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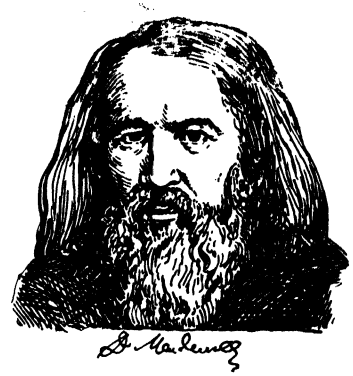
PERIODIC TABLE OF ELEMENTS



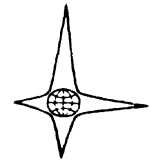
PERIODS	GROUPS OF ELEMENTS I	II	III	IV	V	VI	VII	0	VIII (triads)
1							*1* **H** Hydrogen 1.00797 1	*2* **He** Helium 4.0026 2	
2	*3* **Li** Lithium 6.939	*4* **Be** Beryllium 9.0122	*5* **B** Boron 10.811	*6* **C** Carbon 12.01115	*7* **N** Nitrogen 14.0067	*8* **O** Oxygen 15.9994	*9* **F** Fluorine 18.9984	*10* **Ne** Neon 20.183	
3	*11* **Na** Sodium 22.9898	*12* **Mg** Magnesium 24.312	*13* **Al** Aluminium 26.9815	*14* **Si** Silicon 28.086	*15* **P** Phosphorus 30.9738	*16* **S** Sulphur 32.064	*17* **Cl** Chlorine 35.453	*18* **A** Argon 39.948	
4	*19* **K** Potassium 39.102	*20* **Ca** Calcium 40.08	*21* **Sc** Scandium 44.956	*22* **Ti** Titanium 47.90	*23* **V** Vanadium 50.942	*24* **Cr** Chromium 51.996	*25* **Mn** Manganese 54.9381		*26* **Fe** Iron 55.847 *27* **Co** Cobalt 58.9332 *28* **Ni** Nickel 58.71
	29 **Cu** Copper 63.54	*30* **Zn** Zinc 65.3	*31* **Ga** Gallium 69.72	*32* **Ge** Germanium 9	*33* **As** Arsenic 74.9216	*34* **Se** Selenium 78.96	*35* **Br** Bromine 79.909	*36* **Kr** Krypton 83.80	
5	*37* **Rb** Rubidium 85.47	*38* **Sr** Strontium 87.62	*39* **Y** Yttrium 88.905	*40* **Zr** Zirconium 91.22	*41* **Nb** Niobium 92.906	*42* **Mo** Molybdenum 95.94	*43* **Tc** Technetium [99]		*44* **Ru** Ruthenium 101.07 *45* **Rh** Rhodium 102.905 *46* **Pd** Palladium 106.4
	47 **Ag** Silver 107.870		*49* **In** Indium 114.82	*50* **Sn** Tin 118.69	*51* **Sb** Antimony 121.75	*52* **Te** Tellurium 127.60	*53* **I** Iodine 126.9044	*54* **Xe** Xenon 131.30	
6	*55* **Cs** Cesium 132.905		*57* **La*** Lanthanum 138.91	Hafnium 178.49	*73* **Ta** Tantalum 180.948	*74* **W** Tungsten 183.85	*75* **Re** Rhenium 186.2		*76* **Os** Osmium 190.2 *77* **Ir** Iridium 192.2 *78* **Pt** Platinum 195.09
	79 **Au** Gold 196.967	**Hg** Mercury 200.59	*81* **Tl** Thallium 204.37	*82* **Pb** Lead 207.19	*83* **Bi** Bismuth 208.980	*84* **Po** Polonium [209]	*85* **At** Astatine [210]	*86* **Rn** Radon [222]	
7	*87* **Fr** Francium [223]	**Ra** Radium	*89* **Ac**** Actinium [227]	*104*					

*LANTHANIDES

58 **Ce** Cerium 140.12	*59* **Pr** Praseodymium 140.907	*60* **Nd** Neodymium 144.24	*61* **Pm** Promethium [145]	*62* **Sm** Samarium 150.35	*63* **Eu** Europium 151.96	*64* **Gd** Gadolinium 157.25
65 **Tb** Terbium 158.924	*66* **Dy** Dysprosium 162.50	*67* **Ho** Holmium 164.930	*68* **Er** Erbium 167.26	*69* **Tm** Thulium 168.934	*70* **Yb** Ytterbium 173.04	*71* **Lu** Lutetium 175.97

**ACTINIDES

90 **Th** Thorium 232.038	*91* **Pa** Protactinium [231]	*92* **U** Uranium 238.03	*93* **Np** Neptunium [237]	*94* **Pu** Plutonium [244]	*95* **Am** Americium [243]	*96* **Cm** Curium [247]
97 **Bk** Berkelium [247]	*98* **Cf** Californium [249]	*99* **Es** Einsteinium [254]	*100* **Fm** Fermium [253]	*101* **Md** Mendelevium [256]	*102* [256]	*103* **Lr** Lawrencium [257]



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ГОСУДАРСТВЕННОЕ
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ХИМИЧЕСКОЙ ЛИТЕРАТУРЫ
МОСКВА

B. NEKRASOV

TEXT-BOOK OF GENERAL CHEMISTRY

TRANSLATED FROM THE RUSSIAN
BY
J. VEGODA

TRANSLATION EDITOR
D. SOBOLEV

PEACE PUBLISHERS
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This book is a text-book of general chemistry for college students specialising in chemistry. It will also be useful as an aid to students of non-chemical colleges and to persons studying chemistry by way of self-education.

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TO THE READER

Peace Publishers would be glad to have your opinion regarding this book, its translation, design and printing, and to receive any suggestions from you.

Please write to 2, Pervy Rizhsky Pereulok, Moscow, U.S.S.R.

I. *INTRODUCTION*
ATOMIC AND MOLECULAR THEORY

I-1. The Development of Chemistry. As far as is known at present *the science of substances and their transformation* originated in Egypt, the most technically advanced country of the ancient world. Long before the present era, significant progress had already been made in such branches of production as the working of precious metals, the glass making and dyeing.

In Egypt, chemistry was considered to be a "divine" science and was kept entirely in the hands of the priests who carefully concealed

Fig. 1. Ancient Egyptian drawing representing the working of gold

it from all uninitiates. Nevertheless, some knowledge did leak outside the borders of Egypt. It reached Europe through Byzantium and later through Spain after the conquest of the latter by the Arabs (711 A. D.). The Arabs changed the original name "chēmeia" to "alchemy", by attaching to the word the prefix "al" which is characteristic of Arabic. The concept of "alchemy" subsequently characterised a whole epoch in the history of chemistry.

In order to understand the specific features of development of European alchemy, it is necessary to examine briefly the conditions under which the alchemists worked. In contrast to the centralised system of management of the economy in ancient Egypt, medieval European production was greatly scattered and was carried out by small guilds independently of one another. Technically, it was based wholly on the passing on of recipes from father to son. Therefore, those engaged in production displayed no interest in science. At the same time, trade with the East had developed on a fairly wide scale. However, owing to the difficulties and dangers of transportation, which were due, in the main, to the feudal division of Europe, it was only possible to convey rather expensive materials that required little space. As a result, imports into Eupore consisted almost exclusively of luxury items, for which the sole means of payment was gold. Owing to this, the alchemists devoted their activities to the search

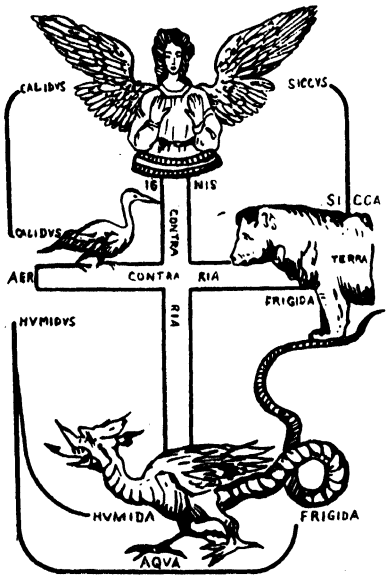


Fig. 2. Alchemist's drawing showing the relation between the elements: Ignis—fire; Terra—earth; Aqua—water; Aer—air; Contraria—the opposites; Siccus—dry; Frigidus—cold; Humidus—wet; Calidus—warm

for the "philosopher's stone" which was supposedly able to turn any metal into gold.

The restricted scope of this work deprived the alchemists of a most important source of knowledge—the *criterion of practice*, i. e., the possibility of testing their theoretical ideas through their widespread practical application.

Divorced from practice, the theoretical outlook of the alchemists did not develop but remained fixed at the level of the concepts of the philosophy of Aristotle (384-322 B. C.). Aristotle taught that the basic elements of nature were abstract "principles", namely: cold, heat, dryness and wetness. Arranging these in pairs and assigning them to "primary matter", Aristotle concluded that there were four "basic elements"—earth, air, fire and water, according to the scheme:

DRYNESS

Earth Fire

COLD HEAT

Water Air

WETNESS

To these Aristotelian "principles" and "elements", the alchemists subsequently added solubility (salt), combustibility (sulphur), and metallicity (mercury).

Fig. 3. An alchemist's laboratory

According to the theoretical system of the alchemists, any substance could be derived from these basic "principles" by combining them in suitable proportions. No wonder, therefore, that so many people firmly believed in the possibility of producing the "philosopher's stone". In search of it, the alchemists discovered many new substances (mainly salts) and developed the basic methods for their purification, and this was the most important achievement of the age of alchemy. The results of their work were kept strictly secret, and many of their discoveries were lost.

A fundamental change took place in alchemy in the first half of the 16th century. The underlying cause of this was the impending change in the very structure of society in a number of the most advanced European countries. The development of the productive forces which had outgrown the framework of feudal society, greatly strengthened the influence of the young and at that time progressive bourgeois class, in whose interests it was to use all means of increasing production and facilitating trade. There arose a need for a wide exchange of

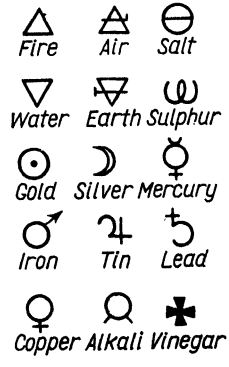


Fig. 4. Alchemical symbols

experience and this was made possible by the advent of printing. At the same time, there appeared new demands called to life chiefly by the requirements of medicine and expanding industry.

The main reformers of alchemy were Paracelsus (1493-1541) and Agricola (1494-1555). "The aim of chemistry lies not in making gold and silver, but in the preparation of medicines", wrote Paracelsus. He considered that all living things consisted of three elements in different proportions: salt (body), mercury (soul) and sulphur (spirit). Diseases stemmed from a deficiency of one of these "elements" in the organism. Consequently, diseases could be cured by introducing the lacking element into the organism. The success of a number of new methods of treatment using simple inorganic compounds, as proposed by Paracelsus (instead of the organic extracts which had been used earlier), induced many physicians to join his school and become interested in chemistry. Chemistry received a great impetus for its further development, having found wide practical application.

Agricola worked in the field of mining and metallurgy. In his extensive work "De re metallica" he collected and generalised all the experience gained in production up to that time, supplementing it with his own investigations and observations. Agricola's book served as the basic manual on mining and metallurgy for more than two hundred years, and some of the methods for testing ores, described by him, are still used today.

An immediate consequence of the work of Agricola and his followers was that the advances made in production methods were utilised by European industry. This led to a rapid expansion of production in Western and Central Europe in the 16th century. It was also during that period that a completely independent Russian industry began to develop. Available evidence shows that smelting of metals, salt extraction and the production of potash, saltpetre, gunpowder, and other items were carried out on a large scale in the State of Muscovy in the 16th century.

By the 17th century, practice had so greatly outstripped theory, which stagnated at the level of the alchemists' ideas, that this contradiction could no longer be tolerated. Aristotle's system, which had for a long time inhibited development, had to be abandoned. In 1661, Boyle (who established the well-known gas law $pv = \text{const}$) denounced this system. In his work "The Sceptical Chymist" he subjected the alchemists' ideas to devastating criticism.

However, while opposing the views of the alchemists, Boyle failed to develop a new general theory, which was more and more urgently needed. A new general theory of chemistry developed about 1700 by Stahl was based on the experience gained in metallurgical processes, which involved reactions of combustion, oxidation and reduction.

Fig. 5. Drawing from Agricola's book: prospecting for ore deposits

Fig. 6. Drawing from Agricola's book: the working of silver

According to this theory, all substances capable of combustion or oxidation contain a special substance called "phlogiston" * which escapes on combustion or oxidation. Essentially, both processes consist in the removal of phlogiston. Adding phlogiston to an oxidised substance (an ore) from a phlogiston-rich substance (coal) results in an unoxidised substance such as a metal. Considering various reactions of combustion and oxidation from this point of view, the phlogiston theory unified and somewhat substantiated almost all the experimental data accumulated up to that time. In addition, it introduced a number of new problems which demanded scientific investigation. It was at the time when the phlogiston theory was prevalent, that most of the gases were discovered. Various metals, oxides and salts were subjected to detailed study. However, the principal merit of the phlogiston theory was that it finally ousted the obsolete ideas of Aristotle.

The basic contradiction of the phlogiston theory lay in the fact that the weight of an oxidised metal is always *greater* than that of an unoxidised metal, whereas quite the reverse should have been expected because upon oxidation the metal *lost* phlogiston. Adherents of the phlogiston theory tried to account for this increase in weight by attributing a "negative" weight to phlogiston, but this explanation was too far-fetched. In spite of numerous attempts, no one ever succeeded in isolating and studying phlogiston. Further discoveries either did not fit into the framework of the theory, or could only be reconciled with it by advancing supplementary hypotheses which often contradicted its principles. Therefore, at the end of its almost century-long domination, the phlogiston theory, which had hitherto aided the progress of science, became an obstacle to its further development.

I-2. The Beginnings of Modern Chemistry. Chemistry, as an exact science, was born during the time when the phlogiston theory reigned supreme. Specifically, it can be considered to have emerged in the middle of the 18th century, when M. V. Lomonosov first formulated the *Law of Conservation of Mass*. This fundamental law of chemistry states that *in any chemical reaction the initial mass of the reacting substances is exactly equal to the final mass of the products*. The law of conservation of mass provides a scientific basis for quantitative analysis and, thereby, makes possible the exact study of the composition of substances and the course of chemical reactions.

Simultaneosly with the formulation of the law of conservation of mass, Lomonosov put forward a very important idea: "There is no doubt that the air particles flowing continuously over a burning substance combine with it and increase its weight". The correctness

* From the Greek, "phlogistos"—combustible.

of this idea (and that of the law of conservation of mass) was confirmed experimentally by Lomonosov in 1756. By heating metals in tightly sealed glass vessels, he proved that when no external air is addmitted, the weight of the burnt metal remains unchanged. This result not only refuted the phlogiston theory, but laid the basis for a new interpretation of oxidation processes.

Consistent application of quantitative methods of investigation typical of Lomonosov's work was also characteristic of the later work of Lavoisier, who totally disproved the phlogiston theory and replaced it with new concepts. In the experiments which he carried out between 1772 and 1777, Lavoisier proved that combustion is not a reaction of *decomposition* in which phlogiston is given off but is, on the contrary, a reaction of *combination* in which the burning substance combines with oxygen from the air. The mysterious and elusive "phlogiston" thus became quite innecessary. At the same time, all the basic conceptions underwent a fundamental change: the oxide, hitherto regarded as an element, was now found to be a complex substance whereas the metal, which had been considered a complex substance, proved to be an element. Lavoisier uprighted the "upside-down" phlogiston theory, thus laying the foundation of the present-day system of chemistry. Many of Lavoisier's contemporaries did not share the new views, but by about 1800 they were accepted and became widespread.

It was Lomonosov's law and the new system of chemistry that made it possible to raise a problem which at the turn of the 19th century was the point of controversy between Berthollet and Proust. Essentially, the problem was whether substances combine in definite quantitative proportions, depending on their nature, or whether these proportions are not fixed but vary, depending solely on the quantities of the substances that take part in the reaction. In the first case, any two elements could be expected to form only a few compounds differing greatly in composition, while in the second, a whole series of compounds of gradually varying composition would result. From this it followed that in the first case, the composition of any given substance should be quite definite and independent of the way the compound had been obtained, while the second precluded any definite composition. On the whole, therefore, the point at issue was whether the composition of substances changed stepwise or continuously.

Berthollet was an advocate of the theory of continuous change in composition, while Proust adhered to the theory of stepwise change. After a debate of several years (1801-1807), chemists accepted the views of Proust. Thus was established the second fundamental law of chemistry—the *Law of Constant Composition* which states that *every chemical compound has a fixed and constant composition*. Hence,

the composition of a chemical compound does not depend on the method of its preparation.

This law made it possible to determine the proportions by weight in which different chemical elements combine with one another. These proportions were studied and put into a system, mainly by Dalton, in a period of several years beginning with 1803. He introduced into science the concept of combining weights of the elements, which came to be known later as "equivalent weights". *The equivalent weight of an element is the weight which will combine with or displace one part* (more precisely 1.008) *by weight of hydrogen.* The importance of this concept for chemistry lies in the fact that *elements always combine with one another in definite proportions by weight, depending on their equivalent weights (the law of definite proportions).* Consequently, the composition of any compound can be expressed in whole numbers of equivalent weights of its constituent elements.

The numerical values of equivalent weights can easily be found if we know the percentage composition of a compound of the element in question with another of established equivalent weight.

Example 1. Find the equivalent weight of oxygen from the percentage composition of water: hydrogen 11.2%, oxygen 88.8%.

If 11.2 parts by weight of hydrogen correspond to 88.8 parts of oxygen, then 1.008 parts of hydrogen correspond to E parts of oxygen.

Obviously, $E = \frac{1.008 \times 88.8}{11.2} = 8.0$ which is the equivalent weight of oxygen.

Example 2. Copper forms a compound with oxygen, which when analysed is found to have the following composition: copper 79.9%, oxygen 2.01%.

The equivalent weight of copper is calculated by proportion:

79.9 parts by wt. of copper correspond to 20.1 parts of oxygen

E parts by wt. of copper correspond to 8 parts of oxygen

$$\text{Hence, } E \text{ for copper} = \frac{8 \times 79.9}{20.1} = 31.8$$

Besides the compound considered in example 2, known as *cupric* oxide, there is another, called *cuprous* oxide which has a different percentage composition, namely: copper 88.8% and oxygen 11.2%. If the equivalent weight of copper in cuprous oxide is calculated from these data, it will be found to be 63.6, i. e., *exactly twice* that of cupric oxide.

A consideration of this and similar cases led Dalton to formulate the *Law of Multiple Proportions: when two elements combine to form more than one compound, the several weights of one element that combine with a fixed weight of the second are in the ratio of small whole*

numbers. Nitrogen oxides are a good example of the operation of this law:

Oxide	Percentage composition		Parts by weight of oxygen per part by weight of nitrogen	Relative content of oxygen (by weight)
	Nitrogen	Oxygen		
Nitrous oxide	63.7	36.3	0.57	1
Nitric oxide	46.7	53.3	1.14	2
Nitrous anhydride . . .	36.8	63.2	1.71	3
Nitrogen dioxide	30.4	69.6	2.28	4
Nitric anhydride	25.9	74.1	2.85	5

The fact that elements combine in definite proportions, led to the conclusion that the structure of matter was *discrete*. This conclusion was arrived at by Dalton on the basis of extensive experimental data which he collected, and it was he who introduced into chemistry

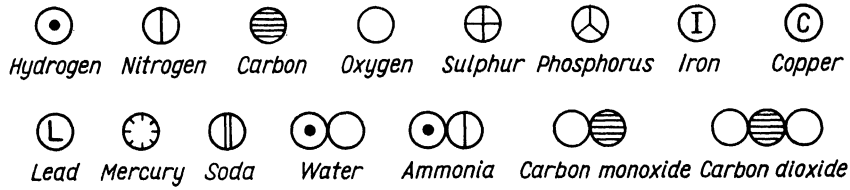


Fig. 7. Dalton's chemical symbols

the concept of *atoms* as *minute particles of which all substances are composed*. "The theory of multiple proportions would be a mystery without the atomic hypothesis", wrote Dalton to Berzelius, one of the most prominent chemists of the first half of the 19th century.

The atomic theory substantiated all the theoretical ideas of chemistry and marked the transition to the modern stage of development of this science. "Neue Epoche beginnt in der Chemie mit der Atomistik..." * ("A new epoch begins in chemistry with the advent of the atomic theory".)

I-3. Atoms and Molecules. From the point of view of the atomic theory, a *chemical element* is a *species of atoms characterised by a definite set of properties*. The properties of all the atoms of any one element are the same, and differ from those of the atoms of any other

* Friedrich Engels. "Dialektik der Natur", Berlin, 1958.

element. A *simple substance* is the result of combination of *like* atoms, and this is the mode of existence of elements in the free state. The combination of *different* atoms gives rise to a *complex substance*, i. e., a chemical compound. By means of suitable operations, any complex substance can be split up into its constituent elements.

After the general acceptance of the atomic theory, it was essential to interpret the weight ratios of reacting elements on the basis of this theory. To do this, it was necessary first to determine the weights of the atoms, if not absolute, then at least relative—the so-called *atomic weights* of the elements. The latter could be determined by taking the weight of the atom of any one element as a unit and expressing the weights of the atoms of the other elements in terms of this arbitrary unit. Hydrogen is the lightest of all the known elements: therefore, it was natural that the weight of the hydrogen atom was, at first, taken as the unit of atomic weight.

However, when determining the atomic weights of the other elements, a difficulty arose. The well-known fact that hydrogen combines with oxygen in the ratio of 1 : 8 by weight was found to be insufficient for determining the atomic weight of oxygen—it was also necessary to know *how many* atoms of hydrogen and oxygen form a molecule of water. If it is assumed that in water one atom of hydrogen is combined with one atom of oxygen, the atomic weight of oxygen will be equal to 8; if there are two atoms of oxygen per atom of hydrogen, the atomic weight of oxygen will be 4; if there is one atom of oxygen to each two atoms of hydrogen, it will be 16, etc. Since Dalton was not able to solve this problem, he accepted the simplest assumption, namely, that the water molecule is composed of one atom of hydrogen and one atom of oxygen. It followed that the atomic weight of oxygen was 8. About this time—in 1813—Berzelius introduced abbreviated symbols for the chemical elements, using the initial letters of their Latin names. In accordance with Dalton's assumption, water was denoted by the formula HO.

When determining the atomic weight of an element which had more than one equivalent, e. g., copper, there was the question which atomic weight to adopt. This question could be answered only arbitrarily. Still greater difficulties were encountered in determining the formulas of complex substances. All this showed that a purely gravimetric approach to the study of chemical problems, while making it possible to substantiate the atomic theory, did not provide any possibilities for its further development.

The development of the atomic theory was given a new impetus by the work of Gay-Lussac, the author of the well-known *Law of the Thermal Expansion of Gases** (if the temperature changes by one

* Also known as Charles' law.

degree, the volume of a gas changes by 1/273 of its volume at zero). Beginning with 1805, Gay-Lussac made a study of the ratios by volume in which gases take part in chemical reactions, and in 1808, he summarised the results of his work in the following *Law of Combining Volumes: in any chemical reaction, the volumes of all gaseous products and reactants measured at the same pressure and temperature may be expressed in ratios of small integers.*

This law attracted general attention, since with its aid it was hoped to establish definite values for the atomic weights. Berzelius who enjoyed great authority among chemists, accepted the simplest assumption that equal volumes of elementary gases (i. e., gases representing simple substances) contain equal numbers of *atoms*, and the majority of other scientists followed his example. Hence, it followed that the atomic weights of elements are related to one another as the weights of equal volumes in the gaseous state.

However, this new theory disagreed, in many cases, with experimental data. For example, it was thought that the reaction between nitrogen and oxygen to form nitric oxide should be formulated as

$$N+O=NO$$

One volume of nitrogen plus one volume of oxygen should yield *one* volume of nitric oxide. However, it was found that in this reaction the volume of the gases did not alter, i. e., the two volumes of the reactants yielded *two* volumes of the product. Similar discrepancies between experiment and theory were found in a number of other reactions.

In order to eliminate these difficulties Avogadro put forward the following hypothesis (1811): *equal volumes of all gases* at the same pressure and temperature *contain the same number of molecules.* This hypothesis introduces the concept of *molecules* as the *smallest particles of a substance capable of independent existence.*

Avogadro assumed that the molecules of elementary gases are *diatomic*, i. e., consist of two atoms. According to this point of view, the reaction between nitrogen and oxygen to form nitric oxide should be written as $N_2+O_2=2NO$, i. e., two volumes yield two volumes. The results obtained in Gay-Lussac's other experiments were plausibly explained in a similar manner.

In spite of this, Avogadro's hypothesis was not accepted by his contemporaries. The main reason for its non-acceptance was the then prevalent view of the nature of chemical reactions, developed by Berzelius. Anticipating the results of much later research, Berzelius held that many chemical phenomena are based on electrical phenomena. He visualised the combination of two elements as the mutual attraction between oppositely charged atoms. According to Berzelius, the atoms of metals possess a surplus positive charge, while the atoms

of non-metals have a surplus negative charge. It followed that molecules consisting of two like atoms could not exist. Avogadro's hypothesis could not, therefore, be accepted before the defeat of Berzelius' electrochemical theory, which was valid, in the main, for most inorganic compounds.

This theory was undermined by its very protogonists who insisted on its applicability in *all* fields of chemistry and in *all* cases, and this often led to contradictions with the experiment. Berzelius' theory was disproved by new data obtained in the rapidly developing field of organic chemistry, and was completely abandoned by about 1840. However, by then Avogadro's hypothesis was almost forgotten, and it was generally accepted only around 1860 (owing to the work of Cannizzaro). This hypothesis is now considered to be a *law* since it has been confirmed by a great deal of experimental data.

I-4. Molecular Weight. If, under the same conditions, equal volumes of two gases contain equal numbers of molecules, it is obvious that the weight of a molecule of one gas bears the same ratio to the weight of a molecule of the other, as the weight of a given volume of the first gas bears to the weight of an equal volume of the second gas. The ratio of the weight of a given volume of one gas to the weight of the same volume of another gas is called the *density* of the first gas relative to the second. Since hydrogen is the lightest gas, it is most convenient to take its weight as the basis for determining the relative weights of the molecules of different substances, i. e., their *molecular weights*. Density relative to hydrogen is denoted by D_H. From the foregoing it follows that the ratio of the molecular weight of any gas under investigation (M_x) to the molecular weight of hydrogen (M_H) is equal to the density of the gas relative to hydrogen:

$$\frac{M_x}{M_H} = D_H \text{ or } M_x = M_H \times D_H$$

It remains to establish how many atoms constitute one molecule of hydrogen. This will determine the choice of a unit for molecular and atomic weights, as a reasonable one would be the weight of the smallest particle of hydrogen—its atom.

This problem was solved on the basis of Gay-Lussac's experiments. For example, when hydrogen reacts with chlorine, one volume of hydrogen and one volume of chlorine form two volumes of hydrogen chloride. Depending on the number of atoms in the molecules of hydrogen and chlorine, the reaction between them must be represented by one of the following equations:

1) $H + Cl = HCl$
2) $H_2 + Cl_2 = 2HCl$
3) $H_3 + Cl_3 = 3HCl$, etc.

Obviously, the second equation agrees with the experimental results. Similarly, the volume ratios in the reactions of hydrogen with oxygen, nitrogen and other gases could be accounted for only by assuming the hydrogen molecule to be diatomic.

Thus, if the weight of the hydrogen atom is taken as unity, the weight of its molecule (M_H) must be two, and the formula for calculating molecular weights becomes:

$$M_x = 2D_H,$$

i. e., *the molecular weight of a substance in the gaseous state is equal to twice its density relative to hydrogen*. Consequently, to determine the molecular weight, it is sufficient to know the weight of a certain volume of the given substance in the gaseous state and the weight of an equal volume of hydrogen under the same conditions.

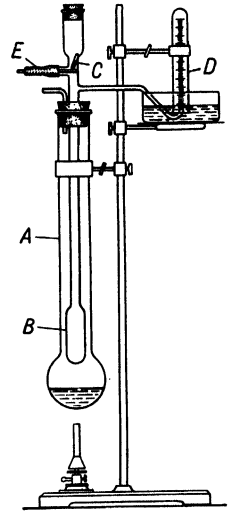


Fig. 8. Apparatus for determining molecular weight

Example. The weight of a certain volume of gaseous chlorine was found to equal 1.5805 g. The weight of an equal volume of hydrogen under the same conditions was 0.0449 g. Find the molecular weight of chlorine.

The density of chlorine relative to hydrogen will be $1.5805/0.0449 = 35.2$. The molecular weight is equal to twice the density, i. e., 2×35.2, or 70.4.

At the beginning of this century, it became the practice to take 1/16 of the atomic weight of oxygen as the unit of molecular and atomic weights ("oxygen unit"), this being more convenient, since the atomic weights of many elements became closer to integers. However, the atomic weight of hydrogen then becomes 1.008, so that its molecular weight is 2.016. Thus, to obtain more exact values for molecular weights, the formula $M_x = 2.016D_H$ should be employed (making the molecular weight of chlorine 70.9). However, such accuracy is not necessary for solving most practical problems.

At present (since 1962), the adopted unit of molecular and atomic weight is 1/12 of the atomic weight of the most abundant species of carbon atoms (i. e., the isotope 12C). The carbon unit is a common basis for physical and chemical calculations, which had not existed earlier. In practice, the atomic weights of the overwhelming majority of elements did not alter on changing over to this new unit.

1) On the basis of Avogadro's law, it is possible to determine the molecular weights not only of gases, but of substances which are liquid or solid under ordinary conditions, and which can be vaporised without decomposition.

An apparatus of the type shown in Fig. 8 is usually employed for this purpose. A liquid with a boiling point higher than that of the substance being investigated is poured into the outer vessel (*A*). On heating this liquid to boiling, a high temperature is produced throughout the whole of vessel (*A*). A carefully weighed quantity of the substance under investigation is placed in a thin-walled glass ampoule (*C*). When the glass rod (*E*) is pulled out, the ampoule drops into the heated vessel and breaks to pieces. The substance in the ampoule vaporises and the resulting vapour forces some air into the graduated tube (*D*) previously filled with water, the volume of the displaced air being equal to that of the vaporised substance. Knowing this volume (reduced to normal temperature and pressure) and the weight of the substance under investigation, it is easy to calculate the density of the vapour and the molecular weight (in the vaporised state). If the vessel (*B*) is not made of glass but of a high-melting metal, and the outer vessel (*A*) is replaced by an electric furnace, this method can be used at temperatures up to 1500° C.

An important corollary follows from Avogadro's law, relating the weights of different substances to the volumes they occupy in the gaseous phase. *A quantity of substance whose weight in grams is numerically equal to its molecular weight is called the gram-molecule* (abbreviated *mole*). The *gram-equivalent* and the *gram-atom* are defined analogously. Obviously, a mole of one substance is as many times larger than that of another, as the weight of a molecule of the first is greater than the weight of a molecule of the second. Hence, *gram-molecular* (or proportional) *quantities of all substances contain the same number of molecules.* Consequently, if the substances are gaseous and are at the same temperature and pressure their gram-molecular weights must occupy equal volumes.

The volume occupied by one gram-molecule of a gas at "normal" temperature and pressure (0° C and 760 mm Hg respectively) * is calculated in the following way. We know from experiment that one litre of hydrogen at N.T.P. weighs 0.0899 g, one litre of oxygen weighs 1.4289 g and one litre of nitrogen weighs 1.2506 g. The respective molecular weights are 2.016, 32.00 and 28.02. Dividing the molecular weights by the weights of one litre, we get in all cases practically the same number, namely **22.4.** Thus, *one gram-molecule of any gas at N. T. P. occupies a volume of 22.4 litres.*

This number should be memorised since by using it we can easily calculate the weight of one litre (and, consequently, any other volume) of any gas at N. T. P., so that there is no need to remember the separate figures.

Example. Calculate the weight of 200 ml of chlorine at N. T. P. The molecular weight of chlorine is equal to 70.9. The weight of one litre is $70.9/22.4 = 3.165$ g. The weight of 200 ml is then $3.165/5 = 0.633$ g.

* Abbreviated N.T.P.

The calculation can be extended to cases where the temperature and pressure are other than normal. For this purpose use is made of the *Clapeyron-Mendeleyev equation*:

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

where P = pressure,
V = volume,
m = weight,
M = molecular weight of the gas,
R = gas constant,
T = absolute temperature (equal to $273 + t$, where t is the Celsius temperature).

In chemical calculations, it is usual to express P in millimetres of mercury (mm Hg), V in millilitres, and m and M in grams. Since a gram-molecule of any gas ($m = M$) at 0° C (273° by the absolute scale) and 760 mm Hg occupies a volume of 22,400 ml, the numerical value of the constant R is $\frac{760 \times 22{,}400}{273} = 62{,}360$. Thus, the formula becomes: $PV = 62{,}360 \frac{m}{M} T$, which makes it easy to calculate any one quantity in the equation if the rest are known.

Example. What is the weight of 400 ml of hydrogen at 700 mm Hg and 20° C?

Substituting the known values into the equation, we get: $700 \times \times 400 = 62{,}360 \times \frac{m}{2.016} \times 293$. From the calculation, we find: $m = 0.0309$ g.

These calculations do not give *completely* accurate results, as the gas laws only approximate the properties of real gases. However, when the temperature and pressure do not differ greatly from N. T. P., this degree of accuracy is sufficient for practical purposes.

I-5. Atomic Weight. The determination of molecular weights made it possible to arrive at reliable values for *atomic* weights. In some cases, the latter could be determined quite simply. For instance, if the molecular weight of chlorine is known to be 70.9 and its molecule consists of two atoms, the atomic weight of chlorine is 35.45.

In more general cases, the problem was solved by taking advantage of the equivalent weights of the element and the molecular weights of its volatile compounds (Cannizzaro, 1850). An example of this was carbon which was known to have two different equivalents, namely 3 and 6. Obviously, the atomic weight of carbon must be either the smallest value of its equivalent weight, or a multiple of the latter, i. e., 3, 6, 9, 12, 18, etc.

The true value was selected on the basis of Avogadro's law. Since the molecule of any carbon compound cannot contain less than one atom of carbon, the *smallest* proportion of the element in the molecular weight must correspond to its atomic weight. Therefore, it was necessary to determine the molecular weights of several volatile carbon compounds, calculate the proportion of carbon from their percentage composition in each case, and choose the smallest value from all the figures obtained. These determinations gave a value of 12. Thus, the atomic weight of carbon must be 12. By way of example, the relevant figures for methane, ether, alcohol and carbon dioxide are given below.

Properties	Methane	Ether	Alcohol	Carbon dioxide
Molecular weight . . .	16	74	46	44
Percentage of carbon . .	75.0	64.9	52.2	27.3
Proportion of carbon in molecular weight . .	12	48	24	12

The atomic weights of elements that do not form volatile compounds could be determined by using the empirical *rule of atomic heat capacities* (Dulong and Petit, 1819): the heat capacity of one gram-atom of an element in the solid state, i. e., the product of the atomic weight of the element and its specific heat under ordinary conditions is approximately a constant whose mean value is 6.2 (specific heat is the quantity of heat required to raise the temperature of one gram of a substance by one degree). This rule was first applied to the determination of atomic weights about 1850.

For example, copper has two equivalent weights, 31.8 and 63.6. The atomic weight of copper must be equal either to the smaller value or to one of its multiples, i. e., it could be 31.8, 63.6 or 95.4, etc. It was known from experiment that the specific heat of copper at normal temperatures is 0.093 cal/g *. Dividing the mean value of the atomic heat by the specific heat, we obtain 6.2/0.093 = 67, i. e., a value close to the second of the possible values for the atomic weight of copper. Consequently, the second value is the correct one.

The establishment of universally accepted atomic weights was of great importance for the development of chemistry. It made it possible to generalise and put into a system all the accumulated knowl-

* The calorie (cal) is the amount of heat required to raise the temperature of one gram of water by one degree (from 19.5° C to 20.5° C). The amount required for one kilogram is a kilocalorie (kcal).

edge of the properties of the elements, and it was Mendeleyev who succeeded in doing this around 1870.

Mendeleyev proceeded from the idea that the most essential property of the atom was its mass, the magnitude of which must serve as the basis for any chemical classification of the elements. When he arranged the elements in the order of increasing atomic weights, he discovered a *periodicity* in the change of their chemical properties: it was found that for each element, after a certain number of others, there is another element which is similar to the first. On the basis of a comprehensive analysis of this chemical similarity, Mendeleyev discovered the periodic law and constructed the Periodic Table which is shown in its modern form on the fly-leaf. In this table, the elements are numbered according to their position (atomic number), and their chemical symbols, names and atomic weights are also given. The atomic weights of the radioactive elements (given in square brackets) are those of the most stable atoms (except U and Th) or of the best known isotopes.

The periodic table of the elements provided chemists with a new method for determining atomic weights. It was first used by Mendeleyev himself to correct the atomic weights of a number of elements.

For instance, consider the element *indium*. Only one equivalent weight of indium was known, viz., 38.3 (approximately). Its atomic weight, therefore, could be equal to 38.3, 76.6, 114.9, 153.2, etc. No volatile compounds of indium were known. If the atomic weight of indium is assumed to be 38.3, the element falls in the position after chlorine in the table, i. e., the position now occupied by potassium (atomic number 19, the elements of group 0 not being known at that time). However, indium is quite dissimilar in its properties to the other elements in the same vertical series; consequently, this assumption must be rejected. If the atomic weight is taken to be 76.6 (as was then thought), indium would take the place of selenium (No. 34). However, as in the previous case, the properties of indium are not at all similar to those of the other elements in this vertical series. The next possibility is that indium has an atomic weight of 114.9, and this puts the element in a position where it would have an atomic number 49, i. e., in the same column as aluminium (No. 31—gallium—was unknown), to which it is very similar in properties. Hence, the atomic weight of indium must be equal to 114.9. Subsequently, this and all the other atomic weights indicated by Mendeleyev were confirmed by experiment. Owing to the periodic table, the determination of the atomic weight of an element was reduced to a more exact determination of its equivalent.

Comparing the atomic and equivalent weights of individual elements, we find that the atomic weight is either equal to the equivalent, or is twice, three times, etc., the equivalent weight. The number indicating how many times greater the atomic weight is than the

equivalent weight, i. e., the quotient obtained on dividing the atomic by the equivalent weight, is called the *valency* of the element. Thus, since the atomic weight of hydrogen is equal to its equivalent weight, hydrogen is a *monovalent* element; as the atomic weight of oxygen is 16 and its equivalent weight 8, oxygen is *divalent*, etc. An element possessing two or more different equivalent weights (e. g., copper) will obviously have more than one valency.

The physical meaning of "valency" will be clear from the following reasoning. If the atomic weight of an element, say, oxygen, is twice its equivalent weight, this means that in compounds, one gram-atom of the element corresponds to two gram-atoms of a monovalent element. In other words, one atom of oxygen is capable of combining with two atoms of a monovalent element (e. g., hydrogen). Consequently, *valency is the number of monovalent atoms with which an atom of the element in question can combine (or the number of such atoms it can displace)*.

Valency is often indicated by attaching the corresponding number of lines to the symbol of the element. In this sense we may speak of valencies or units of valency.

The concept of valency was outlined during the fifties of last century. This concept was of particular importance to chemistry since it formed the basis for the theory of the structure of chemical compounds, one of the guiding theories of present-day chemistry.

I-6. Chemical Formulas and Equations. The confusion which existed in chemical symbols before Avogadro's hypothesis was recognised is difficult to imagine. Inasmuch as there were no generally accepted atomic weights, each chemist was guided in this matter by the considerations he thought most correct. These considerations changed frequently as a result of this or that experiment and this led to alterations in the expressions for the composition of chemical compounds, that is in *chemical formulas*. There was no generally accepted symbol even for water. As to the formulas of more complex substances, disagreement was often so great that chemists could hardly understand one another.

All these problems were settled with the adoption of unified atomic weights. Chemists had finally found a common language. Indeed, determination of the simplest formula of a particular compound no longer presented any difficulties; it was only necessary to know its percentage composition (as determined by chemical analysis) and the atomic weights of its constituent elements.

Example 1. A compound consisting of carbon and chlorine contains 7.8% C and 92.2% Cl. The respective atomic weights are 12.0 and 35.5. Determine the formula of the compound.

The reasoning is as follows. In a compound of given percentage composition, the higher the atomic weight of an element, the smaller the relative number of its atoms in the molecule. Therefore, in order to find the relative number of atoms of each element in the molecule of the compound, the percentages must be divided by the corresponding atomic weights. Such division results in the numbers 0.65 and 2.60 for carbon and chlorine respectively.

These numbers give the relative number of atoms in the molecule. However, both of these numbers are fractional, whereas a molecule can only contain a whole number of atoms. In order to obtain integers we divide both numbers by the smaller one. The resulting figures 1 and 4 directly indicate the number of atoms of each of the elements in the simplest formula, which is, consequently, CCl_4. All these calculations are most conveniently laid out in the following manner:

Elements in the compound	Percentage composition	Atomic weight	Ratio of atoms	Number of atoms in simplest formula
C	7.8	12.0	0.65	1
Cl	92.2	35.5	2.60	4

Example 2. Determine the simplest formulas for copper oxides:

Elements in the compound	Percentage composition	Atomic weight	Ratio of atoms	Number of atoms in simplest formula
1) Cu . . .	88.8	63.5	1.4	2
O . . .	11.2	16.0	0.7	1
2) Cu . . .	79.9	63.5	1.25	1
O . . .	20.1	16.0	1.25	1

The respective empirical formulas will be Cu_2O and CuO.

Example 3. Determine the simplest formula for glycerine:

Elements in the compound	Percentage composition	Atomic weight	Ratio of atoms	Number of atoms in simplest formula
C	39.14	12.0	3.26	1
H	8.70	1.0	8.70	2.67
O	52.16	16.0	3.26	1

It would seem that the glycerine molecule must contain 2.67 atoms of hydrogen. This, of course, is impossible. The result of the calculation shows that actually the glycerine molecule contains not one atom of carbon and one of oxygen but a larger number of them, and a correspondingly larger number of hydrogen atoms. Since the ratio of the atoms cannot change, let us try doubling, trebling, etc., all the numbers of atoms, until the figure for the number of hydrogen atoms becomes an integer. On multiplying by 2, the ratio becomes 2 : 5.34 : 2. The figure for hydrogen is again far from being an integer. Multiplying by 3, we get 3 : 8.01 : 3. Thus, the simplest formula for glycerine will be $C_3H_8O_3$.

Example 4. Determine the simplest formula for ethane:

Elements in the compound	Percentage composition	Atomic weight	Ratio of atoms	Number of atoms in simplest formula
C	80.0	12.0	6.67	1
H	20.0	1.0	20.0	3

Hence, the calculation gives the formula CH_3.

From the simplest formula for a substance the formula weight (equal to the sum of the corresponding atomic weights) can be calculated, and this can be compared with that found by experiment:

Method of determination	Carbon tetrachloride	Cuprous oxide	Cupric oxide	Glycerine	Ethane
From simplest formula	153.8	143.1	79.5	92.1	15.0
By experiment . .	154	—	—	92	30

As can be seen from the above table, the molecular weight determination confirms the formulas of carbon tetrachloride and glycerine, but in the case of ethane the molecular weight is apparently given by the doubled formula C_2H_6. Hence, the *simplest* formula expresses the atomic composition of a compound only when it has been confirmed by determination of its molecular weight. In other words, to determine the *true* formula of a compound, we must know not only the percentage content and atomic weights of its constituent elements, but its molecular weight as well.

Although there are several methods for determining molecular weights, there exist a number of substances to which none of these

methods are applicable (for example, both copper oxides). In all such cases, we have to confine ourselves to the simplest formulas and take them conditionally as the true ones.

If the formula of a compound is known, it is easy to calculate its percentage composition. This is done by adding up the atomic weights to obtain the formula weight, after which the percentage of each constituent is calculated by simple arithmetic. Calculations of this type are met with quite frequently.

Example. Calculate the percentage composition of H_2SO_4. The formula weight of sulphuric acid is $2 \times 1.0 + 32.1 + 4 \times 16.0 = 98.1$. Hence,

$$\%H = \frac{2.0 \times 100}{98.1} = 2.04; \quad \%S = \frac{32.1 \times 100}{98.1} = 32.70;$$

$$\% O = \frac{64.0 \times 100}{98.1} = 65.26$$

The determination of the chemical formula of a compound can often be simplified considerably if the valencies of the corresponding elements are known. Let us first consider a compound consisting of the atoms of only two elements, say, aluminium and oxygen. Aluminium is trivalent and oxygen, divalent. From the valency concept it follows that the atoms in a compound cannot have free valencies. Therefore, the total number of valencies of aluminium atoms must be equal to the total number of valencies of oxygen atoms. The smallest number divisible both by 3 and 2 (the least common multiple) is 6. Hence, the total number of valencies of both aluminium and oxygen must be equal to six. But each atom of aluminium is trivalent and, consequently, the molecule must contain two aluminium atoms. Similarly, the number of oxygen atoms must be three. Thus, the simplest formula for the compound of aluminium and oxygen is Al_2O_3.

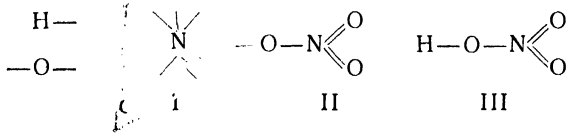
Not all compounds, the formulas of which can be derived according to valencies, exist in reality. The possibility of their formation depends, firstly, on the chemical properties of the elements and, secondly, on the external conditions. Therefore, the derivation of a formula from valencies has any sense at all only when it is known that the properties of the elements allow for the formation of the corresponding compound.

If a compound contains three or more different elements, additional data is required to obtain the formula on the basis of valencies. For example, to determine the formula of nitric acid which consists of H, O and N, additional data must be had besides the valency of nitrogen which is equal to five in this compound (the valencies of hydrogen and oxygen are 1 and 2 respectively), otherwise the problem will remain indeterminate and allow for several different solutions.

Knowing, however, that a molecule of nitric acid contains one atom of hydrogen and one atom of nitrogen not linked directly with each other, we obtain only one quite definite formula.

Starting with the atom of highest valency, the reasoning is as follows. If the pentavalent nitrogen atom is not linked directly with hydrogen, then all its valencies must be linked with oxygen atoms. Since the latter is divalent, two atoms of oxygen may be attached completely to the nitrogen atom while the third oxygen atom will be attached to it through one valency only. Thus, the third oxygen atom is left with one free valency. At the same time, the nitric acid molecule must also contain one atom of hydrogen. This is obviously attached to the oxygen atom. Thus, no free valencies remain, and the formula for nitric acid will be HNO_3.

