{30} = {}_{14}Si^{30} + e^{+} $$

The half-life period of radiophosphorus equals 3 minutes and 15 seconds.

Similar processes occur when boron and magnesium nuclei are bombarded with helions, "radionitrogen" ${}_{7}N^{13}$ (half-life 14 minutes) resulting in the first case, and "radiosilicon" ${}_{14}S^{27}$ (half-life 3 minutes and 30 seconds) in the second.

Frédéric Joliot-Curie, a prominent French physicist, Professor of the University of Paris, was born in 1900.

Joliot-Curie was a pupil of the outstanding French physicist Paul Langevin and a co-worker of Marie Curie-Sklodowska in whose laboratory Joliot-Curie, together with his wife Irène Curie, discovered artificial radioactivity. For this discovery he and Irène Curie were awarded the Nobel Prize.

In 1948 Joliot-Curie constructed the first French nuclear reactor, in which a nuclear chain reaction was achieved.

Joliot-Curie was in the front ranks of the struggle for peace and democracy, and up to the day of his death (1958) was President of the World Peace Council.

Although the amount of artificially obtained radioactive substances was exceedingly small, their nature was nevertheless successfully established by chemical means, which gave the grounds for writing the above equations.

The results obtained by Irène Curie and Frédéric Joliot-Curie opened up a new wide sphere for investigations. Soon a number of analogous works appeared. Especially interesting among them were those in which neutrons were employed to bombard the nuclei. This was a very appropriate choice, as neutrons, being neutral particles, penetrate atomic nuclei much more easily, giving rise to new nuclei. In this way dozens of new radioelements were obtained with half-lives ranging from a few seconds to several days. Many of these elements were successfully isolated by chemical means.

Unlike helium bombardment, the radiations in all the latter cases consisted of electrons. The mechanism of formation of radioelements when irradiated with neutrons is evidently as follows: upon capturing the neutron, the nucleus ejects a proton, turning into a new unstable nucleus with an atomic number one unit lower. The latter decays, emitting an electron and again forming the same nucleus as before; for instance:

$$ {}_{26}Fe^{56} + {}_{0}n^{1} = {}_{25}Mn^{56} + {}_{1}H^{1} $$
$$ {}_{25}Mn^{56} = {}_{26}Fe^{56} + e^{-} $$

Over 400 radioactive isotopes of chemical elements are known at present, with electron or positron radioactivity, and with half-lives



Frédéric Joliot-Curie
(1900 1958)

ranging from fractions of a second to several months. The total number of varieties of atoms found in nature or obtained by artificial means amounts to approximately 700.

In studying the reactions of formation of radioactive isotopes a very interesting phenomenon called *nuclear isomery* was observed, consisting in the fact that two radioactive atoms may possess the same nuclear charge and the same mass number, but different radioactive properties. Thus, for instance, irradiation of bromine by neutrons gave rise to two different radiobromines, $_{35}Br^{80}$, having half-lives of β-decay of 18 minutes and 4.2 hours. Such atomic nuclei are called isomeric; having identical compositions, they are apparently different in structure and in different energy states.

266. Transuranium Elements. The use of neutrons for the bombardment of atomic nuclei not only led to the preparation of radioactive isotopes for all the known elements, but also enabled scientists to solve a problem which had long interested them, that of the possibility of existence of transuranium elements, i.e., elements with atomic numbers exceeding 92.

The first transuranium element was discovered in 1940 in a study of the effect of neutrons on uranium. It was found that neutrons with an energy of 25 electron-volts are easily absorbed by U^{238} nuclei, resulting in a very unstable β-radioactive isotope of U^{239} uranium with a half-life period of 23 minutes. Emitting beta particles, U^{239} changes into a new element with an atomic number of 93. This new element was named *neptunium* (Np) by analogy with the planet Neptune, which follows the Uranus in the solar system.

particles possessing energies of 35 Mev. These elements were named *berkelium* (Bk) and *californium* (Cf) in honour of the town and state in which they were synthesized.

Both elements were prepared in very small quantities (the total quantity of californium obtained did not exceed 10,000 atoms) but nevertheless they were successfully isolated and their radioactive and chemical properties studied. The new elements were isolated chemically by the chromatographic method (see p. 420), using special synthetic resins.

In 1954 foreign periodicals reported the production of two more elements, following californium in the Mendeleyev Table and having the nuclear charges 99 and 100, in cyclotrons and nuclear reactors.