For better clarity, *structural formulas* are used, in which the bonds between the atoms are shown as lines (one line corresponding to one valency of *each* of the atoms at links). The step-by-step construction of the formula for nitric acid can be schematically represented as follows:



I II III

Structural formulas give a much more comprehensive picture than ordinary formulas for the substances in question, since they show not only the number of atoms of each element in the molecule but also how these atoms are linked with one another.

It is often necessary to solve the converse problem, that is, to find the valencies of the elements when the formula of the compound is known. If it is given in structural form, the valencies of all the elements are immediately obvious. In ordinary formulas for substances consisting of only two elements, it is sufficient, as a rule, to know the valency of one of them in order to find the valency of the other.

Example. Given the formula N_2O_5, find the valency of nitrogen in this compound.

Since the 5 oxygen atoms have a total of 10 valencies, these must be matched by the 10 valencies of the nitrogen atoms. But in this molecule there are 2 nitrogen atoms, which means that each must have five valencies. Thus, in this compound nitrogen is pentavalent.

In the case of substances consisting of three or more elements, the problem becomes more complicated: to determine the valency of one of the elements, it is necessary to know the valencies of all the other elements and, moreover, to have some additional information about the structure of the molecule.

Example. Determine the valency of sulphur in sulphuric acid (H_2SO_4).

It is known that hydrogen is monovalent and oxygen, divalent (the atoms of the latter not being linked with each other). However, this is not enough, since depending on the way of reasoning, different solutions will result. For example: 1) the four oxygen atoms have eight valencies in all, while the two hydrogen atoms have two valencies; in all there are 10 valencies which should correspond to the valency of sulphur, i. e., the sulphur would be decavalent; 2) the four oxygen atoms have eight valencies altogether; but two of them are spent on linking with hydrogen and, consequently, the sulphur atom takes up the other six valencies, i. e., it is hexavalent. If, in addition, it is known that in sulphuric acid the hydrogen is not directly linked with the sulphur, only the second solution becomes possible. Thus, sulphur in sulphuric acid is hexavalent.

The concept of valency can also be extended to a whole group of atoms which make up a molecule of a substance. Thus, in nitric acid, the NO_3 group is linked with one atom of hydrogen and is, therefore, monovalent. In sulphuric acid the SO_4 group is linked with two atoms of hydrogen, i. e., it is divalent, etc. If such an atomic group is visualised as being without hydrogen, it will obviously have free valencies (in the above examples, there will be one and two, respectively) and, hence it will not be capable of stable independent existence. Such *groups of atoms with free valencies* are called *radicals* (e. g., NO_3 and SO_4 are often called *acid radicals* and the monovalent radical OH is called the *hydroxyl* radical). The concept of radicals considerably simplifies the derivation of a formula from the valencies, since in writing down many chemical reactions, the radicals may be carried over from one formula to another without change.

Example. In the reaction between aluminium and sulphuric acid, hydrogen is given off and aluminium sulphate is formed, i. e., as a result of the reaction aluminium links with the SO_4 radical. Write the formula for aluminium sulphate.

It is known that aluminium is trivalent and the acid radical SO_4, divalent. The least common multiple of two and three is 6; hence, this molecule contains two atoms of aluminium and three SO_4 radicals, i. e., the formula will be $Al_2(SO_4)_3$. If the formula is known, then knowing the valency of the radical, it is possible to determine the valency of the metal, and vice versa.

Now that we know how to derive chemical formulas for substances we can tackle the problem of completing *chemical equations.* While formulas provide an abbreviated notation for the composition of substances, equations provide an abbreviated notation for chemical reactions.

In chemical equations, the formulas of all the initial substances (reactants) are written on the left, and all the substances obtained as a result of the reaction (products) are written on the right. A coefficient is placed before each formula to indicate how many molecules of each substance enter into the reaction or are obtained as a result of the reaction (if the coefficient is equal to one, it is left out). Here is how the equation for the reaction between aluminium oxide and sulphuric acid is completed, step by step:

1) Write on the left-hand side of the equation the formulas of all the reactants and join them with plus signs:

$$Al_2O_3 + H_2SO_4 \rightarrow \qquad (I)$$

2) Put down tentative formulas for the reaction products (neglecting the valencies for the time being), and join these with plus signs. The expected composition of the products can be outlined from the results of their analysis and by observing the course of the reaction, or from a knowledge of the chemical properties of the reactants and their constituent elements:

$$Al_2O_3 + H_2SO_4 \rightarrow Al \mid SO_4 + H \mid O \qquad (II)$$

3) Correct all the tentative formulas taking into account the valencies of their constituent elements (or radicals):

$$Al_2O_3 + H_2SO_4 \rightarrow Al_2(SO_4)_3 + H_2O \qquad (III)$$

4) Balance the number of atoms of each element (or the number of radicals) on each side of the equation by putting the appropriate coefficients in front of the formulas:

$$Al_2O_3 + 3H_2SO_4 = Al_2(SO_4)_3 + 3H_2O \qquad (IV)$$

Since most chemical reactions take place in aqueous solution the numbers of oxygen and hydrogen atoms should normally be balanced after atoms of the other elements.

Of course there is no need to copy the equation four times as has been done in the example for the sake of clarity. Above, the equation was balanced in stages only to demonstrate the correct line of reasoning, which will help to avoid mistakes in balancing more complicated equations.

The equation of a chemical reaction makes it possible to carry out various calculations connected with it. It must be borne in mind that the symbol for each element has *two meanings simultaneously*; *atomic and gravimetric*. On the one hand, the symbol O, for instance, means *one atom* of oxygen. On the other hand, the same symbol denotes the *gravimetric quantity corresponding to the atomic weight*, i. e., 16 weight units of oxygen. The first meaning is used when deriving formulas according to valencies, and the second, during chemical calcula-

tions. It does not matter what weight units are used in the latter case, as long as they are the same for all the elements involved in the calculation.

Example 1. How much sulphuric acid will react with 100 g of Al and how much aluminium sulphate and hydrogen will result? The equation for the reaction is:

$$2Al + 3H_2SO_4 = Al_2(SO_4)_3 + 3H_2$$

The calculation is carried out as follows:

1) From the atomic weights of the elements, calculate the total weights of all the atoms and molecules in the reaction (taking into account the coefficients):

$2Al$	+	$2H_2SO_4$	=	$Al_2(SO_4)_3$	+	$3H_2$
2×27.0		$3(2\times 1.0+32.1+4\times 16.0)$		$2\times 27.0+3(32.1+4\times 16.0)$		3×2.0
54.0		294.3		342.5		6.0

2) Work out the respective proportions.

a) If 54.0 g of Al react with 294.3 g of sulphuric acid, 100 g of aluminium will react with x g of the acid:

$$\begin{array}{l} Al \quad H_2SO_4 \\ 54.0 - 294.3 \\ 100 - x \end{array} \qquad x = \frac{294.3\times 100}{54.0} = 543 \text{ g}$$

b) A similar calculation is used for the aluminium sulphate:

$$\begin{array}{l} Al \quad Al_2(SO_4)_3 \\ 54.0 - 342.5 \\ 100 - y \end{array} \qquad y = \frac{342.5\times 100}{54.0} = 632 \text{ g}$$

c) Finally, for hydrogen:

$$\begin{array}{l} Al \quad H_2 \\ 54.0 - 6.0 \\ 100 - z \end{array} \qquad z = \frac{6.0\times 100}{54.0} = 11 \text{ g}$$

Example 2. How much metallic mercury is required to prepare 100 kg of mercuric chloride ($HgCl_2$)?

Since in this case the only element we are interested in is mercury, there is no need to know the equation involved. First, find the molecular weight of mercuric chloride: $200.6 + 2\times 35.5 = 271.6$. Since one molecule of $HgCl_2$ contains one atom of Hg, the solution will be given by the proportion:

$$\begin{array}{l} Hg \quad HgCl_2 \\ 200.6 - 271.6 \\ x - 100 \end{array} \qquad x = \frac{200.6\times 100}{271.6} = 73.9 \text{ kg}$$

The above examples show how important it is to master chemical calculations. Without them, efficient organisation and control of production would be unthinkable. The actual output, is usually expressed as a *percentage of the theoretical* yield, i.e., the maximum possible amount according to the equation for the reaction. The actual yield depends essentially on the nature of the chemical process and the techniques used in carrying it out; besides, it gives an idea of the performance.

Suppose, for example, that 27 kg of $AgNO_3$ was obtained from 20 kg of pure silver. The molecular weight of the compound is 107.9 + + 14.0 + 3 × 16.0 = 169.9. The theoretical yield is found by the proportion:

$$\begin{array}{cc} Ag & AgNO_3 \\ 107.9 & 169.9 \\ 20 & x \end{array} \qquad x = \frac{169.9 \times 20}{107.9} = 31.5 \text{ kg}$$

The actual output is (27 × 100)/31.5 = 85.7% of the theoretical yield. But as the process of obtaining silver nitrate should not entail any significant losses, it follows that the performance was unsatisfactory.

II. AIR. OXYGEN

II-1. Air. We live at the bottom of a vast ocean of air. The mixture of gases forming the atmosphere is more necessary to us than anything else. A human being can live for several weeks without food and can go for several days without water, but without air he would not last for more than a few minutes. Enormous untapped energy reserves are stored in the air. Owing to the unequal absorption of the sun's rays by different parts of the earth's surface, the air is heated non-uniformly, and this gives rise to winds which could be utilised in the U. S. S. R. to obtain up to 2×10^{13} kilowatt-hours of electric power a year.

The atmosphere has a complex composition. Its chief components can de divided into three groups: *constant*, *variable* and *occasional*. The first group includes *oxygen* (about 21% by volume), *nitrogen* (about 78%) and the so-called *inert gases* (about 1%). The percentage of these constituents is practically independent of the part of the globe from which the sample is taken. The second group includes *carbon dioxide* (0.02-0.04%) and *water vapour* (up to 4%). The presence of occasional constituents depends on local conditions. In the vicinity of metallurgical plants the air often contains sulphur dioxide, while in localities where organic remains are decomposing, ammonia and other substances are often present. Air always has more or less dust in it.

The air surrounding the earth exerts a pressure of more than one kilogram per square centimetre of surface area. It is easy to calculate this pressure, knowing that normal atmospheric pressure will support a 760 mm column of mercury (sp. gr. 13.6). The total pressure of the atmosphere can be broken down into the pressures of its separate gaseous constituents, and in this case it is usual to speak of their *partial* pressures. For example, of the total pressure of 760 mm Hg, the pressure due to oxygen is $760 \times 21/100 = 160$ mm. All life on the earth's surface has developed in conditions of atmospheric pressure, and therefore we do not notice it, in the same way as deep-sea fish do not notice the colossal pressures at great ocean depths. The change in the mean atmospheric pressure with altitude above sea level can be seen from the data given below.

Altitude (km)	0	1	2	3	4	5	20	50	100
Pressure (mm)	760	671	593	524	463	405	41.0	0.40	0.007

Since the weight of one litre of air at N. T. P. is known from experiment (1.293 g), it is possible to calculate the molecular weight

that air would have if it were a single gas. Since one gram-molecule of any gas occupies a volume of 22.4 litres at N. T. P., the *mean molecular weight of air* is equal to $22.4 \times 1.293 = 29$. This figure—**29**—should be remembered, since from it the density of any gas can be calculated relative to air, and this makes it unnecessary to memorise many separate figures.

Example. Calculate the density of chlorine relative to air. The molecular formula of chlorine is Cl_2, and its molecular weight is $35.5 \times 2 = 71$. It follows from Avogadro's Law that a given gas is as many times heavier (or lighter) than air as its molecular weight is higher (or lower) than the mean molecular weight of air. Hence, the density of chlorine relative to air will be $71/29 = 2.45$, i. e., chlorine is approximately 2.5 times heavier than air. Similar calculations are quite frequently encountered in practice.

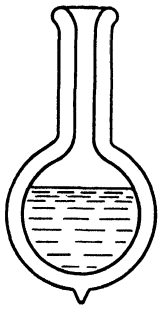


Fig. 9. A Dewar flask

When air is cooled sufficiently, it becomes liquid. Liquid air can be kept for quite a long time in vessels known as Dewar flasks (Fig. 9), having double walls with the air pumped out of the space between them to decrease heat transfer.

Liquid air, which evaporates freely under ordinary conditions, has a temperature of about —190° C. Its composition is not constant because nitrogen evaporates more readily than oxygen. As the nitrogen escapes, the colour of liquid air changes from sky-blue to light-blue (the colour of liquid oxygen).

1) The liquefaction of air was first accomplished at the end of the 19th century. Previous attempts had failed because the essential difference between the gaseous and liquid states of substance was still unclear. It is now known that in both states the molecules are simultaneously attracted to and repelled by each other. Mutual attraction predominates in the liquid state, and mutual repulsion in the gaseous state. Mutual attraction of molecules is practically independent of the temperature, but mutual repulsion, which is due to collisions between the molecules, depends greatly on temperature (since the latter determines the velocity of the molecules and their kinetic energy). Obviously, a gas can be converted to the liquid state only when the attraction prevails over the repulsion or at least becomes equal to the latter. The temperature at which repulsion and attraction are in equilibrium, and there is no difference between the liquid and its vapour, is called the *critical temperature*. The existence of such a temperature was first established by Mendeleyev in 1861.

The critical temperature varies for different substances, that of chlorine, for example, being +144° C. Therefore, if sufficient pressure is applied, chlorine may be converted to its liquid state even without cooling. On the other hand, the critical temperatures of the principal gases the air consists of are very low, being —119° C for oxygen and —147° C for nitrogen. Therefore, air can be converted to its liquid state only after cooling it below these temperatures. Early researchers failed because they endeavoured to obtain liquid air by applying high pressures without cooling sufficiently.

2) A schematic diagram of a liquid air plant is shown in Fig. 10. The air which is first freed from dust, moisture and carbon dioxide, is compressed by the compressor *F* to 200-250 atm (being simultaneously cooled by water), and then passes through the first heat-exchanger *A* after which it is divided into two streams. The larger portion enters the gas-expansion machine *E*. After being cooled considerably in the gas-expansion machine, the air flows through both heat-exchangers where it cools the compressed air it meets and then is discharged from the plant. The other stream of compressed air, which is cooled even further in the second heat-exchanger, *B*, passes through the throttle valve *C* into the expansion chamber *D*, after

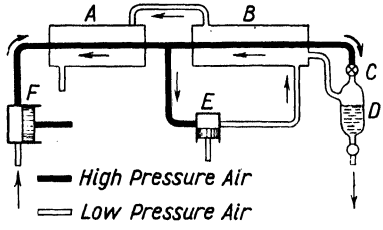


Fig. 10. Diagram of a liquid air plant

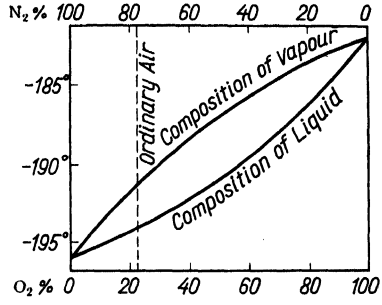


Fig. 11. Boiling point vs. composition of liquid air

which it leaves the plant together with the air from the gas-expansion machine. Shortly afterwards, the temperature of liquefaction of the air is attained in the expansion chamber, and thereupon the air is continuously obtained in the liquid state.

3) The relation between the boiling point of liquid air and its composition is shown in Fig. 11 (in a somewhat simplified form—neglecting the inert gases). As is evident from the diagram, the compositions of the liquid and the vapour vary according to the temperature, the liquid consisting predominantly of oxygen, and the vapour, of nitrogen. For instance, at —190° C the liquid contains about 60% oxygen, while the vapour contains only 30%. Owing to this, as the liquid air evaporates, it becomes richer in oxygen and its boiling point gradually rises.

At the extremely low temperature of liquid air, the properties of many substances change pronouncedly. For instance, sulphur, which is yellow under ordinary conditions, turns white. Liquids and gases, such as alcohol and carbon dioxide, become solid when placed in contact with liquid air. Lead plates, after immersion in liquid air give out a clear metallic ring when struck, while rubber becomes so brittle that a blow will smash it to pieces.

In general, at the temperature of liquid air, chemical reactions are considerably slowed down. However, due to the high concentration of oxygen in liquid air (*concentration is the amount of substance per unit volume or unit weight*), combustible substances when mixed with liquid air burn much more vigorously than they do under ordinary conditions. For example, cotton wool moistened with liquid air flares up like smokeless powder.

On this property is based the important technical application of liquid air for blasting in mines, where cartridges are used containing an inflammable material (for example, coal dust) impregnated with liquid air. This explosive, called *oxyliquit*, has an explosive power close to that of dynamite, but its advantages over the latter are its low cost and safety in handling. Oxyliquits based on liquid oxygen are still more effective.

II-2. The Inert Gases. In 1893, attention was drawn to the discrepancy in the densities of atmospheric nitrogen and the nitrogen obtained by the decomposition of nitrogen compounds. The weight of a litre of nitrogen from the air was 1.257 g while a litre of nitrogen obtained

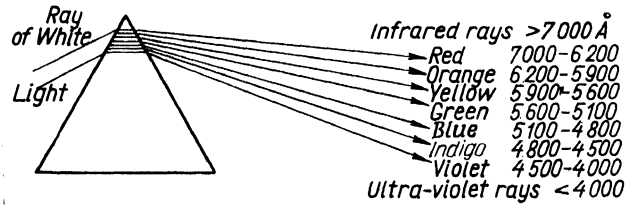


Fig. 12. Splitting up of a sun beam by a prism

by chemical methods weighed 1.251 g. The key to this puzzle was found by carefully reviewing the composition of air. Investigation showed that after all the oxygen and nitrogen had been removed a small quantity of gas remained (about 1%) which would not enter into any chemical reaction. The discovery of the new gas which was called *argon* (Greek, "inert") represented a "triumph" of the third decimal figure. The molecular weight of argon, A, was found to be 39.9. Since its molecule is monatomic, the atomic weight of argon is equal to its molecular weight.

The next inert gas to be discovered was *helium* ("pertaining to the sun"). It was detected on the sun before it was found on the earth. This discovery was made possible due to the method of *spectral analysis* developed during the 1850's.

If a pencil of "white" sunlight is allowed to fall on a glass prism, it splits up into rays having the different colours of the rainbow (Fig. 12). Each ray is characterised by a *definite wavelength* (λ) or *frequency* (ν), i. e., the number of vibrations per second.* On both

* Either of these quantities can easily be transformed into the other since they are related by the equation $\lambda\nu = c$, where c is the velocity of light (3×10^{10} cm/sec). Hence, the smaller λ, the larger ν, and vice versa.

Wavelengths of light and other extremely small lengths are usually measured in the following units: 1 *micron* (μ) $= 0.001$ *mm* $= 10^{-4}$ cm, 1 *millimicron* ($m\mu$) $= 0.001\mu = 10^{-7}$ cm and 1 *angstrom* (Å) $= 0.1$ $m\mu = 10^{-8}$ cm.

sides of the visible spectrum, there are invisible rays, namely, the infrared and ultraviolet rays, which can be detected and studied by various physical methods.

If a volatile sodium salt is introduced into the colourless flame of a gas burner, the flame turns yellow, while a volatile copper compound will colour the flame bluish-green. Each chemical element, if heated sufficiently, emits rays of a characteristic wavelength.

The lengths of light waves are determined by means of the spectroscope. This instrument made it possible to determine the chemical composition of the sun from its spectrum. In 1868, some lines were discovered in the solar spectrum which did not correspond to any known substance. These lines were attributed to a new element which was named helium, He. On earth it was first found in 1895, in the gases given off when the mineral cleveite is heated.

A few years after the discovery of argon and helium (in 1898), three more inert gases were separated from air, these being *neon* ("new")—Ne, *krypton* ("concealed")—Kr and *xenon* ("strange")—Xe. The discovery of these gases was not easy, since 1 m^3 of air contains only 18 ml of neon, 5 ml of helium, 1 ml of krypton and 0.08 ml of xenon along with 9.32 litre of argon.

The last inert gas—*radon*, Rn, was discovered in 1900 while studying certain minerals. Its content in the atmosphere is only 6×10^{-18} % by volume.

The inert gases react chemically neither with each other nor with any other element. In the periodic table, they form a separate *zero* group. Since the inert gases do not display any chemical activity, their positions are determined on the basis of their *physical* properties.

In evaluating the physical properties of any substance, it is usually very important to determine the conditions at which its physical state (gaseous, liquid or solid) changes. In the solid state, the constituent particles of each substance are arranged in a certain strict regularity, while in the gaseous or liquid state, they are in greater or lesser disorder. When a solid substance is heated gradually, the energy of vibration of its particles continuously increases, intensifying their mutual repulsion. Sooner or later, a certain temperature (the *melting point*) is reached at which the mutual attraction of the particles can no longer ensure maintenance of the strict order in their arrangement, and the substance melts.

In liquids, however, the mutual attraction between the molecules is still sufficient to keep them together: only individual molecules, those with the highest velocities at any given moment, succeed in escaping from the surface. Further heating steadily increases the number of such molecules, i. e., the *vapour pressure* of the substance rises. Finally, a temperature is reached, characteristic of each substance

(the *boiling point*), at which the vapour pressure becomes equal to the external pressure. Now evaporation occurs not only at the surface, but in the bulk of the liquid as well; the liquid starts boiling.

Obviously, the boiling point depends greatly on the external pressure. In contrast, slight fluctuations in the external pressure do not change the melting point to any considerable extent.

In practice, it is important to know the temperatures at which changes take place in the physical state at normal atmospheric pressure (760 mm Hg.). These are what is known as the melting and boiling points of a substance, denoted by m.p. and b.p., respectively. Their values for the inert gases are given below.

Properties	He	Ne	A	Kr	Xe	Rn
Atomic number . .	2	10	18	36	54	86
Atomic weight . .	4.003	20.183	39.944	83.80	131.30	222
Melting point (° C)	—272	—249	—189	—157	—111	—71
Boiling point (°C)	—269	—246	—186	—153	—108	—62

1) The melting and boiling points of helium are close to the lowest possible limit to which any substance can be cooled—*absolute zero*. The latter is about —273° C (more exactly, —273.16° C) on the Celsius temperature scale.

On the absolute temperature scale, the readings begin from absolute zero, and this scale is often used in scientific and technical research. The *absolute scale* is very convenient since it includes no negative temperatures. The degree has the same magnitude as that of the Celsius scale (°C). Zero on the latter scale, therefore, corresponds to 273° C on the absolute scale.

2) Helium is stable in the solid state only if under a pressure of not less than 25 atm. When cooled to —271° C at lower pressures, liquid helium changes from its normal form, helium I, to another form known as helium II. While helium I is similar in properties to other liquefied gases, the properties of helium II are quite unusual. It exhibits superfluidity, i. e., an almost complete absence of viscosity, and its thermal conductivity is much higher than that of even the typical metals.

All the inert gases are colourless and consist of *monatomic* molecules. Their solubility rapidly increases from helium to radon. Thus, 100 volumes of water dissolve approximately 1 volume of helium, 6 volumes of argon or 50 volumes of radon at 0° C.

The inert gases have various practical applications. Particularly, the role of helium in the production of low temperatures is especially important, liquid helium being the coldest of all liquids.

II-3. Oxygen. Oxygen is the most abundant element in the earth's crust. The atmosphere contains about 23% of oxygen by weight, water about 89%, the human organism about 65%, sand 53%, clay

56%. The amount of oxygen in the air (atmosphere), water (hydrosphere) and in the solid part of the earth's crust accessible to investigation (lithosphere) accounts for approximately 50% of their total weight.

The study of the chemical changes taking place in the earth's crust is the subject of *geochemistry*. From the point of view of this science, the importance of any element for the chemical reactions occurring in the earth's crust depends on the relative *number of its atoms*. Therefore, it is more correct to compare the abundance of different elements in *atomic* percentages than in percentages by weight. The former are found (I-6) by dividing the weight percentages by the correspon ding atomic weights and expressing each quotient in per cent of the sum of all the quotients. The value obtained for oxygen is 52.3. This means that over half of all the atoms making up the earth's crust are oxygen atoms.

Free oxygen is contained in the atmosphere and consists of diatomic molecules. At ordinary pressures it liquefies at —183° C and solidifies at —219° C. Oxygen is colourless in the gaseous state, but in the liquid and solid states it has a pale blue tint.

Oxygen is prepared in the laboratory by the decomposition of relatively unstable substances rich in the element. The usual procedure is to heat potassium chlorate (Berthollet's salt), which decomposes into potassium chloride and oxygen:

$$2KClO_3 = 2KCl + 3O_2$$

An interesting feature of this reaction is that a little manganese dioxide, MnO_2, added previously to the $KClO_3$ will greatly accelerate it, the amount of MnO_2 remaining unchanged at the end of the reaction. Substances like manganese dioxide *which speed up a reaction but themselves remain chemically unchanged are called catalysts.*

The catalytic activity of a substance is specific, i.e., a good catalyst for one reaction is often found to be quite ineffective for another. On the other hand, if a reaction is catalysed by one substance, a number of other catalysts can usually be selected. Thus, in the decomposition of $KClO_3$, ferric oxide, Fe_2O_3, chromic oxide, Cr_2O_3, and other substances may be used as catalysts instead of MnO_2.

Liquid air is the chief source of *commercial* oxygen. The oxygen separated from it, contains only negligible amounts of nitrogen and the heavier inert gases. Particularly pure oxygen is sometimes prepared by decomposing water with electricity.

1) The nitrogen and oxygen of liquid air (as well as other close-boiling liquids) are usually separated in a *separating column*. The main function of this column is to create an upward current of vapour (*V*) and a downward stream of liquid (*L*) (Fig. 13). A special arrangement of plates brings the two streams into intimate contact, resulting in a continuous exchange of molecules. The molecules of the substance with the lower boiling point (e.g., nitrogen) are more often trapped by the vapour current, and those of the substance with the

higher boiling point (e. g., oxygen), by the stream of liquid. The column operates continuously, and the more plates it contains, the more efficiently the two substances are separated.

2) Oxygen (and other gases which are but sparingly soluble in water and do not react with it chemically) are generally stored in the laboratory in gas holders (Fig. 14). These operate as follows.

First, cocks *A* and *B* are opened, and the vessel is filled with water through funnel *C*. Both cocks are then closed, the plug at *D* is removed, a tube is inserted and the gas is passed through it into the gas holder. The gas displaces the water which flows out through opening *D*. When the whole, or any desired part

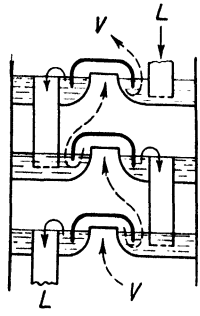


Fig. 13. Diagram of operation of the plates in a separating column

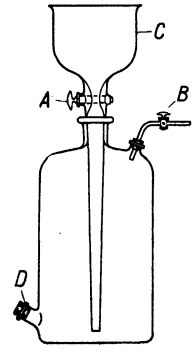


Fig. 14. A gas holder

of the vessel is filled with the gas, opening *D* is closed tightly, water is poured into funnel *C* and cock *A* is opened. Now the gas holder is ready for use. To obtain a stream of gas, it is only necessary to open cock *B* which may also be used to regulate the flow.

3) Larger quantities of oxygen are stored and transported either in steel cylinders (under 150 atm pressure) or in the *liquid* state. For this purpose special tanks are used having a capacity of from a few score kilograms to a few score tons. An oxygen tank is a brass vessel (usually spherical) suspended by chains inside a welded sheet-iron housing. The space between the sphere and the housing is filled with a poor heat conductor such as mineral wool. When in good condition such a tank loses no more than 4 kg of oxygen per ton per hour (due to evaporation through the top opening). Similar tanks are used for storing and transporting large amounts of liquid air.

At 0° C 100 volumes of water will dissolve about five volumes of oxygen, while at 20° C it will dissolve about three volumes of oxygen. Its solubility in water is of great importance to life, because the respiratory process, which is the source of energy for living organisms, requires dissolved oxygen.

From a chemical standpoint *respiration* is essentially the combination of the carbon and hydrogen of organic substances with oxygen from the air. In this respect the process is identical in plants and animals. However, in plants it is accompanied by *nutrition* as a paral-

lel process. Under the action of sunlight, plants synthesise the organic substances they need from carbon dioxide and water, and return free oxygen to the atmosphere. The total amount of oxygen given off by plants during nutrition is about 20 times as great as that which they consume in respiration.

The respiration of living organisms is chemically analogous to the various processes of oxidation taking place in nature. In the restricted sense, the word oxidation is understood as the combination of a substance with oxygen. Since the latter is chemically one of the most active elements, it reacts more or less vigorously with almost all other elements. When oxidation is accompanied by the release of a large amount of heat and light, it is usually called *combustion.* Depending on the nature of the oxidised substance, slow oxidation is called *rusting* (in the case of iron), *smouldering* (in the case of organic remains) or, more often than not, simply *oxidation.*

All oxidation processes take place much more vigorously in pure oxygen than in air. For example, a smouldering splint flares up and burns brightly in oxygen. With the exception of nitrous oxide, which is hardly ever encountered in practice, no other colourless gas produces this effect. Therefore, a smouldering splint is often used as a test for gaseous oxygen.

Oxygen is most frequently used to obtain the high temperatures necessary for melting platinum, quartz and other substances. These temperatures are attained by burning combustible gases, such as hydrogen and illuminating gas, in mixture with pure oxygen instead of with air. A particularly widely used mixture in the welding and cutting of metals is that of oxygen and acetylene (flame temperature about 3000° C). Of great practical importance is the use of oxygen (or oxygen-enriched air) for intensifying various important production processes in the metallurgical and chemical industries.

II-4. Ozone. In 1840 a gaseous substance was obtained which consisted of triatomic molecules, O_3, and differed greatly in properties from normal oxygen (O_2). The new gas which possessed a characteristic odour, was called *ozone* (Greek, "odoriferous").

Like ordinary oxygen, ozone is a *simple* substance. If an element is able to exist in several different forms, these are called its *allotropic modifications.* Hence, ozone is an allotropic modification of oxygen. The probable structural formula for its molecule is O=O= =O with a tetravalent oxygen atom in the middle.

Gaseous ozone is light blue; in the liquid state it becomes dark blue, and in the solid state, almost black. The melting point of ozone is —192° C and its boiling point —111° C. In all its physical states ozone may explode on percussion. It is much more soluble in water than oxygen.

At the earth's surface ozone forms mainly as a result of lightning and the oxidation of certain organic substances. Because of this, considerable quantities of ozone are usually present in the air of coniferous forests, where wood tar is subject to oxidation, and around sea coasts where the seaweeds thrown up by the tide are oxidised. A small amount of ozone in the air is beneficial to the human organism, especially if the respiratory tract is affected by a disease. But in higher concentrations ozone is very toxic.

Ozone is mostly obtained by the action of what is known as a silent discharge (a sparkless electric discharge) on gaseous oxygen. In the laboratory this is accomplished in an apparatus called an ozoniser (Fig. 15). The terminals of the apparatus are connected to the

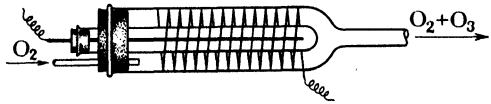


Fig. 15. A simple ozoniser

poles of a high-tension induction coil, and the silent discharge occurs in the gap between the walls of the inside and outside glass vessels. The oxygen leaving the ozoniser contains a small percentage of ozone. The formation of the latter involves a decrease in volume since according to the reaction $3O_2 = 2O_3$, 2 volumes of ozone are obtained from 3 volumes of oxygen.

Ozone can change into oxygen spontaneously, this being attended by a considerable *release* of energy. Consequently, the formation of ozone is accompanied by the *absorption* of the same amount of energy. This follows from the general principle of thermochemistry, according to which, *during the formation of any compound, exactly the same amount of energy is absorbed (or released) as is released (or absorbed) when the compound decomposes into its original substances.*

This principle is a special case of a more general law of nature which was outlined by Lomonosov (in 1748), but was substantiated experimentally and formulated only around the middle of the last century as the *Law of the Conservation and Transformation of Energy: energy cannot arise from nothing or disappear without trace, but its different forms may be converted into one another in strictly definite equivalent proportions.*

The subject of *thermochemistry* is the study of energy changes during chemical transformations. Energy can be evolved or absorbed in various forms, depending on the nature of the process and the conditions under which it takes place. However, in view of the equivalence of different forms of energy, they can all be expressed in thermal units.

Reactions accompanied by the liberation of heat are called *exothermic*, while those in which heat is taken up are called *endothermic*. The energy evolved or absorbed can be indicated in the equation for the reaction, and always refers to the number of gram-molecules (or gram-atoms) of the substances involved in the equation. Thus, for the decomposition and formation of ozone, we have

$$2O_3 = 3O_2 + 69\text{kcal}$$

(exothermic reaction: $\longrightarrow$; endothermic reaction: $\longleftarrow$)

The equation shows that during the decomposition (or formation) of two gram-molecules of ozone (96 g) 69 kcal are evolved (or absorbed).

1) "The question of the amount of heat released or absorbed during chemical reactions is very complicated," wrote D. I. Mendeleyev in 1875, "because chemical processes are accompanied by physical phenomena which may also influence the thermal effect". The total amount of energy evolved or absorbed in a particular chemical reaction is appreciably influenced by passage of the reacting substances from one physical state to another since all such transformations involve the liberation or take-up of energy.

In thermochemistry, the physical states of the reactants and the resultants of a reaction are conventionally indicated by enclosing the formulas of solid substances in brackets, those of liquids in braces (or leaving them without brackets) and those of gases in parentheses. Another way of denoting physical states is to use the initial letters (g), (l) or (s) as subscripts.

Thermochemical equations usually refer to one gram-molecule of the resulting product. In accordance with this, the reaction of decomposition of ozone is written thermochemically as follows:

$$2/3\,(O_3) = (O_2) + 23 \text{ kcal or } 2/3\,O_{3(g)} = O_{2(g)} + 23 \text{ kcal}$$

The absence of any indication regarding the physical states of the substances involved in an equation implies that they are in the state corresponding to the conditions of the reaction, and if these are not specified—to ordinary conditions (room temperature and atmospheric pressure).

Compounds are called *exothermic* if energy is evolved, and *endothermic* if energy is absorbed during their formation. Endothermic substances, such as ozone, always tend to decompose (and the more so, the more endothermic the substance). Therefore, they are all more or less unstable. However, as a rule, they can nevertheless be preserved, because under ordinary conditions they decompose very slowly in most cases. In particular, this refers to ozone in mixture with oxygen. But pure ozone is highly explosive and, therefore, very dangerous to handle.

Ozone readily gives up one atom of oxygen, and hence, is a *very powerful oxidising agent*. Thus, ozone converts almost all metals (except Au, Pt and Ir) into their oxides; it oxidises sulphides to sulphates, ammonia to nitrous and nitric acids, etc. Rubber is very quickly destroyed by ozone, and many other organic substances (e. g.,

alcohol) ignite on coming in contact with it. The very high oxidative power of ozone is its most characteristic chemical property.

II-5. Principal Classes of Compounds. The first classification of the chemical elements into two groups, *metals* and *non-metals*, appeared in the late 18th century. The differences between them were obvious, primarily in their physical properties: metallic lustre, malleability and ductility being characteristic of the first group as distinguished from the second. However, not these external features were the chief criteria for assigning an element to either group, but the chemical nature of the products resulting from the reaction of the element with oxygen and water.

When an element combines with oxygen according to its valency, an *oxide* of the element results. From a structural standpoint any oxide may be regarded as a product of complete substitution of the hydrogen atoms in the *water* molecule by the element in question.

The nomenclature of oxides is derived according to the following rules. If the element is known to have only one oxide the name of the latter is derived by simply adding the word "oxide" to the name of the element. Thus, Li_2O, MgO, Al_2O_3 are called lithium oxide, magnesium oxide and aluminium oxide, respectively. If two oxides are known, the name of that containing relatively less oxygen is derived by attaching the suffix *-ous*, and of that containing more oxygen, the suffix *-ic* to the Latin name of the element and adding the word 'oxide". For example, Cu_2O is cuprous oxide, CuO—cupric oxide; FeO is ferrous oxide, Fe_2O_3—ferric oxide, etc. Oxides containing two or three atoms of oxygen for each atom of the element are often called *dioxides* or *trioxides*, respectively, e.g., NO_2—nitrogen dioxide, CrO_3—chromium trioxide, etc. Finally, if the element forms a larger number of oxides, the rest are usually called *anhydrides* of the acids formed when the oxide reacts with water. An example of this is nitrogen, for which five oxides are known: N_2O—nitrous oxide, NO—nitric oxide, N_2O_3—nitrous anhydride, NO_2—nitrogen dioxide and N_2O_5—nitric anhydride. There are digressions from this nomenclature. For instance, compounds of the type E_2O_3 (where E is a general symbol for an element) are sometimes called "sesquioxides". When an element forms two oxides of the types EO and EO_2, the first is usually termed monoxide and the second, dioxide (instead of attaching the suffixes *-ous* or *-ic* to the element), e.g., CO—carbon monoxide and CO_2—carbon dioxide.

When oxides react with water, *hydroxides* of the corresponding elements result. Metal oxides form *bases*, while non-metal oxides form *acids*. This process consists of the addition of water to the oxide, e. g., $MgO + H_2O = Mg(OH)_2$ base (magnesium hydroxide), $SO_3 + H_2O = H_2SO_4$ acid (sulphuric acid).

The name of a *base* is formed, as a rule, from the name of the corresponding oxide by replacing the word *oxide* with *hydroxide* (compound with the hydroxyl radical). For example, CuOH—cuprous hydroxide, $Cu(OH)_2$—cupric hydroxide, etc. Alongside these names, purely empirical names are in use for some bases. For example, sodium hydroxide is also called caustic soda. The majority of bases are almost insoluble in water. The highly soluble ones, mainly NaOH and KOH, are generally called *alkalis*.

The molecules of each base consist of a metal and, depending on its valency, a definite number of OH radicals. As the hydroxyl radical is monovalent, the valency of the metal can easily be determined from the formula of its base, or the formula of the base from the valency of the metal. The number of hydroxyl radicals in the molecule determines the *acidity* of the base. Thus NaOH is a monoacid base, $Mg(OH)_2$ is diacid base, etc.

The names of *acids* are derived from the names of the elements from which they are formed, e. g., H_2CrO_4—chromic acid, H_3BO_3—boric acid, etc. If an element forms two acids, their names are distinguished by suffixes; the ending *-ic* attached to the name of the element is used for that containing the larger amount of oxygen, and the suffix *-ous* for that with the smaller content of oxygen. Examples are: H_2SO_4—sulphuric acid, H_2SO_3—sulphurous acid, H_3AsO_4—arsenic acid, H_3AsO_3—arsenous acid, etc. Although most acids contain oxygen, some of them do not. The names of such acids usually have the prefix *hydro-* as well as the suffix *-ic*, e. g., HCl—hydrochloric acid, H_2S—hydrosulphuric acid, etc.

It can be seen from the foregoing that the molecules of all acids contain *hydrogen* and an *acid radical*. In most cases, the valency of this radical can be determined directly from the number of atoms of hydrogen in the acid. The valency of an acid-forming non-metal in oxygen-free acids is usually evident from the formula, while in oxyacids it can be found by taking into account that the hydrogen in them is almost always linked with the oxygen. The number of hydrogen atoms that can be displaced by a metal, determines the *basicity* of the acid. Thus, hydrochloric acid is monobasic and sulphuric acid is dibasic.

When a base reacts with an acid (*neutralisation reaction*), a salt and water are formed, e. g.,

$$Mg(OH)_2 + H_2SO_4 = MgSO_4 + 2H_2O$$

The molecule of a *salt* consequently contains a *metal* and an *acid radical*. If the valencies of both are known, it is easy to derive the formula of the salt or, if the formula and the valency of one of the constituents are known, the valency of the other can be determined.

The names of salts are derived from their constituent metals and acids. The metal is named first in the same way as in the correspond-

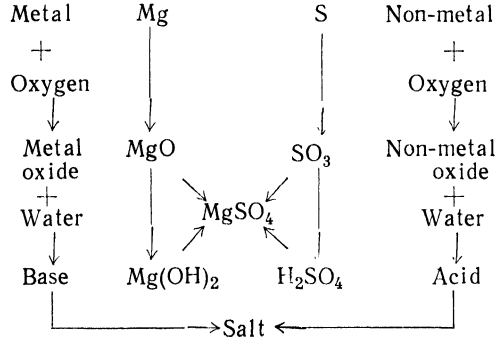
ing oxide, this being followed by the name of the acid changed according to the rules:

(a) in the case of oxygen-free acids the prefix *hydro-* is dropped and the ending *-ic* changes to *-ide*, thus, NaCl—sodium chloride; FeS—ferrous sulphide;

(b) in the case of oxyacids the ending *-ic* changes to *-ate*, and the ending *-ous* (of the acid), to *-ite*. For instance, KNO_3—potassium nitrate, $Fe_2(SO_4)_3$—ferric sulphate, $MgSO_3$—magnesium sulphite.

If the quantity of acid used is insufficient to neutralise the base some of the hydroxyl radicals will remain undisplaced by acid radicals. Then the resulting salt will contain hydroxyl radicals in its molecule, and is called a *basic* salt. Examples of this are $Al(OH)SO_4$—basic aluminium sulphate and $Bi(OH)_2NO_3$—basic bismuth nitrate. On the other hand, if the quantity of base is insufficient, an *acid* salt will form, containing undisplaced hydrogen. For example, $NaHSO_4$—sodium hydrogen sulphate or sodium bisulphate and KH_2PO_4—potassium dihydrogen phosphate. Obviously, only polyacid bases can have basic salts and only polybasic acids can have acid salts.

The above discussion concerning the oxidation products of metals and non-metals can be illustrated by the following diagram.



This diagram was worked out at the turn of the 19th century. It made clear the relationship between the various classes of substances and was thus an important contribution to the progress of chemical theory. However, nowadays it should be regarded as representing only the *extreme* cases of reactions of elements with oxygen and water. The development of the theory of atomic and molecular structure has now made possible a deeper and more general approach to the problem of metallicity and non-metallicity.

II-6. Pure Substances. A very important problem in chemistry is the question of the *purity* of substances. For example, chemical analysis of an impure compound to determine its composition may

result in an incorrect formula. Similarly, when studying the course of chemical reactions the presence of impure substances may lead to erroneous conclusions, i. e., to false ideas concerning the properties of the elements involved. From these examples it is evident that substances used in chemical work must be sufficiently pure.

There are, broadly speaking, two approaches to the problem of testing the purity of a substance, one based on its composition, and the other on its properties. In practice, both approaches are often used simultaneously, since the results supplement each other very well.

The simplest in principle (but not always easily accomplished) method for testing the purity of a substance by its composition is quantitative analysis. Close agreement between the percentages of the elements as determined by analysis and those calculated from the molecular formula usually indicates that the substance contains no significant amounts of impurities. However, since every analysis inevitably involves some inaccuracies, even the most favourable results do not necessarily mean that impurities are totally absent. The kind of impurities present can mostly be determined beforehand by the nature of the compound being tested and its method of preparation. The absence or presence (and the percentage) of specific impurities can be determined by special tests. This constitutes another commonly used method of testing the purity of a substance by its composition.

Purity tests of substances by their properties are based on the *Law of Constant Properties* which states that the *properties of a pure substance are independent of its origin or previous treatment* (Proust, 1806). This law is strictly observed only for gases and liquids, whereas in solids certain properties may vary depending on their treatment. Therefore, the law of constant properties must be used rather cautiously in application to solids.

Of all the different properties of substances, the most suitable for checking their purity are those which can be measured and expressed numerically. If certain constants for a particular substance have been determined accurately, it can be expected on the basis of the law of constant properties that any other specimen of the same substance will have the same values of those constants, *provided it is sufficiently pure*. Therefore, the purity of a substance can be tested by determining certain of its constants and comparing the results with available data for a specimen known to be pure. In practice, the constants most frequently determined are specific gravity, melting point and boiling point.

Since the *specific gravity* is the weight per unit volume, its determination consists essentially in weighing an exactly known volume of the substance. In the case of gases, the results are usually expressed as the weight per litre at N. T. P., while in the case of liquids and solids, they are expressed as the weight per cubic centimetre at the temperature of the experiment.

1) A gas can be weighed in any vessel of exactly known capacity. The specific gravity of liquids and solids is generally determined with the aid of a special vessel called a *pyknometer*. In its simplest form (Fig. 16) this is a small flask with a ground glass stopper having a fine capillary to ensure exact constancy of volume on filling. The volume of the vessel (including the capillary) is found by weighing it filled with water. The specific gravity of a liquid is determined by simply weighing it in a pyknometer. Knowing the weight and volume of the latter, it is easy to find the specific gravity of the liquid. In the case of a solid, the pyknometer is first partially filled with the solid and weighed to find the weight of the sample. Water (or any other liquid of known specific gravity, which will not react with the solid) is then added to fill the pyknometer and it is weighed again. From the difference between the two weights the volume not occupied by the liquid can be determined, this being the volume of the sample. Knowing the weight and volume of the sample, we can easily calculate the required specific gravity.

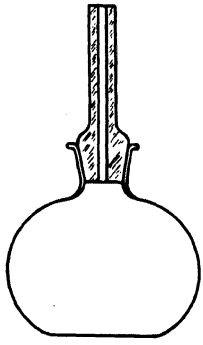


Fig. 16. A pyknometer

2) Rapid but not very accurate determinations of the specific gravity of liquids are often made with a *hydrometer* (Fig. 17). This is a glass float with a scale graduated in specific gravities. The reading is taken where the scale cuts the surface of the liquid.

The temperature at which solids change into liquids and vice versa, is in most cases lowered perceptibly by the presence of impurities. Determination of the melting point is, therefore, a good way of testing the purity of a sample.

In practice, it can be done in two ways: by starting with the solid or with the liquid. In the first case, the *melting* point of the substance is determined, in the second case, the *solidification* (freezing) point. Since the result of both determinations should be the same, the more convenient method is chosen. Usually, the melting point is more convenient to determine.

3) To find the melting point of relatively low-melting substances a simple apparatus of the type shown in Fig. 18 is often used. The substance is ground to a fine powder and packed into a thin-walled glass capillary tube sealed at one end. The capillary tube is bound with an elastic band to a thermometer the bulb of which is immersed in a beaker containing a transparent liquid with a sufficiently high boiling point. The beaker is then heated gently over a slow burner flame, stirring the liquid continuously with a ring-shaped stirrer and observing the state of the substance in the capillary tube. At the moment the contents of the capillary tube become transparent, the reading on the thermometer is noted. This is the melting point of the substance.

Although the *boiling* point is less sensitive to the influence of impurities than the melting (freezing) point, it is often used for testing the purity of substances. The use of this test is especially convenient when the liquids are being purified by distillation (Fig. 19), since the boiling point of a pure liquid should remain unchanged. Conversely, when impurities are present in the substance, the boiling point usually changes in the course of distillation. Thus, two simultaneous indica-

tions of purity are obtained: the numerical value of the boiling point and the degree of its constancy. As the boiling point depends greatly on the external pressure (falling off with decreasing pressure), the latter must be noted during boiling point determinations.

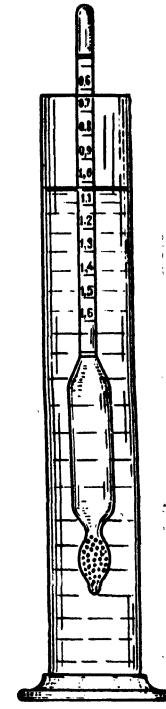


Fig. 17. A hydrometer

4) In testing the purity of substances by determining their boiling points, the possibility of the existence of so-called *azeotropic mixtures* of liquids, i. e., mixtures that boil without changing their composition, must be taken into account. The most familiar example is an azeotropic mixture of alcohol and water (96% by volume of alcohol). Azeotropic mixtures differ from pure liquids in that their composition changes with the pressure as well as their boiling point.

If a substance responds to the appropriate tests like a pure substance, this does not mean that it is entirely free of impurities. Indeed, each testing method is characterised by a definite sensitivity to particular impurities. Therefore, test results indicating the purity of a substance only guarantee that the percentage of impurities in the sample is below a certain limit depending on the sensitivity of the method used.

It follows from the above that in practice there are no absolutely pure substances. At the same time, the percentage of impurities in different samples may vary to a large extent. In the industrial production of chemicals, special terms are used to indicate their degree of purity. Thus, chemicals containing a significant amount of impurities, are designated as "technical grade". Successively purified chemicals are given commercial grades of "pure", "analytical grade" and "chemically pure" according to GOST, the State Standard of the U.S.S.R. For instance, the requirements for sulphuric acid are:

Permissible impurities (%)	Pure	Analytical grade	Chemically pure
Total non-volatile residue . .	0.01	0.002	0.001
Selenium	0.001	0.0005	0.0002
Base metals (Pb, etc.)	0.0005	0.0005	0.0002
Ammonium salts	0.001	0.0003	0.0001
Hydrochloric acid	0.0005	0.0002	0.0001
Nitric acid	0.0005	0.0002	0.0001
Iron	0.0003	0.0001	0.00005
Arsenic	0.00001	0.000003	0.000003

The chemically pure grade is close to the maximum limit of purity of a substance that can be obtained under production conditions. If further purification (which is only required in certain very accurate work) is necessary, it is usually carried out on a laboratory scale. In these cases the purity must be checked by especially sensitive methods such as spectral analysis.

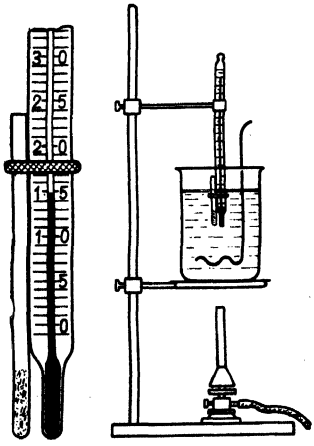


Fig. 18. Apparatus for determining melting point

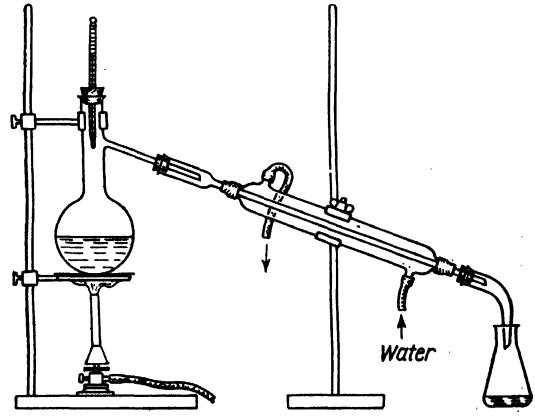


Fig. 19. Apparatus for distilling liquids

The degree of purity of the initial substances required for a particular chemical process may vary widely. At times even "chemically pure" substances have to be further purified, while in other cases "technical grade" chemicals are quite satisfactory. From the point of view of practice, therefore, the purity of a substance is quite relative. Bearing in mind that each subsequent purification greatly increases the cost of the preparation, the use of materials of greater purity than is necessary for the task on hand should be avoided as far as possible.

III. FUNDAMENTALS OF THE INTERNAL STRUCTURE OF SUBSTANCE

III-1. How Real are Atoms and Molecules? The approach of each investigator to the study of nature is governed by the philosophical trend which he consciously or unconsciously follows. Changes in the philosophical systems prevalent in the minds of scientists entail changes in the interpretation of experimental data and in the very direction of the development of science.

The idealistic outlook which permeated natural science at the turn of the century did not leave chemistry unaffected; it fell under the influence of the ideas of "energy" philosophy developed by W. Ostwald, one of the prominent chemists of that time. His world outlook was based on an abstract concept of energy not associated with matter. According to these concepts, matter is not regarded as some objective reality existing independently of the human mind, but only as the concept of spatial coexistence of mass and weight, as a coefficient in equations reflecting natural processes. In this connection, chemical elements are not regarded as definite substances, but as various forms of chemical energy. Obviously, the idea of the real existence of atoms and molecules is not only foreign to the spirit of "energy" philosophy but contradicts its basic principles.

Though many of Ostwald's contemporaries shared his ideas, there were many others who did not agree that the existence of fundamental particles could not be proved. Perrin was one of these scientists, and mainly he is to be credited with direct experimental proof of the real existence of atoms and molecules.

In his work (1908) he proceeded from the *kinetic theory of gases.* According to this theory, only a very small fraction of the volume of a gas (approximately one ten-thousandth part under ordinary conditions) is occupied by its molecules and these are in a perpetual state of random motion. Each molecule collides with other molecules several thousand million times per second and therefore its mean free path equals only a few score millimicrons under ordinary conditions. The approximate path of a gas molecule (greatly magnified), according to the conceptions of the kinetic theory, is shown in Fig. 20.

On striking an obstacle, the molecules exert a pressure on it which is the resultant of the impacts of all the molecules. Obviously, the greater the number of impacts per unit time and the stronger each of them, the greater the pressure exerted. One of the most important conclusions of the kinetic theory is that at any given temperature the mean kinetic energy of the molecules is independent of their nature. In other words, any change in the mass of the molecules will cause

a change in their velocities so that their mean kinetic energy remains constant. Therefore, the pressure must depend only on the *number* of molecules per unit volume.

In the air near the earth's surface, an area of one square centimetre suffers 10^{22} molecular impacts per second. However, it is known that the farther away from the earth's surface, the lower the pressure of the air. Hence, the higher up a layer of gas, the lower its molecular concentration. The kinetic theory enables the change in concentration with altitude to be calculated for particles of any mass.

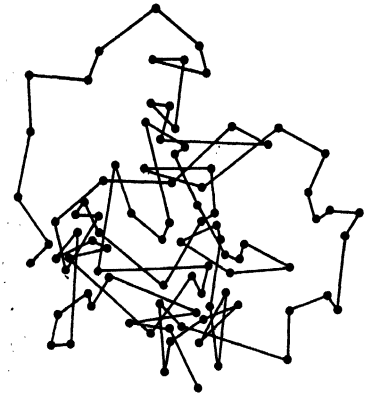


Fig. 20. Path of a gas particle

It was obvious that if calculations based on the kinetic theory could be proved correct in experiments which took into account the behaviour of each individual particle, the concept of atoms and molecules would be substantiated. However, this was difficult owing to the minuteness of molecules.

Perrin eliminated the difficulty by using larger particles. By dint of long painstaking work he succeeded in obtaining spherical particles of some resinous substances having approximately the same radius (of the order of tenths of a micron). These particles could easily be seen under a microscope. Since their radius and the specific gravity of the initial substance were known, it was easy to calculate the mass of each particle. On being shaken with water (or another liquid) in a small glass cell, the particles at first filled the whole volume uniformly but after standing for some time they reached an equilibrium vertical distribution (Fig. 21). By counting up the number of particles per unit volume at different heights with the aid of a microscope (*M*), it is possible to determine whether the results correspond to the requirements of the kinetic theory.

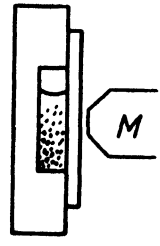


Fig. 21. Diagram of Perrin's experiment

1) The numbers of particles at different heights were counted in a very narrow field of vision, and the mean value of many counts was taken. For example, in one of the experiments with gamboge particles 0.21 μ in radius, counts were made t heights of 5, 35, 65 and 95 μ from the bottom of the chamber. According to theory the ratio of the numbers of particles at these heights should be 100 : 48 : 23 : 11. In the experiment, 13,000 particles were counted, and the relative vertical distribution was found to correspond to the ratio 100 : 47 : 23 : 12.

Perrin's results strikingly agreed with the requirements of the kinetic theory as regards both vertical distribution of particles and verification of other conclusions from this theory. After this no one could object any longer to the real existence of molecules. Even Ostwald was forced to admit that "the atomic hypothesis has been raised to the level of a scientifically substantiated theory". Thus, by about 1910, the molecular and atomic concepts again became generally accepted.

Much earlier, in the latter half of the 19th century, the first attempts were made to approach the problem of the absolute weight and size of atoms and molecules. Although it is obviously impossible to weigh a single molecule, theory indicated another method. It was necessary in some way to determine the number of molecules in a gram-molecule (or of atoms in a gram-atom), this number being known as *Avogadro's number* (N). Although direct counting of the molecules is as impossible as weighing them, Avogadro's number enters into many equations in various branches of physics and can be calculated from these equations. Obviously, if the results of calculations carried out in several independent ways agree, the value found may be considered correct.

Results of Determining Avogadro's Number

Method	$N \times 10^{-23}$	Method	$N \times 10^{-23}$
Blue of the sky	6.04	Radioactive phenomena	6.04
Theory of radiation . .	6.05	Structure of spectral lines	6.08
Vertical particle distribution	6.05	Crystal structure . . .	6.04
Electrical charges of particles	6.02	Surface tension of solutions	6.00

It can be seen that all these values are very close to one another, in spite of the fact that they were obtained by different methods. At present the accepted value of Avogadro's number is 6.02×10^{23}. Some idea of its magnitude may be obtained from this parallel: if the whole of the earth's population (3500 million) were to count the molecules contained in one gram-molecule, and if each person counted one molecule a second without a break, more than 6 million years would be required to complete the operation.

Knowing Avogadro's number the absolute weight of a particle of any substance is easy to find. Indeed, the weight of the unit of atomic and molecular weights is $1/N$, i.e., 1.66×10^{-24} g. The absolute weight of any particle can be found by multiplying its atomic or molecular weight by this value. For instance, an atom

of hydrogen (atomic weight 1.008) weighs 1.67×10^{-24} g. This weight bears approximately the same ratio to that of a small pellet, as the weight of a man to that of the whole globe.

The sizes of individual atoms can also be evaluated by using Avogadro's number. For example, the atomic weight of sodium is 23 and its specific gravity is 0.97. The volume occupied by one gram-atom of sodium (its so-called *atomic volume*) is, consequently, equal to $23/0.97 = 23.7$ cm^3. Since one gram-atom contains 6.02×10^{23} atoms, each atom occupies $23.7/6.02 \times 10^{23} = 3{,}9 \times 10^{-23}$ cm^3 = 39 Å^3, which corresponds to a cube with sides 3.4 Å long.

Actually, it is more correct to regard the atom not as a cube but as a sphere, and determination of the radius of the sodium atom by a more accurate method gives 1.86 Å. The radii of other atoms are also usually expressed in values of the order of angstroms.

III-2. The Complexity of Atomic Structure. Until the end of last century, physics and chemistry had comparatively few points of contact. Only in the 20th century was the sharp division between the two sciences obliterated. The gap between them was filled by two new disciplines, physical chemistry and chemical physics.

Although Lomonosov founded the former (1752), it reached maturity only by the end of the 19th century. Its field is the application of theoretical and experimental methods of physics to common chemical problems. Chemical physics which attained full development in the 20th century deals with the internal structure of atoms and molecules and the changes which it undergoes during the course of chemical reactions.

Atoms "are not indivisible in their nature, but cannot be divided by means now available, and are conserved only in those chemical processes which are now known, but they may be divided in new processes which will be discovered in the future". This prophecy, made by Butlerov in 1886, was not understood or accepted by his contemporaries. Apart from the influence of "energy" philosophy, the conception of atoms as the ultimate particles of matter which are indivisible under all conditions took root in the minds of even those scientists who firmly adhered to the atomic theory. Because of this, the correct interpretation of the important discovery made by Becquerel in 1896, was delayed for several years.

It was known that there were substances that glowed for some time after being previously exposed to light. This phenomenon is called phosphorescence. One of the ways of studying it is by the action of such substances on a photographic plate. While studying various substances in this way, Becquerel noticed that one of the specimens, which happened to contain uranium, exposed the photographic plate *without* being previously illuminated.

Sklodowska-Curie, who took an interest in these experiments and continued them, found that the effect of natural uranium ores on a photographic plate was stronger than that of its pure oxide, despite the larger percentage of uranium in the latter. This suggested that uranium minerals contain some unknown element which is more active than uranium. In 1898, as a result of careful and painstaking work, Curie succeeded in separating two new elements, polonium and radium, from uranium ore. Their effect on a photographic plate was found to be stronger than that of uranium.

This phenomenon, which was later studied mainly on radium compounds, was named *radioactivity*. Experiment showed that the

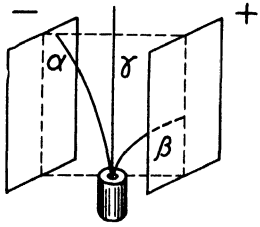


Fig. 22. Splitting up of radioactive radiation in an electric field

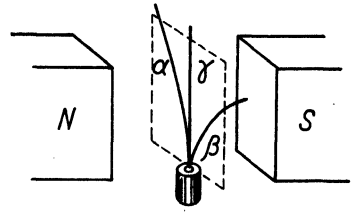


Fig. 23. Splitting up of radioactive radiation in a magnetic field

activity of a substance depends solely on its radium content and is quite independent of the type of compound in which it occurs. The activity of a substance is also independent of external conditions: heating, cooling, the action of light, electricity and so on, have no appreciable effect on it. All these facts led to the conclusion that radioactive phenomena owe their origin to *spontaneous disintegration of atoms* of radium and other radioactive elements, which basically contradicted the established views. This brought up the question of the internal structure of the atom.

The study of radioactive radiation showed it to be complex. If a radioactive substance (enclosed in a lead capsule impenetrable to the rays, with an aperture at the top) is placed in an electric field, the rays split up into three components called *alpha* (α), *beta* (β) and *gamma* (γ) rays (Fig. 22). The first are deflected towards the negative plate, and consist of a stream of particles of relatively large mass which carry a positive electric charge. β-rays are more strongly deflected towards the positive plate and are composed of particles of very small mass carrying a negative electric charge. The last-named, γ-rays are waves similar to those of light but much shorter. A magnetic field has a similar splitting effect on radioactive radiation (Fig. 23). All three types of rays expose photographic plates, cause luminescence in certain substances, etc.

Even before the discovery of radioactivity it was known that when metals are heated (and also when they are exposed to ultraviolet radiation), their surface emits negative electricity. The nature of this electricity was elucidated by experiments on so-called *cathode* rays which were obtained by an electric discharge in a vacuum.

A diagram of the apparatus used for studying cathode rays is shown in Fig. 24. An anode A and a cathode K are sealed into a glass vessel from which the air is pumped out. When a discharge occurs between the electrodes, cathode rays are emitted from the cathode and

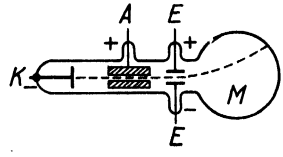


Fig. 24. Diagram of apparatus for investigating cathode rays

some of them pass through the narrow aperture in the anode, then through the gap between the metal plates E, and finally enter the space M where they can be detected by photography or by other methods. If an electric field is set up between the plates E, the rays are deflected towards the plate which is charged positively. This shows that the rays are charged negatively. By altering the conditions (field intensity, etc.), various properties of these rays can be studied.

As a result of these experiments, it was found that cathode rays consist of a stream of negatively charged particles of very small mass. This conclusion was confirmed by subsequent investigations, during which it was found that the particles emitted by metals on heating or illumination are the same as the particles of cathode rays and of β-rays. These particles were named electrons.

Before the experiments with cathode rays, it was thought that the quantity of electricity could change continuously. After them the opposite opinion began to prevail. By the end of the 19th century, an approximate evaluation of the smallest possible quantity of electricity had been made. This tiny charge, "the atom of electricity", corresponds in magnitude to the charge of an electron and is equal to 4.80×10^{-10} absolute electrostatic units *. The concept of the atomic nature of electricity, according to which each electric charge is a multiple of the charge of an electron (e) of either sign, is nowadays generally accepted.

Experiments with metals which are heated or exposed to light show that electrons are the most easily removed parts of the atomic

* The absolute electrostatic unit is a charge which when placed at a distance of 1 cm from an equal charge repels it with a force of one dyne (approximately equal to 1 mg of weight).

structure. Electrons are negatively charged but the atom as a whole is neutral; consequently, inside the atom, the negative charge must somehow be compensated by a positive charge.

The first atomic model suggested by Thomson in 1904 was based on the concept of a positive charge distributed uniformly throughout the volume of the atom, and neutralised by electrons dispersed in this "sea of positive electricity". This model was not developed in detail, since it was disproved by the work of Rutherford.

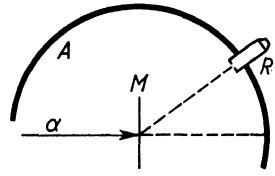


Fig. 25. Diagram of Rutherford's experiment

This scientist carried out his experiments with α-particles. The mass of each of these is 4 atomic mass units (whereas the mass of the electron is only 1/1820 of this unit). They have a positive charge which is twice that of the electron in absolute value. During the radioactive disintegration of an atom, α-particles are expelled at a high initial velocity.

A diagram of the experiment is shown in Fig. 25. A narrow beam of α-particles was directed at a leaf of thin metal foil *M*. Their further behaviour could be observed by means of a device *P* for registering α-particles, which moved along the arc *D*. It was found that the majority of the α-particles passed through the foil without deviation, some were deflected through various angles, and a certain, very small, fraction of approximately 1 particle in every 10,000, rebounded and almost retraced their original path.

The results of these experiments, especially the rebounds, could not be explained on the basis of Thomson's model. Indeed, an α-particle, which possesses a double positive charge, travels at a high velocity and has a relatively large mass, can be sharply thrown back only if it meets an obstacle in its path, which possesses a high positive charge concentrated at a single point. A charge distributed throughout the volume of an atom could not produce such an effect.

Moreover, though each α-particle must pass through many atoms when traversing the metal foil, sharp rebounds were observed very rarely. This also led to the conclusion that the space within the atom is by no means completely filled with positive electricity. On the basis of the results of Rutherford's experiments, the volume of the

positively charged part of the atom, its "nucleus", was approximately assessed in the following way. If the atom is imagined to be enlarged to the size of a sphere 10 m in diameter, the nucleus will be the size of a pin's head. That is why the vast majority of α-particles are not deflected from their rectilinear path, though each of them passes through many thousands of atoms.

Only those α-particles are deflected which pass in the immediate vicinity of the nucleus of one of the atoms in their path (Fig. 26). The only α-particles that rebound are those that impinge directly on a nucleus. Calculation of the relative number of such rebounds made it possible to estimate the size of the nucleus.

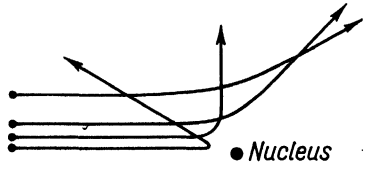


Fig. 26. Deflection of α-particles by a nucleus

Moreover, experiments with α-particles permitted the magnitude of the positive nuclear charge of different atoms to be evaluated. Indeed, the higher the positive nuclear charge, the stronger should be the deflections of the α-particles. The results of the calculation showed that this charge is equal to the lowest electric charge (*e*) multiplied by a number corresponding to approximately *half* the atomic weight of the element.

On the basis of his own research work, Rutherford in 1911 proposed a new "planetary" model which compared the atom to the solar system. At the centre was a very small positively charged nucleus containing almost the whole mass of the atom. The nucleus was surrounded with electrons, the number of which was determined by the magnitude of the positive nuclear charge. However, such a system can be stable only if the electrons are moving since otherwise they would fall upon the nucleus. Consequently, the electrons of the atom must revolve about the nucleus in approximately the same way as the planets move around the sun.

The correctness of the planetary model of the atom was soon proved by further experiments with α- and β-particles. The development of the Wilson cloud chamber in 1911 made it possible to see and photograph their tracks. The method is based on the fact that when air saturated with water vapour is cooled, droplets of mist form almost exlusively around foreign particles, especially those that are electrically charged. The top of the cloud chamber (Fig. 27) and part of its side walls are made of glass while the bottom is a piston which,

when drawn suddenly downwards, expands the air in the chamber, thus lowering its temperature. If the dust is thoroughly removed from the air before the experiment, no cloud will form. But if α- or β-particles are passing through the chamber, they will both knock electrons out of the molecules they encounter, thus producing large numbers of charged particles. Droplets of vapour will immediately form around the latter, so that the tracks of all the passing α- or β-particles will become clearly visible.

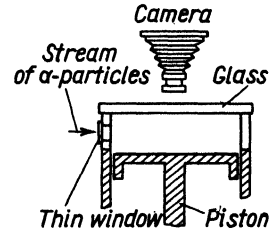


Fig. 27. Diagram of a cloud chamber

A heavy α-particle does not deviate from its rectilinear path after knocking an electron out of a molecule; it is deflected appreciably only when it passes close to the nucleus of an atom. On the other hand, a light β-particle does change its path (especially if its velocity is decreased) after knocking out electrons. Fig. 28 is a cloud-chamber photograph of the ends of the tracks of α- and β-particles, while Fig. 29 shows the ends of two α-particle tracks. Usually the path is rectilinear and it terminates when the velocity of the α-particle has been reduced so much that it ceases knocking electrons out of the molecules it encounters. Tracks similar to the upper one occur very

Fig. 28. Photograph of the track ends of α- and β-particles

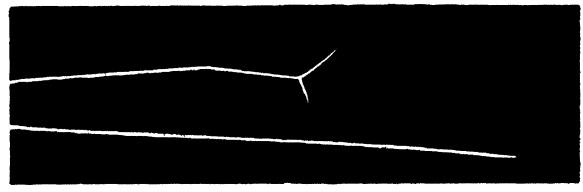


Fig. 29. Tracks of two α-particles

rarely in photographs. The first bend in the track corresponds to the deflection due to passing close to the nucleus of an atom, while the second is due to collision with another nucleus.

Calculations carried out on the basis of such photographs showed that a β-particle passes, on an average, through 10,000 atoms before knocking out an electron, while an α-particle passes through 500,000 atoms without more than two or three times coming close enough to a nucleus to be deflected appreciably. This proves conclusively that the nucleus and the electrons fill negligible part of the space occupied by the atom. The actual volume of the nuclei of all the atoms in the human body is only one millionth of a cubic millimetre.

III-3. Atomic Models. The planetary model of the atom was of great importance as a new and significant step on the road towards an understanding of the internal structure of the atom. However, it could not be refined at first, since the number and arrangement of electrons in the atoms of individual elements were unknown.

The solution to the first problem was supplied by X-ray research. In 1895, while studying the properties of cathode rays, Röntgen discovered that those areas on a glass tube which were being bombarded by a stream of electrons emitted some new kind of radiation which passed readily through glass, wood and other materials, but was stopped by most metals.

An investigation of X-rays showed that they were electromagnetic vibrations similar to visible light, but had a much shorter wavelength

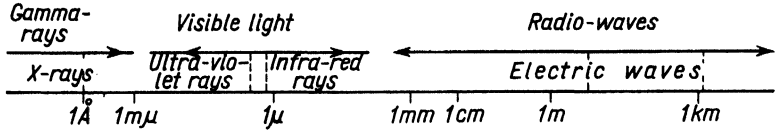


Fig. 30. Electromagnetic spectrum

(0.05 to 20 Å). In the electromagnetic spectrum (Fig. 30), X-rays are located between ultraviolet rays and the γ-rays from radium and partially overlap the latter. Owing to the high penetrating power of X-rays, they are widely used in medicine. By X-raying and photographing, fractured bones, tumour and other maladies can be detected inside living organisms. Fig. 31, for example, is an X-ray photograph of a hand. Very "hard" X-rays, i. e., with a very short wavelength, are also used for X-raying metal castings in order to detect cavities ("blow-holes").

X-rays are emitted when fast electrons impinge on atoms of the elements contained in glass. To make a very rough analogy, X-rays may be compared with the waves formed when a stone hits the still surface of a liquid. The nature of the waves will depend not only on the mass, velocity, size and other characteristics of the stone, but also on the properties of the liquid, and will change when one liquid is substituted for another, for example, when oil is substituted for water. Similarly, given an electron with a definite velocity, the nature of the X-rays, that is, their wavelength, will change, depending on the element whose atom is struck by the moving electron.

Since various elements are contained in glass, the resulting radiation contains rays of various wavelengths, a fact which makes practical application of such rays inconvenient. In order to overcome this, an anode made of an elementary substance is placed opposite the cathode in the X-ray tube (Fig. 32). Electron bombardment of

a uniform anode surface gives X-rays characterised by a definite wavelength.

In 1912, Moseley began a systematic study of the wavelengthso f X-rays obtained from anodes made of different chemical elements. It was found that the change in wavelength is fairly regular as can

Fig. 31. An X-ray photograph

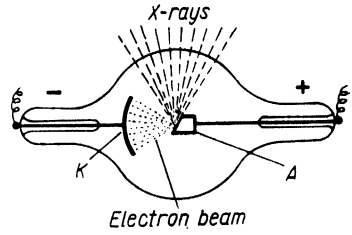


Fig. 32. Diagram of an X-ray tube

be seen from Fig. 33. Mathematical treatment of the results of measurements revealed that the square root of the reciprocal of the wavelength (the "wave number") is a linear function of the atomic number, i. e., the number of the element in the periodic table (Fig. 34).

Theoretically, it would be expected that the higher the charge of the atomic nucleus, the shorter the wavelength,

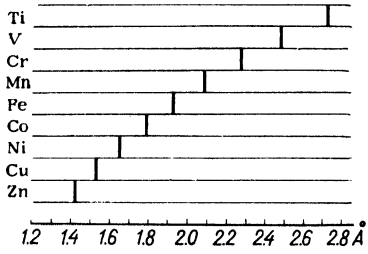


Fig. 33. X-ray wavelengths for the elements from Ti to Zn

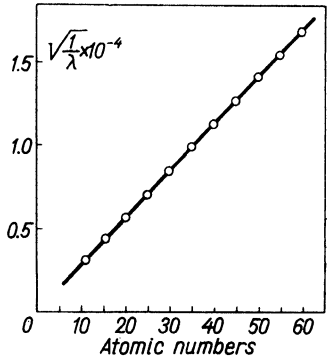


Fig. 34. X-ray wavelengths vs. atomic number

i. e., the larger the reciprocal of the wavelength. The results of Rutherford's experiments showed that the nuclear charge (in electrostatic units) is approximately equal to half the atomic weight. For atoms that are not very heavy, the number of the element in the periodic table is also just equal to approximately half the atomic weight. All this clearly indicated that the *positive nuclear charge is numerically equal to the number of the element in the periodic table.*

Thus, each atomic nucleus has the following basic characteristics: charge Z and mass A. It is now generally accepted that the structural units of all atomic nuclei, "nucleons", are two simple particles with approximately the same mass which is very close to one atomic mass unit. One of these particles, the proton (p) carries one unit of positive charge, while the other, the neutron (n), is electrically neutral. The structure of any atomic nucleus may be expressed by the simple formula $Zp + (A - Z)\,n$. For instance, the nucleus of the fluorine atom ($Z = 9$, $A = 19$) is made up of 9 protons and 10 neutrons.

For the majority of the chemical elements, the nuclei of different atoms may differ somewhat in their number of neutrons ($A - Z$), while the number of protons Z remains constant. For example, the nuclei of carbon atoms always contain 6 protons, but the number of neutrons may be 6 or 7. Therefore, in nature, though most carbon atoms have a mass number of 12 (abbreviated ^{12}C), some have a mass number of 13 (^{13}C). Atoms of the same element which have different mass numbers (i. e., the nearest whole numbers to their masses in atomic mass units) are called isotopes of that element.

Usually, carbon is a natural mixture of ^{12}C (about 98.9%) and ^{13}C (about 1.1%). As the chemical properties of isotopes are practically identical in most cases, the composition of their natural mixture usually remains unchanged during chemical reactions.

Since atoms are neutral, the number of electrons contained in their structure is equal to the nuclear charge, i. e., to the atomic number of the respective chemical element. Determination of this number (Z) made it possible to consider the construction of atomic models.

In general outline, this problem was solved by Bohr in 1913. The most interesting models, from the point of view of chemistry, were worked out by Kossel in 1916. Although in their construction a number of different properties of atoms were taken into account, we may limit our discussion to the chemical aspect of the problem. On passing from the light to the heavier atoms, the nuclear charge increases with each succeeding atom. On the other hand, the chemical properties change in a periodic manner (I-5). Hence, chemical properties are determined by the *relative arrangement* of the electrons in the atom rather than by their total number.

But if this is so, then conversely, the chemical properties may serve as an indication of the arrangement of the electrons. In particular, one would expect a certain periodicity of changes in this arrangement as the nuclear charge successively increases.

It was known that under certain conditions, a molecule of common salt can break up into sodium and chlorine in such a way that the former is charged positively, while the latter is charged negatively. Investigation of these particles showed that the charge of each of them

was numerically equal to the electronic charge. It is natural to explain the origin of both charges by the transfer of one electron from the sodium atom to the chlorine atom. But in common salt, both sodium and chlorine are monovalent, and therefore, one valency unit corresponds to one transferred electron. Then, for example, in the case of calcium which is divalent, one would expect a transfer of two electrons. Indeed, experiment shows that the particle of calcium obtained under these conditions does have two positive charges. In other cases, too,

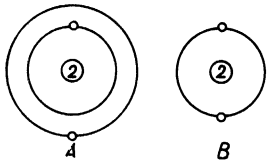


Fig. 35. Possible models of the helium atom

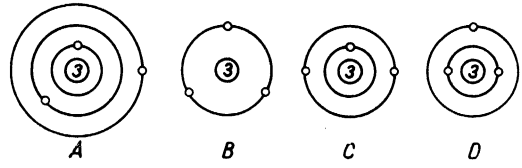


Fig. 36. Possible models of the lithium atom

the valency of the elements corresponds to the number of electrons transferred. The electrons most easily transferred are the *valency electrons*, these being the most remote from the positively charged nucleus of the atom.

Finally, of great importance were considerations concerning the properties of the inert gases. The fact that the elements of this group do not take part in chemical reactions, indicates that the electronic structure of their atoms is particularly stable.

Construction of the simplest model of the hydrogen atom presents no difficulties. In this atom one electron rotates around the nucleus, a *proton*, which has a positive charge of one. For the next element, helium, two models are possible (Fig. 35): two electrons of this atom can rotate in orbits which are either at different distances from the nucleus (A), or at the same distance (B), which is schematically shown by putting them in one orbit. The choice between them can be made on the basis of the chemical properties of helium. If model A were true, the outer electron would not be bound more firmly in helium than in hydrogen. In that case, the properties of helium would resemble those of hydrogen. However, helium is chemically inert. This indicates that both of its electrons are in the same conditions and both are bound very firmly to the nucleus, and therefore model B should be chosen.

The next element, lithium, possesses three electrons. There are four possible models for its atom, which are shown in Fig. 36. Lithium is a metal whose chemical properties resemble those of sodium, and in all its compounds it is monovalent. Evidently, model D is the most suitable. The fact that the stable helium configuration is retained with two of the electrons in the innermost shell, is of fundamental importance.

The element with the atomic number 4, beryllium, is always divalent. This shows that only two electrons in this atom are valency electrons, both of them being in the same shell. It is evident that in beryllium a stable helium pair is maintained, and the two remaining electrons are in the next shell.

Element No. 5, boron, is trivalent. The model of its atom is constructed similarly to the model of beryllium, except that there are three electrons in the second shell from the nucleus. Element No. 6, carbon, is tetravalent, i. e., 2 of its electrons are located in the first shell and 4 in the second. The general trend in the development of atomic structures is already evident: the helium pair is retained in the

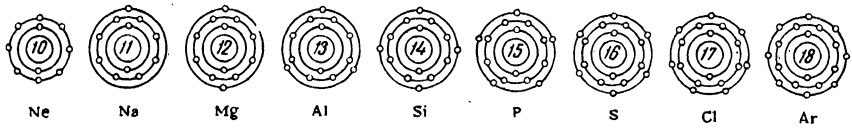


Fig. 37. Electronic models of atoms

first shell, and the second is gradually filled up with electrons. This filling up of the second shell will obviously continue until the number of electrons corresponds to its maximum stability. But when this happens, an atom of an inert gas should result. However, when considering the elements which follow carbon, it is found that nitrogen (2 and 5), oxygen (2 and 6) and fluorine (2 and 7) are chemically active. Only element No. 10, neon, with the structure 2 and 8 is an inert gas. Hence, we may conclude that the *second* electronic shell becomes stable when it contains 8 electrons.

Continuing the examination, it is found that element No. 11, sodium, is monovalent, magnesium divalent, etc. Since in the neon atom, the second electronic shell is already filled, the valency electrons of these elements are in the *third* shell. The electronic models of the elements from neon to argon are shown in Fig. 37.

As the use of complete models of atoms for expressing the structure of chemical compounds is inconvenient, a simplified method of representation is generally employed, in which only the number of electrons in the *outermost* shell is shown:

$$:\dot{\ddot{N}}e: \quad Na \quad \dot{M}g \quad \dot{\ddot{A}}l \quad \dot{\ddot{S}}i \quad \dot{\ddot{P}}\cdot \quad \dot{\ddot{S}}: \quad \cdot\dot{\ddot{C}}l: \quad :\dot{\ddot{A}}:$$

It is self-evident that the above models of atoms represent their structure only very schematically. However, precisely this first step towards an understanding of the structure of the atom—the distribution of electrons in the shells—is of paramount importance for an understanding of chemical properties and processes.

III-4. The Valency Bond. The problem of the nature of the forces which bring about the formation of chemical compounds, arose at the very beginning of the 19th century. However, it could not be satisfactorily solved at that time.

Owing to the development of our knowledge concerning the structure of atoms, it is now possible to approach somewhat closer an explanation of the nature of chemical reactions and their underlying causes. At the same time, it is, of course, necessary to bear in mind that "the human concept of cause and effect always somewhat simplifies the objective connection of phenomena of nature" (Lenin).

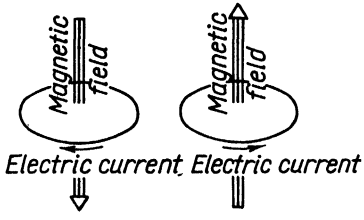


Fig. 38. The corkscrew rule

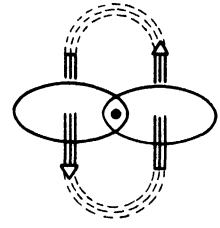


Fig. 39. Interlocking of magnetic fields

As we know, an electric current flowing in a closed circuit sets up a magnetic field whose direction is given by the "corkscrew rule" (Fig. 38). An electron circling in an orbit behaves in a similar manner. At the same time it also rotates about its own axis—this being known as the *spin* of the electron. Since the latter is not a mathematical point, but has a certain (albeit negligible) size, its own rotation also sets up a magnetic field. Each electronic orbit in the atom therefore represents a very tiny magnet.

But the unlike poles of two separate magnets attract each other, while their fields interlock. In order to separate them again, a certain amount of work must be done. Hence interlocking of magnetic fields makes the system more stable.

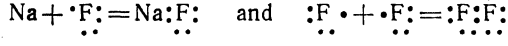
The same must take place in the case of the electronic orbits. For example, the interaction of the magnetic fields in the helium atom is of the type shown in Fig. 39. In the case of more complex atoms most of the electronic orbits must similarly be locked together in pairs. The particular stability of the atomic structures of the inert gases suggests that all their orbits are firmly paired.

When two atoms which have unpaired electrons in their structures come sufficiently close together, their magnetic fields begin to attract each other. As a result, both atoms move still closer together and the fields interlock to form electron pairs. According to Lewis this is how valency bonds between atoms originate.

1) It has been established by calculation that interlocking of magnetic fields accounts for only a very small part of the total energy corresponding to the formation of a valency bond between atoms and which ensures stability of the bond. The principal factor is the *electrical* forces of attraction which develop between the nuclei and the electrons. However, interlocking of the magnetic fields of the two valency electrons is a necessary condition for the appearance of these forces. Therefore, the basic idea of Lewis, concerning the part played by the formation of electron pairs in the establishment of valency bonds between atoms, completely retains its significance.

An electron pair which forms a valency bond is made up of one electron from each of the combining atoms. Therefore, the valency of an element in a particular compound is determined by the number of electrons in the atom which take part in the formation of such electron pairs. At the same time, the *maximum possible* valency of an element is equal to the total number of unpaired (or unstably paired) electrons in the atom. The latter, as a rule, corresponds to the number of the group in the periodic table, to which the element in question belongs.

The process of the formation of NaF and F_2 molecules, for example, can be schematically represented as follows:



From the equations it is evident that an electron pair corresponds to the valency bond (line) of the usual structural formulas.

A problem of primary importance is the position of this pair in relation to the nuclei of the combining atoms. Two essentially different cases are possible. The orbits of the paired electrons may either belong completely to *one* of them, or may be connected in some way with *both* nuclei.

The former is the case when one of the atoms attracts the electron pair forming the valency bond much more strongly than the other atom. Obviously, if the electron pair is drawn completely over to one of the atoms, this atom gains one electron, while the other loses it. Thus, both atoms become electrically charged. *Electrically charged particles formed from atoms* (or groups of atoms) *due to the loss or gain of electrons* are called *ions*. Such, in particular, is the case with the NaF molecule, during the formation of which sodium becomes positively and fluorine negatively charged.

Having unlike charges, the two ions are attracted to each other. But after coming together to a certain degree, they stop at the distance where the attraction is balanced by the mutual repulsion of their electronic shells. A valency bond involving complete transfer of an electron pair to one of the atoms, and subsequent drawing together of the resulting ions, is called an *ionic* (also known as electrovalent or heteropolar) bond. Compounds of this type form when the reacting atoms are of sharply opposite chemical properties.

Formally (according to Kossel) the ionic bond may be regarded as the result of the simple transfer of an electron from one of the atoms to the other (Fig. 40). This way of reasoning is often found to be very convenient, owing to its simplicity. It obviously leads to the same final results as that used above.

According to Kossel, the motive force of a chemical reaction is the "tendency" of atoms to assume the most stable electronic configurations. Such are primarily the structures of the inert gases (and then

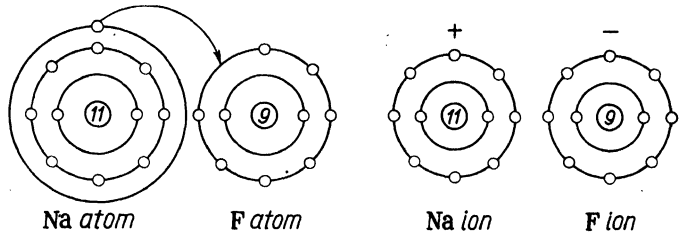


Fig. 40. Diagram of the formation of the NaF molecule according to Kossel

structures having 18 electrons in the outermost shell). Atoms "tend" to acquire the nearest of them by yielding or gaining electrons.

The number of electrons yielded determines the *positive valency* of an atom, while the number of electrons gained determines its *negative valency*. From a consideration of the electronic diagrams in Fig. 37, it follows that Na, Mg and Al should tend more readily towards the structure of neon, and P, S, Cl, to the structure of argon to which they are closer. The former three elements are usually classed as metals and the latter three as non-metals. Generalising this result, it may be said that from the electrochemical point of view, the elements which predominantly yield electrons in chemical reactions are called *metals*, while those which predominantly gain them are called *non-metals*.

However, it is known that many elements may yield or gain electrons, depending on the conditions. Hence, there is no sharp dividing line between metals and non-metals, and this division emphasises only the *predominant tendency* of the type of atom in question and is by no means absolute.

The chief advantage of Kossel's concept is its simplicity and clarity; its main drawback is its limited applicability. Indeed, all organic and many inorganic compounds are non-ionic and therefore cannot be considered from the ionic point of view. At the same time, Lewis's idea of the formation of an electronic pair first, permits all kinds of valency bonds to be covered by a single treatment.

It is obvious that when two *like* atoms combine with one another, no one-sided attraction of an electron pair to form a valency bond

will occur. Consequently, each pair will belong equally to both atoms and the orbits of the electrons forming the pair will be associated with *both* nuclei. A valency bond due to a pair of common electrons belonging equally to both combining atoms is called *non-polar*.

Both combining atoms may differ in chemical nature, but not exhibit such a sharp contrast as between fluorine and sodium. An example of this is the compound of fluorine with hydrogen, the metallic properties of which are much weaker than those of sodium. As a result, the electron pair forming the valency bond is much less strongly drawn towards the fluorine, the more non-metallic element, than in the reaction of the latter with sodium. This case is, consequently, intermediate between the two examples considered above, as is evident from Fig. 41.

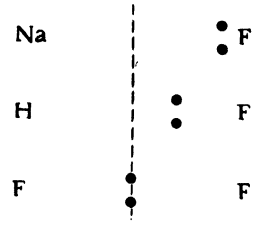


Fig. 41. Diagram of the types of valency bonds

The third principal type of valency bond, the *polar* bond is distinguished by the electron pair being more or less one-sidedly drawn towards one of the combining atoms, but not close enough to warrant the formation of independent ions. In this case, the orbits of its electrons remain associated with both nuclei. Owing to the latter circumstance, polar bonds are often classed together with non-polar bonds under the general name of *covalent* (atomic or homopolar) bonds.

The most important characteristics of a valency bond are its *energy* and *polarity*. Both of these quantities depend, to some extent, on the *length* of the bond (a), i. e., the distance between the nuclei of the atoms forming the bond.

The energy of a bond is the work which must be done to rupture the bond, and it characterises the stability of the latter. Usually, this energy is referred to one gram-molecule, i. e., 6.02×10^{23} bonds, and is expressed in kilocalories. It may vary greatly for different bonds. For example, the energy of the H—H bond is 104 kcal, while that of the Cl—Cl bond is 58 kcal. Hence, the bond between the atoms in a hydrogen molecule is much more stable than in a chlorine molecule.

The polarity of a bond characterises it as to *electrical symmetry*. As can be seen from Fig. 41, ionic and non-polar bonds are essentially extreme cases of the polar bond. If the polarity p of the non-polar bond is taken to be zero, while that of the ionic bond (with singly-charged ions) is taken as unity, then in any intermediate case the value of p can be expressed, in principle, as a simple decimal, for instance, $p_{HCl} = 0.17$. This indicates that the H—Cl bond is much closer to the non-polar than to the ionic type. This quantitative characteristic of the polarity of a bond can be given, as yet, only in a few of the simplest cases.

III-5. Types of the Simplest Molecules. The combination of two atoms through various types of bonds results in the formation of diatomic molecules, as shown in Fig. 42. Since the ionic and non-polar types are, in fact, extreme cases of the polar type, it will be convenient in further discussions to proceed from the latter.

The electric charges in a polar molecule, such as HF, are distributed non-uniformly. As a result of attraction of the binding electron pair

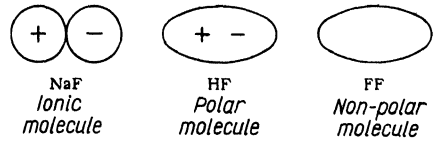


Fig. 42. Different types of molecules

to the fluorine, the part of the molecule containing the fluorine acquires a surplus negative charge, while the part containing the hydrogen acquires a surplus positive charge.

This concept may be approached from a more general point of view. Every molecule contains positively charged particles (atomic nuclei) and negatively charged ones (electrons). For all the particles of either type, a point can be found which will be their electric "centre

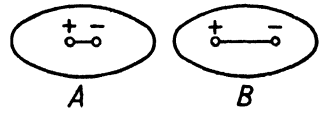


Fig. 43. Molecules of different polarity

of gravity". Its position evidently depends on both the distribution of the particles and the magnitude of their charges. If the electric centre of gravity of all the positive particles coincides with that of all the negative particles, the distribution of electricity in the molecule as a whole will be uniform, and the molecule will be *non-polar*. If the electric centres of gravity do not coincide, the molecule is *polar*. If there is a very marked non-coincidence between the electric centres of gravity, the molecule is of the *ionic* type.

The degree of non-uniformity in the distribution of electricity in the molecule determines its *polarity*. The latter may be characterised quantitatively by introducing the concept of *dipole* which is an arrangement of two equal and opposite electric charges situated at a known distance from each other. If the magnitude of each charge is taken, in all cases, to be equal to the elementary quantity of electricity (the charge of an electron), the distance between them, i. e., the dipole length will represent the polarity of the molecule. Thus, of the molecules shown schematically in Fig. 43, molecule *B* is the

more polar. The numerical values of the lengths of molecular dipoles determined in this way are usually equal to fractions of an angstrom.

1) The so-called *dipole moment* μ (the product of the dipole length by the magnitude of the elementary electric charge) is often employed to characterise the polarity of a molecule instead of the dipole length l. If the dipole moment is known (it is usually determined experimentally), the dipole length can be easily calculated. For example, for the hydrogen chloride molecule, $\mu = 1.04 \times 10^{-18}$, whence $l = (1.04 \times 10^{-18}) : (4.80 \times 10^{-10}) = 0.22 \times 10^{-8}$ cm $= 0.22$ Å.

2) If the dipole length, l, of a diatomic molecule and the distance, d, between the nuclei of its atoms are known from experiment, an estimate of the polarity of the valency bond characteristic of the molecule can be obtained by dividing the former by the latter. For example, for HCl we have $l = 0.22$ Å and $d = 1.28$ Å. Hence the value 0.17 which was given in the previous paragraph.