During the year following the publication of reliable data on the discovery of these elements, five isotopes of element No. 99 and four isotopes of element No. 100 were synthesized. The lighter of these isotopes were obtained by bombarding uranium atoms in the cyclotron with hexa-charged nitrogen ions, possessing energies of over 100 Mev and oxygen ions with energies of 180 Mev. The rest of them were obtained by prolonged radiation of plutonium in nuclear reactors with slow neutrons. The new elements were named *einsteinium* (En) and *fermium* (Fm) in honour of the prominent scientists A. Einstein and E. Fermi. The mass numbers of these elements are 253 and 255, respectively.

Synthesis of each new element has proved, as a rule, more and more complex; an outstanding achievement of human thought and modern experimental technique was the discovery of the new element No. 101 named after the great Russian chemist *mendelevium* (Mv).

Mendelevium was obtained (U.S.A., 1955) by bombarding one of the isotopes of einsteinium, namely, En^{253}, with alpha particles having energies of about 40 Mev. Altogether only seventeen atoms of mendelevium were obtained, but nevertheless G. Sieborg and his collaborators, who synthesized the new element, were able to establish its radioactive and chemical properties.

At present the chemical properties of the first transuranium elements, especially those of plutonium, have been studied in rather great detail.

It is known that neptunium and plutonium chemically resemble uranium. Both elements, like uranium, manifest valencies of 3, 4, 5 and 6, and decrease in stability of their highest valency compounds from uranium to plutonium; therefore, the transfer of neptunium and especially plutonium from its lowest to its highest degree of oxidation requires a more powerful oxidative action than the same transfer in uranium. The stability of the compounds of the highest degree of oxidation continues to decrease in the elements following plutonium,

americium and curium, for which the valency number 3 is characteristic, curium apparently being capable of forming only compounds in which it is trivalent.

The peculiarities of chemical behaviour of the first transuranium elements, the absence of any resemblance between them and the elements of the sixth period of the Periodic Table located above them, rhenium, osmium, etc., as had been supposed at first, led to the assumption that, like in the case of the lanthanide atoms, it was not the second last electron layer that was being filled with electrons in these atoms, but the underlying third last one. This layer begins to fill up right after thorium (No. 90), thus actinium, No. 89, is followed by a series of elements which, by analogy with the lanthanides, may be called actinides.

The production of the other transuranium elements and investigation of their chemical properties show that this assumption was correct and that the elements following actinium resemble the lanthanides chemically. This made it necessary to alter the earlier grouping of the elements of the seventh period. In this period only the first three boxes remained filled, the actinides being placed, like the lanthanides, outside the Table proper (see pp. 90-91).

267. Utilization of Subatomic Energy. The decay of atomic nuclei is accompanied by the release of enormous amounts of energy, exceeding the energy of ordinary reactions by millions of times. No wonder, therefore, that the problem of utilization of subatomic (or nuclear) energy has long drawn the attention of investigators. However, the practical solution of this problem met with a number of obstacles which seemed unsurmountable.

All the nuclear transformations described in the previous paragraph are caused by bombarding nuclei either with helions ejected by natural radioactive elements or with protons and deuterons (heavy hydrogen nuclei), which can be artificially accelerated in special apparatuses, or, finally, with neutrons. But during such bombardments the probability of the flying particles colliding with the nucleus is very low. At best the number of hits leading to nuclear fission equals $1 : 10^4$, i.e., only one particle in 10,000 hits a nucleus, while the other 9,999 particles are lost for the reaction. The most favourable conditions for bombarding nuclei are attained with neutrons, which bear no charge and are therefore not deflected by the nucleus. However, the very production of neutrons by means of nuclear reactions is very inefficient.

But the main obstacle to the practical utilization of nuclear power was that not a single reaction was known which, once started by some external action, would continue subsequently by itself, as is the case, for instance, with the burning of fuel, and certain other chemical reactions.

Entirely new opportunities for the production of nuclear power arose at the beginning of 1939 when Hahn and Strassmann of Germany discovered that when uranium is irradiated with neutrons, the ordinary nuclear reaction is accompanied by another process, namely "fission" of the nuclei of this element into two approximately equal parts, about 10 to 20 times more energy being liberated than in the first case.* At about the same time the Soviet physicists K. Petrzhak and G. Flerov established that aside from their usual radioactive decay uranium nuclei could also split spontaneously, albeit much more slowly. The half-life period of this process equals 10^{15} to 10^{16} years.