3) A detailed characteristic of the intramolecular distribution of electricity requires determination of the degree of electronic saturation of each of the atoms forming the given molecule, and this can be expressed by means of the *effective charge*, δ, of the atom. The effective charge is numerically determined (in e-units) as the algebraic sum of polarities of all the bonds linking any given atom with others. For example, for the HCl molecule we have $\delta_H = +0.17$ and $\delta_{Cl} = -0.17$, while in the water molecule, $p_{HO} = 0.33$, hence $\delta_H = +0.33$ and $\delta_O = -0.66$. This quantitative estimation of the effective charges of atoms is, as yet, only possible for a few of the simplest molecules.

The polarity of a *diatomic* molecule indicates directly the nature of the valency bond between its constituent atoms. The polarity can be roughly estimated in this case from the melting or boiling point of the compound. Both of these are very high for substances with ionic molecules, and very low for substances with non-polar molecules. Compounds with polar bonds occupy an intermediate position. The substances considered above have the following constants:

Substance	NaF	HF	FF
Melting point (°C)	995	—83	—218
Boiling point (°C)	1702	+20	—187

In more complicated cases, the general character of the molecule must be distinguished from the character of the individual bonds. The presence or absence of ions is usually of decisive importance in determining the former. If ions are present, the substance behaves as if it were built up of the simplest ionic molecules, whereas if they are absent, it behaves as if it were built up of simplest polar or non-polar molecules. For example, there are no ionic bonds in SO_3 and its melting point is + 17° C. On the other hand, in Na_2SO_4, the bonds between sodium and oxygen are ionic, and this salt melts only at 885° C. The nature of the individual bonds in a complex compound can be roughly determined (as in the case of diatomic molecules) if the properties of the constituent elements and the order in which their atoms are linked with one another are known.

Although the structural formula of a molecule (I-6) shows the order of linkage of the atoms, it does not at all indicate their relative arrangement in space. However, knowledge of this arrangement is very important in chemistry. At the present time there are a number of methods of determining the spatial structure of molecules, thus giving a much more complete and accurate information on them. By way of example, the structures of certain molecules of types AB and

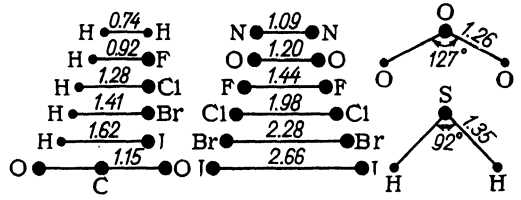


Fig. 44. Arrangement of atomic nuclei in some of the simplest molecules

AB_2 are shown in Fig. 44, the nuclear distances, d, being given in angstroms. For triangular molecules the values of the angles α are also shown.

The distance d between the atomic nuclei may be regarded as being approximately equal to the sum of the radii of the corresponding atoms. These so-called *covalent radii*, i. e., radii of the atoms in molecules with covalent bonds, are given below (in angstroms) for a number of elements.

F	Cl	Br	I	O	S	Se	Te
0.72	0.99	1.14	1.33	0.73	1.04	1.16	1.35

N	P	As	C	Si	Ge
0.74	1.11	1.22	0.77	1.16	1.27

The covalent radius of hydrogen is less constant than the others but is in most cases about 0.30.

The approximate value of d for any particular molecule can be found by simple addition of two covalent radii. For example, for HCl we obtain $d = 0.30 + 0.99 = 1.29$ Å, whereas direct determination gives $d = 1.28$ Å.

4) The quoted covalent radius values correspond to the presence of a *simple* covalent bond between the atoms in question. In the case of double bonds they are reduced by approximately 0.1 Å, and for triple bonds, by approximately 0.2 Å.

III-6. Intermolecular Forces. As everywhere in nature, there are forces of attraction acting between molecules, which are directly proportional to the product of the *masses* of the interacting bodies,

and inversely proportional to the square of the distance between their centres (the universal law of gravitation). However, because of the extremely small masses of individual molecules, these forces are so small that they can be practically neglected. At the same time, it follows from the existence of the solid and liquid states of substances that mutual attraction between molecules undoubtedly exists.

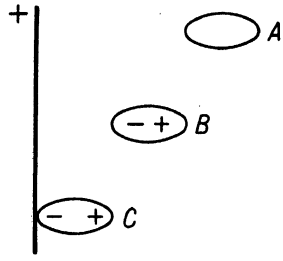


Fig. 45. Polarisation of a non-polar molecule

An explanation of the nature of intermolecular forces became possible only on the basis of the theory of the internal structure of matter. It was found that these forces are of *electric* origin and may manifest themselves in various forms. The simplest of these forms is defined by the *Fundamental Law of Electrostatics* (Coulomb, 1785): *the force of interaction between two electrically charged particles is proportional to the product of their charges, and inversely proportional to the square of the distance between their centres.*

1) When characterising the interaction between particles, it is often necessary to refer to the energy (instead of force) of interaction, this being the work required to completely separate the particles from each other. In this case, the denominator in the equation for the fundamental law of electrostatics is not the square but the first power of the distance.

These so-called *Coulomb* forces play the principal part in the interactions between ions. It is obvious, however, that they cannot act between neutral molecules. The nature of interactions between the latter can be understood only if we first look into the reaction of molecules to an external electric field.

Let us first consider the simplest case of a *non-polar* molecule (*A*, Fig. 45). If in the course of its random motion, it comes sufficiently close to a source of electric field, the latter will appreciably affect the atomic nuclei and electrons in the molecule: all the particles charged similarly to the field will be repelled, while all oppositely charged particles will be attracted. As a result, the electric centres of the positive and negative charges will be displaced relative to each other and a *dipole* will form in the molecule (*B*, Fig. 45). Owing to its presence the molecule is further attracted towards the source of the field, whereupon the dipole becomes larger (*C*, Fig. 45).

The formation of a dipole in a non-polar molecule involves its deformation, i. e., departure from the normal internal structure which is the most stable in the absence of external influences. Therefore, the dipole produced by the action of (or induced by) the external electric field exists only as long as the field operates. The higher the field intensity and the more easily the molecule is deformed, i. e., the

greater its deformability, the larger the magnitude of the induced dipole.

The deformability of a molecule depends on how easily its constituent atomic nuclei and electrons can be displaced relative to one another. Since the outermost electrons are the most loosely bound to the atomic nuclei, their displacement under the influence of the external field plays the chief part in deformation.

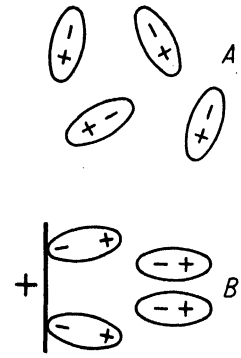


Fig. 46. Polarisation of polar molecules

In the case of *polar* molecules which possess permanent dipoles, the effect of the electric field is manifested somewhat differently than with non-polar molecules. Polar molecules disposed at random in the absence of a magnetic field (*A*, Fig. 46) turn the oppositely charged ends of their dipoles towards the field under the action of the latter, i. e., they are *oriented* in a definite manner relative to the field (*B*, Fig. 46). Simultaneously, the molecules deform and, as a consequence, their dipoles increase. Thus, the *polarisation* of a polar molecule, i. e., the total effect of an electric field upon it consists of two effects—*orientation* of the molecule and its *deformation*:

$$polarisation = orientation + deformation$$

Other things being equal, the greater the dipole, the more readily orientation of the molecule will occur. Therefore, the more polar the molecules, the more they will be attracted and oriented by relatively weak electric fields.

As the intensity of the field rises the deformation of the molecule becomes more and more important. The induced dipole which originates due to the deformation, when added to the permanent dipole, can produce so great a resultant dipole that an initially less polar but more easily deformed molecule may become more polar and be more strongly attracted. Given sufficiently strong fields and ready deformability, the same may occur in non-polar molecules whose polarisation is entirely due to deformation.

Proceeding from the above, we can now turn to the question of molecular interaction. Consider two *polar* molecules quite close to one another. Since the similarly charged ends (poles) of their dipoles are mutually repelled, while the oppositely charged ends attract each other, both of the molecules will strive to orient themselves so as to bring their unlike poles close to each other. In this position (*A*, Fig. 47), the mutual attraction between the unlike poles is only partially compensated by the mutual repulsion between the like poles which are

farther from each other. As a result, there are forces of attraction acting between the molecules, due to the interaction between their *permanent* dipoles; these are called *orientation* forces. Owing to the presence of the latter, the two molecules are drawn together (*B*, Fig. 47) and become more or less firmly bound to each other.

At the same time, each of them deforms to some extent under the influence of the near pole of the neighbouring molecule. The induced dipoles formed as a result of this deformation, interact with each other in a similar manner to permanent dipoles, and this creates what are

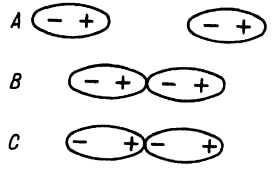


Fig. 47. Diagram of interaction between polar molecules

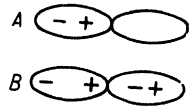


Fig. 48. Diagram of interaction between a polar and a non-polar molecules

known as *induction* forces which also contribute to the mutual attraction between the molecules. The superposition of these forces on the orientation forces is related to the increase in length of the dipoles (*C*, Fig. 47) and results in intensification of the molecular interaction.

The interaction between a polar and a non-polar molecule (*A*, Fig. 48) is distinguished from that considered above only by the fact that first an induced dipole (*B*, Fig. 48) is formed in the non-polar molecule, and this subsequently interacts with the dipole of the polar molecule. On the other hand, the case of interaction between two non-polar molecules demands a fundamentally different interpretation. Indeed, in the absence of permanent dipoles in *both* molecules it would appear that no forces of mutual attraction should arise between them. However, it is known that the inert gases, for example, are converted into the liquid and, subsequently, into the solid state when the temperature is lowered sufficiently. From this it follows that certain forces of attraction do act between the non-polar monatomic molecules of the inert gases.

The nature of these so-called *dispersion* forces was established only comparatively recently (London, 1930). They were found to be closely related to the continuous motion of the internal constituent parts of the molecules, their atomic nuclei and electrons. A model-like idea of dispersion forces can be had from Fig. 49.

Consider two atoms of an inert gas (*A*, Fig. 49) which are close to one another. Owing to the continuous rotation of the electrons and the vibratory movement of the nuclei, a temporary displacement of

certain electron orbits relative to the nucleus may always take place in each of these atoms, resulting in a *temporary* dipole. But each of these dipoles will, by its charges, inevitably influence the orientation of a similar temporary dipole originating in the neighbouring atom, and moreover, this influence will be quite specific—in the sense of a preferable proximity of unlike poles (*B*, Fig. 49) rather than like poles (*C*, Fig. 49). Although dipoles formed in this way can exist only for a very short period, a certain *coordination of orientation* will be maintained in each of their subsequent appearances (*D*, Fig. 49).

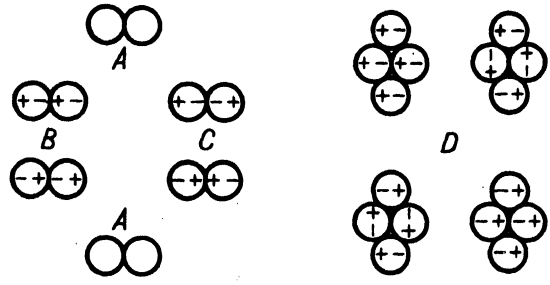


Fig. 49. Diagram of the model treatment of dispersion interaction

The proximity of their unlike poles is practically continuously renewed. This gives rise to forces of attraction constantly acting between particles, which are referred to as dispersion forces.

All the above considered types of interaction between molecules can be combined under the heading of *intermolecular forces* (or "*Van der Waals forces*"*). The relative contribution of each type for each particular case depends, in the main, on two properties of the interacting molecules—their polarity and deformability. The higher the polarity, the more important the role of the orientation forces; the greater the deformability, the more important the role of the dispersion forces. Induction forces depend on both factors, but they usually play only a secondary part.

As regards general manifestation, the fundamental difference between intermolecular forces and Coulomb forces lies in the unique nature of the former. While a Coulomb interaction may be one of attraction (between unlike charges) or repulsion (between like charges), intermolecular forces are always forces of attraction.

However, when particles come very close together, the mutual repulsion between their external electronic shells becomes significant. The forces of repulsion due to these shells are very strong when the particles are in direct contact, but they weaken much more rapidly

* Van der Waals was the first (1873) to derive an equation of state for a gas, with allowance for mutual attraction between the molecules.

than the forces of attraction as the distance between the particles increases (Fig. 50). The result is that the total interaction between particles as they approach each other is at first that of continuously increasing mutual attraction, but this subsequently becomes gradually weaker and, finally, changes to repulsion. The distance between the centres of the particles, d, at which the attraction becomes equal to the repulsion, corresponds to stable equilibrium, and is characteristic of the spatial structure of the particular substance.

III-7. Structure of Solids. In contrast to the more or less mobile particles of gases and liquids, the particles of a solid are capable of only comparatively small vibratory motions about definite points.

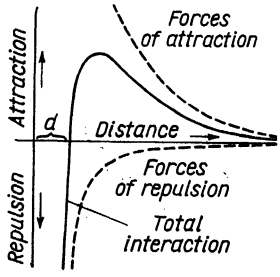


Fig. 50. Forces of attraction and repulsion

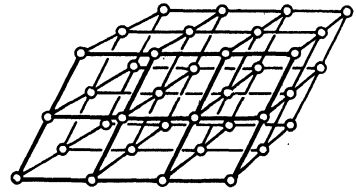


Fig. 51. Example of space lattice

Theoretically, one would expect these points to be arranged in space after a strictly regular pattern and to correspond to the nodes of some type of *space lattice* (Fig. 51).

Direct confirmation of this theoretical conclusion by experiment became possible only after 1912, when it was found that X-rays are refracted in passing through a crystal, and the character of the refraction depends in a regular manner on the arrangement of the particles forming the crystal. A diagram of the arrangement which was used for this purpose is given in Fig. 52.

A narrow pencil of X-rays formed by a slit in a lead screen A is passed through the crystal B and produces a number of spots on the photographic plate C beyond it, surrounding in a regular manner the central spot caused by the unrefracted rays (Fig. 53).

Calculations based on such photographs not only enable determination of the spatial arrangement of the particles but also give indications as to their nature. From this point of view four basic types of solid structures should be distinguished. These are shown schematically in Fig. 54.

As the name indicates, *atomic* structure is characterised primarily by the fact that separate atoms are located at the nodes of the space

lattice. The atoms are linked with one another by ordinary covalent bonds (schematically shown in Fig. 54 as connecting lines). Because of the complete equivalence of all these bonds, there are no grounds to group any of the atoms into separate molecules, and the whole crystal should be regarded as a gigantic single particle.

Solids with atomic structure have high melting points and great hardness.

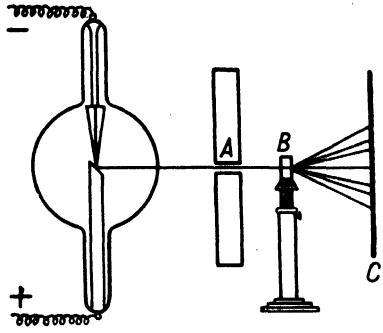


Fig. 52. Arrangement for investigating the internal structure of crystals

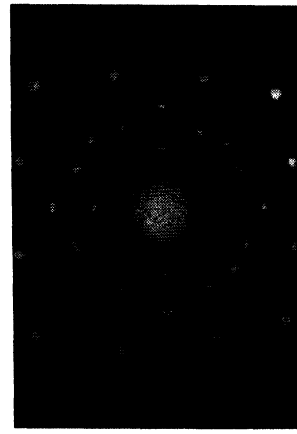


Fig. 53. X-ray photograph of MgO

Both these features are due to the fact that the covalent bonds link the atoms very firmly. A typical example of a solid possessing atomic structure is diamond, in which each carbon atom is linked directly to four other carbon atoms.

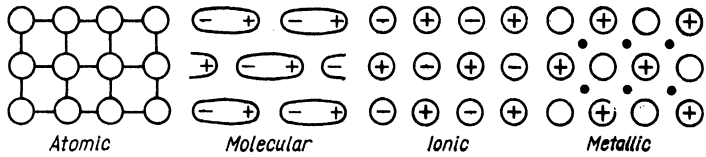


Fig. 54. Basic structures of solids

The specific features of *molecular* structure are due to the presence of non-polar molecules at the nodes of the space lattice, which are linked with one another only by intermolecular forces. Although these molecules may sometimes be monatomic (for the inert gases), the lattice is still molecular in all its properties. The difference between atomic and molecular structures, therefore, depends not so much on the type of particles as on the nature of their interaction. Since intermolecular forces draw the particles together comparatively weakly,

solids of molecular structure usually have low melting points and low hardness.

Ionic structure with separate ions at the nodes of the space lattice is typical of the solid state of substances made up of ionic molecules. As shown in Fig. 54, each ion bears exactly the same relationship to all the ions of opposite sign immediately surrounding it. Thus, on being converted to the solid state, the individuality of the separate molecules is lost: the whole crystal of an ionic compound is a gigantic single particle.

The Coulomb forces acting in ionic structures make for much stronger mutual attraction between the particles than intermolecular forces. For this reason, both the melting points and the hardness of ionic compounds are considerably higher than those of substances made up of polar or non-polar molecules.

1) The forces of attraction between the ions in a crystal are often characterised by the *lattice energy* which is defined as the energy which can be evolved during the formation of one gram-molecule (or gram-equivalent) of crystals from the free gaseous ions. Thus, for NaCl (58.5 g) we have: $(Na^+) + (Cl^-) = [NaCl] + 183$ kcal. It is obvious that when the crystal decomposes into free gaseous ions, the same quantity of energy should be absorbed.

Metallic structure which is characteristic of metals in their solid or liquid states, is more complex than those considered above. This structure contains simultaneously both neutral and ionised atoms, i. e., atoms in which some of the valency electrons have become detached. Since all the atoms of a given metal are identical, each stands the *same* chance of being ionised. In other words, transfer of an electron from a neutral to an ionised atom can take place without the expenditure of energy. In consequence, there is always a continuous exchange of electrons taking place in metallic structures, and they always contain a certain number of *free* electrons, i. e., electrons which do not belong to any particular atom at the moment. In Fig. 54, these free electrons are shown as dots.

The extremely small size of electrons enables them to travel more or less freely throughout the whole of the metal crystal. In this connection, the latter may be regarded as a space lattice of neutral atoms and positive ions in an atmosphere of an "*electron gas*". Since each of the structural elements of the metallic crystal is not linked preferentially with any other, the crystal as a whole is a gigantic single particle.

The presence of free electrons in all metallic structures accounts for the *common* properties of the metals. These include such characteristic external features as opacity, metallic lustre and, in most cases, grey colour. The high electrical and thermal conductivity of metals is due to the free movement of the electrons. The comparatively ready mechanical deformability of typical metals makes it possible to shape

metals as desired by suitable treatment (according to Lomonosov's definition, "a metal is a bright body which can be forged"). All these features sharply distinguish metals from solid substances with atomic or ionic structures (such as diamond or NaCl).

Thus, the common properties of metals are due to the presence of free electrons in them. The greater the concentration of the latter, the more clearly expressed are the specific features of the metallic state. However, in different metals, the concentration of free electrons may vary widely. On the other hand, the individual features of the neutral atoms and positive ions occupying the nodes of the space lattice must manifest themselves. Therefore, alongside common properties, each metal also possesses its own characteristic properties. In particular there is a wide variation in the melting points of different metals. For instance, sodium melts at about 100° C, while chromium melts at about 1900° C.

2) The examples quoted show that the forces of attraction acting in metals must be complex in nature. Most probably, the *metallic* bond which is the sum of all these forces, is basically the net result of the simultaneous presence of ordinary covalent bonds (between neutral atoms) and Coulomb attraction (between ions and free electrons). The contribution of each of these components determines the manifestation of "metallic" properties in the solid and liquid metal. On the other hand, the vapour of a metal consists of individual molecules (usually monatomic) and behaves like other gaseous substances. The metal bond is characteristic, consequently, only of the solid and liquid states: it is a property not of individual particles but of an *aggregate* of particles.

After considering the solid state, it would be well to discuss the internal structure of *liquids*. Until comparatively recently, it was thought that liquids, like gases, are characterised by complete absence of orderly arrangement of their particles. However, actually this is not so. Although the particles of a liquid are able to move freely, they preferentially occupy definite positions in relation to each other. The liquid state may be roughly compared to the situation in a dance hall with a large number of dancing couples which, though they keep constantly changing places, coming together and going apart, nevertheless preserve, on the whole, a certain order.

Thus, there is a certain order in the relative positions of the particles of a liquid. As it approaches the freezing point, i. e., the solid state, the orderliness of internal structure becomes more clearly defined. On the other hand, as the liquid approaches the boiling point, i. e., the gaseous state, the disorder of relative arrangement of the particles increases. Thus, from the point of view of internal structure, the liquid state is actually *transitional* between the solid and gaseous states.

At the beginning of this section, it was stated that X-ray investigation of substances enables exact determination of the spatial arrangement of particles.

Thus it has become possible to find the *sizes* (or rather, the *spheres of action*) of individual atoms and ions, and this is of great importance to chemistry. For example, the radius of the Na^+ ion is 0.98 Å

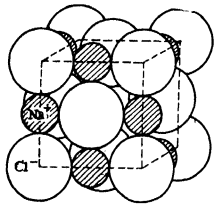


Fig. 55. Packing of ions in a NaCl crystal

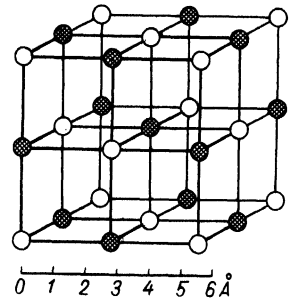


Fig. 56. Diagram of the structure of a NaCl crystal

and that of the Cl^- ion, 1.81 Å. Both ions can be roughly represented as spheres arranged in the NaCl crystal in the manner shown in Fig. 55. Usually, the crystalline structures of substances are represented more schematically, disregarding the sizes of the particles and showing only their relative position (Fig. 56).

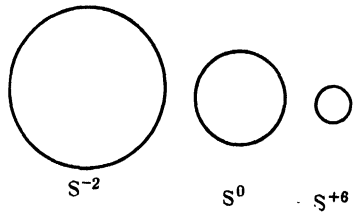


Fig. 57. Influence of valency state on size of atom

The radii (spheres of action) of neutral Na and Cl atoms are equal to 1.86 and 0.99 Å, respectively. Comparison of the ionic and atomic radii shows how greatly yielding or gaining of electrons by an atom influences the size of its ions.

For the case of one and the same element this influence is distinctly seen in Fig. 57, which gives the sizes of a sulphur atom in the neutral (S^0), negative divalent (S^{-2}) and positive hexavalent (S^{+6}) states magnified 50 million times. It will often be necessary later to deal with the sizes of atoms and ions, since many properties of substances depend greatly on them.

IV. HYDROGEN. WATER

IV-1. Hydrogen. Hydrogen is one of the most abundant elements: it accounts for about 1% of the weight of all the three layers of the earth's crust (atmosphere, hydrosphere and lithosphere) which in terms of atomic percentages amounts to 17.0.

The bulk of the element occurs in the combined state. Water contains about 11% by weight of hydrogen, clay contains about 1.5%, etc. Hydrogen enters into the composition of oil, various natural gases and all living organisms in the form of carbon compounds.

Free hydrogen is often present in volcanic gases. It is formed during the decomposition of certain organic remains. A small quantity of hydrogen is also given off by green plants. The atmosphere contains about 0.00005% of hydrogen by volume.

Hydrogen can be prepared by various methods. The simplest in principle is the decomposition of water by the action of certain metals, during which the corresponding hydroxide or oxide is formed together with hydrogen. Thus, sodium and calcium decompose water at ordinary temperatures; magnesium decomposes it on heating; zinc decomposes it when strongly heated with steam, and iron when still more strongly heated. The reactions take place, e. g., in accordance with the equations:

$$2Na + 2H_2O = 2NaOH + H_2$$

$$Zn + H_2O = ZnO + H_2$$

Hydrogen is given off much more vigorously when the same metals react with dilute acids: sodium and calcium react explosively, magnesium reacts very violently, zinc and iron, somewhat more slowly. The action of zinc on dilute hydrochloric (or sulphuric) acid in accordance with the reaction

$$Zn + 2HCl = ZnCl_2 + H_2$$

is the usual method used in the laboratory for the preparation of hydrogen.

1) When preparing hydrogen by the action of an acid on zinc, use is generally made of the apparatus for obtaining gases (the Kipp generator) shown in Fig. 58. This apparatus is very convenient, since the stream of hydrogen can be turned on or off as desired.

To charge the apparatus, some zinc granules are put into the globe *C* (the lower opening of which is covered with copper gauze) through the opening *B*. The opening *B* is closed with a rubber stopper carrying a tube fitted with a cock *D*. The latter is opened and dilute hydrochloric acid (1 : 2) or sulphuric acid (1 : 10) is poured into the apparatus through the opening *H* until the acid fills the reservoir *A* and covers all the zinc in the globe *C*. The cock is then

closed and a funnel *F* with water in it (to prevent escape of the acid vapour) is inserted into the opening *H*. After this, the apparatus is ready for use. When the cock is opened, the acid from the globe *E* passes into the globe *A* and from there enters the globe *C*, where it reacts with the zinc. When the cock is closed, the acid is displaced from the globe *C* into *A*, and thence back into the globe *E*, and the reaction ceases. The opening *G* which is closed with a stopper, is used for flushing the apparatus.

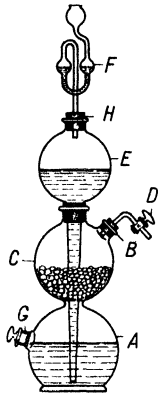


Fig. 58. Apparatus for producing gases

Hydrogen is colourless and odourless. Its melting and boiling points are very low (m. p. —259°, b. p. —253°). It is only slightly soluble in water in a ratio of 2 : 100 by volume. A very characteristic feature of hydrogen is its solubility in many metals.

Since hydrogen is the lightest of gases, its molecules move faster than any others. Therefore, hydrogen has the highest *rate of diffusion*, i. e., it disperses in a space or passes through various fine pores, etc., faster than any other gas. Due to this it has a high thermal conductivity. Thus, a heated object can be cooled six times more rapidly by hydrogen than by air.

2) According to the kinetic theory, the general expression for the mean velocity of a gas particle is $v = 14{,}530\sqrt{T/M}$ cm/sec, where T = absolute temperature and M = molecular weight. Hence, under identical conditions, the *mean velocities of the molecules of different gases are inversely proportional to the square roots of their molecular weights.* If the relative rates of diffusion, v, of two gases (which are directly proportional to the mean velocities of their molecules) and the molecular weight of one of them are known from experiment, the molecular weight of the other can be found from the relation $v_1 : v_2 = \sqrt{M_2} : \sqrt{M_1}$.

3) The molecular velocities referred to above, are *mean* velocities. The actual velocities of individual molecules may differ greatly from one another, and a rise in temperature of a gas causes not only a general increase in velocities but more equal distribution of velocities among the individual molecules (Fig. 59). Though in all cases, most of the particles have velocities close to the mean velocity, a gas always also contains molecules which move much faster.

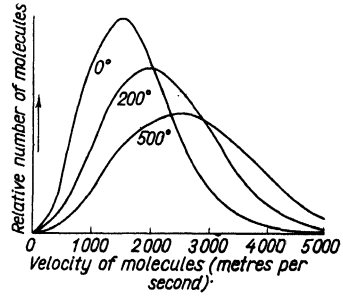


Fig. 59. Velocity-distribution curves of hydrogen molecules

The velocity distribution curves for all gases are similar to those shown in Fig. 59. Of course, the velocity of a particular molecule is not a constant value, but only represents its state at a given moment. In general, the probability of a particular velocity is the same for all the molecules of a given gas.

The chemical role of hydrogen is extremely varied. Its derivatives, called *hydrides*, are known for many elements. The hydrogen atom

can either yield its single electron to form a positive ion (which is a bare proton) or gain one electron, and change into a negative ion with the electronic configuration of helium (Fig. 60). However, the first possibility is never realised in its pure form, because hydrogen forms polar, and not ionic bonds with the typical non-metals.

On the other hand, ionic structures containing an H^- ion are known. Compounds of this type are formed by direct interaction of the most active metals (Na, Ca, etc.) with hydrogen on heating. They are typical

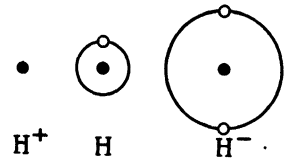


Fig. 60. Atom and ions of hydrogen

salts similar to the corresponding products of fluorine and chlorine. However, because of their instability with regard to water and air, these compounds are rarely encountered in practice.

Hydrogen combines with many non-metals, such as oxygen, chlorine, sulphur and nitrogen forming a more or less polar bond. All these compounds, except those with oxygen, will be dealt with when discussing the corresponding elements.

Hydrogen does not support the combustion of the usually combustible substances. Thus a lighted candle will be extinguished in it. But oxygen and some other elements will burn in an atmosphere of hydrogen. It can be seen, therefore, that the concept of "supporting" or "not supporting" combustion is relative. Usually it refers to the combustion of carbon compounds.

Hydrogen burns in pure oxygen and in air, the combustion product being water. The reaction between hydrogen and oxygen when a mixture of these gases, "detonating gas", is ignited, is much more vigorous and explosive.

The reaction of formation of water from its elements is highly exothermic

$$2H_2 + O_2 = 2H_2O + 137 \text{ kcal}$$

Besides combining directly with oxygen, hydrogen is able to take oxygen away from many other elements. As a result, the oxide is converted into the free element, e. g., according to the equation:

$$CuO + H_2 = H_2O + Cu$$

However, these reactions in which hydrogen is a *reducing agent* take place only on heating.

Experiment shows that the chemical activity of hydrogen sometimes greatly increases. This is observed when the substance reacting with it is present where the hydrogen is prepared (for example, by the action of zinc on an acid). The increased activity "*in the nascent state*" was attributed to the fact that in this case the hydrogen is available for the reaction in the form of atoms rather than molecules. Indeed, in reactions for the preparation of hydrogen, the latter must be given off initially as individual atoms. If a substance capable of reacting with these atoms is present, the reaction takes place before any H_2 molecules are formed.

This idea was confirmed when *atomic* hydrogen was obtained in the gaseous state and its reactivity was studied. It was found to be considerably more active than molecular hydrogen. Thus, atomic hydrogen combines with sulphur, phosphorus and other elements even under ordinary conditions, reduces the oxides of many metals, displaces certain metals (Cu, Pb, etc.) from their salts and enters into other reactions of which ordinary molecular hydrogen is quite incapable under the same conditions.

4) Atomic hydrogen is obtained by the action of a silent electric discharge on ordinary hydrogen. In this process, part of the molecules decompose into atoms which do not instantly recombine into molecules under reduced pressure, making it possible to study the chemical properties of atomic hydrogen.

The increased activity of atomic hydrogen can be explained as follows. When ordinary hydrogen takes part in chemical reactions, the hydrogen molecule has to decompose first into atoms. But this reaction of decomposition (*dissociation into atoms*) is strongly endothermic:

$$H_2 + 104 \text{ kcal} = 2H$$

Obviously the energy consumed in this reaction (*energy of dissociation*) must be compensated by the energy liberated during the interaction between the hydrogen atoms and the substance they react with. Consequently, it may be expected that hydrogen reactions in which less than 104 kcal are evolved per two gram-atoms of hydrogen will not take place spontaneously. In the case of reactions of substances with *atomic* hydrogen, such expenditure of energy for dissociation is not required. Therefore, here a considerably wider range of reactions are possible.

The large amount of energy evolved during the formation of a hydrogen molecule, explains its stability under ordinary conditions. At the same time it suggests the possibility of *thermal dissociation* (decomposition on heating) of the H_2 molecule by imparting a sufficient amount of heat to it. Experiment shows that appreciable thermal dissociation of hydrogen begins only at approximately 2000° C and increases with the temperature. Contrariwise, when the temperature is lowered, the individual atoms recombine into molecules.

5) The union of hydrogen atoms into molecules takes place considerably more rapidly on the surface of metals than in the gas itself. In this case, the metal absorbs the energy liberated during the formation of the molecules, and is heated to a very high temperature. The latter fact makes possible the technical application of atomic hydrogen for the welding of metals.

A diagram of the device used for the purpose is shown in Fig. 61. An electric arc is struck between two tungsten rods, and a stream of hydrogen is passed

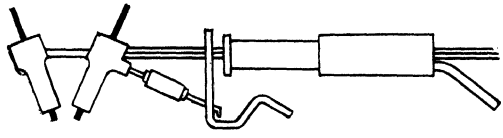


Fig. 61. Welding torch for producing atomic hydrogen flame

through the arc via tubes fitted to the rods. Part of the H_2 molecules split up into atoms, which then recombine on the metal surface situated at a small distance from the arc. The metal can be heated in this way to a temperature above 3500° C. Under these conditions, separate pieces of metal can be welded together strongly and rapidly. The great merit of the "atomic hydrogen flame" is its uniformity of heating which enables even very thin metal parts to be welded.

Hydrogen has various practical applications. In the chemica-industry hydrogen serves as a raw material for obtaining many important products such as ammonia; in the fuel industry it is used for the production of artificial gasoline from coal, etc. The high temperature (up to 2500° C) obtained when hydrogen is burnt in oxygen, is used for processes such as the fusing of quartz.

Industrially, hydrogen is produced mainly by the reaction of carbon monoxide with steam at high temperatures according to the reaction $H_2O + CO = CO_2 + H_2$, or by separating it from coke-oven gas by cooling the latter to low temperatures. Sometimes use is made of the action of steam on red-hot iron or the decomposition of water by an electric current. Hydrogen is transported in steel cylinders in which it is kept under high pressure.

IV-2. The Hydrogen Atom. Although the problem of the structure of the simplest atom—the hydrogen atom—appeared to be solved by the planetary model proposed in 1911, the model itself had internal contradictions. Indeed, according to the concepts of classical electrodynamics, an electron revolving about a nucleus should continuously radiate energy in the form of electromagnetic waves. Two important conclusions follow from this. 1) Because of the constant radiation of energy, the radius of the orbit of the electron should successively decrease; ultimately, the electron should fall on to the nucleus, annihilating the atom as such. 2) Owing to the *gradual* change in speed of rotation of the electron, the electromagnetic radiation of the atom should consist of a continuous series of rays of various wavelengths.

In other words, the spectrum of hydrogen should be *continuous*, i. e., should contain lines corresponding to all possible wavelengths.

Neither conclusion is true to fact: no self-annihilation of the hydrogen atom occurs, and its visible spectrum consists of a series of separate lines corresponding to definite wavelengths (Fig. 62).

Thus, either the planetary model or the theory based on classical electrodynamics must have been incorrect. Actually both were at fault.

Even before the advent of the planetary model of the atom, the thesis of continuous radiation in the classical electromagnetic theory of light had been rejected. "...To a thesis stating that *there are no*

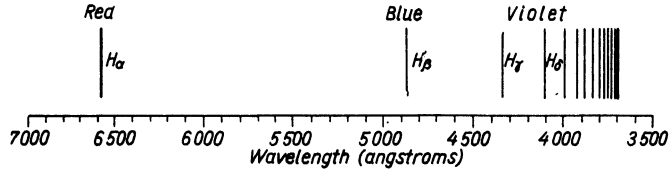


Fig. 62. Visible spectrum of hydrogen (Balmer series)

leaps and that there is only continuity, an *antithesis* may justifiably be opposed according to which, in reality, *changes always come about in leaps, only we see a number of tiny leaps rapidly following one another as merging into one continuous process*" (Plekhanov).

The *quantum theory* (Planck, 1900) was such an antithesis.

According to this theory, energy is not radiated continuously but in definite packets which are multiples of a certain "quantum of action", h. The magnitude of a radiated quantum of energy is the greater, the higher the frequency of the radiation, i. e., the shorter its wavelength (II-2). For example, rays at the violet end of the spectrum have more energy than those at the red end. In the electromagnetic spectrum (Fig. 30), γ-rays have the highest energy, while radio waves have the lowest. The magnitude of a quantum of energy (E in ergs *) for any electromagnetic radiation, can be calculated from the equation $E = h\nu$, where h is the quantum of action (6.62×10^{-27} erg·sec) and ν is the frequency of vibration of the ray. The quantum theory has been confirmed by ample experimental data and is now universally recognised.

Starting from the planetary concept and the quantum theory, Bohr, in 1913, constructed a model of the hydrogen atom which was free of the contradictions referred to above. This model was worked out on the basis of the following postulates.

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* An erg is approximately equal to the energy acquired by 1 mg in falling from a height of 1 cm.

1) An electron cannot rotate around the nucleus in any orbits at all, but only in a *limited number of definite* orbits. It rotates in these "permissible" orbits *without radiating energy.*

2) The orbit closest to the nucleus corresponds to the most stable (*normal*) state of the atom. When energy is imparted to the atom from outside, the electron can pass to one of the outer orbits, and the further out from the nucleus this orbit, the greater the store of energy of the electron. In other words, the electron is at a *higher energy level.* An atom which has an electron at one of the higher energy levels is called an "*excited*" atom in contrast to an atom in the normal state.

3) The atom absorbs or radiates energy only when the electron jumps from one orbit to another. The difference between the energies of the initial state, E_i, and the final state, E_f, is taken up or given off in the form of a quantum of radiant energy (a *photon*), and corresponds to a ray with a frequency of vibration determined by the relation $h\nu = E_i - E_f$.

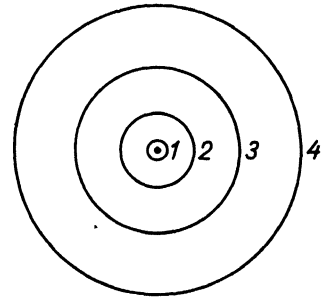


Fig. 63. Possible electronic orbits in the hydrogen atom according to Bohr

These concepts enabled calculation of the radii of the different electron orbits in the hydrogen atom "allowed" by the quantum conditions. The ratio of their radii was found to be $1^2 : 2^2 : 3^2 : 4^2 : \ldots n^2$. The quantity n came to be known as the *principal quantum number.* As can be seen from the above, n can take on different values corresponding to the natural series of integers.

The radius of the orbit closest to the nucleus ($n = 1$) was found to be 0.53 Å for hydrogen. The electron rotates in this orbit at a rate of about 2200 km per second. Fig. 63 is a diagram of the first four possible orbits for the hydrogen atom. The speed of rotation of the electron in the second orbit is one half, and in the third orbit, one third, etc., of that in the first orbit.

The work which must be done in order to remove the electron of the hydrogen atom from an orbit, is inversely proportional to the square of the principal quantum number of the orbit. Therefore, it is nine times easier, for example, to remove the electron from the third orbit than from the first.

The calculated frequency of the rays which result when the electron jumps from one orbit to another, was found to agree almost exactly with the frequency of the lines of the experimentally observed hydrogen spectrum. As is evident from Fig. 64, jumps from various remote orbits to the orbit with $n = 1$ correspond to the lines of the series in the ultraviolet region; jumps to the orbit with $n = 2$ correspond to the

lines of the Balmer series (Fig. 62); and jumps to the orbits with $n = 3$, 4 and 5 correspond to the lines of the three series in the infrared region. The latter two series were discovered experimentally after the theory of the hydrogen atom had been developed, and on the basis of its predictions.

If sufficient energy is imparted to an atom, it *ionises*, i. e., splits up into an electron and a positively charged ion (a proton in the case

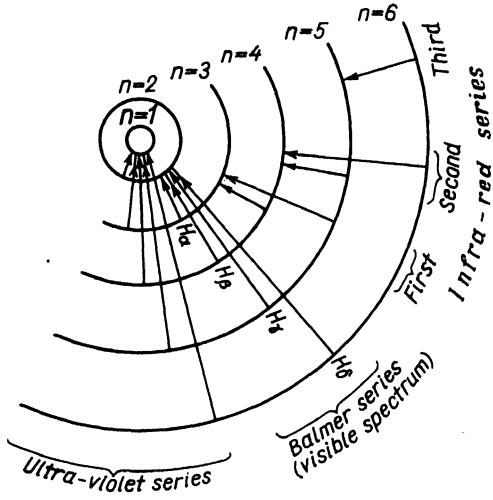


Fig. 64. Diagram of the origin of the hydrogen spectrum

of hydrogen). The energy necessary to do this corresponds to $n = \infty$ (Fig. 65) and is called the *ionisation energy* (I). It is determined from the spectrum, and for the normal state of the hydrogen atom is equal to 313 kcal per gram-atom:

$$H + 312 \text{ kcal} = H^+ + \ominus$$

The ionisation energy can be calculated for the excited states of the hydrogen atom from the equation $I = 312/n^2$.

The theory of the hydrogen atom was further developed in 1916 by Sommerfeld who showed that besides circular orbits, an electron can move in elliptical orbits and that there are as many possible types of orbits corresponding to each energy level as there are units in its principal quantum number. The latter determines the length of the major semi-axis of a given family of ellipses (in the particular case of a circle, it determines its radius). The length of the minor semi-axis is determined by the "*azimuthal*" quantum number, k, which also takes on the values of consecutive integers but cannot be greater than the principal quantum number.

The major semi-axis of the ellipse is given by the equation $a = n^2r$, and the minor semi-axis is given by the equation $b = nkr$, where r is the radius of the orbit (0.53 Å) when the atom is in its normal state. For example, for the principal quantum number 3, three types of ellipse are possible, their designations being 3_1, 3_2 and 3_3, which shows that the ratio of the major semi-axes to the minor semi-axes is 3 : 1, 3 : 2 and 3 : 3. The last is a particular case of an ellipse—a circle—the only one considered by the initial theory.

A model of the possible electronic orbits for the hydrogen atom according to Sommerfeld is shown in Fig. 66.

The energy levels corresponding to each of them are schematically compared in Fig. 67 (*B*) with the energy levels (sublevels) corresponding only to the circular orbits (*A*). Sommerfeld's refinement of the model of the hydrogen atom made it possible to account for the fine structure of spectral lines.

It is evident from Fig. 67 that the most elongated elliptical orbits correspond to the lowest energy level. Therefore, these orbits are the first to be filled with electrons during the building up of each new shell in *multi-electron* atoms. These *electronic shells*, i. e., sets of electrons with the same principal quantum number, are often denoted by the letters *K*, *L*, *M*, *N*, *O*, *P*, *Q*, in the order of their distance from the nucleus.

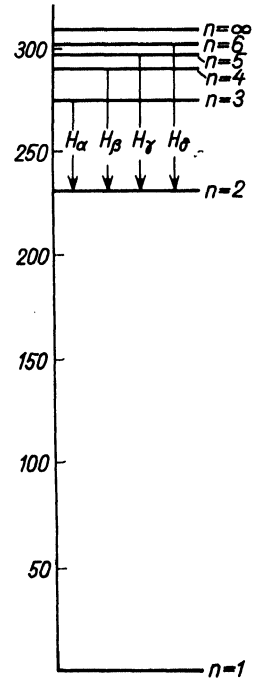


Fig. 65. Energy levels of the hydrogen atom (kcal/gram-atom)

Fig. 68 shows a model of the sodium atom constructed on the basis of this concept, in which the *K* and *L* shells are already completed and the *M* shell is beginning to be filled. The single electron of this shell is linked with the nucleus much more loosely than the others and therefore functions as a "valency" electron. Fig. 69 is a model of the argon atom, in which the *M* shell is completely filled with 8 electrons. The next element, potassium, has the same kind of elongated orbit in its *N* shell, as the sodium atom in its *M* shell.

In heavy atoms the lines of the visible spectrum are due to the jumps of only the outermost electrons, whereas jumps in shells closer to the nucleus give lines corresponding to ultraviolet rays or X-rays. The ionisation energy for these atoms is the energy required to remove the least firmly bound electron, i. e., one of those occupying the outermost orbits.

The work required to remove an electron from an atom is often expressed by indicating the *ionisation potential*. The latter is defined

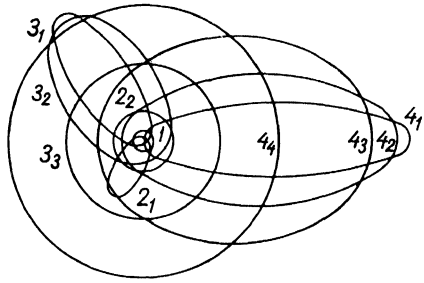


Fig. 66. Possible electronic orbits in the hydrogen atom after Sommerfeld

as the minimum electric field intensity in volts, at which a free electron accelerated by the field becomes capable of ionising a given atom (by knocking out its outer electron). For example, the ionisation potential of the hydrogen atom is equal to 13.6 volts. The ionisation energy is in a simple relation to the ionisation potential: *ionisation energy* (kcal/mole) = *ionisation potential* (volts) × 23.06. Therefore, the work needed to ionise an atom may be expressed either in the form of ionisation energies or in the form of ionisation potentials.

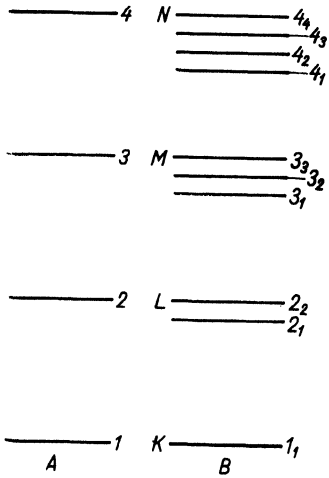


Fig. 67. Diagram of the energy levels for circular and elliptical orbits

The ideas considered above do not contradict the simplified atomic models (Fig. 37), but only refine them. Indeed, the distribution of electrons in shells is maintained in the Bohr and Sommerfeld models and corresponds to that given in the preceding section. Of course, none of these models come close to representing the structures of atoms in all their complexity. However, they certainly give a correct idea of certain basic features of the structure, and should be considered in this light.