The experiments on irradiating uranium with neutrons were repeated by Joliot-Curie in France, as well as by American physicists. It was established that the fragments resulting from the fission of uranium nuclei were unstable isotopes of various lighter elements which changed into stable isotopes as a result of subsequent β-decay. At the same time, the most important peculiarity of this new nuclear reaction was detected: it was found that the nuclear fission of uranium caused by neutrons is accompanied by the emergence of from one to three new neutrons of very high kinetic energy. These "secondary" neutrons are capable of causing new fissions if they hit intact uranium nuclei, this fission again being accompanied by the emergence of neutrons, etc.

Thus appeared the possibility of a nuclear chain reaction with the emission of neutrons, which enabled the reaction to proceed independently, once started. If more than one neutron forms instead of each neutron, which causes nuclear fission, and each of the new neutrons, in its turn, splits a nucleus, the speed of the reaction will increase indefinitely and an explosion will result.

Further investigation of the fission of uranium nuclei by neutrons showed that the reaction is much more complicated than was thought at first. The trouble is that natural uranium consists chiefly of two isotopes, 99.3 per cent of U^{238} and 0.7 per cent of U^{235}. The first, heavier isotope, can be split only by very fast neutrons. Therefore, most of the neutrons hitting U^{238} nuclei, though absorbed by them, do not cause fission. On the contrary, U^{235} nuclei are easily split by neutrons, mainly slow ones. The chain reaction is possible only with the isotope U^{235}, and in order to accomplish it the secondary neutrons must be considerably slowed down. This can be achieved by making the neutrons pass through a substance of small atomic weight, called a **moderator**. The most suitable moderators are hydrogen (especially its heavy isotope, deuterium), beryl-

* The nuclei of thorium and protactinium are subject to similar fission when irradiated with neutrons.

lium and carbon (as graphite), whose nuclei absorb most of the energy of neutrons upon elastic recoil of the latter from them.

In natural uranium, which consists mainly of U^{238} and contains very little U^{235}, the chain reaction cannot develop with slow electrons, as the secondary electrons are captured by the U^{238} nuclei before their velocity can be moderated sufficiently, and so do not cause further fission. Therefore to carry out a chain reaction, U^{235} must be separated from U^{238}.

The capture of neutrons by U^{238} nuclei leads to the formation of the β-active isotope U^{239}. A study of the further transformations of this isotope, as stated in the previous paragraph, led to the discovery of the first transuranium elements, neptunium and plutonium, and it was established moreover, that plutonium nuclei are split by slow neutrons just as readily as U^{235} nuclei, liberating immense quantities of energy and ejecting new neutrons.

Such were the new scientific facts which became known before the beginning of World War II. They opened out quite ponderable possibilities for the unharnessing of tremendous quantities of energy.

The most important problem that still remained to be solved was primarily the separation of uranium isotopes and the isolation of pure U^{235}, as it seemed probable that this isotope could be used as an explosive of unprecedented destructive power.

The separation of isotopes even in laboratory conditions entails immense experimental and technical difficulties. Though many methods of isotope separation are known, they are all extremely complex, clumsy and of low efficiency. In this case the problem was further complicated by the very insignificant content of U^{235} in natural uranium. However, all these difficulties were overcome. As a result of numerous investigations and the painstaking work of scientists and engineers, plants were erected for the separation of uranium isotopes and they began to produce considerable amounts of U^{235}.

It should be noted that the chain reaction of nuclear fission can proceed only in a large enough lump of U^{235}. Otherwise the majority of the neutrons formed by the fission of the U^{235} nuclei may emerge from the lump before they collide with other uranium nuclei, thus interrupting the chain reaction. The least amount of U^{235}, with which a chain reaction is just possible, is called its **critical mass.** Smaller lumps of U^{235} will not explode. But if small lumps, the total mass of which exceeds the critical, are brought together quickly, a violent reaction ensues resulting in an explosion.

This is the basic principle of the "atomic bomb", the first variant of which consisted of two pieces of U^{235}, separated from one another and enclosed in a shell of a special material serving as a neutron reflector. The mass of each of these pieces of "explosive" was a little more than half the critical.

If these pieces of U^{235} are united very rapidly by means of an ordinary explosive placed in the common outer shell together with the pieces of uranium, an explosion of tremendous force results. It will suffice to mention that the temperature at the point of explosion of the first specimens of atomic bombs reached several million degrees, and the pressure several million atmospheres.

Together with the separation of uranium isotopes, investigations were also carried out in many countries with the aim of accomplishing a controllable chain reaction in *unseparated* uranium.