1) The mid-twenties of this century marked a turning point in the progress of the theory of atomic structure, due to the influence of a new physical concept suggested by de Broglie in 1924. If it followed from the quantum theory and was experimentally confirmed by studies of collisions between photons and electrons, that *each electromagnetic wave simultaneously possesses the*

properties of a particle, then according to de Broglie, the converse is also true: *each moving particle simultaneously possesses the properties of a wave.*

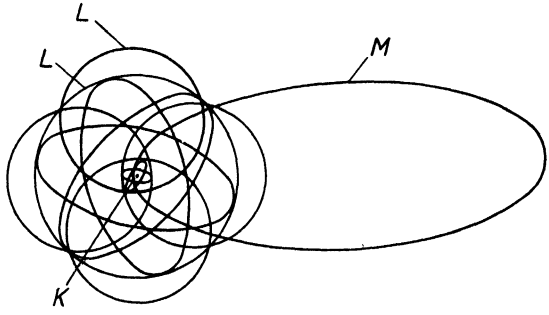


Fig. 68. Model of sodium atom

The quantitative interdependence between the wave and corpuscular properties of matter is given by *de Broglie's equation*, $\lambda = \frac{h}{mv}$, where h is the quantum of action, m is the mass of the particle, v, its velocity, and λ is the corresponding wavelength. This equation can be used to calculate the mass of the quantum of radiant energy ($v = c = 3.00 \times 10^{10}$ cm/sec) corresponding to any wavelength. At the same time, it is possible to calculate the wavelength associated with a particle with any given mass and velocity. For example, a photon corresponding to the $H\alpha$ line of the Balmer series ($\lambda = 6563$ Å $= 6.563 \times 10^{-5}$ cm) has a mass of $m = 3 \times 10^{-33}$ g, i. e., its mass is approximately 1/300,000 that of an electron. On the other hand, an electron with a velocity of, say, 6×10^8 cm/sec has a wavelength of $\lambda = 1.21 \times 10^{-8}$ cm $= 1.21$ Å, i. e., its wavelength is in the X-ray range.

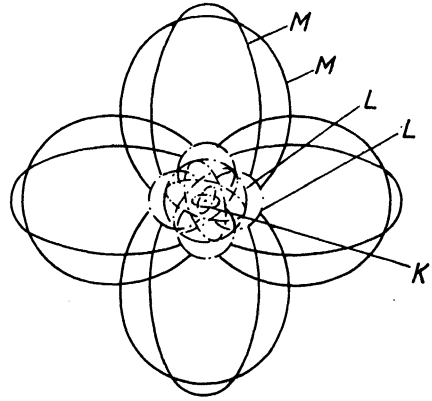


Fig. 69. Model of argon atom

This corollary of the theory was soon confirmed directly by experiment. It was found that an electron beam incident upon a crystal, undergoes diffraction in precisely the same way as X-rays. Somewhat later, the same was established for hydrogen and helium atoms. Since diffraction is a characteristic property of waves, these results conclusively proved the correctness of these ideas.

2) *Wave mechanics* which was developed on the basis of these ideas, approaches the problem of atomic structure from the point of view of the *principle of uncertainty* (Heisenberg, 1925). According to the latter, the nature of the motion of an electron cannot in principle be accurately determined. The model concept of the atom with its *definite* electronic orbits must, therefore, be replaced by a description in which only the *probability* of an electron being at a certain point in space is estimated. Though this probability estimate is based on structural data, it is calculated purely mathematically, by means of the so-called wave equation (Schrödinger, 1926).

The wave-mechanical approach to atomic problems supplied the key to a number of problems which had earlier been obscure, and also made it possible to obtain certain quantitative results with considerably greater accuracy than before. However, the renunciation of graphical clarity which is characteristic of wave mechanics considerably lowers the cognitive value of this method.

IV-3. Chemical Equilibrium. If gaseous hydrogen and oxygen are mixed under ordinary conditions, there will be practically no reaction between them. Only after the mixture of gases is heated, will any appreciable quantities of water begin to form. It has been established experimentally that at 400° C, 80 days are required for hydrogen and oxygen to combine completely, at 500° C this will require 2 hours and at 600° C the reaction takes place explosively, i. e., instantaneously.

Thus, the rate of formation of water from its elements, i. e., the reaction rate, depends greatly on the external conditions. To make a quantitative study of this dependence possible, it is first of all necessary to specify the units of measurement. *The rate of a chemical reaction is characterised by the change in concentration of the reacting substances in unit time.* The concentration is most usually expressed in moles per litre, and the time, in seconds, minutes, etc., depending on the rate of the reaction in question.

In studying any object, we always isolate it in some way from the surrounding space. *A substance or a mixture of substances in a definite limited volume* (e. g., in the volume of its container) is called a *system* in chemistry, and the different substances making up the system are called its *components.* Henceforth it will be assumed that the system in question is either a gas or a solution.

The molecules of any system can interact only when they collide. The more often this takes place, the more rapidly the reaction will proceed. However, the number of collisions depends primarily on the concentration of the reactants: the higher the concentration, the more numerous the collisions. A graphic example illustrating the influence of the concentration is the sharp difference in intensity of combustion of substances in oxygen and in air (which contains about 20% of oxygen).

The general formulation of the influence of the concentration on the rate of a chemical reaction is given by the *Law of Mass Action* (Guldberg and Waage, 1867): *the rate of a chemical reaction is directly proportional to the product of the concentrations of the reactants.* Thus, for the reaction $A + B = C$, we have $v = k[A][B]$, where v is the rate, k is the *rate constant* and [A] and [B] are the concentrations of the reactants A and B. If more than one particle of a substance take part in the reaction, its concentration must be raised to a power equal to the number of particles of that substance involved in the equation for the reaction. For example, the expression for the rate of the reaction

taking place according to the equation $2H_2 + O_2 = 2H_2O$ will be: $v = k[H_2]^2[O_2]$.

1) Whereas in gaseous mixtures or solutions any of the particles can collide with each other, in processes involving the participation of a solid obviously only the particles on its surface are available for the reaction. Therefore, in this case, the rate of the process depends on the surface area rather than on the volumetric concentration. Hence, the finer the solid particles, the more favourable the conditions for the reaction.

Besides the concentrations of the reactants, the reaction rate must be influenced by the *temperature*, since raising the temperature increases the velocity of motion of the molecules, thus increasing the number of collisions.

Experiment shows that *each 10-degree rise in temperature, approximately trebles* the rate of the majority of reactions. Meanwhile, according to the kinetic theory, the increase in the number of collisions due to such a rise in temperature is very small, and can by no means account for such an acceleration of the reaction.

This divergence between theory and practice is, however, only a seeming one. As a matter of fact, each collision between reactant particles does not necessarily result in chemical reaction—collisions may occur without causing any change in the molecules. Chemical interaction will occur only if the colliding molecules are sufficiently *active*, i. e., possess a large supply of energy.

The relative number of "effective" collisions is determined primary by the nature of the reactants. Therefore, given the same total number of collisions between molecules, the rates of different reactions may be extremely varied. On the other hand, a rise in temperature increases not only the total number of collisions, but also the number of effective collisions, and that is why the reaction rate increases so rapidly on heating. For different substances, the number of active molecules increases to a different degree on heating; hence the difference in acceleration of various reactions.

2) The number characterising the acceleration of a reaction due to raising the temperature 10° C is often called the *temperature coefficient of the action*. For most reactions, the values of these coefficients under ordinary conditions lie between 2 and 4. As the temperature is raised, the coefficients decrease and gradually approach unity.

If the mean value of the temperature coefficient of the action is 3, heating from a certain initial temperature, t_i, to a certain final temperature, t_f, will speed up the reaction by 3^w times, where $w = (t_f - t_i)/10$. For example, raising the temperature 100° C will speed up the reaction by 59 thousand times. At the same time, the increase in the number of molecular collisions per unit time is proportional to $\sqrt{T}$, where T is the absolute temperature. If the temperature has been raised, for instance, from 0° to 100° C, the number of collisions increases only by $\sqrt{373}/\sqrt{273} = 1.2$ times.

3) The period during which the molecules are in contact when they collide is estimated to be of the order of 10^{-12} sec. In such a short period, only particles which are sufficiently reactive, succeed in reacting.

Such *active* molecules may include those which are the "fastest" and possess considerable kinetic energy (cf. Fig. 59) at the moment of collision. They may also include excited molecules in which some electrons are not at the normal level, but at some higher energy level. Finally, active molecules include all those whose internal structure (distance between atomic nuclei, etc.), at the moment of collision, differs from the most stable structure. In all these cases, the surplus energy of the molecule determines its increased chemical activity.

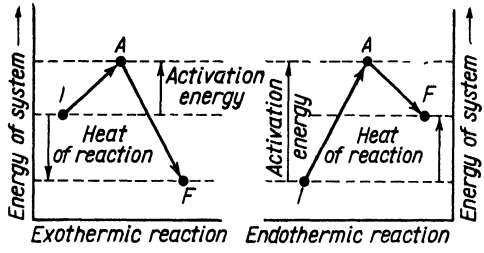


Fig. 70. Diagram of the course of activated reactions

4) The energy necessary to activate the original particles is called the *activation energy* of the corresponding reaction. As can be seen from the diagrams in Fig. 70, the energy used to convert the reactants *I* to the activated state *A* is later wholly or partially evolved during the transformation to the resultants, *F*. Therefore, the heat of reaction, determined by the difference between the energy of the reactants and the resultants, is independent of the activation energy. At the same time, the activation energy, which may vary widely in different cases, is the basic factor determining the reaction rate: the higher the activation energy, the fewer the molecules that possess it at a given temperature, and the slower the reaction. As a rule, processes with activation energies less than 10 kcal/mole are immeasurably rapid at ordinary temperatures, while those with activation energies over 30 kcal/mole are immeasurably slow.

The temperature coefficient of the action also depends on the magnitude of the activation energy. At ordinary temperatures, values of 2, 3 and 4 for the temperature coefficient correspond to activation energies of 14, 21 and 28 kcal/mole, respectively.

At about 1000° C hydrogen and oxygen react explosively to form water, while at 5000° C water explosively decomposes into hydrogen and oxygen. Writing this schematically, we have:

$$\text{hydrogen} + \text{oxygen} \underset{\text{at } 5000^\circ\text{C}}{\overset{\text{at } 1000^\circ\text{C}}{\rightleftharpoons}} \text{water}$$

It is obvious that at certain temperatures, *both* reactions must be possible. This actually occurs in the range from 2000° to 4000° C, where both the formation of water molecules from hydrogen and oxygen, and the decomposition of other water molecules into hydrogen

and oxygen, take place *simultaneously*. Consequently, under these conditions, the reaction between hydrogen and oxygen becomes perceptibly *reversible*. In general, *reactions are called reversible when they take place simultaneosly in opposite directions*. When writing them down, the equality sign is often replaced by arrows pointing in opposite directions:

$$2H_2 + O_2 \rightleftarrows 2H_2O$$

The following expressions may be drawn up for the rates of these two reactions proceeding in opposite directions according to the above equation:

$$v_1 = k_1 [H_2]^2 [O_2] \quad \text{and} \quad v_2 = k_2 [H_2O]^2$$

If $v_1 > v_2$, more molecules of water will be formed than decomposed per unit time. If $v_1 < v_2$, the number of molecules decomposed will exceed the number formed. Finally, if $v_1 = v_2$, the number of water molecules decomposed and formed per unit time will be equal.

Suppose a mixture of hydrogen and oxygen is heated to 3000° C. At first, there will be no molecules of water, and $v_2 = 0$. On the other hand, the rate v_1 is high, since there are many molecules of hydrogen and oxygen. In the next instant, when some of the molecules have succeeded in combining, the rate v_2 becomes appreciable, and the rate v_1 slightly decreases (since the concentrations of hydrogen and oxygen become smaller). As more water is formed, v_2 continues to increase, while v_1 continues to decrease. Finally, a moment arrives when both rates become equal.

If the initial substance is water, instead of oxygen and hydrogen, similar results will be obtained in the same way. In either case, when the rates of both reactions become equal, *chemical equilibrium* is established, and this is manifested by the fact that the concentrations of hydrogen, oxygen and water vapour remain constant for any length of time provided the conditions are not changed.

It follows that *chemical equilibrium is a dynamic equilibrium*: it is not characterised by the discontinuation of the process, but by the fact that both reactions proceed in opposite directions at the *same* rate. Molecules of water are continuously formed and decomposed, but the number of molecules formed in unit time is equal to the number of those that decompose. Therefore, to all appearances, no change takes place in the system.

5) A number of different methods are used for studying chemical equilibria. One of the most common is "freezing" of the equilibrium. The method is based on the fact that at sufficiently low temperatures, the reaction rate drops practically to zero. If, for example, a refractory metal tube is filled with a mixture of hydrogen and oxygen, which is then kept for some time at a temperature of 2000° C, an equilibrium corresponding to this temperature will be established between the initial gases and the water vapour in the tube. If the tube is now

cooled very rapidly the equilibrium will not have time to shift, and it will remain fixed because of the extreme slowness of reactions at low temperatures. Therefore, analysis of the contents of the tube will give results corresponding to the position of the equilibrium at 2000° C. As a check, the experiment is repeated, and the equilibrium is reached from the opposite direction: in this case, water is placed in the tube, instead of the hydrogen-oxygen mixture. The results of both experiments should agree, since exactly the same position of equilibrium is attainable from both directions.

Using the above expressions for the rates of the forward and reverse reactions, we can approach the important concept of the *equilibrium constant*. At equilibrium $v_1 = v_2$ whence we have:

$$k_1 [H_2]^2 [O_2] = k_2 [H_2O]^2$$

To separate the concentrations from the velocity constants, we divide both sides of the equation by $k_2[H_2]^2[O_2]$:

$$\frac{k_1}{k_2} = \frac{[H_2O]^2}{[H_2]^2 [O_2]}$$

But the quotient of k_1 divided by k_2, which are constant under given external conditions, is also a constant. This constant is called the equilibrium constant, and is denoted by the letter K.

Thus, we have:

$$\frac{[H_2O]^2}{[H_2]^2 [O_2]} = K$$

From the above, there follows a practical rule for deriving expressions for the equilibrium constant: write the product of the concentrations of the substances on the right-hand side of the equation in the numerator, and of the substances on the left-hand side—in the denominator (or vice versa). The concentration of each substance is raised to the power numerically equal to the number of its particles involved in the equation for the reaction. The numerical value of the constant indicates the position of the equilibrium for the temperature in question, and does not change when the concentrations of the reactants are altered.

6) The data obtained for the reaction $H_2 + I_2 \rightleftarrows 2HI$ at 445° C can serve as a simple example to illustrate the experimental determination of the equilibrium constant. Fig. 71 shows that equilibrium is approached from both sides, the same state of equilibrium is obtained in this system after approximately two hours (78% HI, 11% H_2 and 11% I_2 vapour, by volume). The experimental values of the equilibrium concentrations (in moles per litre) when various non-equivalent proportions of the reacting substances were present, and the values of the equilibrium constant calculated from them, are given below:

$$\frac{[H_2]\,[I_2]}{[HI]^2} = K$$

$[H_2]$	0.0268	0.0099	0.0032	0.0017	0.0003
$[I_2]$	0.0002	0.0020	0.0078	0.0114	0.0242
$[HI]$	0.0177	0.0328	0.0337	0.0315	0.0202
K	0.017	0.018	0.022	0.020	0.018

As can be seen from the above data, in spite of considerable differences in the relative concentrations of H_2 and I_2, the value of K remains fairly constant. Its mean value can be taken as 0.02.

Calculations associated with equilibrium constants constitute the subject matter of one of the most important branches of physical chemistry. However, even in qualitative form, the expression for the equilibrium constant provides a valuable indication of how the concentrations of the separate components of the equilibrium system influence each other.

Suppose an excess of hydrogen is introduced into the system $2H_2+O_2 \rightleftarrows 2H_2O$, thus increasing the denominator in the above expression for the equilibrium constant. In this case, the latter will remain constant only if there is a corresponding decrease in the concentration of oxygen and an increase in the concentration of water vapour. In practice, this means that to make the fullest possible use of the oxygen under given external conditions, the concentration of hydrogen must be increased. On the other hand, if the fullest possible use is to be made of the hydrogen, an excess of oxygen must be introduced into the system.

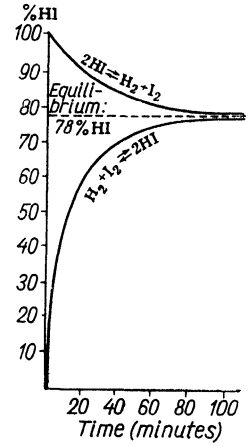


Fig. 71. Two-way approach to equilibrium

The same effect—more efficient use of one of the reacting substances—may sometimes be obtained by decreasing the concentration of the other substance participating in the reaction. Suppose the system $2H_2+O_2 \rightleftarrows 2H_2O$ is enclosed in a vessel impervious to water vapour and oxygen, but which allows hydrogen to pass through. Then the latter will leave the system, thus decreasing the denominator in the expression for the equilibrium constant. As K is constant, the inevitable result will be further decomposition of the water vapour and accumulation of free oxygen in the vessel.

Up till now, we have only considered equilibrium systems under constant external conditions. The general effect of a change in the external conditions is governed by *Le Châtelier's Principle of Equilibrium Shift* (1884) which can be expressed as follows: *if an external stress is applied to a system in equilibrium, the equilibrium will shift continuously in the direction indicated by the stress until the growing reaction in the system becomes equal to the external stress.*

The operation of Le Châtelier's principle can be vividly illustrated by the following mechanical system. Consider a spring attached to a fixed support. If left alone, the system will obviously be in equilibrium. If an external force of compression or extension is applied to the spring, the equilibrium of the system will shift in the direction

indicated by the external action—the spring will be compressed or extended respectively. However, elastic forces will appear in the spring and will increase with increasing strain, i. e., a reaction begins to grow in the system. Finally, a point is reached where the reaction becomes equal to the external action, and a new state of equilibrium is established, corresponding to the compressed or extended spring. Thus, the equilibrium has shifted relative to its initial position in the direction indicated by the external action.

Le Châtelier's principle covers very wide field. That is why its general expression sounds rather vague. Below, the principle will be considered in application to the external conditions of greatest importance to chemistry, viz., temperature and pressure.

The equation $2H_2 + O_2 \rightleftarrows 2H_2O + 137kcal$ shows that when hydrogen and oxygen combine heat is given off while when water decomposes into its elements heat is absorbed. If the system is in equilibrium at a certain temperature, and heat is applied, the equilibrium will shift successively in the direction of the formation of higher and higher concentrations of free hydrogen and oxygen. But according to the law of mass action, the exothermic reaction of combination will simultaneously be speeded up, i. e., a reaction gradually grows up in the system. Obviously, a new state of equilibrium will be established only when the concentrations of hydrogen and oxygen increase to such a point that the amount of heat evolved during their reaction becomes equal to the amount supplied from without in the same time.

The more heat imparted to the system, the more favourable for the decomposition of the water, i. e., the *endothermic* reaction. Conversely, removal of heat from the system by cooling hinders the decomposition of water and thus favours more complete combination of hydrogen with oxygen, i. e., the exothermic reaction. Hence, *on heating an equilibrium system, the equilibrium shifts in the direction of the endothermic reaction, while on cooling, the equilibrium shifts in the direction of the exothermic reaction.*

For the gaseous system $2H_2 + O_2 \rightleftarrows 2H_2O$, there are 3 molecules on the left-hand side of the equation and 2 molecules on the right. Applying Avogadro's law, we find that if all the water vapour were to decompose into hydrogen and oxygen, the system would occupy 3 volumes, while if no decomposition occurred at all, the system would occupy 2 volumes. Actually, the number of volumes occupied by the system must be intermediate, depending on the position of equilibrium; a shift of the latter towards the formation of water vapour results in a decrease in volume, and a shift towards the decomposition of the water vapour, in an increase in volume.

A change in the external pressure exerted on a gaseous system should cause a corresponding change in its volume. Increasing the

pressure will decrease the volume and vice versa. Suppose the pressure exerted on the system is raised. This will shift equilibrium towards the formation of water vapour, i. e., the relative concentration of the latter will increase. But according to the law of mass action the decomposition of water vapour into its elements by virtue of which the volume increases will be accordingly speeded up. This results in an increased reaction of the system. Obviously a new state of equilibrium will be established only when the concentration of the water vapour is such that the pressure exerted by the system itself becomes equal to the pressure exerted on the system from without.

Thus, as the external pressure on the system $2H_2 + O_2 \rightleftarrows 2H_2O$ is increased, the equilibrium shifts towards the formation of water, while a decrease in the pressure will shift the equilibrium towards its decomposition. The equilibrium of the dissociation, i. e., the reversible decomposition, of water into hydrogen and oxygen at various temperatures and pressures, is shown in Fig. 72. The effect of an increase or a decrease in pressure can be determined by comparing the degrees of dissociations at any one temperature.

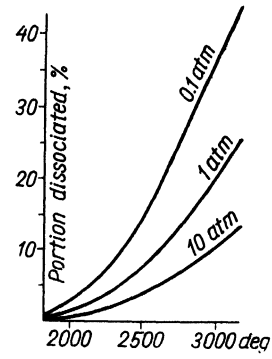


Fig. 72. Equilibrium of the thermal dissociation of water

As in the above case of the dissociation of water, the external pressure affects the position of equilibrium of all other reversible reactions between gases involving a change in volume. The change in volume is due to the different number of molecules on the left- and right-hand sides of the equation for the reaction.

From this follows the version of Le Châtelier's principle in application to the effect of pressure on the equilibrium of reversible gas reactions: *increasing the pressure shifts the equilibrium towards the formation of a smaller number of molecules, while decreasing the pressure shifts it towards the formation of a larger number of molecules.* Obviously, if the total number of molecules in the left- and right-hand sides of the equation for the reaction is equal, a change in pressure will not affect the position of chemical equilibrium.

Since the volume occupied by solid and liquid substances alters very little in the course of a reaction, a change in pressure has hardly any effect on the equilibrium shift in such ("condensed") systems. In mixed cases, when substances in various physical states are in equilibrium, usually only the number of molecules of the substances which are *gaseous* under the conditions of the experiment are of practical value for determining the effect of pressure on the equilibrium.

Example. Consider the system $CO_2 + C \rightleftarrows 2CO$. Counting up the number of particles formally (2 on the left and 2 on the right) it might be inferred that pressure does not affect the equilibrium of this system. But actually, only CO_2 and CO are gases (whereas C is a solid). Therefore an increase in pressure will shift the equilibrium to the left, and a decrease in pressure, to the right.

If the equilibrium in any reversible reaction shifts very greatly in one direction the reaction will appear *irreversible* under the given conditions, i. e., it can proceed in only one direction. For example, when hydrogen combines with oxygen at 600° C, it appears that no free molecules of hydrogen and oxygen remain. Actually, they are always present in very small numbers, and just as many are formed from water in unit time as combine to form water.

Thus, in reality reactions are reversible throughout the whole range of temperatures at which the substances in question can exist. But practically reversibility is detectable only within a certain narrower range. For instance, the reversibility of the reaction of formation of water (under ordinary pressures) is practically detectable only between 2000 and 4000° C.

With this broader approach, most chemical processes are found to be reversible, but often the equilibrium is so far displaced in one direction that their reversibility is practically imperceptible until an appropriate change in external conditions is effected. Owing to this abundance of reversible reactions, the study of equilibria and the conditions for their displacement is especially important to chemistry.

IV-4. Water. The total amount of water on earth is estimated to be 2×10^{18} tons. About 3/5 of this is concentrated in the oceans and seas. Of the remaining 2/5, a comparatively small part exists in the form of ice, inland water and water vapour in the atmosphere, while the major portion forms part of the solids in the earth's crust.

Natural waters always contain impurities. Some of these are in suspension, others in solution. Most of the suspended particles can be removed by settling, or, more rapidly, by filtering the water through thick layers of sand, etc. In the laboratory, filter (unsized) paper is usually employed for this purpose. Dissolved substances are mostly removed from water by distillation, the result being known as *distilled water.*

1) An installation of the type usually employed in towns for the purification of river water is shown in Fig. 73. The first operation is to add a small quantity of aluminium sulphate to the water, which causes a bulky precipitate of aluminium hydroxide to separate out, and this entraps various particles suspended in the water thus promoting their subsequent precipitation in the settling tank. The clarified water is filtered through a thick layer of sand, after which it is disinfected with chlorine, and only then enters the mains.

Water consists of 11.2% of hydrogen and 88.8% of oxygen by weight. To form water, one volume of oxygen combines with two volumes of hydrogen.

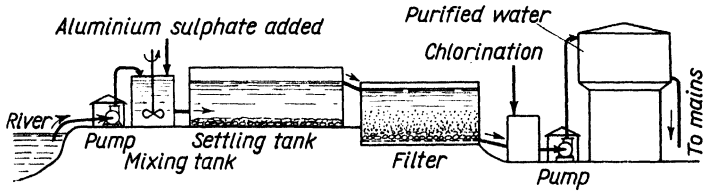


Fig. 73. Diagram of the purification of river water

As can be seen in Fig. 74, both atoms of hydrogen in the water molecule are arranged on the same side of the oxygen atom. As a consequence of this and the high polarity of H—O bonds (0.33), the whole H_2O molecule possesses a high polarity (dipole length 0.39 Å).

Determinations of the molecular weight of water vapour show that it corresponds to the simplest formula—H_2O. On the other

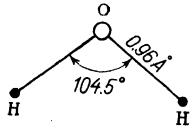


Fig. 74. Arrangement of atomic nuclei in the water molecule

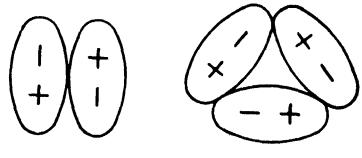


Fig. 75. Association of polar molecules

hand, in the liquid state water is *associated*, i. e., alongside simple molecules it contains more complex formations corresponding to the general formula $(H_2O)_x$, where $x = 2, 3, 4$, etc. These molecular aggregates are continually forming and breaking up, as can be expressed by the following equation:

$$xH_2O \rightleftarrows (H_2O)_x$$

2) Broadly speaking, association of molecules may be due to high polarity. As is evident from Fig. 75, molecules possessing a permanent dipole are able to combine in twos, threes, etc., owing to the mutual attraction between their opposite poles. However, the forces of attraction involved are not large, and in the case of water dipole association is of secondary importance.

3) The formation of *hydrogen bonds* is the main factor in the association of water molecules. These bonds form as a result of the drawing together of the hydrogen of one water molecule and the oxygen of another according to the

scheme: $O—H\cdots O—H$ (with the second H above the first O and the first H below the first O). This is made possible by the presence of considerable effective charges both in the hydrogen ($\delta = +0.33$) and in the oxygen ($\delta = -0.66$) of the water molecule.

Since the original bond between the hydrogen and its "own" oxygen is not lost, the hydrogen atom is thus linked with two oxygen atoms simultaneously, and hence links the two molecules of water to each other. Similarly, three, four, and more molecules of water may join together.

The hydrogen bond is much less stable than ordinary valency bonds (its energy in the case of water is 5 kcal per gram-atom). That is why molecules associated in this way may separate and then associate again in other combinations, etc.

A necessary condition for the formation of hydrogen bonds is sufficiently high polarity of the hydrogen valency bonds in the initial molecules. Since this condition is best satisfied by the bonds F—H, O—H and N—H, substances characteristically apt to associate through the formation of hydrogen bonds are usually encountered among compounds containing these bonds.

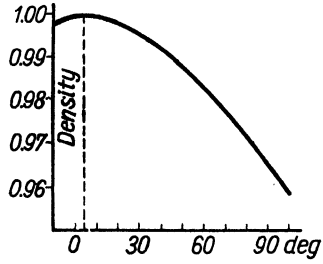


Fig. 76. Water density vs. temperature

In thin layers liquid water is colourless, but in thick layers it has a bluish-green colour. In contrast to almost all other substances, the density of which continuously increases on cooling, water has highest density at +4° C (Fig. 76).

Pure water hardly conducts electricity. It has a higher *specific heat* than any other liquid or solid, i. e., a greater amount of heat is required to raise the temperature of water an equal number of degrees than for the same weight of any other liquid or solid. Conversely, on cooling water loses more heat than an equal quantity of any solid or liquid substance.

At low temperatures, water evaporates relatively slowly, but its vapour pressure increases rapidly on heating.

Temperature (°C)	0	5	10	15	20	25	30	40	50	75	100
Vapour pressure (mm Hg)	4.6	6.5	9.2	12.8	17.5	23.8	31.8	55.3	92.5	289.1	760.0

The above values are the partial pressures of water vapour in air enclosed in a confined space above the liquid water. Such air will be saturated with water vapour, meaning that it cannot hold any more of it at the given temperature. Usually air contains from 30 to 70% of the maximum possible quantity of water vapour.

If air which is not saturated with water vapour is cooled, a state of saturation is gradually attained, after which the excess water

vapour begins to separate out in the form of a mist or—in the case of abrupt cooling—in the form of rain. If the whole process takes place at lower temperatures, the result is, respectively, hoarfrost or snow. Some of the exquisite patterns formed by snowflakes are shown in Fig. 77.

When the vapour pressure of a liquid becomes equal to the external pressure, the liquid begins to boil. The boiling point of water

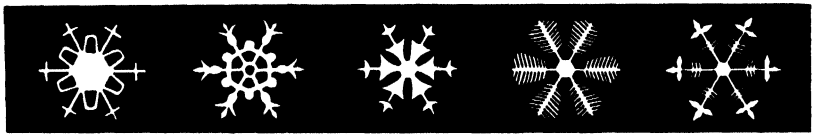


Fig. 77. Shapes of snowflakes

at normal atmospheric pressure is 100° C. Decreasing the pressure obviously lowers the boiling point, and vice versa. Some data for near-normal and high pressures are set out below.

Atmospheric pressure (mm Hg)	730	740	750	760	770	780
Boiling point of water (°C)	98.9	99.3	99.6	100.0	100.4	100.7
Pressure (atm)	2	4	6	8	10	20
Boiling point of water (°C) . .	120	143	158	170	179	211

The above data show that the boiling point of water rises very rapidly with growing pressure.

4) In order to convert a substance from the liquid to the gaseous state, work has to be performed to overcome the mutual attraction of its molecules (and the external pressure). The magnitude of this work expressed in calories is called the *heat of vaporisation* of the particular substance. It depends on the temperature at which evaporation takes place, decreasing as this temperature rises, and dropping to zero at the critical temperature (374° C for water). For water at 100° C we have: $\{H_2O\} + 9.7$ kcal $= (H_2O)$. The same quantity of heat is evolved when the vapour is converted into the liquid. Boiling water cannot be heated above 100° C at atmospheric pressure, because any excess heat supplied is used up for evaporation. It should be noted that water has a higher heat of vaporisation (per unit weight) than any other liquid.

5) If the dissolved gases are removed from water and it is then uniformly heated, taking care to protect it from jarring, a temperature considerably higher than 100° may be attained before the water begins to boil vigorously. If such *superheated* water is stirred, boiling usually begins immediately. In practice, water has been superheated to temperatures above 200° C. Superheating is frequently encountered in the boiling of liquids—in this case they boil "with bumping". In order to eliminate superheating and other associated effects, very fine glass ("capillary") tubes are sometimes introduced into the liquid, since the air retained in the tubes promotes uniform boiling.

When water is cooled to 0° C, it is converted to the solid state—ice. The specific gravity of ice is 0.92, i. e., it is lighter than water.

This fact is of great importance to natural life, as because of it the ice formed in water reservoirs remains on the surface of the water and protects the deeper layers from further cooling. If ice were heavier than water, all the water reservoirs in cold and temperate zones would be a mass of ice and would melt on the surface only in summer. The properties of water are, in this respect, anomalous, i. e., they depart from the general rule, since the density of the vast majority of substances is higher in the solid state than in the liquid.

Like water, ice can evaporate. It is well known, for example, that wet laundry dries even in a heavy frost. It has also been established that in winter, up to 30% of all the fallen snow evaporates. However, ice evaporates much slower than water since the vapour pressure of ice at low temperatures is very low:

Temperature (°C)	—50	—30	—20	—10	—8	—6	—4	—2	0
Vapour pressure (mm Hg) . . .	0.03	0.3	0.8	1.9	2.3	2.8	3.3	3.9	4.6

The evaporation of ice is no exception. Any solid has a vapour pressure (which is usually very low and cannot be measured directly). In some cases, however, it is high enough to be noticeable. An example is naphthalene, which is used to protect clothes from moths.

Since in the equilibrium system water $\rightleftarrows$ ice, the volume of the ice is greater than the volume of the same amount of water, it may be expected that on increasing the pressure, the equilibrium will shift to the left. In practice, this means that at high pressures ice will melt below 0° C. Indeed, experiment shows that each atmosphere of excess pressure lowers the melting point of ice by approximately 0.01° C. Thus, the shift of the melting point is extremely small. This is due to the fact that the volume of ice is only slightly smaller than the volume of the same amount of water.

6) If very pure water is cooled while carefully protecting it from jarring, it can be supercooled, i. e., it can be made to reach temperatures below zero without forming ice. However, such *supercooled* water is very unstable—if a small crystal of ice is introduced, it immediately solidifies. In practice, water has been supercooled to —72° C.

7) Under ordinary conditions water is stable in the liquid state. The state of supercooled or superheated water is called *metastable*. The characteristic feature of this state is that, though it is more or less stable intrinsically, this stability is easily upset by various effects. Imagine a cone slightly truncated parallel to its base. The stable state of the substance would correspond to such a cone standing on its base, and the metastable state, to the same cone standing on its apex.

8) As in the case of evaporation, the temperature of ice does not rise above 0° C while it is melting, because all the excess heat supplied from without is consumed in melting the ice (*the heat of fusion*): $[H_2O] + 1.4$ kcal $= \{H_2O\}$. When water freezes, the same amount of heat is evolved.

Using the above data for the evaporation of water and ice and for the melting of the latter, we can construct a *phase diagram* for water. In this diagram the temperature is usually plotted on the abscissa axis and the pressure on the ordinate axis. A schematic (i. e., not to scale) phase diagram for water is given in Fig. 78. *AC* is the vapour pressure of liquid water, *AB*, the vapour pressure of ice and *AD* is the pressure dependence of the melting point of ice.

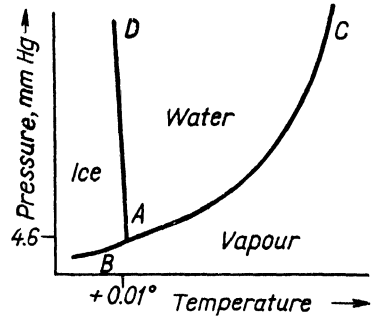


Fig. 78. Phase diagram of water

As was pointed out above (IV-3), in chemistry a substance or a mixture of substances contained in a definite limited volume is called a system. A system may be *homogeneous* or *heterogeneous*. The former is an accumulation, *uniform* in composition and internal structure, of particles, similar or different, but intimately mixed with one another. Examples of such homogeneous systems are water, a solution of sugar or salt, a mixture of gases or a uniform solid. Conversely, a system is heterogeneous if it consists of several accumulations of particles, *differing* in composition or internal structure and *separated by their interfaces*. Examples of heterogeneous systems are: systems consisting of two immiscible liquids, ice and water, a mixture of solids, etc.

The component parts of a heterogeneous system separated from each other by interfaces are called its phases. A *phase* is thus the homogeneous part of a heterogeneous system. For example, a system consisting of two immiscible liquids is a two-phase system, while a mixture of several solids consists of as many phases as there are substances, etc. Obviously, any homogeneous system is also a single-phase heterogeneous system.

Turning to Fig. 78, we see that the diagram is divided into three areas, each of which corresponds to the region of stability of one of the physical states of water, i. e., one of the phases of the three-phase system: ice—water—water vapour. The lines separating these regions correspond to the conditions of temperature and pressure under which two phases are stable:

Line *AC* . . . . . water $\rightleftarrows$ vapour equilibrium
" *AD* . . . . . ice $\rightleftarrows$ water equilibrium
" *AB* . . . . . ice $\rightleftarrows$ vapour equilibrium

The three lines intersect at *A*. Hence, at the temperature (+0.01° C) and pressure (4.6 mm Hg) corresponding to this point, all three

phases can exist in stable equilibrium, and it is therefore known as the *triple* point.

The position of the triple point in the phase diagram characterises the changes in physical states typical of the substance at ordinary pressure. If it lies below 760 mm, the substance on heating will pass first from the solid into the liquid, then into the gaseous state. If the triple point lies above 760 mm, the substance will pass from the solid state directly into the gaseous, i. e., it *sublimates* on heating. From this it follows that to liquefy a sublimable substance, it must be heated at a sufficiently high pressure.

9) The amount of heat necessary to sublimate a substance is called its *heat of sublimation*. For example, for iodine: $[I_2] + 15$ kcal $= (I_2)$. The sublimation temperature is defined as the temperature at which the vapour pressure of a sublimable substance reaches 760 mm Hg.

A phase diagram can be constructed for any substance. It is very convenient, since it enables direct determination of the conditions of stability of a given phase or phase equilibrium. That is why such diagrams have found wide application.

Chemically, water is a very reactive substance. It combines with the oxides of many metals and non-metals, reacts with active metals and takes part in various other reactions. Therefore, manifestations of the chemical properties of water will be encountered throughout the whole of this course.

IV-5. Hydrogen Peroxide. Besides water, hydrogen is known to form another compound with oxygen, namely *hydrogen peroxide*, H_2O_2. In nature, it forms as a by-product of the oxidation of many substances by atmospheric oxygen, and traces of it are always contained in precipitations and the sap of certain plants. Some hydrogen peroxide also forms in the flame of burning hydrogen, but it decomposes when the combustion products are cooled.

The heat of formation of hydrogen peroxide from its elements cannot be determined directly but can be found indirectly by applying the *Law of Constant Heat Summation* established by Hess (1840). This law states that *the total amount of heat evolved or absorbed in a series of consecutive chemical reactions is equal to the amount of heat evolved or absorbed in any other series of reactions with the same initial substances and final products.*

The essence of this law is reflected vividly in the following mechanical analogy: the total work performed by a load lowered without friction does not depend on its path, but only on the difference between the initial and final heights. Similarly, the total amount of heat evolved or absorbed in any chemical reaction depends only on the difference between the heats of formation (from the elements) of

its final products and its initial substances. If all these values are known, the total amount of heat evolved or absorbed in the reaction can be calculated by subtracting the total heats of formation of the initial substances from the total heats of formation of the final products. Hess's law is often used in calculating the heats of reactions for which direct experimental determination is difficult or impossible.

In application to H_2O_2 the calculation can be carried out proceeding from two different methods for the formation of water.

1. Suppose the combination of hydrogen and oxygen results first in hydrogen peroxide which then decomposes into water and oxygen.

The processes can be represented by the following equations:

$$2H_2 + 2O_2 = 2H_2O_2 + 2x \text{ kcal}$$
$$2H_2O_2 = 2H_2O + O_2 + 47 \text{ kcal}$$

The heat evolved in the latter reaction is easily found by experiment. Adding both equations term by term and cancelling identical terms, we get:

$$2H_2 + O_2 = 2H_2O + (2x + 47) \text{ kcal}$$

2. Suppose the combination of hydrogen and oxygen results directly in water:

$$2H_2 + O_2 = 2H_2O + 137 \text{ kcal}$$

Since in both cases, the initial substances and the final products are the same, $2x + 47 = 137$, whence $x = 45$ kcal. This is the heat of formation of one gram-molecule of hydrogen peroxide from its elements.

In practice, the simplest way of obtaining hydrogen peroxide is by the action of dilute sulphuric acid or carbon dioxide on barium peroxide, BaO_2. As a result of the reactions

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2$$
$$BaO_2 + CO_2 + H_2O = BaCO_3 + H_2O_2$$

the barium salts which form together with the hydrogen peroxide are insoluble in water, and the liquid can be removed from these salts by filtration. H_2O_2 is usually marketed as a 3% or a 30% aqueous solution.

Pure hydrogen peroxide is a syrupy liquid with a specific gravity of 1.5. Thin layers are colourless, but thick layers have a bluish colour. Solid hydrogen peroxide (white crystals) melts at —2° C. When heated under ordinary conditions it decomposes, but under greatly reduced pressure it can be distilled without decomposing.

Hydrogen peroxide readily dissolves many salts, and is miscible with water (as well as with alcohol and ether). A dilute solution of

H_2O_2 has an unpleasant "metallic" taste. A strong solution will cause burns on the skin, the burnt spot turning white.

The structural formula of hydrogen peroxide, H—O—O—H, shows that the two oxygen atoms are linked directly with each other. This bond is unstable, which accounts for the instability of the molecule. Indeed, anhydrous H_2O_2 may decompose explosively into water and oxygen. It is much more stable in dilute aqueous solutions.

1) The spatial structure of the H_2O_2 molecule is rather complex: the H—O bonds (d = 1.01 Å) form angles of about 100° with the O—O bond (d = 1.48 Å), two bonds being in one plane, and the third approximately normal to it.

2) The purer the hydrogen peroxide, the more slowly it decomposes on storing. The compounds of certain metals (Cu, Mn, etc.) are especially active catalysts for H_2O_2 decomposition, and even traces of them have an appreciable effect.

An alkaline medium favours the catalytic decomposition of hydrogen peroxide. An acid medium, on the contrary, retards decomposition. For these reasons, solutions of H_2O_2 are often acidified with sulphuric acid. Hydrogen peroxide decomposes more rapidly under the action of heat and light, and should therefore be stored in a cool dark place.

Hydrogen peroxide is a *powerful oxidising agent*, i. e., it readily yields its extra (as compared with water) oxygen atom. Thus, paper, sawdust and other combustible substances will ignite under the action of anhydrous or even 65% H_2O_2.

The practical application of H_2O_2 is based on its oxidising properties. Highly concentrated hydrogen peroxide is used as a source of oxygen in jet engines. Very weak solutions of H_2O_2 are widely used as a gargle and for washing wounds. Hydrogen peroxide is also extensively employed for bleaching silk, furs, feathers, etc., since it destroys the colouring matter with hardly any effect on the material.

The *oxidising* decomposition characteristic of hydrogen peroxide can be represented schematically as follows:

$$\begin{matrix} H-O & H \\ | & \diagdown \\ H-O & H \end{matrix} \rangle O + O \quad \text{(for oxidation)}$$

For example, black lead sulphide is oxidised by hydrogen peroxide to the white sulphate:

$$PbS + 4H_2O_2 = PbSO_4 + 4H_2O$$

This reaction is used for the restoration of pictures.

The *reducing* decomposition in accordance with the equation

$$\begin{matrix} H-O & O \\ | & \| \\ H-O & O \end{matrix} + 2H \quad \text{(for reduction)}$$

which is less characteristic of hydrogen peroxide, is much less common. For example, it reacts with ozone as follows:

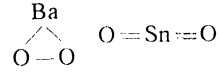
$$O_3 + H_2O_2 = H_2O + 2O_2$$

Hydrogen peroxide also possesses very weak *acidic* properties. It reacts with the hydroxides of certain metals to form corresponding *peroxides*, and these should therefore be regarded as *salts of hydrogen peroxide*. The reaction

$$Ba(OH)_2 + H_2O_2 = BaO_2 + 2H_2O$$

is an example of this.

From the point of view of molecular structure salts of hydrogen peroxide are distinguished by the presence of a *peroxide chain* consisting of two oxygen atoms. The molecules of normal oxides (II-5), contain no such chain. This can be seen by comparing, for example, the structural formulas of barium peroxide and stannic oxide:

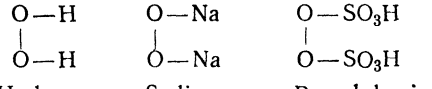


For this reason the behaviour of peroxides and normal oxides towards acids is different—the former react to form hydrogen peroxide, while the latter produce water:

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2$$
$$SnO_2 + 2H_2SO_4 = Sn(SO_4)_2 + 2H_2O$$

Whether an oxygen compound is a peroxide or a normal oxide can be determined by studying the products of its reaction with acids.

The hydrogen atoms of hydrogen peroxide can be replaced not only by a metal, but by certain acid radicals. In the latter case, acids containing a peroxide chain in their molecule result; these are called *peroxyacids*. They are, consequently, derivatives of hydrogen peroxide (and like the latter, they possess powerful oxidising properties). One example of these is persulphuric acid, the schematic formula of which is given below together with the formulas of hydrogen peroxide and sodium peroxide.



V. SOLUTIONS

V-1. Disperse Systems. If a substance is dispersed throughout another substance (a medium), as very fine particles, the system is called a *disperse* system. Depending on the physical state of the dispersed substance and the medium, the following 9 types of disperse system are possible (G—gaseous state, L—liquid state and S—solid state; the first letter refers to the dispersed substance, and the second, to the medium):

G+G	G+L	G+S
L+G	L+L	L+S
S+G	S+L	S+S

In chemistry, the most important disperse systems are those in which the medium is a liquid.

The properties of disperse systems, primarily, their stability, greatly depend on the size of the dispersed particles. If the latter are very large relative to the molecules, the disperse system is unstable, and the dispersed substance will settle quite rapidly (or rise to the top, if it is lighter than the medium). Such fairly unstable disperse systems containing comparatively coarse dispersed particles are called *suspensions.*

On the other hand, if the dispersed substance is in the form of separate molecules, quite stable systems result, which will not separate, no matter how long they are allowed to stand. Such systems are called *molecular solutions* (usually, simply *solutions*).

Finally, the intermediate range is occupied by *colloidal* solutions, in which the size of the dispersed particles varies between the sizes of the particles in suspensions and those in molecular solutions.

Although there is no sharp boundary between these ranges, it may be roughly stated that systems in which the dispersed particles are larger than 100 mμ are suspensions, while those in which the dispersed particles are smaller than 1 mμ are molecular solutions. The particles in the majority of suspensions can be seen either with the naked eye or through a microscope (the resolving power of which is about 200 mμ). The finer particles in colloidal solutions can be seen with the aid of an ultramicroscope which enables observation of light scattered from objects down to 2 mμ in size.

1) In an ordinary microscope the object is observed in *transmitted* light, whereas the underlying principle of the ultramicroscope is observation of the light *reflected* by the object (Fig. 79). This makes visible tiny objects which cannot be seen through an ordinary microscope. Similarly, dust particles con-

tained in the air normally cannot be seen, but if a narrow ray of sunlight enters a darkened room, a vast number of moving dust particles become visible in it. However, they become invisible again, if the ray is observed along its path instead of from the side.

Depending on the physical state of the dispersed substance, suspensions fall into *suspensions* proper and *emulsions*. The former result when the dispersed particles are solid, while in the second, the dispersed particles are liquid. In both cases, other things being equal, the larger the size of the suspended particles and the difference between the specific gravities of the dispersed substance and the medium, the less stable the system.

Suspensions play an appreciable role in nature and in engineering. Thus, river water always contains suspended particles, which on settling in places where the current slows down, form deposits of sand, clay, etc. In particular, the extraction of gold by washing auriferous sands is based on the difference in the specific gravities of the suspended particles. Colloidal solutions are of still greater importance, since many processes taking place in living organisms are connected with them. They also play an important part in engineering.

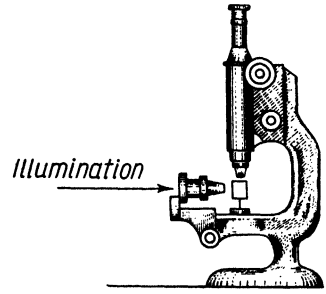


Fig. 79. An ultramicroscope

Finally, the most important and most frequently encountered disperse systems are molecular solutions, which will be dealt with in the next section.

An example of a complex disperse system is milk, the basic constituents of which (not counting water) are fat, casein and lactose. The fat is in the form of an emulsion, and when the milk is allowed to stand, it gradually rises to the top (creams). The casein is contained in the form of a colloidal solution and does not separate out spontaneously, but can be easily precipitated (as curds) if the milk is acidified with vinegar, for example. Under natural conditions the separation of casein takes place when milk turns sour. Finally, lactose is in the form of a molecular solution and can be separated out only by evaporating the milk.

V-2. Molecular Solutions. As has already been stated in the previous section, molecular (or *true*) solutions consist of individual molecules of the dispersed substance and the medium mixed with each other; they are, therefore, homogeneous systems.

Though equivalent proportions between the dispersed substance (in this case—the *solute*) and the medium (*solvent*) are not main-

tained on dissolving, solutions cannot be regarded as mere mechanical mixtures. In certain features they resemble chemical compounds. In particular, during dissolution energy is always absorbed or evolved (*heat of solution*) and a change in volume takes place.

Both effects are, as a rule, fairly small but become appreciable in some cases. For example, when alcohol and water are mixed a small decrease in volume and an appreciable evolution of heat are always observed. Heats of solution may sometimes be quite considerable. Thus, dissolving ammonium nitrate results in intense cooling, but when potassium hydroxide is dissolved the liquid becomes very hot. The two processes can be represented by means of the following equations:

$$NH_4NO_3 + aq + 6 \text{ kcal} = NH_4NO_3 \cdot aq$$
$$KOH + aq = KOH \cdot aq + 13 \text{ kcal}$$

The symbol aq (abbreviation for the Latin aqua—water) denotes a large, unspecified quantity of water.

Studies of solutions by various methods have shown that many of them contain what are known as *solvates* (or *hydrates*, in the particular case of aqueous solutions) which are more or less unstable compounds of the solute particles with molecules of the solvent. Solvate formation sometimes changes the properties of the dissolved substance so extensively that it can be detected by direct observation. For example, anhydrous copper sulphate is colourless, whereas its aqueous solution is blue.

Generally speaking, the more polar the particles of the solute and the solvent, the easier it should be for solvates to form and the more stable they should be. Since of all the common solvents, the most polar is water, more often than not one has to deal with hydrates.

Hydrated water is sometimes so firmly linked with the solute that when the latter is separated out of solution, it forms part of its crystals. Such crystalline formations containing molecules of water are called *crystal hydrates* (*crystal solvates* in the general case). When water is contained as a structural element in crystals of other substances, it is called *water of crystallisation*. The composition of crystal hydrates is usually expressed by indicating in the formula of the substance the number of molecules of water of crystallisation per molecule of the substance. For example, the formula of the crystal hydrate of copper sulphate—blue vitriol—is $CuSO_4 \cdot 5H_2O$. Like the aqueous solution of copper sulphate, the crystal hydrate is blue.

The composition of solvates is probably variable. The solution also contains free solvent molecules. That is why, as a rule, solutions do not show the equivalence characteristic of chemical compounds in the proportions between solute and solvent.

Thus, solutions cannot be classed as chemical compounds of definite composition, nor can they, on the other hand, be regarded as mere mechanical mixtures. Occupying an intermediate position, solutions are liquid dissociated systems consisting of solvent and solute particles, and definite, unstable, but exothermic compounds between them, of which there may be one or several, depending on the nature of the constituents. These lines contain the essence of the *chemical* theory of solutions as developed by Mendeleyev. This theory differs radically from the "physical" theory which regards the solvent only as an inert medium and denies the presence of solvates in solutions, i. e., in fact classes them as simple mechanical mixtures. At present, the chemical theory of solutions is universally recognised.

A solute behaves like a gaseous substance in some respects. Just as one gas freely pervades another, one substance dissolves in a dilute solution of another almost as readily as in the pure solvent. Diffusion processes take place in solutions in the same way as in gases, only much more slowly, and owing to this diffusion the concentration of the solute gradually becomes and remains uniform throughout the entire volume of the solution.

The process of dissolving is itself closely connected with diffusion. When a solid substance is introduced into water, for example, the molecules of its surface layer dissolve and, as a result of diffusion, they disperse through the volume of the solvent. A second layer of molecules then comes away from the surface, and these, in turn, disperse throughout the volume, etc.

The process of dissolving would continue in this way until any amount of the solid passed completely into solution, were it not for the fact that an opposite process—the separation of molecules from the solution—takes place. The dissolved molecules, which are in continual motion, may stay on the surface of the undissolved solute when they collide with it, and form a new layer. It is obvious that their reverse separation will be the more intense, the higher the concentration of the solution. But as the substance dissolves, its concentration continually increases, and finally reaches a value at which just as many molecules separate out in unit time as are dissolved. A solution in this state is called *saturated*: it contains the maximum possible quantity of solute (under given external conditions). From the above it follows that the equilibrium in the system undissolved solute—saturated solution is a *dynamic* equilibrium, and under constant conditions such a system can exist indefinitely without perceptible change.

Any solution, the concentration of which is lower than that of a saturated solution is *unsaturated*. In contrast to a saturated solution such a solution can still dissolve a certain quantity of substance under constant external conditions. Apart from these terms, the

following designations are also used in practice: a solution containing little solute, is called *dilute*, while one containing a great deal of solute is called *concentrated*.

The concentration of a solution may be expressed in various ways. For example, the number of *gram-molecules* of solute contained in one litre of solution,* may be specified. Concentrations specified in this way are called *molar* concentrations (M). They are usually denoted as follows:

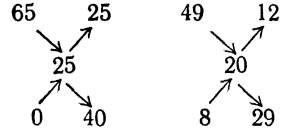
M = molar solution (1 mole per litre),
$2M$ = two molar solution (2 moles per litre),
$0.1M$ = a decimolar solution (0.1 mole per litre), etc.

Molar solutions are very convenient in that equal volumes of the same concentration contain the same number of molecules of solute. Consequently, if one molecule of substance A reacts with one molecule of substance B and the molarity of their solutions is the same, equal volumes of each solution must be taken to obtain complete reaction; if one molecule of A reacts with two molecules of B, the volume of solution B must be twice as large as that of solution A, etc.

1) The concentration of solutions is sometimes expressed as the number of gram-molecules of solute in 1000 g of solvent. Concentrations expressed in this way are known as *molal* concentrations (m). Their chief merit is that they are independent of the temperature (being purely gravimetric). As regards the way in which they are denoted, all that was said above about molar solutions applies to molal solutions.

2) Concentrations of solutions are sometimes also expressed as the number of grams of solute in a certain volume of solution, or in a certain volume of solvent, and very often they are expressed as the percentage by weight of solute (in 100 g of solution). In industry, the concentration of solutions is often characterised by their specific gravity.

3) If more dilute or stronger solutions have to be prepared from solutions of a definite percentage composition, the necessary quantity by weight of the initial liquids can easily be found by applying the so-called *blending rule*. The latter is a method of calculation which will become clear from the following examples. Suppose that it is required: 1) to prepare a 25% solution from a 65% solution and water (0%) and 2) to prepare a 20% solution from a 49% and an 8% solution.



According to the scheme, it is necessary: 1) to add 40 parts by weight of water to 25 parts by weight of the 65% solution; 2) to add 12 parts by weight of the 49% solution to 29 parts by weight of the 8% solution.

The *solubility* of a substance under given conditions is defined as the concentration of its saturated solution under those conditions. Unfortunately, there is no theory so far which would enable gener-

alisation of the results of separate investigations and deduction of the general laws of solubility. This is due largely to the fact that the solubility of different substances depends on the temperature in very different ways.

The only guiding principle that gives some help is the long-standing empirical rule that *like dissolves in like*. In the light of modern views concerning the structure of molecules, its meaning is that if the solvent molecules are non-polar or of low polarity, e. g., benzene or ether, substances with non-polar or low-polarity molecules will dissolve readily in it, while substances with highly polar molecules will be less soluble in this solvent, and ionic substances will hardly dissolve at all. On the other hand, a solvent with pronouncedly polar molecules, e. g., water, will, as a rule, readily dissolve substances with polar or partially polar molecules, but will hardly dissolve substances with non-polar molecules.

4) The polarity of a solvent can be characterised by its *dielectric constant*, ε. The latter shows how many times weaker the attraction or repulsion between two electric charges in a given medium is, compared to vacuum ($\varepsilon = 1$). Other things being equal, the more polar the molecules of the medium, the weaker the interaction. At ordinary temperatures, the dielectric constants of water, alcohol, ether and benzene are 81, 27, 4 and 2, respectively.

Although the physical state of the solute and the solvent may vary greatly (V-1), in practice one has to deal almost exclusively with solutions in liquids, mainly in water. Therefore, mainly aqueous solutions will be considered below.

The solubilities of *gases* in liquids differ very widely. For example, under ordinary conditions one volume of water can dissolve 0.02 volume of hydrogen or 400 volumes of hydrogen chloride. Most gases dissolve more readily in less polar solvents than in water. The solubility of gases in liquids almost always *decreases* on heating. Liquids can usually be freed completely of dissolved gases by boiling.

The relation between the solubility of a gas and the pressure is expressed by the *Law of Solubility of Gases* (Henry, 1803): *the solubility of a gas in a liquid is directly proportional to its partial pressure*. Consequently, reducing the partial pressure decreases the solubility. An example of this is ordinary carbonated water, which is a saturated aqueous solution of carbon dioxide prepared under a pressure of 760 mm Hg of the latter. When this water comes in contact with the air, in which the partial pressure of CO_2 is only 0.2 mm Hg, the dissolved carbon dioxide is given off vigorously. Figures for the solubilities of different gases usually refer to a partial pressure of 760 mm Hg, i. e., to saturation of the liquid by the gas in question under atmospheric pressure.

When *liquids* dissolve in liquids, there may be various cases. For example, alcohol and water are completely miscible, but water

and benzene are almost insoluble in one another. The most common case is that of limited mutual solubility, which is observed, for example, in the system water—ether. On heating, the solubility of liquids in liquids changes differently: in some cases it increases, while in others it decreases.

The solubility of *solids* in liquids varies very widely for different solutes and solvents. In most cases, the solubility *increases* with the temperature. The relationship between solubility and temperature is best expressed graphically in the form of *solubility curves*, three typical forms of which are shown in Fig. 80. As can be seen from the diagram, the solubility of NaCl increases very slowly with the temperature, while that of KNO_3 increases very rapidly.

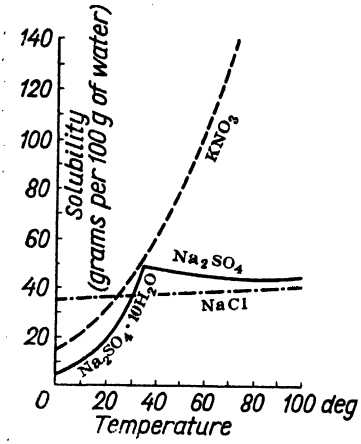


Fig. 80. Solubility curves

The solubility curve for sodium sulphate is more complicated. At 32.4° C its crystal hydrate decomposes and is converted into the anhydrous salt. This corresponds to the break in the solubility curve which is actually a combination of two separate curves: up to 32.4°, the saturated solution is in equilibrium with a precipitate of the formula $Na_2SO_4 \cdot 10H_2O$, while above this temperature, it is in equilibrium with the anhydrous salt Na_2SO_4. The sharp break in the curve shows that the solubilities of the two substances are substantially different. The same is observed in the case of crystal hydrates with different water contents: each of them has a characteristic solubility.

5) The variation in solubility with temperature is often taken advantage of for the purification of substances by *repeated crystallisation*. For example, if a hot saturated solution of a salt which is contaminated with impurities is cooled, a considerable portion of the salt will precipitate. At the same time, the impurities will remain in solution, as the latter is not saturated with them even in the cold. Any solid substance, the solubility of which depends greatly on the temperature, can be purified in this manner.

If the solubility of a substance varies little with temperature, it cannot be purified by repeated crystallisation. Such substances are purified by boiling down their saturated solutions, i. e., by removing part of the water from the latter. A certain portion of the substance will then crystallise out, while the impurities remain in solution.

Many (but far from all) solids form *supersaturated* solutions quite readily. The characteristic feature of such solutions is that the solute content in them is higher than that corresponding to its normal solubility under the same conditions. A supersaturated solution can

be prepared, for example, by carefully cooling a solution which is saturated at a higher temperature. If a "seed" is introduced in the form of a small crystal of the solute, all the excess of the latter (over the content corresponding to normal solubility) crystallises out. This shows that supersaturated solutions, unlike saturated solutions, are unstable systems and are able to exist only when there is no solid-phase solute in contact with them.

V-3. Properties of Solutions. The formation of a solution involves a change not only in the properties of the solute but in those of the solvent, as well. As applied to *dilute* solutions, these changes may

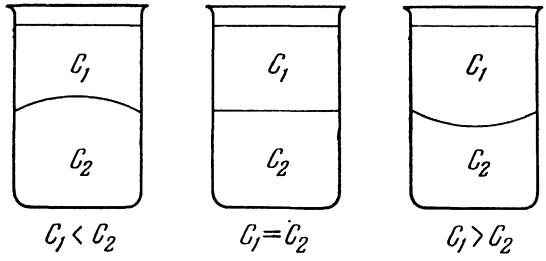


Fig. 81. Osmosis

be of two types: those dependent on, and those practically independent of the nature of the solute. The former include changes in colour, volume, etc., and are specific for each solute. The principal reason for the changes of the latter type is the decrease in the concentration of free solvent molecules due to dispersion of the other substance in it. Obviously, this decrease will be the greater, the larger the share of the total volume occupied by the solute molecules (together with their solvation sheaths), i. e., the higher its concentration.

One of the phenomena directly connected with changes in the concentration of the free molecules of the solvent is *osmosis*. This phenomenon takes place when two solutions of different concentration are in contact, being separated only by a *semipermeable* membrane which allows the molecules of the solvent to pass, but obstructs passage of the solute particles. Osmosis consists in spontaneous transfer of the solvent from one part of the system to the other.

Suppose a vessel divided in the middle by an elastic semipermeable membrane contains solutions, the molar concentrations of which are C_1 and C_2 in the upper and lower parts, respectively (Fig. 81). If $C_1 = C_2$, the concentration of the solvent will be the same in both solutions. Therefore, the number of solvent molecules passing through the membrane in both directions in unit time will also be the same. As a result, the total volumes of both solutions will remain unchanged.

However, it will be different if $C_1 \neq C_2$. Suppose, for example, that the upper solution is more dilute ($C_1 < C_2$). Since the concentration of the solvent is higher in the upper part, more molecules of the solvent will pass downwards than upwards through the semipermeable membrane in unit time. As a result, the volume of the upper solution will decrease, while that of the lower one will increase (the elastic membrane will bulge upwards). However, the downward passage of the solvent will lead to a simultaneous increase in C_1 and decrease in C_2, i. e., the concentrations will gradually become equal. When C_1 becomes equal to C_2, osmosis will cease.

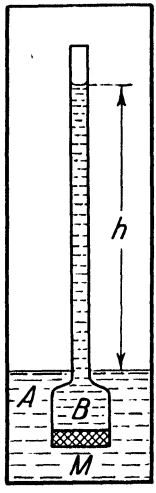


Fig. 82. Determining osmotic pressure

If the upper solution is more concentrated ($C_1 > C_2$), its volume will be similarly increased at the expense of the lower solution (the elastic membrane will bulge downwards). Osmosis ceases when the same number of solvent molecules pass through the semipermeable membrane in both directions in unit time. Solutions that satisfy this condition are called *isotonic*.

The osmotic properties of a solution (with respect to the pure solvent) can be quantitatively described by introducing the concept of *osmotic pressure*. This is the additional pressure which must be applied to a solution in order to stop osmosis. The effect of the pressure is to promote the escape of solvent molecules from the solution.

In Fig. 82, where A denotes a pure solvent, B—a solution and M—a semipermeable membrane, the osmotic pressure is determined by the height h of the liquid column. The higher the initial molar concentration of the solution, the higher the pressure, i. e., the higher the liquid in the tube will rise due to osmosis.

Most organic tissues possess the property of semipermeability. Therefore, osmotic phenomena are exceedingly important to life. The processes of food assimilation, metabolism, etc., are closely connected with the different permeabilities of tissues to water and various dissolved substances. On the other hand, osmotic phenomena elucidate certain points concerning the relation of an organism to its environment. For instance, owing to osmosis fresh-water fish cannot live in sea water, nor salt water fish in river water.

1) Departure of the cells of any tissue of the organism from their normal state usually involves sensations of pain. If we open our eyes under the water when bathing in a river, colic rapidly sets in owing to stretching of the cells of the eye tissue as a result of osmosis. The latter occurs because the total molar concentration of dissolved substances in the cell fluid of the eye tissue

is higher than the concentration of dissolved substances in river water. Sea water is considerably closer to isotonic with the cell fluid of the eye tissues. Therefore, it is possible to dive in sea water with open eyes without experiencing any painful sensations.

The *lowering of the vapour pressure* is another important consequence of the decrease in the concentration of free solvent molecules on formation of a solution.

It is known that a liquid is in equilibrium with its vapour when the number of molecules evaporating from its surface is equal to the number settling on its surface from the gaseous phase. Since part of the surface of the solution is occupied by more or less solvated molecules of the non-volatile solute, the number of solvent molecules evaporating from it in unit time decreases accordingly. Therefore, in the case of a solution, an equilibrium state is established at a lower vapour pressure than for the pure solvent.

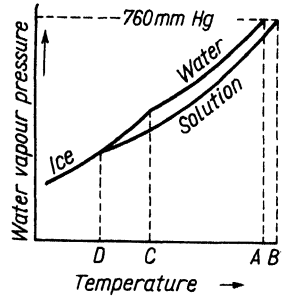


Fig. 83. Vapour pressure of water and of a solution

2) It is this, among other things, that causes the *deliquescence* of certain solid substances in the air. When coming into contact with a solid, the water vapour contained in the air may form a slight amount of solution on its surface. If the water vapour pressure over this liquid is lower than its partial pressure in the air, the vapour will continue to condense, and this will make the solid substance dissolve further. This continues until the concentration of the solution drops so low that the water vapour pressure over it becomes equal to the partial pressure of the water vapour in the air.

The most commonly known deliquescent substance is calcium chloride, which is sometimes placed between double window frames in winter: by absorbing water vapour from the air it prevents frosting of the panes.

If the vapour pressures of pure water and a solution are plotted against the temperature, the curve for the solution will be below the curve for the water (Fig. 83). From this, important conclusions follow concerning the boiling and freezing points of solutions.

A liquid begins to boil when its vapour pressure becomes equal to the external pressure, which under ordinary conditions is 760 mm Hg. As can be seen from Fig. 83, this occurs at a higher temperature, *B*, for a solution than for the pure solvent, *A*. The *elevation of the boiling point* depends, of course, on the concentration of the solution.

On the other hand, a liquid freezes when its vapour pressure becomes equal to the vapour pressure of the corresponding solid phase. From Fig. 83, it can be seen that the vapour pressure of ice is reached at a lower temperature, *D*, by a solution than by pure water, *C*. Hence it follows that solutions freeze at lower temperatures than pure solvents, and the *depression of the freezing point* depends on

the concentration of the solution. Thus, ocean water which contains 3.5% of dissolved salts freezes at —1.9° C instead of at 0° C.

V-4. Ionisation Hypothesis. Quantitative studies of the dependence of the properties of dilute solutions on the concentration of solutes showed that all these properties—vapour pressure lowering, boiling point elevation, freezing point depression, and osmotic phenomena—obey the same law, namely, the Raoult-Van't Hoff *Law of Dilute Solutions* (1886), which states that the *properties of dilute solutions vary in direct proportion to the number of dissolved particles*, i. e., to the molecular concentration of the solute.

This made it possible to develop methods for determining the molecular weights of many substances whose vapour density could not be measured. Although it is possible to use any of the above-mentioned common properties of dilute solutions for such determinations, the most frequently employed is depression of the freezing point. The reasoning will be clear from the following example.

Example. Studies of aqueous solutions of substances with known molecular weights show that when one gram-molecule is dissolved in 1000 g of water, the freezing point is depressed by 1.86° C. Consequently, according to the Raoult-Van't Hoff law, if $^1/_2$ gram-molecule is dissolved, the freezing point should be depressed by 0.93° C, if 0.1 gram-molecule is in solution, it should be depressed by 0.186° C, etc. Suppose it is required to determine the molecular weight of glucose. Analysis of this compound gives CH_2O as the simplest formula (the sum of the atomic weights is 30). Obviously, the true formula of glucose is $(CH_2O)_x$, where x may be equal to 1, 2, 3, etc. In order to find the value of x, 30 g of glucose is dissolved in 1000 g of water, and the freezing point of the resulting solution is determined. The experiment shows that it is depressed by 0.31° C, i. e., by 1/6 of 1.86° C. Consequently, 30 g corresponds to 1/6 gram-molecule, i. e., $x = 6$, and the true formula of glucose is $C_6H_{12}O_6$.

The theory of dilute solutions, which reduced the change in various properties to one simple law, was not, however, free of inherent contradictions which, as usual, served as an impetus to its further development. While fully confirmed by experiment for aqueous solutions of organic substances and solutions in other solvents, such as benzene, the conclusions of the theory were found to be inapplicable to aqueous solutions of acids, bases and salts. For example, a solution containing one gram-molecule of NaCl (58.5 g) per 1000 g of water showed a freezing point depression of 3.36° C, i. e., much greater than the theory demanded. The same was observed in the case of other aqueous solutions of salts, acids and bases—the depression of the freezing point (and the change in the other common

properties of solutions) was always *greater* than that expected theoretically.

The cause of this, could be sought along two lines: either the theory was incorrect with regard to aqueous solutions of acids, bases and salts or it was correct in this case, too, and the apparent departures from it were due to incorrect calculation of the number of dissolved particles. Since the effects were always larger than those required by the theory, it might be thought that dissolving, say, 100 molecules of NaCl would give more than 100 particles in the solution, i. e., that part of the molecules of common salt break down into smaller particles.

The problem was solved on the basis of the results of a study of the electrical conductivity of solutions. It was known that solutions in such solvents as benzene do not conduct electricity, and that only acids, bases and salts, i. e., those substances for which departures from the Raoult-Van't Hoff law are observed, conduct it in aqueous solution.

The *ionisation hypothesis* put forward by Arrhenius in 1887, related these special features of acids, bases and salts to their electrical conductivity in solution, and not only qualitatively explained both phenomena, but made it possible to calculate one of them from the results obtained in studying the other.

Essentially, the ionisation hypothesis consisted in the statement that molecules of acids, bases and salts in aqueous solution dissociate partly into separate *ions*. The more ions there are, the higher the electrical conductivity of the solution. But as the molecules dissociate into ions, the total number of dissolved particles increases, since two (or more) particles result from each molecule. Therefore, the Raoult-Van't Hoff law turned out correct for aqueous solutions of acids, bases and salts, too, if ions are regarded as separate particles as well as molecules.

Arrhenius, being a supporter of the "physical" theory of solutions (V-2), made no allowance for the interaction between the solute and the solvent, and believed that molecules dissociate into *free* ions, for example, according to the equation:

$$NaCl = Na^+ + Cl^-$$

Such isolated treatment of the ionisation process could not lead to a correct understanding of this process, which became possible only on the basis of a synthesis of Arrhenius' concepts and the chemical theory of solutions.

The first to point out the need for such a synthesis was the Russian scientist I. A. Kablukov (1891), who stated the problem in the following words: "It is our opinion that on breaking down the molecules of a dissolved body into ions water combines with the latter

to form unstable compounds which are in a state of dissociation; Arrhenius holds that the ions move freely like the separate atoms originating from the dissociation of halide molecules at a high temperature".

According to Kablukov the ions in aqueous solutions are not free, but are *hydrated*, and hydration is the principal cause of the ionisation of the molecules. In order to distinguish hydrated ions from

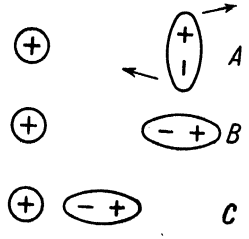


Fig. 84. Orientation of a polar molecule near an ion

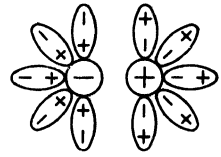


Fig. 85. Orientation of dipoles about an ionic molecule

free (unhydrated) ions, the positive charges of the former are denoted by dots and the negative charges, by dashes. Thus, the ionisation of NaCl in solution should be represented not as given above, but by the equation:

$$NaCl = Na^{\cdot} + Cl'$$

Kablukov's interpretation of the ionisation of solutes is now universally recognised.

Positively charged ions are usually called *cations*, and negatively charged ions, *anions*. The dissociation of ionic molecules into separate ions can be represented as follows. The polar water molecules orient themselves around each of the ions of a molecule of, say, NaCl in solution, as shown schematically in Fig. 84 for the case of Na^+. In position *A*, the negative end of the dipole is attracted to the ion, while the positive end is repelled. As a result, the molecule turns into position *B*. But the magnitudes of the positive and negative charges of the dipole are equal, while their distances from the ion are different. Therefore, the attraction is stronger than the repulsion, and the molecule is drawn towards the ion (*C*).

It is obvious that similar phenomena will occur in the vicinity of the negative ion. Thus, the water molecules attracted to the ions collect around them, as shown in Fig. 85. But the ions are attracted by the dipoles with the same force as the latter are attracted by the ions. As a result, the attraction between the ions is weakened so greatly that the energy of molecular motion in the solution is sufficient to separate them from each other.

In the case of solvents less polar than water, the dipoles orient themselves around the ions to a much smaller degree. The consequent weakening of the forces of attraction between the ions is accordingly less significant, and, as a result, the energy of molecular motion in the solution may prove insufficient to separate them from each other. That is why no dissociation of molecules into ions is observed, as a rule, in such low-polarity solvents as benzene, and is comparatively weak in solvents of intermediate polarity, such as alcohol.

1) Since the crystals of most salts consist of free ions, their dissolving may begin with separate cations and anions (always in equivalent proportions), and not molecules as such, passing into solution. The partial formation of molecules is, in this case, a secondary process which takes place in the solution. The final outcome, corresponding to the equilibrium state, obviously remains the same as that discussed above in the more general approach to ionisation in solutions.

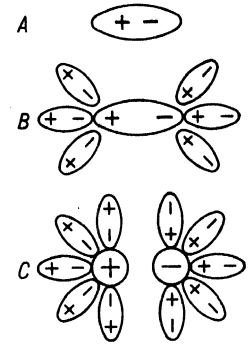
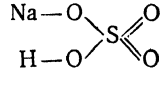


Fig. 86. Transformation of polar structure into ionic structure

Ionisation is observed in aqueous solutions not only in the case of ionic molecules, but also for certain molecules which are polar in the free state. An example of this is HCl. The preliminary stage of dissociation in such cases is conversion of the polar structure into an ionic structure under the influence of the water molecules; this is schematically shown in Fig. 86. The particles of water attracted to the ends of the dissolved polar molecule (*A*) cause the poles of the dipole to separate (*B*), which may result in the molecule acquiring an ionic structure (*C*).

2) The main factor that enables the polar bonds of a solute to ionise, is usually not the total polarity of the solvent (as characterised by the dielectric constant), but the presence in the solvent molecule of an atom capable of sufficiently active interaction with one of the atoms of the polar bond (most frequently, with a hydrogen atom).

In the case of more complex molecules, ionisation proceeds primarily along ionic bonds and, subsequently, along those of the polar bonds which are capable of being transformed into ionic bonds with sufficient ease. Dissociation into ions does not, as a rule, occur along low-polarity and non-polar bonds. As an example, consider sodium bisulphate:



In this molecule, the Na—O bond is ionic, the H—O bond is markedly polar and the bonds between the sulphur and the oxygen

are of low polarity. The $Na^{\cdot}$ ions split off first, then the $H^{\cdot}$ ions, but no ions whatsoever are formed along the sulphur—oxygen bonds.

V-5. Electrolytic Dissociation. Substances that conduct electricity in aqueous solution—salts, bases and acids—are called *electrolytes*, while those which do not conduct electricity are called *non-electrolytes*. In connection with this, after experimental confirmation, the hypothesis of ionisation came to be known as the *theory of electrolytic dissociation*.

The ions formed on dissociation of different electrolytes should naturally differ in character. In salt molecules dissociation always results in the formation of cations of the metal and anions of the acid radical. Therefore, *salts* may be defined as *compounds that yield ions of a metal and of an acid radical in aqueous solution*. Examples:

$$KNO_3 = K^{\cdot} + NO_3' \qquad Na_2SO_4 = 2Na^{\cdot} + SO_4''$$
$$MgCl_2 = Mg^{\cdot\cdot} + 2Cl' \qquad MgSO_4 = Mg^{\cdot\cdot} + SO_4''$$

In molecules of bases, of the two oxygen bonds—one with a metal and one with hydrogen—the former is the more readily ionised. Therefore, dissociation results in metal cations (which may be dissimilar) and hydroxyl anions (OH') which are common to all bases. Thus, *bases* may be defined as *compounds that yield hydroxyl ions in aqueous solution*. Examples:

$$NaOH = Na^{\cdot} + OH' \qquad Ba(OH)_2 = Ba^{\cdot\cdot} + 2OH'$$

The number of hydroxyl groups capable ot ionising, determines the *acidity* of the base (II-5).

Finally, acids dissociate to form hydrogen cations and anions of an acid radical. These radicals may be different but a feature common to all acids is the formation of hydrogen ions in aqueous solution. Consequently, *acids* may be defined as *compounds that yield hydrogen ions in aqueous solution*. Examples:

$$HNO_3 = H^{\cdot} + NO_3' \qquad H_2SO_4 = 2H^{\cdot} + SO_4''$$

The number of hydrogen atoms capable of ionising determines the *basicity* of the acid.

1) The free hydrogen ion, i. e., the nucleus of a hydrogen atom—a bare proton—combines instantly in solution with one molecule of water, to form a complex *oxonium* ion, H_3O^+. The latter is further hydrated like all ordinary ions. Therefore, its charge in solution is denoted by a dot ($H_3O^{\cdot}$) instead of a plus. Oxonium ion formation plays an important part in the dissociation of acids, and is the principal cause of the conversion of the polar structure of an acid molecule into an ionic structure. Consequently, the dissociation into ions of, for example, a molecule of HCl would be more accurately expressed by the equation $H_2O + HCl = H_3O^{\cdot} + Cl'$. However, this is not necessary, since in the usual notation the hydrogen ion is understood to be hydrated ($H^{\cdot}$, not H^+).

2) The definitions of acids and bases given above from the point of view of the classical theory of electrolytic dissociation are applicable only to aqueous solutions. In order to be able to take account of the chemical nature of these substances in non-aqueous media, a *proton* theory of acids and bases was worked out by Brönsted in 1923, based on the following definitions: acids are substances which *donate* protons; bases are substances which *accept* protons.

According to the proton theory, the relation between an acid and a base is given by the following scheme: base + proton = acid. In a system of two substances capable of reacting with a proton, the base is always the one which is more firmly linked with the proton, i. e., has a higher *proton affinity*. For example, in the series $NH_3—H_2O—HF$ proton affinity decreases from left to right. Therefore, in a mixture with ammonia, water behaves as an acid, while in a mixture with HF, it behaves as a base:

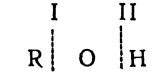
$$NH_3+H_2O=NH_4^++OH^- \quad \text{and} \quad H_2O+HF=H_3O^++F^-$$

While in the case of acids, the proton interpretation coincides with the usual treatment and only extends it to non-aqueous solutions, an essentially different approach results in the case of bases. Thus, NaOH is considered to be a base not because it is capable of yielding a hydroxyl ion, but because this hydroxyl ion is capable of receiving a proton (to form an H_2O molecule). Consequently, the base is not NaOH as a whole but only the OH^- ion.

Since water is always in equilibrium with its hydrogen and hydroxyl ions: $H_2O \rightleftarrows H^\cdot + OH'$, each change in concentration of either of these ions necessarily involves an equivalent change in the concentration of the other. Therefore, in aqueous solutions, both the classical and the proton approach practically lead to the same results.

As has already been noted (V-4), the nature of the electrolytic dissociation of a particular molecule is, to a considerable extent, predetermined by the polarity of its valency bonds. Other things being equal, the more polar the bond, the more readily it is ionised. However, the polarity of the bond between any two elements is not a permanent property of the latter, but also depends more or less on the other elements combined with them. For example, the polarity of the bond between oxygen and hydrogen in compounds of the ROH type depends on the chemical nature of the atom or radical R. If the latter possesses clearly defined metallic properties, the bond between R and O is highly polar (up to and including its conversion into the ionic type), whereas the O—H bond, in this case, has low polarity. On the other hand, if the atom or radical R possesses clearly defined non-metallic properties, the bond between it and oxygen has low polarity, and the O—H bond becomes highly polar. Roughly speaking, the nature of both bonds depends on the relative ease with which the oxygen detaches electrons from R or H.

From the foregoing it follows that compounds of the ROH type may dissociate, generally speaking, in two ways:



Predominance of one or the other way depends on the relative polarity of the R—O and O—H bonds. For example, Na is considerably more metallic than hydrogen, and therefore, NaOH dissociates, in practice, only as a base (I). On the other hand, in nitric acid ($HONO_2$), the NO_2 radical is considerably more non-metallic than hydrogen, and it dissociates, in practice, only as an acid (II).

What will result when R is not very different from hydrogen in its chemical nature? Obviously in this case, the polarities of both

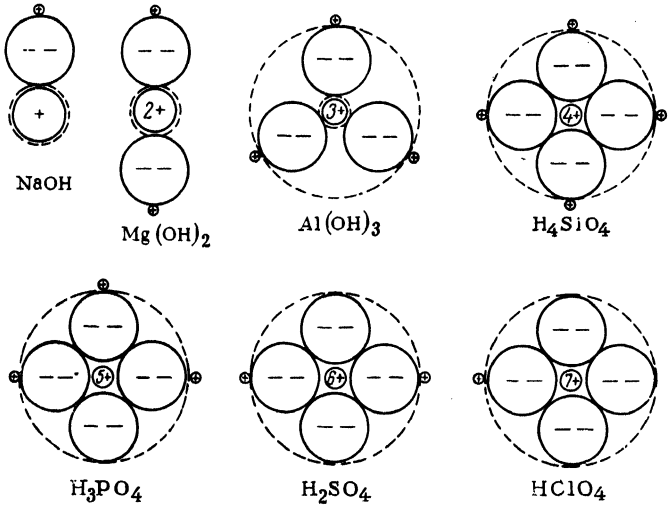


Fig. 87. Type of dissociation depending on charge and radius R

bonds will be close to each other, and therefore both ways of dissociating should be possible. *Compounds which are able to lose both hydrogen ions and hydroxyl ions under the same conditions,* are called *amphoteric.* Predominance of one or the other kind of dissociation of amphoteric compounds will depend on the relative polarity of the bonds in question.

Starting from simplified concepts concerning the formation of ionic bonds in all cases (III-4), we can graphically trace the relation between the kind of dissociation of compounds of the ROH type and the charge and radius of R. The schemes shown in Fig. 87 refer to derivatives of the elements of the third period from sodium to chlorine. The dotted lines indicate the observed trends of dissociating.

The larger the charge of each of two oppositely charged particles and the smaller its radius, the stronger the forces of attraction between them. Owing to its very small size, the hydrogen ion in NaOH and $Mg(OH)_2$ is bound to the oxygen atom more firmly than the metal ion (in spite of the larger charge of magnesium). Owing to

this, both substances dissociate as bases. As a result of the increase in the charge of R and the decrease in its radius when R is aluminium, the two bonds become close in nature, and $Al(OH)_3$ is a typical amphoteric electrolyte. Finally, in the remaining four compounds (Fig. 87), owing to further increase in the charge of R and the decrease in its radius, the bond between the oxygen and the hydrogen becomes weaker, and these compounds dissociate as acids.

It follows from the above that, theoretically, the amphoteric state is a common property of electrolytes of the ROH type. However, the *probability* of dissociation in either way (which is determined chiefly by the nature of the bonds) is, in many cases, so different that for practical purposes only one of these ways need be considered. Thus, the division of compounds of the ROH type into two opposite classes—bases and acids—which was outlined as far back as the beginning of the 19th century (II-5), preserves its significance to a certain extent.

The simplest amphoteric compound is *water*, which produces H^+ and OH^- ions on dissociation. However, this dissociation is so small that the concentration of hydrogen and hydroxyl ions in pure water is only 10^{-7} g-ions/litre each.

Experiment shows that the content of ions in water does not change in time. Hence it follows that ionisation is accompanied by the reverse process, i. e., the formation of undissociated molecules from ions (*molarisation*). A similar reverse reaction must also take place in a solution of an electrolyte: if the ions collide during their random motion, they may reform a molecule. Thus, *electrolytic dissociation is a reversible process*: at any given moment ions are being formed due to the ionisation of molecules, and molecules are being formed due to the collisions between ions. It is obvious that, as a result, equilibrium will be established: just as many molecules will be formed in unit time as are dissociated. For example, in the case of NaCl, this may be represented by the scheme:

$$\xrightarrow{\text{ionisation}}$$

$$NaCl \rightleftarrows Na^+ + Cl^-$$

$$\xleftarrow[\text{molarisation}]{}$$

Ionic molecules such as NaCl are often called "ion pairs".

The quantitative characteristic of the equilibrium state of an electrolyte is given by its *degree of dissociation*, i. e., *the ratio of the number of molecules dissociated into ions to the total number of dissolved molecules*. This ratio is often multiplied by 100 to express the dissociated fraction as a percentage of the total number of molecules. The numerical values of the degrees of dissociation can be found

from the deviations of electrolytes from the Raoult-Van't Hoff law in its molecular form.

Example. From the depression of the freezing point, find the degree of dissociation of NaCl in a solution containing one gram-molecule of the salt (58.5 g) per thousand grams of water. The normal depression for such a solution should be 1.86° C, whereas actually it amounts to 3.36° C (V-4). Since in determining the degree of dissociation, it is important to know only the ratio between dissociated and dissolved molecules, and not this absolute numbers, the reasoning is quite simple. Suppose that 100 molecules of NaCl are dissolved, and that in the absence of dissociation these should give a depression of 1.86° C. Actually, the depression was larger by $3.36 : 1.86 = 1.80$ times. Consequently, the depression found corresponds to that which would be produced by 180 and not by 100 dissolved particles, i. e., of the 100 molecules taken, such a fraction dissociated into ions that in all, 180 particles were formed. This can only happen if 80 out of every 100 dissolved molecules have dissociated into ions, since we then have: 20 undissociated molecules + 80 $Na^{\cdot}$ ions + + 80 Cl' ions, giving 180 particles in all. Thus, the degree of dissociation of NaCl in this solution is equal to 0.80, i. e., 80% of all the dissolved molecules are dissociated.

Changes in concentration of a solution may affect ionisation and molarisation variously. Since the former process is influenced only by the particles of water immediately surrounding the electrolyte molecule, dilution has no substantial effect on the rate of ionisation. On the other hand, the rate of molarisation decreases appreciably, because it depends on the number of collisions between unlike ions, which decreases on dilution of the solution. As a result, the equilibrium is displaced, *and the degree of dissociation of the electrolyte increases when the solution is diluted.* Consequently, when discussing the degree of dissociation of electrolytes, the concentration of their solutions should be indicated.

In working with solutions of electrolytes, it is convenient to use what are known as *normal* concentrations. A *solution is said to be normal (N) if it contains one gram-equivalent of solute per litre.* Gram-equivalent or normal weights are found by dividing the molecular weight of the electrolyte by the number of valency bonds between the ions forming its molecule. For example, the equivalent weights of HNO_3, $Ba(OH)_2$, and $Al_2(SO_4)_3$ are M, $M/2$ and $M/6$, respectively. The main advantage of this method of expressing the concentrations of electrolytes is that *any* alkali, for instance, will react with *any* acid of the same normality in equal volumes. As to methods of expressing the concentration, all that was said above about molar solutions (V-2) applies to normal solutions.

Different electrolytes of equal normality are dissociated to a different degree. The simplest case is that of salts, where the bond between the metal and the acid radical is usually of an ionic nature. However, here, too, the conditions for dissociation may vary in some cases. For example, the NaCl molecule is built up of singly charged ions, while that of $MgSO_4$ is built up of doubly charged ions. Obviously, in the latter case, the forces of attraction between the ions must be greater. Hence, other things being equal, the degree of dissociation of a salt of the type $\overset{++}{M}\overset{--}{A}$ will be lower than for a salt of the type $\overset{+}{M}\overset{-}{A}$. Salts of the $\overset{++}{M}\overset{-}{A}_2$ and $\overset{+}{M}_2\overset{--}{A}$ types, e. g., $MgCl_2$ and Na_2SO_4, will be intermediate in this respect.

The table below shows the experimentally found degrees of dissociation of different types of salts, as well as those of certain acids and bases; the figures vary over a wide range, but are always greater than the degree of dissociation of water which also appears in the table.

Degree of Dissociation (α) in 0.1 *N* Solutions

Electrolyte	α	α, %	Electrolyte	α	α, %
Salts			Acids		
Types $\overset{+}{M}\overset{-}{A}$	0.80-0.90	80-90	CH_3COOH . .	0.014	1.4
			H_2CO_3	0.0017	0.17
" $\overset{++}{M}\overset{-}{A}_2$	0.70-0.80	70-80	HCN	0.0001	0.01
" $\overset{+}{M}_2\overset{--}{A}$			H_2O	2×10^{-9}	2×10^{-7}
" $\overset{++}{M}\overset{--}{A}$	0.35-0.45	35-45	Bases		
Acids			KOH, NaOH	0.90-0.95	90-95
HNO_3, HCl . .	0.90-0.95	90-95	$Ba(OH)_2$ . .	0.77	77
H_2SO_4	0.60	60	NH_4OH . . .	0.014	1.4
HF	0.08	8			

Electrolytes that are 30 per cent or more dissociated under the conditions indicated are usually termed *strong*, those dissociated between 30 and 3 per cent—*medium strength*, and below 3 per cent—*weak* electrolytes. As is evident from the above table, all *salts* (with very few exceptions which will be indicated in the following) are *strong* electrolytes.

3) The experimentally found degrees of dissociation of strong electrolytes are only apparent in the sense that they do not correspond to the actual degree of dissociation of the corresponding molecules into ions. This discrepancy is due to the electrostatic interaction between the ions, which is rather pronounced in solutions of strong electrolytes (where ions are numerous) and affects the results of the experimental determinations (reducing them). If allowance is made

for this interaction it is found that in dilute solution strong electrolytes are dissociated almost completely (at one time it was even thought that they were completely dissociated). On the other hand, for weak electrolytes (solutions of which contain relatively few ions) this interaction is insignificant and the apparent degrees of dissociation practically coincide with their true values. In spite of the discrepancy between the actual and apparent degrees of dissociation of strong electrolytes, the latter can still be used for comparing the strength of acids, bases and salts, since their apparent degrees of dissociation are approximately proportional to the true values.

That undissociated molecules are actually present in aqueous solutions of strong electrolytes can sometimes be detected by direct experiment. Thus, there is an appreciable vapour pressure of HCl over concentrated hydrochloric acid, while $AgClO_4$, a typical strong electrolyte, can be partially extracted from its aqueous solutions (above 2.5 *M*) by benzene. Obviously, the existence of undissociated molecules in sufficiently concentrated solutions of strong electrolytes, as established by these facts, leaves no grounds to deny, *in principle*, their presence in more dilute solutions.

Electrolytes with multivalent ions dissociate *stepwise*, this being most clearly observed in polybasic acids. For example, the first ionisation step of phosphoric acid is:

$$H_3PO_4 \rightleftarrows H^{\cdot} + H_2PO_4'$$

Owing to the negative charge of the H_2PO_4' ion, the second hydrogen ion is detached with much greater difficulty than the first, and therefore, the second step of ionisation

$$H_2PO_4' \rightleftarrows H^{\cdot} + HPO_4''$$

is far less complete than the first.

The last hydrogen ion has to break away from a doubly charged negative ion. Therefore, the third stage of ionisation in a solution of phosphoric acid,

$$HPO_4'' \rightleftarrows H^{\cdot} + PO_4'''$$

hardly occurs at all.

Electrolytic dissociation is a reversible process resulting in establishment of an equilibrium. For example, for acetic acid we have:

$$CH_3COOH \rightleftarrows CH_3COO' + H^{\cdot}$$

Applying the law of mass action to this equilibrium, we obtain:

$$\frac{[CH_3COO'][H^{\cdot}]}{[CH_3COOH]} = K$$

In this case the equilibrium constant K refers to the electrolytic dissociation of CH_3COOH, and is therefore called the *dissociation constant*. The higher its value, the more ionised is the compound in question.

4) If the molar concentration of an electrolyte which is dissociated into two ions is denoted by C, and its degree of dissociation is denoted by α, the concentration of each of the ions will be αC, and the concentration of the undis-

sociated molecules will be $(1-\alpha)C$. Consequently, according to the law of mass action, we have:

$$\frac{\alpha C \cdot \alpha C}{(1-\alpha)C} = K, \quad \text{or} \quad K = \frac{\alpha^2}{1-\alpha} C$$

This expression, known as the *dilution law*, relates the degree of dissociation and the dissociation constant, and permits the one to be calculated from the other. The experimental data for acetic acid are given below as an example.

C	0.001	0.005	0.01	0.05	0.1	0.2
α	0.124	0.060	0.042	0.019	0.014	0.0095
$K \times 10^5$	1.80	1.82	1.83	1.85	1.85	1.82

In view of the low value of α in not very dilute solutions, $1-\alpha$ may be regarded as equal to 1 in approximate calculations for weak electrolytes. The dilution law then takes the form $K = \alpha^2 C$, whence $\alpha = \sqrt{K/C}$.

5) From the above expression for the dissociation constant of CH_3COOH given in the main text, it can be seen that when $[CH_3COOH] = [CH_3COO']$, the concentration of hydrogen ions becomes numerically equal to the dissociation constant. In a solution of a weak monobasic acid this situation arises when it is half neutralised by a strong alkali. Determination of hydrogen ion concentration in such a solution, consequently, enables the value of the dissociation constant to be found directly. Similar reasoning is valid for weak monoacid bases.