As mentioned above, no chain reaction based on slow neutrons can develop in natural uranium, owing to the absorption of the neutrons by U^{238} nuclei. But if small pieces of uranium are distributed at equal distances through a mass of graphite serving as the moderator, the fast neutrons emitted by the split U^{235} nuclei are slowed down as they pass through the layer of graphite and collide with the light carbon nuclei. After this, when they enter new pieces of uranium they are absorbed very little by U^{238} nuclei. Therefore a considerable part of them is captured by U^{235} nuclei, causing their fission. In these conditions, the chain reaction takes place much less violently than in pure U^{235}, and more important, its rate can be controlled. However, a considerable quantity of very pure uranium is required to sustain the process.

A unit consisting of lumps (blocks) of uranium distributed at definite distances through a mass of graphite, is called a nuclear reactor or uranium pile.

The first experimental nuclear reactor, constructed by the Americans, was started in December 1942. It contained about 6 tons of pure uranium, the least quantity necessary for its operation.

Besides the fission of U^{235} nuclei and the release of an immense amount of energy, another very important process takes place during the operation of a reactor. This is the gradual accumulation of plutonium in the reactor as a result of the absorption of some of the neutrons by U^{238} nuclei. As plutonium is a different element than uranium, it can be separated from it chemically.

The Americans constructed a huge plant for the production of plutonium in Hanford (State of Washington), which began to put out plutonium in December 1944. Plutonium, like U^{235}, was used by the Americans to make atomic bombs.

At the high temperatures developed during the explosion of the atomic bomb, synthesis of light complex nuclei from simpler ones becomes possible in principle. Such is, for instance, the synthesis of helium from the hydrogen isotopes H^2 and H^3. Such processes, referred to as **thermonuclear**, are accompanied by the liberation of colossal amounts of energy. The use of thermonuclear processes in the

so-called hydrogen bomb has made it possible to produce a weapon many times more powerful than the atomic bomb.

Processes of a similar kind evidently take place in the depths of the sun and the stars and are the source of the colossal amounts of luminous energy emitted by them over billions of years.

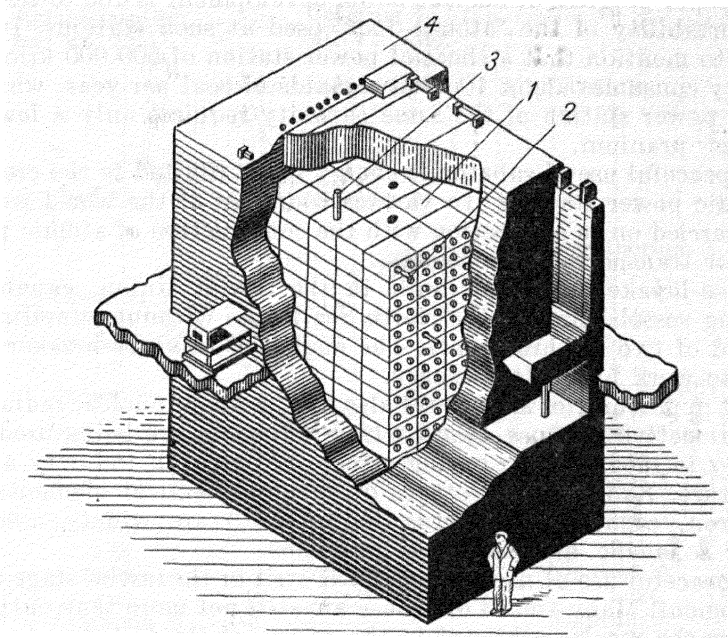


Fig. 160. Nuclear reactor:
1—graphite blocks; 2—uranium rods; 3—cadmium control rod; 4—concrete shielding

Subatomic energy was first used to create a weapon of unprecedented destructive force. For a certain, very short time, the Americans owned the monopoly of producing this weapon. However, very soon the Soviet Union put an end to the monopoly of the U.S.A. in this field. At the same time the Soviet Union has fought and continues to fight persistently for complete ban of nuclear and other types of weapons of mass destruction.

Striving to set the energy of the atomic nucleus to work for the good of mankind, the Soviet Union pioneered the utilization of atomic energy for peaceful purposes. In June 1954 the first industrial atomic power station of 5,000 kilowatts capacity was started in the U.S.S.R., this energy being obtained at the expense of uranium nuclear fission. The experience gained as a result of the operation of this

station has made it possible to undertake the construction of even larger atomic power stations. In the course of the next few years several atomic power stations totalling 2 to 2.5 million kilowatts will be erected in the U.S.S.R. Atomic power stations are now being built also in England, the U.S.A. and other countries.