Since the dissociation constant does not alter with changes in concentration of the solution, it provides a more general characteristic of the electrolyte than the degree of dissociation. This is true, however, only of weak electrolytes, the solutions of which contain comparatively few ions. On the other hand, strong electrolytes are appreciably influenced by electrostatic interaction between their ions, which results in deviations from the law of mass action and changes in the values of K on diluting the solutions. Therefore, in the table below, dissociation constants are given only for several weak electrolytes.

Dissociation Constants

Electrolyte	K	Electrolyte	K
H_3PO_4 K_1	7×10^{-3}	H_2O_2 K_1	2×10^{-12}
K_2	6×10^{-8}	CH_3COOH	2×10^{-5}
K_3	3×10^{-12}	HCN	7×10^{-10}
H_2CO_3 K_1	4×10^{-7}	H_2O	2×10^{-16}
K_2	5×10^{-11}	NH_4OH	2×10^{-5}

The effect of the increase in the charge of the dissociating particle during consecutive dissociation can be seen by comparing the constants corresponding to the ionisation of the first, second and third hydrogen atoms of phosphoric acid (K_1, K_2, K_3).

6) It has been found possible to extend the law of mass action to strong electrolytes by replacing the total, analytically determined concentration, C, by *effective* concentrations (i. e., those which manifest themselves in action)—so-called *activities*, a. The relation between these two values is given by the expression $a = fC$, where f is the *activity coefficient*. The latter is a quantity which represents the total of interactions between force fields, taking place in the given system. Therefore, its physical meaning does not lend itself to unambiguous interpretation, and it remains an essentially empirical factor.

The activity coefficient of a substance can be determined by several experimental methods. Usually, there is good agreement between the results of independent determinations. The value of the activity coefficient of a solute depends on the concentration of the solution, its general composition, temperature, etc.

By taking advantage of the fact that the dissociation constant of a weak electrolyte is constant at a given temperature, the concentration of its separate ions in solution can be altered artificially. This method is often employed to reduce the concentration of hydrogen or hydroxyl ions, i. e., the *acidity* or *alkalinity* of the solution.

Suppose, for example, that it is required to reduce the acidity of a solution of acetic acid. According to the foregoing, we have for acetic acid:

$$\frac{[CH_3COO'][H^\cdot]}{[CH_3COOH]} = K$$

If the concentration of CH_3COO' ions is increased, then the concentration of hydrogen ions must decrease since K is constant. An increase in the concentration of CH_3COO' ions can be effected very simply by adding some salt of acetic acid, such as CH_3COONa. Since this salt is strongly dissociated, it will provide many CH_3COO' ions, and there will be a marked decrease in the acidity of the solution. Similarly, addition of an ammonium salt, say, NH_4Cl, to an ammonium hydroxide solution will reduce the concentration of OH' ions, i. e., the alkalinity of the solution.

When the law of mass action is applied to the dissociation of pure water, we have:

$$\frac{[H^\cdot][OH']}{[H_2O]} = K \quad \text{or} \quad [H^\cdot][OH'] = K[H_2O]$$

Denoting $K[H_2O]$ by K_w, we obtain $[H^\cdot][OH'] = K_w$. The quantity K_w is equal to the product of the concentrations of the hydrogen and hydroxyl ions in water, and is, therefore, called the *ion product of water*. Its numerical value can easily be found, since K and $[H_2O]$ are known: the dissociation constant of water, K, equals 1.8×10^{-16}, while the concentration of undissociated water molecules is, owing to insignificant dissociation, practically equal to the total number of gram-molecules of water per litre, i. e., $1000/18 = 55.56$. Consequently, $K_w = 1.8 \times 10^{-16} \times 55.56 = 1 \times 10^{-14}$.

The ion product of water is an extremely important value, since it enables the concentration of OH' ions to be found for any aqueous solution with a known concentration of $H^{\cdot}$ ions and vice versa. For example, in 0.1 N acetic acid, the hydrogen ion concentration is 1.4×10^{-3} g-ions/l. Hence, in this solution,

$$[OH'] = \frac{K_w}{[H^{\cdot}]} = \frac{1 \times 10^{-14}}{1.4 \times 10^{-3}} = \frac{10 \times 10^{-15}}{1.4 \times 10^{-3}} = 7.1 \times 10^{-12}$$

For pure water, $[H^{\cdot}] = [OH'] = \sqrt{K_w} = 10^{-7}$ g-ions/l.

By using the ion product of water, the acidity or alkalinity of any solution can be expressed in terms of hydrogen ion concentration.

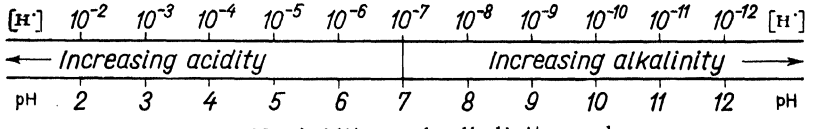


Fig. 88. Acidity and alkalinity scale

In a neutral solution, $[H^{\cdot}]$ (often denoted by C_H) is, according to the foregoing, equal to 10^{-7}. Obviously, it is higher in an acid solution and lower in an alkaline. Thus, as a solution becomes more and more acid, C_H will pass through the values 10^{-6}, 10^{-5}, 10^{-4}, etc. And, conversely, as the solution becomes more and more alkaline, we shall have: $C_H = 10^{-8}$, 10^{-9}, 10^{-10}, etc.

The quantitative designation of the acidity or alkalinity of a solution may be still further simplified by using the *hydrogen ion concentration index* (pH). This index is defined by the relation: $pH = -\log C_H$. Thus a neutral solution will have $pH = 7$, an acid solution will have $pH = 6, 5, 4$, etc., and an alkaline solution will have $pH = 8, 9, 10$, etc. (Fig. 88). Of course, the pH index may also have any intermediate value between these integers.

In practice, the acidity or alkalinity of a solution is conveniently determined by means of *indicators*—substances which change colour depending on the relative concentrations of $H^{\cdot}$ and OH' ions. The best known indicator is *litmus*, which turn red when there is a surplus of $H^{\cdot}$ ions, i. e., in acid solution, blue when there is a surplus of OH' ions, i. e., in alkaline solution, and violet in neutral solution. If a filter paper impregnated with litmus ("litmus paper") is immersed in the solution to be tested, its colour shows at once whether the solution is acid, alkaline or neutral.

7) The colour change of different indicators occurs at different hydrogen ion concentrations, which is important for chemical analysis. For example, litmus changes its colour (red to blue) at approximately $pH = 7$, methyl orange (red to yellow) at $pH = 4$, and phenolphthalein (colourless to pink), at $pH = 9$.

With the aid of a set of different indicators, the pH value of a solution can be found very accurately.

The ionisation of an electrolyte rarely involves an appreciable evolution or absorption of heat. Therefore, as a rule, it is hardly influenced by minor changes in temperature.

Water is a special case, since its dissociation is accompanied by a considerable absorption of heat:

$$H_2O + 13.7 \text{ kcal} \rightleftarrows H^{\cdot} + OH'$$

Therefore, *the degree of dissociation of water sharply increases on heating*. This phenomenon will be encountered further on, as it is of great importance for certain reactions in aqueous solutions.

V-6. Ionic Reactions. The discussion in the previous section shows that in a dilute solution of a strong electrolyte the solute is almost exclusively in the form of ions. Since the latter are not directly linked with each other, each of them possesses its own definite properties, whatever the compound in which it was introduced into the solution. For example, no matter what the acid, the hydrogen ions always cause litmus to turn red, impart a sour taste to the solution, etc. Therefore, certain properties of a dilute solution of a strong electrolyte are essentially the sum total of the properties of its individual constituent ions.

Concentrated solutions of strong electrolytes and solutions of weak electrolytes are different in this respect. Along with ions, these solutions contain considerable quantities of undissociated molecules, the properties of which may be substantially different from those of their ions.

If dilute solutions of two electrolytes, AX and BY, are mixed (A and B being positive ions, and X and Y, negative), the liquid will contain all the four possible ions: $A^{\cdot}$, $B^{\cdot}$, X' and Y'. Since they are in continuous random motion, they may collide at times in the following combinations:

1) $A^{\cdot} + B^{\cdot}$ 3) $A^{\cdot} + X'$ 5) $A^{\cdot} + Y'$
2) $X' + Y'$ 4) $B^{\cdot} + Y'$ 6) $B^{\cdot} + X'$

Owing to the likeness of charges, collisions of the first two types will not result in combination. But collisions of the other four types may lead to the formation of molecules; cases 3 and 4 will produce the initial substances, while cases 5 and 6 will produce new substances, AY and BX. The possibility of formation of each of the four substances in the solution is represented by the equation

$$AX + BY \rightleftarrows AY + BX$$

which shows that, regardless of whether the initial substances are AX and BY or AY and BX, the same equilibrium state finally results.

The position of equilibrium in such a system depends on the properties of the substances which may be formed. The principal factor is the probability of formation of one or other of them, which depends on the relative number of collisions between the corresponding ions.

Suppose the concentrations of all four ions are approximately the same, as, for example, in the system:

$$NaNO_3 + HCl \rightleftarrows HNO_3 + NaCl$$

where all the substances participating in the reaction are almost equally strongly dissociated. The chances of formation of each of the substances are, in this case, approximately equal. Schematically, this is denoted by the equal lengths of the arrows above and below the equation.

If one of the substances is more weakly dissociated than the others, the corresponding ions, in forming it, will combine into undissociated molecules, their concentration in the solution will decrease, and the chances of formation of substances by the reverse reaction will be reduced. As a result, the equilibrium will shift towards the formation of the slightly dissociated substance. This is the case, for instance, in the system:

$$CH_3COONa + HCl \rightleftarrows CH_3COOH + NaCl$$

Owing to the comparatively weak dissociation of acetic acid, the concentrations of CH_3COO' and $H^{\bullet}$ ions are drastically reduced. This reduces the probability of their reaction with $Na^{\bullet}$ and Cl' ions which would lead to the formation of CH_3COONa and HCl. Comparing this system with the preceding one, we have:

System		System	
$NaNO_3 + HCl \rightleftarrows HNO_3 + NaCl$		$CH_3COONa + HCl \rightleftarrows CH_3COOH + NaCl$	
Much: $Na^{\bullet}$, NO', $H^{\bullet}$, Cl'		$Na^{\bullet}$, Cl', CH_3COOH	
Little: $NaNO_3$, HCl, HNO_3, NaCl		CH_3COO', $H^{\bullet}$, CH_3COONa, HCl, NaCl	

If a salt of hydrocyanic acid, which is a very weak acid, is taken instead of CH_3COONa, the equilibrium will shift still further to the right,

$$NaCN + HCl \rightleftarrows HCN + NaCl$$

From this, there follows an extremely important rule: *reactions between ions proceed in the direction of the formation of slightly dissociated substances.* The equilibrium in the last considered reaction is so far displaced to the right that the reaction can be regarded as

practically irreversible. Hence, it follows, among other things that *strong acids liberate weak acids from their salts.*

A decrease in the concentration of certain ions in a solution and the attendant equilibrium shift may be caused not only by the formation of a slightly dissociated compound, but also by one of the substances leaving the "sphere of the reaction". If, for example, one of the resultants of a reaction is volatile under the conditions of the experiment, it will be driven off from the system as a gas, and thus reduce the possibility of the reverse reaction. In most cases, volatile compounds are also only slightly dissociated, but the opposite is also possible. Thus, if we take dilute solutions of NaCl and H_2SO_4, then in the system

$$2NaCl + H_2SO_4 \rightleftarrows Na_2SO_4 + 2HCl$$

an equilibrium will be established, which is displaced somewhat to the left (because H_2SO_4 is less dissociated than HCl). But if NaCl and H_2SO_4 solutions are concentrated, the equilibrium can be displaced completely to the right by heating, owing to evolution of the hydrogen chloride (a volatile substance is often denoted by an arrow pointing upwards):

$$2NaCl + H_2SO_4 \rightleftarrows Na_2SO_4 + 2HCl\uparrow$$

More often than not, one has to deal with the formation of sparingly soluble substances which leave the sphere of the reaction in the form of a precipitate (often denoted by an arrow pointing downwards). It is apparent that in this case the concentration of the corresponding ions also decreases, and the possibility of a reverse reaction is also reduced. For example, in the system

$$AgNO_3 + HCl \rightleftarrows HNO_3 + AgCl\downarrow$$

the equilibrium is practically wholly displaced to the right, owing to the low solubility of AgCl.

In ionic form, the equation for the previous reaction is written as:

$$Ag^{\cdot} + NO_3' + H^{\cdot} + Cl' = H^{\cdot} + NO_3' + AgCl\downarrow$$

Since the $H^{\cdot}$ and NO_3' ions remain unchanged, they can be excluded from the equation. The latter then takes the form:

$$Ag^{\cdot} + Cl' = AgCl\downarrow$$

The equation in this more general form shows that the formation of a white, practically insoluble precipitate of AgCl takes place in all cases when an $Ag^{\cdot}$ ion encounters a Cl' ion, regardless of the nature of the other ions. Therefore, $AgNO_3$ can serve as a means of detecting

the presence or absence of Cl′ ion in a solution, i. e., as a *test* for Cl′ ion. In turn, HCl can be used as a test for the $Ag^{\cdot}$ ion.

Since strong electrolytes are almost completely dissociated in very dilute solutions, the solubility of slightly soluble salts is sometimes conveniently expressed by means of the *solubility product*, S, which is the *product of the concentrations of the ions of a slightly soluble strong electrolyte in its saturated solution.* For example, in a saturated solution of AgCl under ordinary conditions, $[Ag^{\cdot}] = [Cl'] = 1 \times 10^{-5}$ gram-ions/litre. Hence, $[Ag^{\cdot}][Cl'] = 1 \times 10^{-10}$. In the general case of a slightly soluble strong electrolyte of the type A_xB_y, the expression for S has the form: $S = [A]^x[B]^y$. The numerical values of the solubility products for various substances may differ widely. They are very important in chemical analysis.

The reactions considered above are combined under the general heading of *exchange* or *double decomposition reactions*, since in these reactions one pair of substances is formed from another pair by simple exchange of ions. Theoretically, double decompositions are always *reversible*, a definite state of equilibrium corresponds to each system under given conditions. This equilibrium shifts (often practically completely) towards the formation of slightly dissociated, sparingly soluble or highly volatile substances.

Processes are often encountered involving sparingly soluble compounds, both among the reactants and the resultants, for example:

$$CaCO_3\downarrow + Na_2SO_4 \rightleftarrows CaSO_4\downarrow + Na_2CO_3$$

$$BaCO_3\downarrow + Na_2SO_4 \rightleftarrows BaSO_4\downarrow + Na_2CO_3$$

The equilibrium in these systems shifts towards the formation of the least soluble substance. Since the solubility of $CaCO_3$ ($S = 5 \times 10^{-9}$) is much lower than that of $CaSO_4$ ($S = 6 \times 10^{-5}$), the equilibrium in the first system is greatly displaced to the left. On the other hand, $BaCO_3$ ($S = 8 \times 10^{-9}$) is more soluble than $BaSO_4$ ($S = 1 \times 10^{-10}$), and therefore, the equilibrium in the second system is shifted to the right.

It is not uncommon for both slightly dissociated and sparingly soluble substances to be formed simultaneously in a given system. If both result from the same direction of the reaction, equilibrium will shift still further than when only one of them is formed. However, it is more usual for the slightly dissociated substance to form when the reaction proceeds in one direction, and the sparingly soluble substance, when it proceeds in the opposite direction.

In these systems the equilibrium shifts towards the formation of the substance that binds the corresponding ion more completely. Since this depends both on the solubility of the sparingly soluble electrolyte and on the degree of dissociation of the slightly dissociated substance, either direction may predominate. For example,

in the systems

$$FeS\downarrow + 2H^{\cdot} \rightleftarrows Fe^{\cdot\cdot} + H_2S \quad \text{and} \quad CuS\downarrow + 2H^{\cdot} \leftrightarrows Cu^{\cdot\cdot} + H_2S$$

hydrogen sulphide is the slightly dissociated substance in either case. Nevertheless, in the first system the equilibrium is practically completely displaced to the right, while in the second it is practically completely displaced to the left. This is due to the fact that S^{2-} ions are more completely bound in hydrogen sulphide than in ferrous sulphide, while cupric sulphide, being much less soluble than FeS, binds the S^{2-} ions even more completely than H_2S.

Many cases where substances practically insoluble in water are dissolved by acids are due to the formation of slightly dissociated compounds. An example is the above reaction in which FeS is dissolved, and which is based on the formation of the slightly dissociated H_2S.

1) A salt of a weak acid should dissolve in stronger acids the more rapidly, the higher the $H^{\cdot}$ ion concentration in the solution of the strong acid, i. e., the stronger it is. As a rule, this is what actually happens. However, apparent exceptions are sometimes observed. For instance, $CaCO_3$ will dissolve in weak acetic acid much more rapidly than in strong sulphuric acid. In this case (and in similar cases) dissolving is retarded by the formation of a layer of a sparingly soluble product of the reaction ($CaSO_4$) on the $CaCO_3$ surface, which obstructs the reaction between the $CaCO_3$ and the acid.

Water is one of the least dissociated substances formed in ionic reactions. Therefore, equilibrium shifts in ionic reactions are frequently due to the formation of water. Besides the reactions between bases and acids (*neutralisation reactions*), these also include reactions between bases and acid anhydrides and between metal oxides and acids.

If we represent a neutralisation reaction in the ionic form, we obtain, for example,

$$Na^{\cdot} + OH' + H^{\cdot} + Cl' = Na^{\cdot} + Cl' + H_2O$$

or, cancelling the ions which remain unchanged during the reaction:

$$\mathbf{H^{\cdot} + OH' = H_2O}$$

The last expression is the *general* equation for neutralisation reactions, and shows that in all cases when $H^{\cdot}$ ions encounter OH' ions they combine to form water. In this process, both the "acidic" properties of the $H^{\cdot}$ ions (or the acid) and the "alkaline" properties of the OH' ions (or the base) disappear, and the solution acquires the "neutral" character peculiar to water, due to equal concentrations of $H^{\cdot}$ and OH' ions. Hence the name "neutralisation reaction", which is essentially a special case of double decomposition.

2) Fig. 89 shows the variation in acidity and alkalinity of the solution for different cases of neutralisation (in 0.1 *N* solutions). If both the acid and the base are strong electrolytes (HCl and NaOH), the instant when they are in equivalent proportions is characterised by a very abrupt change in the pH, i. e., by a sharp change in the acidity or alkalinity of the solution. On the other hand, when a weak acid reacts with a weak base (CH_3COOH and NH_4OH), the change is rather smooth. In mixed cases, the neutralisation curve becomes unsymmetrical. The differences in nature of neutralisation curves are of great importance in quantitative chemical analysis.

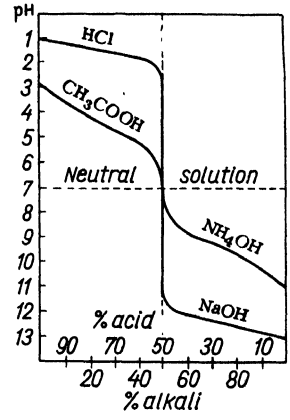


Fig. 89. Change of pH during neutralisation

Up till now, we have considered ionic reactions involving equivalent quantities of the reactants. An increase in the concentration of one of them will shift the position of equilibrium in the system. This is very important in practice, since the yield of the product obtained can often be raised considerably by increasing the concentration of one of the reactants. In general, reversibility of processes is avoided as far as possible in chemical engineering, and attempts are always made to shift the equilibrium in the more advantageous direction. As has already been pointed out (IV-3), the law of mass action and Le Châtelier's principle provide the necessary guides.

In many cases, the acidity or alkalinity of the solution decides the direction of the process. A simple example is the dissociation of an amphoteric electrolyte. Thus, $Zn(OH)_2$ may dissociate into ions both as a base and as an acid. Consequently, the following equilibria are simultaneously characteristic of this compound:

$$\underset{\text{dissociation as base}}{Zn^{\cdot\cdot} + 2OH' \rightleftarrows ZnOH^{\cdot} + OH'} \rightleftarrows \underset{\text{in acid solution}}{\overset{\text{in alkaline solution}}{\rightleftarrows}} Zn(OH)_2 \equiv H_2ZnO_2 \rightleftarrows H^{\cdot} +$$

$$\underset{\text{dissociation as acid}}{+ HZnO_2' \rightleftarrows 2H^{\cdot} + ZnO_2''}$$

As the arrows show, in alkaline solution the equilibrium is displaced in the direction of dissociation as an acid, since the $H^{\cdot}$ ions formed are bound by the hydroxyl ions of the solution to form slightly dissociated water molecules. On the other hand, in acid solution the OH' ions are bound by the $H^{\cdot}$ ions of the solution to form water, and therefore, the equilibrium shifts towards dissociation as a base. The possibility of an equilibrium shift in both directions explains, why amphoteric hydroxides, which are practically insoluble in water, dissolve readily in both acids and in alkalis.

3) The dissolving of an amphoteric hydroxide in acids and alkalis can also be described on the basis of the *addition* of hydrogen or hydroxyl ions to the hydroxide, according to equations such as:

$$Zn(OH)_2 + 2H^{\cdot} \rightleftarrows Zn(OH)(OH_2)^{\cdot} + H^{\cdot} \rightleftarrows Zn(OH_2)_2^{\cdot\cdot}$$

$$Zn(OH)_2 + 2OH' \rightleftarrows Zn(OH)_3' + OH' \rightleftarrows Zn(OH)_4''$$

This method of description, which is essentially more correct in the majority of cases, is somewhat arbitrary with respect to determining the number of molecules of water or hydroxyl ions bonded to the central element. If the hydrated state of all the ions is taken into account, then, as far as the results are concerned, this method is equivalent to that discussed in the main text. For example, $ZnO_2'' + 2H_2O \rightleftarrows Zn(OH)_4''$, i. e., the composition of the two final products differs only by two molecules of water. Since both ions are hydrated by an unknown number of these molecules, this difference does not actually affect their composition.

4) The hydrogen ion concentration at which an amphoteric compound dissociates equally in both directions, is known as its *isoelectric point.* In the case of $Zn(OH)_2$, the latter lies at about pH = 11. If an amphoteric compound is sparingly soluble, the isoelectric point also corresponds to its minimal solubility.

V-7. Hydrolysis. When various substances are dissolved in water a chemical reaction of an exchange nature often occurs. Such processes are grouped under the heading of *hydrolysis.*

In general, *hydrolysis is an exchange reaction of substances with water.* In this case, the equilibrium of the dissociation of water,

$$H_2O \rightleftarrows H^{\cdot} + OH'$$

is displaced owing to binding of one (or both) of its ions by the ions of the solute to form a slightly dissociated or a sparingly soluble product.

The following discussion will be confined to the hydrolysis of salts, which, in practice, is by far the most common case of hydrolysis.

1) When considering possible systems, other than aqueous, hydrolysis should be regarded as a special case of *solvolysis*, i. e., as *an exchange reaction between the solute and the solvent.*

When a salt formed by a strong base and a strong acid, such as NaCl, dissolves, the water dissociation equilibrium does not shift, since the ions of such a salt do not form slightly dissociated products with $H^{\cdot}$ and OH' ions. Therefore, in the system

$$NaCl + HOH \rightleftarrows NaOH + HCl$$

the only remaining slightly dissociated compound is water itself. As a result, the equilibrium of the reaction is almost wholly shifted to the left, i. e., practically no hydrolysis of NaCl occurs, and there is no appreciable surplus of either $H^{\cdot}$ or OH' ions in the solution.

It is different when a salt of a strong base and a weak acid (CH_3COONa), or vice versa, (NH_4Cl), dissolves. In the former case, the $H^{\cdot}$ ion will be partially bound, while in the latter, the OH' ion will be partially bound due to the equations:

$$CH_3COO' + HOH \rightleftarrows CH_3COOH + OH'$$
$$NH_4 + HOH \rightleftarrows NH_4OH + H^{\cdot}$$

Since both CH_3COOH and NH_4OH are much more dissociated than water, both these equilibria are greatly displaced to the left. Therefore, hydrolysis of the salts in accordance with the equations

$$CH_3COONa + HOH \rightleftarrows CH_3COOH + NaOH$$
$$NH_4Cl + HOH \rightleftarrows NH_4OH + HCl$$

takes place only to an insignificant extent. Nevertheless, the first solution contains a certain surplus of OH' ions, while the second solution contains a certain surplus of $H^{\cdot}$ ions.

Obviously, if both substances forming the salt—the base and the acid—are slightly dissociated, the equilibrium of the hydrolysis, say,

$$CH_3COONH_4 + HOH \rightleftarrows CH_3COOH + NH_4OH$$

should be shifted further to the right. In other words, the hydrolysis of a salt formed by a *weak* base and a *weak* acid will be, generally speaking, more complete than if only one of these substances is slightly dissociated.

The acidity or alkalinity of solutions of such salts depends on the relative strength of the acid and the base. If their strengths are equal, the solution may be neutral, which is the case, for example, in the hydrolysis, of CH_3COONH_4. Thus, neutrality of a solution does not, in itself, prove that the salt is not hydrolysed.

In practice, one mostly has to deal with the hydrolysis of salts with a multiply charged ion of the *weak* constituent (acid or base) and singly charged ions of the *strong* constituent. Hydrolysis of such compounds, e. g., $CuCl_2$ and Na_2CO_3, results, as a rule, in *basic* or *acidic* salts, respectively:

$$CuCl_2 + HOH \rightleftarrows Cu(OH)Cl + HCl$$

or

$$Cu^{\cdot\cdot} + HOH \rightleftarrows Cu(OH)^{\cdot} + H^{\cdot}$$

$$Na_2CO_3 + HOH \rightleftarrows NaHCO_3 + NaOH$$

or

$$CO_3'' + HOH \rightleftarrows HCO_3' + OH'$$

Hydrolysis of such salts does not usually proceed any further, i. e., to formation of the free weak base or acid, owing to the accumulation of $H^{\cdot}$ or OH' ions, respectively, in the solution. Exceptions are those cases where the basic or acidic properties of the multivalent constituent are extremely weak. In such cases hydrolysis often proceeds practically to completion.

2) Individual possible cases of hydrolysis of salts are compared below (from the point of view of the acidity or alkalinity of the solution and the nature of the products obtained). The basis for the comparison is, on the one hand, the strength of the corresponding acids and bases, and, on the other hand, the type of salt with regard to valency of the cation and the anion.

I. *Strong base, weak acid.* The solution is *alkaline.* The following cases are possible, depending on the valency of the cation or the anion.

a) *Cation and anion monovalent.* The hydrolysis products are a free acid and a free base, e. g.:

$NaCN + H_2O \rightleftarrows NaOH + HCN$ or, in ionic form, $CN' + H_2O \rightleftarrows HCN + OH'$

b) *Cation monovalent, anion multivalent.* This is the most typical case. Hydrolysis gives *acid salts* and a free alkali, e. g.:

$$Na_3PO_4 + H_2O \rightleftarrows Na_2HPO_4 + NaOH \quad \text{or} \quad PO_4''' + H_2O \rightleftarrows HPO_4'' + OH'$$

In a large volume of water hydrolysis proceeds further:

$$Na_2HPO_4 + H_2O \rightleftarrows NaH_2PO_4 + NaOH \quad \text{or} \quad HPO_4'' + H_2O \rightleftarrows H_2PO_4' + OH'$$

However, it does not reach the stage of formation of a free weak acid owing to the accumulation of free alkali (OH' ions) in the solution.

c) *Cation multivalent, anion monovalent.* This case is rather rare. Hydrolysis results in a *basic salt* and a free acid. But the solution is alkaline since it contains more OH' ions from the basic salt (formed by the strong base) than $H^{\cdot}$ ions from the weak acid, e. g.:

$$Ba(CN)_2 + H_2O \rightleftarrows Ba(OH)CN + HCN \quad \text{or} \quad CN' + H_2O \rightleftarrows HCN + OH'$$

d) *Cation and anion multivalent.* This case is never encountered in practice, as the compounds of this group are all insoluble in water.

II. *Weak base, strong acid.* The solution is *acid.*

a) *Cation and anion monovalent.* Hydrolysis gives a free base and a free acid, e. g.:

$$NH_4NO_3 + H_2O \rightleftarrows NH_4OH + HNO_3 \quad \text{or} \quad NH_4^{\cdot} + H_2O \rightleftarrows NH_4OH + H^{\cdot}$$

b) *Cation multivalent, anion monovalent;* this is the most typical case. Hydrolysis results in *basic salts* and a free acid, e. g.:

$$AlCl_3 + H_2O \rightleftarrows Al(OH)Cl_2 + HCl \quad \text{or} \quad Al^{\cdot\cdot\cdot} + H_2O \rightleftarrows Al(OH)^{\cdot\cdot} + H^{\cdot}$$

In a large volume of water hydrolysis proceeds further:

$$Al(OH)Cl_2 + H_2O \rightleftarrows Al(OH)_2Cl + HCl \quad \text{or} \quad Al(OH)^{\cdot\cdot} + H_2O \rightleftarrows Al(OH)_2^{\cdot} + H^{\cdot}$$

However, it does not reach the stage of formation of a free weak base owing to the accumulation of free acid ($H^{\cdot}$ ions) in the solution.

c) *Cation monovalent, anion multivalent.* This is a very rare case. The result of hydrolysis is an *acid salt* and a free base. In this case, the solution contains more $H^{\cdot}$ ions from the acid salt (formed by the strong acid) than OH' ions from the weak base, e. g.:

$$(NH_4)_2SO_4 + H_2O \rightleftarrows NH_4HSO_4 + NH_4OH \quad \text{or} \quad NH_4^{\cdot} + H_2O \rightleftarrows NH_4OH + H^{\cdot}$$

d) *Cation and anion multivalent.* Hydrolysis results in a *basic salt* and a free acid, e. g.:

$$Fe_2(SO_4)_3 + 2H_2O \rightleftarrows 2Fe(OH)SO_4 + H_2SO_4 \quad \text{or} \quad Fe^{\cdot\cdot\cdot} + H_2O \rightleftarrows Fe(OH)^{\cdot\cdot} + H^{\cdot}$$

III. *Weak base, weak acid.* In this case the alkalinity or acidity of the solution depends on the relative strengths of the acid and the base. The nature of the hydrolysis products depends on the strengths of the acid and the base

as well as on the valencies of the cation and the anion. For example, aluminium acetate hydrolyses to form basic salts, according to the equations:

$$Al(CH_3COO)_3 + H_2O \rightleftarrows Al(OH)(CH_3COO)_2 + CH_3COOH$$

$$Al(OH)(CH_3COO)_2 + H_2O \rightleftarrows Al(OH)_2CH_3COO + CH_3COOH$$

while aluminium sulphide, a salt of a much weaker acid, is hydrolysed to the free base and the free acid:

$$Al_2S_3 + 6H_2O \rightleftarrows 2Al(OH)_3 + 3H_2S$$

IV. *Strong base, strong acid.* Solutions of such salts are *neutral* to litmus, since they are practically unhydrolysed. This group includes NaCl, Na_2SO_4, $BaCl_2$, etc.

From the above it follows that the *degree of hydrolysis* (i. e., *the ratio of the number of hydrolysed molecules to the total number of dissolved molecules*, which is usually expressed in per cent) depends, primarily, on the chemical nature of the constituent ions of the salt in question. In the majority of cases, the degree of hydrolysis is low. Thus, in 0.1 *N* solutions of CH_3COONa and NH_4Cl it is about 0.01% at 25° C, i. e., only one molecule in ten thousand is hydrolysed. When both the acid and the base are weak, the degree of hydrolysis is higher, being about 0.5% for CH_3COONH_4 under the same conditions. Similarly, the degree of hydrolysis is higher in the case of very weak acids or bases; for example, it is about 1.3% for a 0.1 *N* solution of NaCN. Finally, the hydrolysis of salts of a very weak base and a very weak acid often proceeds practically to completion.

As hydrolysis is a reversible process, its equilibrium depends on all the factors that affect the equilibrium of any ion exchange reaction. For example, it shifts towards decomposition of the initial salt if the products obtained (mostly in the form of basic salts) are sparingly soluble. By adding an excess of one of the substances formed during the reaction (usually an acid or an alkali) to the system, it is possible to shift the equilibrium in the opposite direction in accordance with the law of mass action. On the other hand, the addition of excess water, i. e., dilution of the solution, leads to more complete hydrolysis, again in accordance with the law of mass action. For example, the dependence between the degree of hydrolysis, *h*, and the concentration, *c*, for the reaction

$$Na_2CO_3 + HOH \rightleftarrows NaHCO_3 + NaOH$$

at 25°C is:

c (moles/litre) . . .	0.2	0.1	0.05	0.01	0.005	0.001
h (%) . . .	1.7	2.9	4.5	11.3	16	34

As indicated above (V-5), the degree of dissociation of water increases sharply with rising temperature (whereas for most other electrolytes it changes only slightly). Therefore, if a solution is heated,

the concentration of $H^{\cdot}$ and OH' ions increases substantially, and this raises the probability of formation of slightly dissociated molecules of a weak acid or base. Therefore, *heating a solution greatly increases the degree of hydrolysis.* For instance, in the case of the reaction

$$CrCl_3 + HOH \rightleftarrows Cr(OH)Cl_2 + HCl$$

at $c = 0.01$ moles/litre, the temperature dependence of the degree of hydrolysis, is:

Temperature (°C) . . .	0	25	50	75	100
h (%) . . .	4.6	9.4	17	28	40

Hence, we get the following general rules concerning the displacement of hydrolytic equilibrium. If it is desired to shift the equilibrium towards the maximum possible decomposition of a salt, dilute solutions should be used at high temperatures. Conversely, if the minimum possible hydrolysis is desired, strong solutions should be used at low temperatures. In the latter case, it is also very useful to add an excess of one of the hydrolysis products (acid or alkali) to the solution. These directions are often found useful in chemical practice.

3) Besides its purely chemical applications, hydrolysis is of great importance in many processes occurring in living organisms. For example, the biological role of certain salts contained in blood ($NaHCO_3$ and Na_2HPO_4) chiefly consists in maintaining a definite concentration of hydrogen ions. This is accomplished by a shift in the hydrolysis equilibrium according to the equations:

$$HCO_3' + H_2O \rightleftarrows H_2CO_3 + OH' \text{ and } HPO_4'' + H_2O \rightleftarrows H_2PO_4' + OH'$$

If an excess of $H^{\cdot}$ ions occurs in the blood for some reason or other, these ions are bound by hydroxyl ions, and the above equilibria shift to the right, while if there is an excess of OH' ions, the equilibria shift to the left. Owing to this, the pH of the blood in a normal person fluctuates only slightly about the mean value of 7.4, which is essential for normal functioning of the organism.

4) The biological effect of the hydrogen ion concentration also extends to plant organisms. For most successful growth, each variety of land plant requires a definite concentration of hydrogen ions in the soil. For example, potatoes grow best of all on slightly acid soils (pH = 5), lucerne—on slightly alkaline soils (pH = 8), and wheat—on neutral soils (pH = 7). Marine plants are more handicapped in this respect, since the oncentration of hydrogen ions in sea water is maintained at an approximately constant level of pH = = 7.9-8.4, due to the hydrolysis of carbonates.

V-8. Chemistry and Electricity. *Displacement reactions* differ fundamentally from the ion exchange reactions considered in the previous sections. In double decomposition the already existing ions are drawn together into different combinations, while in displacement reactions one ion is converted into a neutral atom, and a new ion is simultaneously formed. Consequently, displacement reactions involve a *transfer of electrons.*

Of the simplest processes of this type, the most frequently encountered are cases where metals react with acids. An example is the reaction generally used for obtaining hydrogen:

$$Zn + 2HCl = ZnCl_2 + H_2$$

Since HCl and $ZnCl_2$ are strong electrolytes, and the H_2 molecule does not dissociate into ions, the ionic form of the above equation is:

$$Zn + 2H^{\cdot} + 2Cl' = Zn^{\cdot\cdot} + 2Cl' + H_2$$

or, cancelling the constituents that remain unchanged,

$$\mathbf{Zn + 2H^{\cdot} = Zn^{\cdot\cdot} + H_2}$$

Thus, neutral zinc atoms are converted into ions, and hydrogen ions into neutral atoms (which then combine into molecules). Apparently, the net result of the process is the transfer of electrons from zinc to the hydrogen ions.

The last equation shows that the reaction depends directly on the nature of the metal and the hydrogen ion concentration. While the $H^{\cdot}$ ion concentration determines the rate of the reaction, the chemical nature of the metal determines the practical possibility of its initiation. Indeed, the transfer of electrons to the hydrogen ions can occur only if the metal yields these electrons with sufficient readiness. Hence, hydrogen cannot be displaced by any metal that reacts with an acid, but only by those that possess sufficient chemical activity. For example, zinc and iron displace hydrogen from acids, but copper and silver do not.

The activity of metals, i. e., their readiness to yield electrons, can be compared still more vividly than in their reactions with acids by observing reactions in which one metal is displaced by another from solutions of their salts. The chemical process which takes place in this case, also involves the transfer of electrons from one element to another, which can be seen, for example, from the following equations:

$$Zn + CuSO_4 = ZnSO_4 + Cu \quad \text{or} \quad \mathbf{Zn + Cu^{\cdot\cdot} = Zn^{\cdot\cdot} + Cu}$$

Thus, a reaction in which one metal is displaced by another consists essentially of the transfer of electrons from an atom of the first metal to an ion of the second. For example, in the series Zn, Fe, Cu, Ag each preceding metal will displace those following it from their salts, whereas no reverse displacement is observed. This shows that the stability of the electronic bonds in the metals increases from Zn to Ag.

The reaction between zinc and copper according to the above equation may be divided into two stages:

$$Zn = Zn^{\cdot\cdot} + 2\ominus \quad \text{and} \quad 2\ominus + Cu^{\cdot\cdot} = Cu$$

Obviously, if the transfer of electrons could be brought about through a metal conductor instead of directly, a stream of electrons, i. e., an

electric current, would flow through the conductor from the zinc to the copper.

Fig. 90. is a diagram of a voltaic or galvanic cell, a device which enables the transfer of electrons through a conductor. Vessel *A* and tube *C* connecting both vessels are filled with $ZnSO_4$ solution, while vessel *B* is filled with $CuSO_4$. A zinc plate is immersed in the first vessel, and a copper plate in the second. If the two plates are connected by a wire, *e*, an electric current will flow through it in the direction indicated by the arrow.

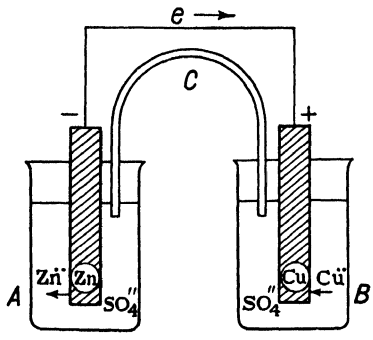


Fig. 90. A galvanic cell

The origin of the current is directly connected with the different concentrations of free electrons in the individual metals (III-7), and their tendency towards equalisation when the metals are in contact. At the boundary between the metal and the solution of its salt, there are simultaneous equilibria (for singly charged ions)

$$\underset{\text{metal}}{M} \rightleftarrows \ominus + M^+ \quad \text{and} \quad M^+ + aq \underset{\text{solution}}{\rightleftarrows} M^{\cdot}$$

or, if combined:

$$M + aq \rightleftarrows \ominus + M^{\cdot}$$

Decreasing the concentration of free electrons in the metal (below its usual value) will make the equilibrium shift *to the right*, i. e., towards formation of additional positive ions and their passage into solution. On the other hand, an increase in the concentration of free electrons makes the equilibrium shift *to the left*, i. e., towards conversion of the positive ions into neutral atoms (and deposition of the latter on the surface of the metal).

Since the concentration of free electrons is higher in zinc than in copper, the zinc electrode is denoted by a minus and the copper electrode by a plus. When the two electrodes are connected with a wire, some of the electrons pass through it from the zinc to the copper, and the zinc plate becomes positively charged, while the copper plate becomes negatively charged. The positive charge on the zinc is instantly neutralised by $Zn^{\cdot\cdot}$ ions passing into solution. The negative charge on the copper is also instantly neutralised by deposition of $Cu^{\cdot\cdot}$ ions on the electrode (and conversion of these ions into neutral atoms). Simultaneously, a corresponding number of $Zn^{\cdot\cdot}$ ions passes through the connecting tube *C* from vessel *A* to vessel *B*. All these processes occur continuously (until all the zinc is dissolved or the copper salt

is completely decomposed). Thus, in a galvanic cell, *electric current is generated by a chemical reaction.*

1) If a small piece of zinc is put into a solution of a copper salt, particles of metallic copper will deposit instantly on its surface. When dropped into a solution of an acid, this "copper plated" zinc reacts with it much more vigorously than pure zinc. This is due to the fact that the Zn—Cu *galvanic couple* works like a galvanic cell; electrons pass from the zinc to the copper and from the latter to the hydrogen ions in solution (Fig. 91). As a result, gaseous hydrogen is deposited on the copper instead of on the zinc and does not prevent the further passage of $Zn^{\bullet\bullet}$ ions into solution. The same always occurs when acids act on a metal which is in contact with another, less active metal.

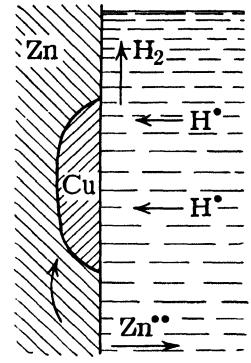


Fig. 91. A galvanic couple

The case of a Zn—Cu couple is by no means an exception. If the conditions in the device shown in Fig. 90 are suitably selected, electric current can be produced by means of any displacement reaction.

The greater the difference in the concentrations of free electrons, the more intensive their transfer from one metal to the other, i. e., the higher the voltage of the electric current. If the charge on each of the rods is known, and the voltage of the current is measured, the relative activity of different metals can be evaluated, and this value can serve as a criterion for arranging them in what is known as the *electromotive series.* The general form of the latter is:

...K...Ca...Mg...Zn...Fe...Sn...**H**...Cu...Ag...Au

The most important rules following from the electromotive series are given below.

1) Each metal will displace from their salts all the others situated to the right of it in the electromotive series.

2) All metals situated to the left of hydrogen will displace it from acids, while those situated to the right of it will not.

3) The farther two metals are from one another, the higher the voltage of a galvanic cell made up of them.

2) If one half of the device in Fig. 90, say, beaker *A*, is separated from the other, then at the place of contact between the electrode (the zinc plate) and $ZnSO_4$ solution, an equilibrium will be established between the atoms and ions of zinc: $Zn \rightleftarrows Zn^{\bullet\bullet} + 2\ominus$. The positive ions will be in solution, and the electrons in the plate. Owing to this, the layer of solution adjacent to the electrode will be positively charged, while the electrode itself will be charged negatively, and there will be a difference of potentials between them. A similar phenomenon will take place in beaker *B* if it is isolated, except that the difference of potentials will not have the same value. If this difference of potentials could be measured, the tendency of the ions of any given metal to pass into solution could thus be quantitatively characterised.

However, there are no methods for direct measurement of these differences of potentials. Therefore, in order to obtain numerical data, an indirect method must be used, based on the fact that the total voltage developed by a voltaic cell is equal to the algebraic sum of all the potential differences in the cell.

If a platinum electrode coated with an active layer of platinum black is immersed in a solution containing $H^{\cdot}$ ions, e. g., H_2SO_4, and gaseous hydrogen is allowed to bubble around it, the hydrogen will cover the platinum, and at the surface of this *hydrogen electrode*, an equilibrium will be established between hydrogen molecules, hydrogen atoms and hydrogen

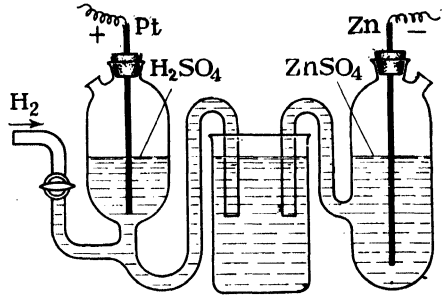


Fig. 92. Determination of electrode potential

ions: $H_2 \rightleftarrows 2H \rightleftarrows 2H^{\cdot} + 2\ominus$. Conventionally taking the difference of potentials between the hydrogen electrode and the acid solution as equal to zero, and combining this electrode with, say, a zinc electrode (Fig. 92), it will be found that the difference of potentials between Zn and the solution of its salt (the *electrode potential* of zinc) is exactly equal to the voltage produced by this element. In a similar way, the relative electrode potentials of most other metals can be determined. The charge on the electrode will be negative if the metal is more active, and positive if it is less active than hydrogen. The table contains data (E_0 in volts) relating to molal solutions (for the corresponding ion), ordinary temperatures and a hydrogen pressure of atmosphere. A change in either of these conditions causes a change in the electrode potentials, because the equilibria $M \rightleftarrows M^{\cdot} + \ominus$ and $H_2 \rightleftarrows 2H \rightleftarrows 2H^{\cdot} + 2\ominus$ shift accordingly.

Electrode Potentials

Metal	Ion	E_0	Metal	Ion	E_0
K	$K^{\cdot}$	−2.92	Sn	$Sn^{\cdot\cdot}$	−0.14
Ca	$Ca^{\cdot\cdot}$	−2.87	H_2	$2H^{\cdot}$	±0.00
Mg	$Mg^{\cdot\cdot}$	−2.38	Cu	$Cu^{\cdot\cdot}$	+0.34
Zn	$Zn^{\cdot\cdot}$	−0.76	Ag	$Ag^{\cdot}$	+0.80
Fe	$Fe^{\cdot\cdot}$	−0.44	Au	$Au^{\cdot\cdot\cdot}$	+1.42

3) Knowing the electrode potentials of the metals, the *electromotive force* (voltage) of a galvanic cell made up of any given couple can be calculated by

subtracting the potential of the negative electrode from the potential of the positive electrode. For example, for the couple Zn—Cu, we have $E = +0.34 - (-0.76) = 1.10$ volts.

4) The relation between the electrode potential E_c and the molal concentration of the ion, C, is given for ordinary conditions by the equation $E_c = E_0 + (0.06/n) \log C$, where n is the valency of the ion. This relation makes it possible to obtain a more accurate value for the electromotive force of a galvanic cell by taking into account the concentrations (more precisely, the activities) of the electrolytes which it contains.