The rapid progress of nuclear power development is due to the high transportability of the "atomic fuel" used at such stations. It will suffice to mention that a thermal power station of 500,000 kilowatts capacity consumes about 100,000 carloads of coal per year, while an atomic power station of the same capacity requires only a few carloads of uranium.

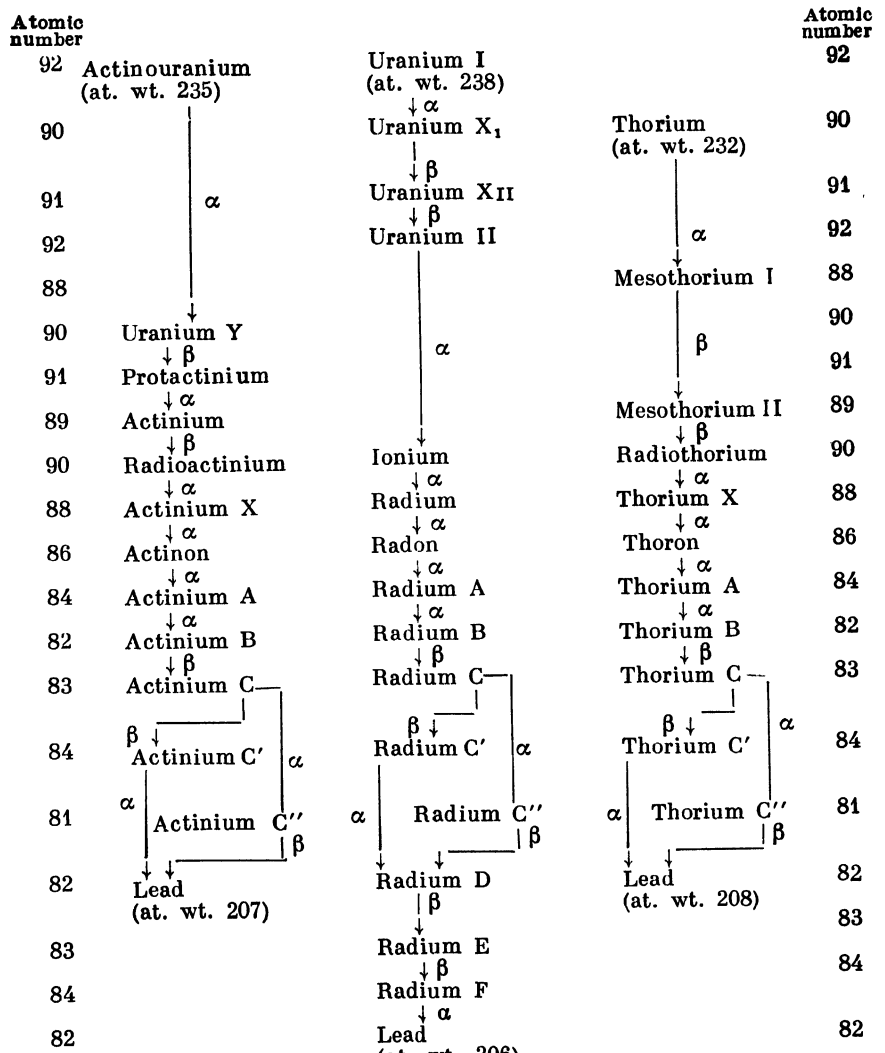
The peaceful use of subatomic energy is not limited to the creation of atomic power stations. In various countries of the world work is being carried on in connection with the construction of atomic power units for transportation purposes.

An ice-breaker has been built in the Soviet Union, capable of escorting vessels through the North Sea Route without refuelling for a period of two or three years. The engine of this ice-breaker will be set to work by nuclear energy.

Great opportunities are offered also by the use of nuclear radiations and radioactive isotopes. Radioactive radiations are being used successfully in medicine for curing certain diseases, in industry and in agriculture. Radioactive isotopes of various chemical elements (cobalt, iron, carbon, phosphorus, iodine, etc.) are widely used for solving scientific and technical problems.

The peaceful use of nuclear energy is still in the initial stage of its development. Many trends of its use are still not more than outlined. However the results achieved in the course of the last decade are a graphic illustration of the fact that the use of the energy of the atomic nucleus opens out wide opportunities before mankind for the development of the productive forces and for further technical progress.

TRANSFORMATIONS OF RADIOACTIVE ELEMENTS



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TO THE READER

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