The generation of an electric current by means of chemical reactions in galvanic cells of various types is widely practised. However,

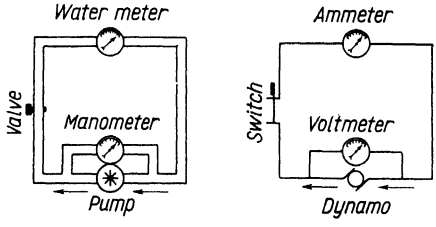


Fig. 93. Analogy between a water and an electrical system

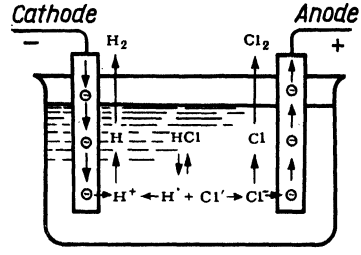


Fig. 94. Diagram of electrolysis

this is more frequently accomplished by dynamos, which may be likened to pumps for the transfer of electrons from one part of a circuit to another.

A flow of electrons, called electric current, is, in general, very similar to a flow of water, as is evident from the comparative diagrams of a water system and an electrical system (Fig. 93). Like the pump, the dynamo transfers electrons from one part of the system to the other. The voltage of the current (analogous to the pressure of the water) is measured with a voltmeter, the quantity of electricity which is flowing (analogous to the quantity of water which is flowing) is measured with an ammeter, and the role of the valve in the water system is played by a switch.

5) The *voltage* of an electric current is measured in *volts*. An idea of the size of this unit may be gained from the fact that the galvanic cell shown in Fig. 90 yields about 1.1 volts, while lighting systems in the U. S. S. R. generally use voltages of 127 or 220 volts. The unit of *quantity of electricity* adopted in engineering is the *coulomb* (6.25×10^{18} times the charge of an electron). If one coulomb per second passes through a conductor, the *current intensity* is one *ampere*. The product of the voltage and the current intensity is its *power* (ability to do work), measured in *watts*: the voltage multiplied by the amperage is equal to the wattage. Therefore, for example, at a voltage of 100 volts a 50 watt electric lamp conducts a current of 0.5 ampere.

If a vessel containing a solution of an electrolyte, e. g., HCl, is cut into an electric circuit (Fig. 94), a phenomenon known as *electro-*

lysis takes place. Owing to the work of the current source, electrons will be transferred from one electrode (the *anode*) to the other (the *cathode*). This will cause a deficiency of electrons at the anode and a surplus of electrons at the cathode. The Cl' ions in the solution will be repelled by the negative electrode and attracted to the positive electrode; the reverse will be true of the $H^{\cdot}$ ions. Thus, the former will travel towards the anode, and the latter towards the cathode. For this reason the negatively charged ions are usually called anions (moving towards the anode), and the positively charged ions cations (moving towards the cathode).

Since the current source pumps electrons from the anode, one electron is removed from each Cl' ion that reaches the anode, and it is converted into a neutral atom. These atoms thereupon combine by pairs into molecules and are evolved as gaseous chlorine. Simultaneously, the cathode (which contains a surplus of electrons) yields electrons to the $H^{\cdot}$ ions reaching it, and converts them into neutral hydrogen atoms. The latter combine by pairs to form molecules, and gaseous hydrogen escapes from the vessel.

Thus, when an electric current is allowed to flow through a solution of an electrolyte, the following processes take place at the electrodes:

a) At the anode, anions are converted into neutral atoms (or groups of atoms) by *yielding* electrons.

b) At the cathode, cations are converted into neutral atoms (or groups of atoms) by *gaining* electrons. Both of these processes cease only when all the electrolyte is used up. It is obvious that, essentially, electrolysis consists in *causing chemical reactions by means of electric current.*

If we modify the previous example somewhat by taking, say, $CuCl_2$ instead of HCl, the process at the anode will remain the same, but at the cathode metallic copper will be deposited instead of hydrogen being given off. If suitable conditions are chosen (current intensity, composition of the solution, etc.), the copper can be deposited in a thick and even layer. Electroplating of one metal with another is widely employed in present-day technique (for nickel-plating, gold-plating, etc.).

The process will be slightly different if a copper anode is used in the electrolysis of $CuCl_2$. As Cu atoms give up electrons more readily than Cl' ions, $Cu^{\cdot\cdot}$ ions will pass from the anode into solution in this case, instead of chlorine being liberated. The electrolysis will, consequently, be essentially the transfer of copper from the anode to the cathode. This transfer is of great technical value, since it permits metals to be purified by electrolysis.

As was pointed out above, the ease with which an element can be converted from the atomic to the ionic state depends upon its chemical activity. Consequently, different voltages must be applied to

convert different ions into neutral atoms. Indeed, the further a metal is to the left in the electromotive series, the more difficult it is to deposit it from a solution by electrolysis.

Some important methods of separating different metals are based on the difference in the voltages required to deposit them. For example, given a solution of a mixture of Zn and Cu salts, the copper can be made to deposit on the electrode and the zinc to remain in solution by suitably adjusting the voltage.

6) Since the ions of water are more easily discharged at the electrodes than the ions of many electrolytes, during the electrolysis of, say, Na_2SO_4, hydrogen is liberated at the cathode (due to the $H^{\cdot}$ ions of water), and oxygen at the anode (according to the equation: $2OH' - 2\ominus = H_2O + O$). As a result, the region around the cathode becomes enriched with $Na^{\cdot}$ and OH' ions, and the region around the anode with SO_4'' and $H^{\cdot}$ ions, i. e., free alkali accumulates in the former, and free acid in the latter.

Thus, for the conversion of different ions into neutral atoms, different voltages are required, depending on the chemical nature of the ion. There is a much simpler relation for the quantity of electricity consumed during electrolysis. Independently of its chemical nature, each singly charged ion receives or gives up one electron, each doubly charged ion receives or gives up two electrons, etc. Consequently, one gram-ion of any monovalent element will be discharged by the same quantity of electricity, while the quantity of electricity needed to discharge one gram-ion of any divalent element, is twice as large, etc. This relation becomes still more general when applied to equivalent weights, since in this case the differences connected with the ionic charges are eliminated. The *Law of Electrolysis* (Faraday, 1834) which is valid for all electrolytes states that *the same quantities of electricity liberate equivalent weights of elements*, and 96,500 *coulombs* (26.8 ampere-hours) *will liberate one gram-equivalent of any element*. Faraday's law makes possible various calculations connected with electrolysis.

Example. A current of 5 amperes is passed for 10 minutes through solutions of $AgNO_3$, $CuSO_4$ and $AuCl_3$ connected in series in a direct-current circuit. Determine how much silver, copper and gold will be deposited on the cathodes in this time. Since one ampere corresponds to a flow of one coulomb per second, $5 \times 60 \times 10 = 3000$ coulombs will have passed through the solutions during the experiment. Hence,

$$\frac{107.9 \times 3000}{1 \times 96{,}500} = 3.36\ \text{g of Ag}, \qquad \frac{63.5 \times 3000}{2 \times 96{,}500} = 0.99\ \text{g of Cu}$$

$$\text{and } \frac{197.0 \times 3000}{3 \times 96{,}500} = 2.04\ \text{g of Au will be deposited.}$$

7) The law of electrolysis provides a very convenient method for determining equivalent weights. All we have to know for this purpose is the weight of the element deposited by a known quantityof electricity.

Example. On passing a current of 1A for 15 minutes through a solution of a cadmium salt, 0.524 g of metallic cadmium was deposited. Find the equivalent weight of cadmium. From the law of electrolysis, we have: $E_{Cd} = (0.524 \times 96{,}500)/(15 \times 60 \times 1) = 56.2$.

8) Since the electronic charge is known to be equal to 4.80×10^{-10} absolute electrostatic units (III-2) or 1.602×10^{-19} coulombs, it is easy to calculate Avogadro's number from the law of electrolysis: $96{,}500/1.602 \times 10^{-19} = 6.02 \times 10^{23}$.

After considering electrolysis, the nature of the electrical conductivity of solutions becomes clear. Reverting to Fig. 94, it is easy to see that no current, i. e., flow of electrons, passes through the liquid at all. Since, however, the number of electrons received by the anode is equal to the number of electrons given up by the cathode during the same period, the current *in the external circuit* flows just as it would if the electrons passed directly through the liquid. That is why we speak of the "electrical conductivity" of a solution.

Obviously, solutions that do not contain ions, i. e., solutions of non-electrolytes, will not conduct current. The electrical conductivity of solutions of electrolytes depends, above all, on the *concentration* of the ions; the higher the concentration, the higher the electrical conductivity.

The second factor affecting electrical conductivity is the ionic *charge*. It is obvious that, other things being equal, a larger quantity of electricity can be "transferred" by, say, doubly charged ions than by singly charged ions, since each of the former yields (or gains) two electrons at a time. In order to eliminate the effect of the ionic charge in comparative studies of electrical conductivity, normal concentrations of solutions are used. In this case, the higher charge of the ion is compensated by its smaller content.

Finally, the third important factor is the *mobility* of the ions, which characterises the velocity with which they move in the solution. The faster the ions move, the greater number of them will be discharged both at the anode and at the cathode per unit time and, consequently, the higher will be the electrical conductivity of the solution. The actual velocities of individual ions are close to one another and are very low at normal voltages (of the order of centimetres per hour). OH' ions and especially H^+ ions are much more mobile than the others, the former by approximately 3 times and the latter by approximately 5 times. Therefore, solutions of strong acids and bases are better conductors of electricity than solutions of salts at the same normal concentration. With rising temperature, the mobility of the ions increases, and hence, the electrical conductivity of solutions also increases, as a rule.

The very low absolute velocities of ions are partially due to their *hydration* (V-4). As a result of hydration, a "cloud" of water molecules is formed around the ion and moves together with it towards the electrode, thereby greatly retarding its motion.

VI. THE PERIODIC TABLE OF THE ELEMENTS

VI-1. The Work of Mendeleyev. Of all the fundamental theoretical concepts of modern chemistry, the most ancient is that of the atomic and molecular structure of matter. The earliest known development of this concept is attributed to the Hindu philosopher Kanyadha who lived apparently some time before 500 B. C. In surprising agreement with the views of a much later period, he taught that substances consist of minute particles, each of which is, in turn, composed of several still smaller particles that are indivisible. These views were widespread in ancient Asia. It is possible that their influence extended to Europe and influenced the teachings of the ancient Greek philosophers Leuccippus (500-428 B. C.) and his pupil Democritus (460-370 B. C.), who are usually considered to be the founders of the atomic and molecular concepts.

Aristotle was a resolute opponent of these ideas. Under the influence of his natural scientific ideas, which prevailed for about 2000 years, the atomic and molecular concepts were forgotten. They began to re-emerge only in the 17th century. Of the scientists who developed these ideas, special mention should be made of Lomonosov (1711-1765), whose atomic and molecular theory was considerably ahead of its time in depth of treatment.

The introduction of the concept of atoms on an experimental basis is credited mainly to Dalton. By generalising the results of his own investigations and those of others, he formulated the laws of definite and multiple proportions (I-2), and explained them by the existence of atoms of the reacting elements.

Attempts to classify the chemical elements began shortly after the acceptance of the concept of atoms. Beginning with Döbereiner in 1817, a number of different scientists had worked on this most important chemical problem. However, only Mendeleyev scored a decisive success in this field.

The work of his predecessors lacked the most important feature—a unified theoretical generalisation. All of them had looked for and found only more or less suitable versions of a classification which was considered by them to be an end in itself. Mendeleyev, on the other hand, sought and discovered the *natural law* which should be graphically reflected in *any* classification.

In February 1869, Mendeleyev published the table shown below. The text accompanying it contains all the most important features of the *Periodic Law* which was revealed in detail a year later. The basic principles are as follows:

a) "The elements, if arranged according to their atomic weights, exhibit an obvious *periodicity* of properties".

b) "The atomic weight determines the character of the element just as the magnitude of the particle determines the properties of a complex body. Therefore, for example, S and Te, Cl and I, etc., exhibit very obvious differences as well as similarities."

c) "We must expect the discovery of many yet *unknown* elements, for example, elements analogous to Al and Si, whose atomic weight would be between 65 and 75".

d) "The atomic weight of an element may sometimes be amended if its analogues are known."

e) "Certain *analogues* of the elements can be foretold from their atomic weights."

Trial System of Elements
Based on Their Atomic Weights and Chemical Resemblance

			Ti=50	Zr=90	?=180
			V=51	Nb=94	Ta=182
			Cr=52	Mo=96	W=186
			Mn=55	Rh=104.4	Pt=197.4
			Fe=56	Ru=104.4	Ir=198
			Ni=Co=59	Pl=106.6	Os=199
H=1			Cu=63.4	Ag=108	Hg=200
	Be=9.4	Mg=24	Zn=65.2	Cd=112	
	B=11	Al=27.4	?=68	Ur=116	Au=197?
	C=12	Si=28	?=70	Sn=118	
	N=14	P=31	As=75	Sh=122	Bi=210?
	O=16	S=32	Se=79.4	Te=128?	
	F=19	Cl=35.5	Br=80	I=127	
Li=7	Na=23	K=39	Rb=85.4	Cs=133	Tl=204
		Ca=40	Sr=87.6	Ba=137	Pb=207
		?=45	Ce=92		
		?Er=56	La=94		
		?Yt=60	Di=95		
		? In=75.6	Th=118?		

In the following year, 1870, an article by Lothar Meyer appeared, in which he alluded to the work of Mendeleyev and presented a system of the elements differing somewhat in form but "essentially identical to the Mendeleyev system". Concluding his article, Meyer wrote that it would be premature to change the accepted atomic weights on such precarious grounds.

Mendeleyev approached the problem in quite a different way. Being deeply convinced that the had discovered one of the most important laws of nature, Mendeleyev boldly used it *as the basis* for

appraising the available experimental data. In order to establish the periodic law in all its harmony, he had to arrange certain elements (Os, Ir, Pt, Au, Te, I, Ni, Co) in an order that was in contradiction with their atomic weights known at the time, to *change* their values (cf. I-5) for a number of other elements (In, La, Y, Er, Ce, Th, U) and, finally, to assume the existence of a number of *as yet undiscovered* elements. It required the genius of Mendeleyev to go as far as this and to give in an article (1871) a comprehensive statement of the periodic law together with a periodic table which differed but little from its present form:

		Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII transitional to group I
		H 1							
Typical elements		Li 7	Be 9.4	B 11	C 12	N 14	O 16	F 19	
First period	Series 1	Na 23	Mg 24	Al 27.3	Si 28	P 31	S 32	Cl 35.5	
	» 2	K 39	Ca 40	— 44	Ti 50 ?	V 51	Cr 52	Mn 55	Fe Co Ni Cu 56 59 59 63
Second period	» 3	(Cu) (63)	Zn 65	— 68	— 72	As 75	Se 78	Br 80	
	» 4	Rb 85	Sr 87	(Y) (88 ?)	Zr 90	Nb 94	Mo 96	— 100	Ru Rh Pd Ag 104 104 104 108
Third period	» 5	(Ag) (108)	Cd 112	In 113	Sn 118	Sb 122	Te 128 ?	I 127	—
	» 6	Cs 133	Ba 137	— 137	Ce 138 ?	—	—	—	—
Fourth period	» 7	—	—	—	—	—	—	—	Os Ir Pt Au
	» 8	—	—	—	—	Ta 182	W 184	—	199? 198? 197 197
Fifth period	» 9	(Au) (197)	Hg 200	Tl 204	Pb 207	Bi 208	—	—	
	» 10	—	—	—	Th 232	—	U 240	—	
Higher salt oxide		R_2O	R_2O_2 or RO	R_2O_3	R_2O_4 or RO_2	R_2O_5	R_2O_6 or RO_3	R_2O_7	R_2O_8 or RO_4
Higher hydrogen compound				(RH_5 ?)	RH_4	RH_3	RH_2	RH	

Going beyond mere assumption of the existence of still undiscovered elements, Mendeleyev supplied details of their chemical properties on the basis of the periodic law. He reasoned in the following way. "If, in a certain group, there are elements R_1, R_2 and R_3, and in

a series containing one of these elements, for example, R_2, there is an element Q before it and an element T after it, the properties of R_2 are determined by the properties of R_1, R_3, Q and T. For instance, the atomic weight of $R_2 = 1/4 (R_1 + R_3 + Q + T)$. By way of illustration, selenium is in group VI between sulphur (S = 32) and tellurium (Te = 127), while in the 5th series, arsenic (As = 75) comes before it and bromine (Br = 80) comes after it. Hence, the atomic weight of selenium is 1/4 (32 + 127 + 75 + 80) = 78.5—a figure close to the actual atomic weight".

The properties of the elements with probable atomic weights of 44, 68 and 72 were predicted in great detail. Concerning this Mendeleyev wrote in his article in 1871, that it would be an important gain for the theoretical aspect of the subject if even one of the expected elements were definitely discovered and its properties were found to be such as visualised from comparisons based on the natural system.

In 1875, Lecoq de Boisbaudran discovered a new element that he named gallium, Ga, which possessed an atomic weight of 69.7. Four years later, Nilson and Cleve isolated an element with an atomic weight of 45.1, and named it scandium, Sc. Finally, in 1886, Winkler discovered germanium, Ge, and showed that its atomic weight was equal to 72.6. A thorough study of all three elements and their most important compounds showed excellent agreement between the experimentally determined properties and those predicted by Mendeleyev. The data for germanium are an example:

Predicted by Mendeleyev (1871)	Found by Winkler (1886)
Atomic weight ~ 72	Atomic weight 72.6
Specific gravity ~ 5.5	Specific gravity 5.35
The metal will not displace hydrogen from acids	The metal does not dissolve in HCl and dilute H_2SO_4
Formula of oxide, EO_2	Formula of oxide, GeO_2
Specific gravity of oxide ~ 4.7	Specific gravity of oxide 4.70
Oxide will be fairly easily reduced to the metal	GeO_2 is reduced to the metal on heating in a stream of hydrogen
Basic properties of hydroxide will be very weak	Basic properties are not characteristic of $Ge(OH)_4$
Its salts will be readily decomposed by water	Germanium salts are readily decomposed by water
The chloride with the formula ECl_4 will be a liquid, b. p. about 90° C and sp. gr. about 1.9	$GeCl_4$ is a liquid, b. p. 83° C; sp. gr. 1.887

This is how Winkler evaluated Mendeleyev's discovery in his article:

"There is no doubt whatsoever that the element discovered recently is no other than the eka-silicon predicted 15 years ago by Mendeleyev. It would hardly be possible to find a more striking proof of the correctness of the theory of periodicity than the fact that the recently discovered element turned out to be the hypothetical eka-silicon. This is not merely the confirmation of a daring theory; here is an obvious broadening of the chemical outlook, a big stride forward in the field of knowledge."

According to Mendeleyev's definition, the essence of the periodic law is that the *properties of the elements* (and, consequently, those of simple and compound bodies formed by them) *are periodic functions of their atomic weights*. At first, it was very coldly received by the majority of his contemporaries. Only the subsequent confirmation of a number of atomic weights that had been changed by Mendeleyev, and especially the discovery of Ga, Sc and Ge and the agreement between their predicted and actual properties, cleared the way to universal recognition of the periodic law. It was generally accepted by about 1890.

The significance of Mendeleyev's work for science in general can be best expressed in the words of Engels: "...war Mendelejew eine wissenschaftliche Tat gelungen, die sich der Leverriers in der Berechnung der Bahn des noch unbekannten Planeten Neptun kühn an die Seite stellen darf". (F. Engels, Op. cit. "Dialektik", S. 60). ("Mendeleyev ... accomplished a scientific feat, which may be safely placed alongside that of Leverrier who calculated the orbit of the as yet unknown planet Neptune").

In chemistry the periodic law ushered in a new epoch, and its value for this science is quite exceptional.

VI-2. Development of the Periobic Law. "The periodic law awaits not only new applications, but improvements, elaboration and fresh forces", Mendeleyev pointed out in 1889. The first serious test to which the law was exposed, shortly after its universal recognition, was the discovery of *argon* in 1893. According to its atomic weight (39.9), the new element should have been placed in the periodic system between potassium (39.1) and calcium (40.1), where there was no vacancy for it. Only after helium had been found on earth, and other inert gases had been discovered, did it become clear that they were all members of a special, "zero" group which should come after the seventh group in the table. Thus, the danger to the existence of the periodic law, initiated by the discovery of argon, turned into its opposite (the periodic system of the elements became more extensive and complete) with the discovery of the rest of the inert gases. "It seems

that the future holds in store for the periodic system not destruction, but elaboration and development", wrote Mendeleyev in 1905.

The next important stage in the development of the periodic law is connected with the work of Moseley (III-3) who, in 1912, showed that the actual basis for the law is not the atomic weights but the positive nuclear charges of the atoms, numerically expressed (in electronic charge units) by the atomic numbers of the corresponding elements. In principle, this change in the interpretation of the periodic law causes no objections, since the refinement of general formulations on the basis of new experimental data is a necessary condition for the development of science.

Moseley's investigations confirmed the correctness of the arrangement in the system of those elements that were not placed correctly from the point of view of their atomic weights. Except for Os, Ir, Pt and Au, whose atomic weights were subsequently adjusted, there were two such cases at the earliest stage in the development of the system: Mendeleyev placed cobalt (58.9) before nickel (58.7), and tellurium (127.6) before iodine (126.9). This departure from the general principle of arrangement according to atomic weights was dictated by the properties of these elements, tellurium being very similar in properties to selenium but quite different from bromine, while iodine, on the other hand, is very similar to bromine but quite unlike selenium. After the discovery of the inert gases, there was a third departure: argon (39.9) was placed before potassium (39.1). From the point of view of the new basis for the law—nuclear charges—all these discrepancies were eliminated; it was found that the appropriate place for cobalt was actually No. 27, for nickel, No. 28, etc.

At the same time, the extremely important problem of the number of as yet undiscovered elements was clarified. The form of the periodic system adopted at that time, on the one hand, suggested the existence of a number of elements transitional between hydrogen (which was placed in group I) and helium, and, on the other hand, gave rise to considerable confusion as to the number and arrangement of the elements in the interval between Ba and Ta. Moseley's work proved conclusively that there could be no new elements between hydrogen and helium and that the total number of elements between Ba and Ta was 16.

Although the *number* of elements between barium (No. 56) and tantalum (No. 73) was thus definitely established, their *arrangement* in the system remained unclear. The theory of atomic structure supplied the solution to this problem.

The transition from lighter to heavier atoms may be visualised as resulting from the successive introduction of protons into the nucleus and of corresponding number of electrons into the outer sphere of the atom. In this case, the question arises whether the additional

electrons will form a *new* shell or whether they will be included in one of the *existing* shells. This problem can be solved on the basis of general considerations concerning the comparative stability of different possible structures, on the one hand, and on the basis of similarities in spectra, on the other. This was done by Bohr in 1922.

It was found, for example, that the transition from argon (No. 18) to potassium (No. 19) involved the formation of a new electronic shell; the transition from potassium to calcium (No. 20) involved the inclusion of an additional electron in the existing outer shell, while the most stable structure of scandium was 2, 8, 9, 2, which corresponded to inclusion of the next electron in the *second outermost* shell.

Of the elements following scandium, titanium has the structure 2, 8, 10, 2, vanadium—2, 8, 11, 2, etc. Further additions to the second outermost shell only cease with copper (No. 29), the atom of which has the structure 2, 8, 18, 1. The distribution of electrons in the shells of atoms of still heavier elements is shown in the table on page 162, which is the periodic system of the elements in the form proposed by Werner.

When considering the elements directly following barium (2, 8, 18, 8, 2), it was found that in lanthanum (No. 57), the new electron is included in the *second outermost* shell, and in the lanthanide atoms (Nos. 58, 59, etc.)—in the *third outermost* shell. This shell acquires maximum stability, however, only when it is filled up to a certain limit. This limit is reached when there are 32 electrons in the shell, which corresponds to element No. 71.

In the next element, No. 72, the new electron must be included in the *second* outermost shell. This element should, consequently, have the structure 2, 8, 18, 32, 10, 2, and should be chemically *analogous to zirconium* (2, 8, 18, 10, 2) *and not to the lanthanides preceding it.* Therefore, it should be looked for not in ores where lanthanides are usually found (and where element No. 72 had been sought in vain for many years), but in zirconium minerals. Indeed, element No. 72 (Hf) was discovered in a zirconium ore in 1923.

The discovery of hafnium at last made it possible to establish definitely the arrangement of the lanthanides in the periodic system; since, in passing from one element to the next throughout this group the new electron is invariably added to a deep-seated electronic shell, they must all be placed in the same group, namely the *third* group. The *actinides*, i. e., the elements following actinium (No. 89), are now also placed all in the third group.

However, the basic significance of the theory of atomic structure for the periodic law is not merely more accurate determination of the position of certain elements. As Mendeleyev pointed out in 1889, "we do not understand the origin of the periodic law". By supplying

PERIODIC SYSTEM OF THE ELEMENTS (after Werner)

1 H 1																2 He 2
3 Li 1 2											4 Be 2 2	5 B 3 2	6 C 4 2	7 N 5 2	8 O 6 2	9 F 7 2	10 Ne 8 2
11 Na 1 8 2		1	2	3	4	5	6	7	8	9	12 Mg 2 8 2	13 Al 3 8 2	14 Si 4 8 2	15 P 5 8 2	16 S 6 8 2	17 Cl 7 8 2	18 A 8 8 2
19 K 1 8 8 2	20 Ca 2 8 8 2	21 Sc 2 9 8 2	22 Ti 2 10 8 2	23 V 2 11 8 2	24 Cr 1 13 8 2	25 Mn 2 13 8 2	26 Fe 2 14 8 2	27 Co 2 15 8 2	28 Ni 2 16 8 2	29 Cu 1 18 8 2	30 Zn 2 18 8 2	31 Ga 3 18 8 2	32 Ge 4 18 8 2	33 As 5 18 8 2	34 Se 6 18 8 2	35 Br 7 18 8 2	36 Kr 8 18 8 2
37 1 Rb 8 18 8 2	38 2 Sr 8 18 8 2	39 2 Y 9 18 8 2	40 2 Zr 10 18 8 2	41 1 Nb 12 18 8 2	42 1 Mo 13 18 8 2	43 2 Tc 13 18 8 2	44 1 Ru 15 18 8 2	45 1 Rh 16 18 8 2	46 0 Pd 18 18 8 2	47 1 Ag 18 18 8 2	48 2 Cd 18 18 8 2	49 3 In 18 18 8 2	50 4 Sn 18 18 8 2	51 5 Sb 18 18 8 2	52 6 Se 18 18 8 2	53 7 I 18 18 8 2	54 8 Xe 18 18 8 2
55 1 8 Cs 18 18 8 2	56 2 8 Ba 18 18 8 2	57—71 Rare earths	72 2 10 Hf 32 18 8 2	73 2 11 Ta 32 18 8 2	74 2 12 W 32 18 8 2	75 2 13 Re 32 18 8 2	76 2 14 Os 32 18 8 2	77 2 15 Ir 32 18 8 2	78 1 17 Pt 32 18 8 2	79 1 18 Au 32 18 8 2	80 2 18 Hg 32 18 8 2	81 3 18 Tl 32 18 8 2	82 4 18 Pb 32 18 8 2	83 5 18 Bi 32 18 8 2	84 6 18 Po 32 18 8 2	85 7 18 At 32 18 8 2	86 8 18 Rn 32 18 8 2
87 1 8 Fr 18 32 18 8 2	88 2 8 Ra 18 32 18 8 2	89 2 9 Ac 18 32 18 8 2	90 2 10 Th 18 32 18 8 2	91 2 10 Pa 20 32 18 8 2	92 2 9 U 21 32 18 8 2												

Rare-earth Elements

57 2 9 La 18 18 8 2	58 2 8 Ce 20 18 8 2	59 2 8 Pr 21 18 8 2	60 2 8 Nd 22 18 8 2	61 2 8 Pm 23 18 8 2	62 2 8 Sm 24 18 8 2	63 2 9 Eu 25 18 8 2	64 2 9 Gd 25 18 8 2	65 2 8 Tb 27 18 8 2	66 2 8 Dy 28 18 8 2	67 2 8 Ho 29 18 8 2	68 2 8 Er 30 18 8 2	69 2 8 Tm 31 18 8 2	70 2 8 Yb 32 18 8 2	71 2 9 Lu 32 18 8 2

the picture of the step-by-step development of atomic structures, which is accompanied *by a periodic recurrence of similar electronic formations*, the theory of the structure of atoms revealed the physical meaning of the periodic law. It may be said that only with the development of this theory did we really come to understand its essence.

VI-3. Structure of the Periodic Table. Mendeleyev's table of the elements (see fly-leaf), which is a graphic expression of the periodic law, consists of *periods* and *groups*. In all, there are seven periods in the table, of which three are *short* and four are *long*. Each period (except the first and the last) includes elements, the electronic structures of which are intermediate between the structures of two consecutive inert gases:

He (2)—Ne (2,8)—A (2, 8, 8)—Kr (2, 8, 18, 8)—Xe (2, 8, 18, 18, 8)—
—Rn (2, 8, 18, 32, 18, 8)

The first of the short periods contains only hydrogen and helium, while the other two contain 8 elements each. Of the long periods, the fourth and the fifth contain 18 elements each, the sixth contains 32 elements, and the seventh remains incomplete. The general nature of the changes in electronic structure of the atoms in the individual periods is clearly conveyed by the comparison below.

Periods	Atomic numbers	Elements	Number of electrons in different shells						
			K $n=1$	*L* 2	*M* 3	*N* 4	*O* 5	*P* 6	*Q* 7
1	1 → 2	H → He	1 → 2						
2	3 → 10	Li → Ne	2	1 → 8					
3	11 → 18	Na → A	2	8	1 → 8				
4	19 → 36	K → Kr	2	8	8 → 18	1 → 8			
5	37 → 54	Rb → Xe	2	8	18	8 → 18	1 → 8		
6	55 → 86	Cs → Rn	2	8	18	18 → 32	8 → 18	1 → 8	
7	87 →	Fr →	2	8	18	32	18 →	8 →	1 →

1) The electron has three degrees of freedom of movement in space (corresponding to the three coordinate axes), and an additional degree of freedom associated with its own rotation. Therefore, in order to fully characterise an electron, it is necessary and sufficient to indicate four quantum numbers.

Consequently, in order to give a detailed description of the atoms, a system of four quantum numbers—n, l, m_l and m_s — was developed. Of these, the *principal* quantum number, n, retained its original meaning, while l was introduced in place of the azimuthal quantum number, k, with which it is related by the expression: $l = k - 1$. Since the original azimuthal quantum number could assume any integral value in the series $k = 1, 2, 3 \ldots n$, l (which has retained the name of the *azimuthal* quantum number) can assume any integral value in the series $l = 0, 1, 2, \ldots (n - 1)$.

The so-called *magnetic* quantum number, m_l, is related to the magnetic moment of the electron arising from its movement n its orbit. It may assume all the integral values from $-l$ to $+l$, i. e., it may have $2l+1$ different values. For example, when $l=3$, the values of m_l will be: -3, -2, -1, 0, $+1$, $+2$, $+3$.

The so-called *spin* quantum number, m_s, is also connected with a magnetic moment of the electron—in this case not with the orbital movement but with that arising from its own rotation, i. e., its spin. This quantum number can assume only two values, $+\,^1/_2$ and $-\,^1/_2$.

The *exclusion principle* (Pauli, 1925), which is an important physical generalisation, asserts that *no atom can contain simultaneously two electrons with all their quantum numbers equal.*

2) In classifying spectra, it is customary to divide the electrons of each *shell* defined by the *principal* quantum number n, into *subshells*, each corresponding to an *azimuthal* quantum number l. The numerical values of the latter are usually replaced by conventional letters in accordance with the series shown below:

Value of l	0	1	2	3	4
Spectroscopic symbol	*s*	*p*	*d*	*f*	*g*

In characterising a particular subshell of electrons, its principal quantum number is first denoted by a figure and then its azimuthal quantum number by a letter. For example, the symbol $3d$ signifies that the subshell of electrons is in the third shell and has the value $l=2$. The number of electrons in the subshell is indicated by attaching it as superscript to the corresponding letter. For example, the symbol $3d^{10}$ means that the $3d$ subshell contains 10 electrons.

The spectroscopic description of the electronic structure of an atom includes all the individual symbols of its subshells, arranged in increasing order, first of n and then of l. For example, for Ne with its 10 electrons we have $1s^2 2s^2 2p^6$. This description shows that two electrons in the neon atom are in the first shell and have the value $l=0$; two of the eight electrons in the second shell also have $l=0$, and for the other six $l=1$.

3) From the possible values of m_l corresponding to the different values for l, the maximum capacity of the individual subshells of any particular shell can be found. This capacity is often expressed as the number of independent cells, each of which is capable of accommodating one electron pair:

Subshell	*s*	*p*	*d*	*f*	*g*
Maximum capacity	2	6	10	14	18
Number of cells	1	3	5	7	9

As the atomic number increases the subshells fill up in such a way that each additional electron strives to occupy the lowest energy level (of those yet unfilled), since this corresponds with its most stable bond with the nucleus. The distribution of electrons in the subshells of each atom can be seen from the table (p. 165).

The *groups* of the periodic table include elements according to chemical similarity. In all, there are nine groups in the table. Of these, the zero group consists of the inert gases, while the eighth group contains only elements belonging to the long periods. In each of the remaining groups, the elements belonging to the short periods (which Mendeleyev called "typical" elements), are followed by *two subgroups* of elements of the long periods.

Distribution of Electrons in Atoms

Layer	K	L	M			N					
n	1	2	3			4					
l	0	0	1	0	1	2	0	1			
Subgroup	1s	2s	2p	3s	3p	3d	4s	4p			
1 H	1										
2 He	2										
3 Li	2	1									
4 Be	2	2									
5 B	2	2	1								
6 C	2	2	2								
7 N	2	2	3								
8 O	2	2	4								
9 F	2	2	5								
10 Ne	2	2	6								
11 Na	2	2	6	1							
12 Mg	2	2	6	2							
13 Al	2	2	6	2	1						
14 Si	2	2	6	2	2						
15 P	2	2	6	2	3						
16 S	2	2	6	2	4						
17 Cl	2	2	6	2	5						
18 A	2	2	6	2	6						
19 K	2	2	6	2	6		1				
20 Ca	2	2	6	2	6		2				
21 Sc	2	2	6	2	6	1	2				
22 Ti	2	2	6	2	6	2	2				
23 V	2	2	6	2	6	3	2				
24 Cr	2	2	6	2	6	5	1				
25 Mn	2	2	6	2	6	5	2				
26 Fe	2	2	6	2	6	6	2				
27 Co	2	2	6	2	6	7	2				
28 Ni	2	2	6	2	6	8	2				
29 Cu	2	2	6	2	6	10	1				
30 Zn	2	2	6	2	6	10	2				
31 Ga	2	2	6	2	6	10	2	1			
32 Ge	2	2	6	2	6	10	2	2			
33 As	2	2	6	2	6	10	2	3			
34 Se	2	2	6	2	6	10	2	4			
35 Br	2	2	6	2	6	10	2	5			
36 Kr	2	2	6	2	6	10	2	6			

Layer	K	L	M	N				O			P
n	1	2	3	4				5			6
l				0	1	2	3	0	1	2	0
Subgroup				4s	4p	4d	4f	5s	5p	5d	6s
37 Rb	2	8	18	2	6			1			
38 Sr	2	8	18	2	6			2			
39 Y	2	8	18	2	6	1		2			
40 Zr	2	8	18	2	6	2		2			
41 Nb	2	8	18	2	6	4		1			
42 Mo	2	8	18	2	6	5		1			
43 Tc	2	8	18	2	6	5		2			
44 Ru	2	8	18	2	6	7		1			
45 Rh	2	8	18	2	6	8		1			
46 Pd	2	8	18	2	6	10		0			
47 Ag	2	8	18	2	6	10		1			
48 Cd	2	8	18	2	6	10		2			
49 In	2	8	18	2	6	10		2	1		
50 Sn	2	8	18	2	6	10		2	2		
51 Sb	2	8	18	2	6	10		2	3		
52 Te	2	8	18	2	6	10		2	4		
53 I	2	8	18	2	6	10		2	5		
54 Xe	2	8	18	2	6	10		2	6		
55 Cs	2	8	18	2	6	10		2	6		1
56 Ba	2	8	18	2	6	10		2	6		2
57 La	2	8	18	2	6	10		2	6	1	2
58 Ce	2	8	18	2	6	10	2	2	6		2
59 Pr	2	8	18	2	6	10	3	2	6		2
60 Nd	2	8	18	2	6	10	4	2	6		2
61 Pm	2	8	18	2	6	10	5	2	6		2
62 Sm	2	8	18	2	6	10	6	2	6		2
63 Eu	2	8	18	2	6	10	7	2	6		2
64 Gd	2	8	18	2	6	10	7	2	6	1	2
65 Tb	2	8	18	2	6	10	9	2	6		2
66 Dy	2	8	18	2	6	10	10	2	6		2
67 Ho	2	8	18	2	6	10	11	2	6		2
68 Er	2	8	18	2	6	10	12	2	6		2
69 Tm	2	8	18	2	6	10	13	2	6		2
70 Yb	2	8	18	2	6	10	14	2	6		2
71 Lu	2	8	18	2	6	10	14	2	6	1	

Layer	K	L	M	N	O				P		Q
n	1	2	3	4	5				6		7
l					0	1	2	3	0	1	2	0
Subgroup					5s	5p	5d	5f	6s	6p	6d	7s
72 Hf	2	8	18	32	2	6	2		2			
73 Ta	2	8	18	32	2	6	3		2			
74 W	2	8	18	32	2	6	4		2			
75 Re	2	8	18	32	2	6	5		2			
76 Os	2	8	18	32	2	6	6		2			
77 Ir	2	8	18	32	2	6	7		2			
78 Pt	2	8	18	32	2	6	9		1			
79 Au	2	8	18	32	2	6	10		1			
80 Hg	2	8	18	32	2	6	10		2			
81 Tl	2	8	18	32	2	6	10		2	1		
82 Pb	2	8	18	32	2	6	10		2	2		
83 Bi	2	8	18	32	2	6	10		2	3		
84 Po	2	8	18	32	2	6	10		2	4		
85 At	2	8	18	32	2	6	10		2	5		
86 Rn	2	8	18	32	2	6	10		2	6		
87 Fr	2	8	18	32	2	6	10		2	6		2
88 Ra	2	8	18	38	2	6	10		2	6		2
89 Ac	2	8	18	32	2	6	10		2	6	1	2
90 Th	2	8	18	32	2	6	10		2	6	2	2
91 Pa	2	8	18	32	2	6	10	2	2	6	1	2
92 U	2	8	18	32	2	6	10	3	2	6	1	2
93 Np	2	8	18	32	2	6	10	5	2	6		2
94 Pu	2	8	18	32	2	6	10	6	2	6		2
95 Am	2	8	18	32	2	6	10	7	2	6		2
96 Cm	2	8	18	32	2	6	10	7	2	6	1	2
97 Bk	2	8	18	82	2	6	10	9	2	6		2
98 Cf	2	8	18	32	2	6	10	10	2	6		2
99 Es	2	8	18	32	2	6	10	11	2	6		2
100 Fm	2	8	18	32	2	6	10	12	2	6		2
101 Md	2	8	18	32	2	6	10	13	2	6		2
102 No	2	8	18	32	2	6	10	14	2	6		2
103 —	2	8	18	32	2	6	10	14	2	6	1	2

A serious drawback of the usual version of the periodic table was that it did not reveal the relationship between the typical elements of each group and the members of its left and right subgroups. Thus, from the table it followed that in group V, for instance, antimony is similar to arsenic, niobium to vanadium, and phosphorus to nitrogen. However, it remained unclear how vanadium and arsenic were related to phosphorus.

In solving this problem, chemists were for a long time guided by the more conspicuous individual properties of the elements, selected at random. Thus, when considering group V, they proceeded from the existence of hydrogen compounds of the type EH_3 for both phosphorus and arsenic and the absence of such a compound for vanadium. On this ground, the arsenic subgroup was regarded as the "principal" subgroup of group V, a direct continuation of its typical elements. On the other hand, the vanadium subgroup was regarded as "subordinate" and completely cut off from phosphorus and nitrogen. As a result, there was nothing to justify placing the elements of the vanadium subgroup in group V at all. Since the same was the case with other groups, many chemists thought it more proper to legalise the situation as it stood by rearranging the periodic table as proposed at that time, in particular, by Werner (1905).

After the electronic structures of atoms and their determinative influence on the properties of the elements had been established, it became clear that these structures constitute the decisive feature which must serve as the basis for any chemical classification. This found expression in the periodic system adopted by Bohr (p. 167)*, which was based on the similarities in electronic structures of the *neutral atoms*. As can be seen from this system (see connecting lines), the division into "principal" and "subordinate" subgroups is fully preserved. Thus, the impression was created that a theoretical basis was provided for spontaneously formed conceptions.

Bohr's approach to the interpretation of the periodic system is, however, rather one-sided. As a matter of fact, the structure of the neutral atoms may have a determinative significance only in the case of *simple* substances and the reactions in which they participate. But when it comes to the properties of *complex* substances and the reactions between them, the determining factors are the structures of the atoms in the valency states corresponding to the compounds in question. Hence, a sufficiently profound interpretation of the periodic system is possible only if the structural peculiarities of the atoms in all their characteristic valency states as well as in their neutral state are taken into account.

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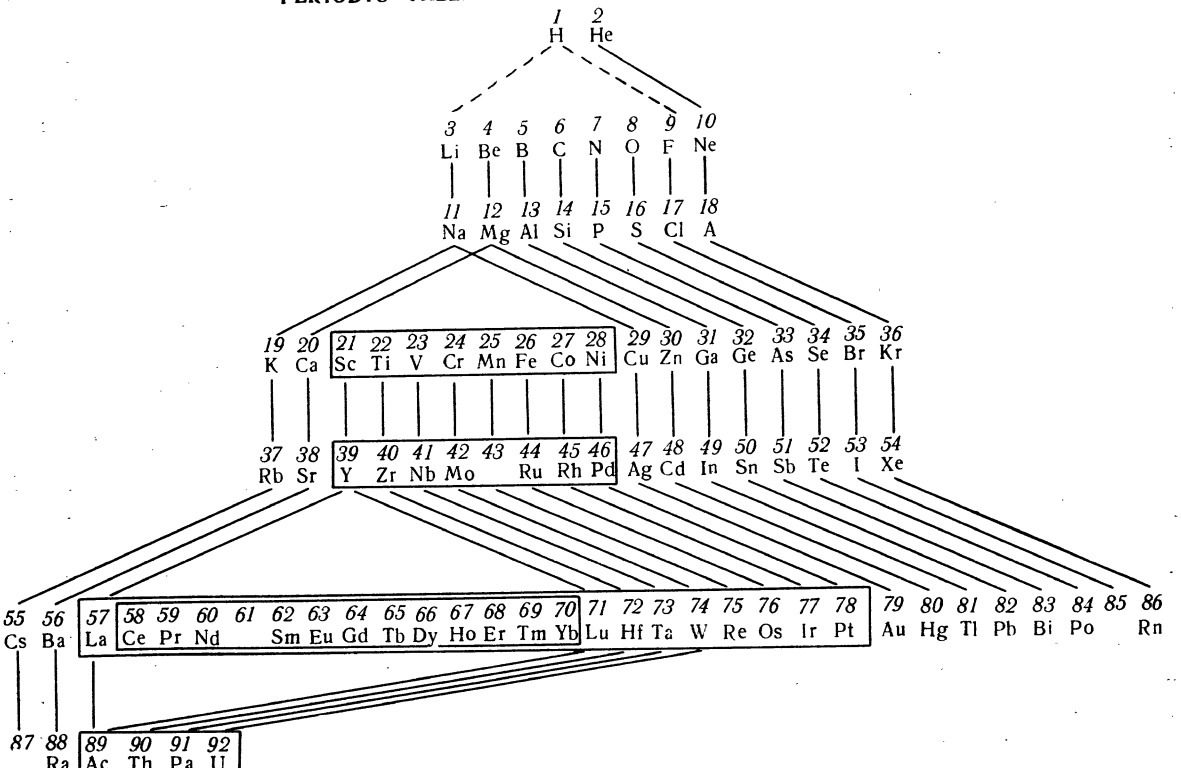
* The frames enclose elements whose atoms undergo completion of inner electron shells: the second (single frame) or third (double frame) from the outside.


PERIODIC TABLE OF ELEMENTS (after Bohr)
1 H
2 He
3 Li
4 Be
5 B
6 C
7 N
8 O
9 F
10 Ne
11 Na
12 Mg
13 Al
14 Si
15 P
16 S
17 Cl
18 A
19 K
20 Ca
21 Sc
22 Ti
23 V
24 Cr
25 Mn
26 Fe
27 Co
28 Ni
29 Cu
30 Zn
31 Ga
32 Ge
33 As
34 Se
35 Br
36 Kr
37 Rb
38 Sr
39 Y
40 Zr
41 Nb
42 Mo
43
44 Ru
45 Rh
46 Pd
47 Ag
48 Cd
49 In
50 Sn
51 Sb
52 Te
53 I
54 Xe
55 Cs
56 Ba
57 La
58 Ce
59 Pr
60 Nd
61
62 Sm
63 Eu
64 Gd
65 Tb
66 Dy
67 Ho
68 Er
69 Tm
70 Yb
71 Lu
72 Hf
73 Ta
74 W
75 Re
76 Os
77 Ir
78 Pt
79 Au
80 Hg
81 Tl
82 Pb
83 Bi
84 Po
85
86 Rn
87
88 Ra
89 Ac
90 Th
91 Pa
92 U

VI-4. Electronic Analogues. The correct grouping of analogous elements is a necessary preliminary condition for a rational consideration of the factual material of general chemistry on the basis of the periodic law. In this grouping one cannot be guided merely by the closeness of certain properties, since the similarity of the elements must follow not only from the formal resemblance between them, but also from their regular differences reflecting the development of the atomic structures in the particular series. It is these structures as the determining factor in the chemical behaviour of the elements that must serve as the basis for a correct grouping of analogues.

If neutral atoms and elementary ions, i. e., ionised atoms, were structureless spheres, their properties would be determined only by the magnitudes of their charges and radii. Actually, the *structure of their electronic shells* is of enormous importance. The *outermost* shell plays the decisive role with respect to chemical properties. The dependence of the properties of the atoms and ions on the *second* outermost shell is much less pronounced (the more electrons there are in the outermost shell and the fewer there are in the second outermost shell, the weaker the influence of the structure of the latter). The importance of the structure of the still more deep-seated electronic shells is almost zero. Therefore, in grouping elements into analogues, the structure of only the outermost shell need be considered as a first approximation, and the second outermost shell may be regarded only as a correction term.

With this in mind, consider the elements Mg, Ca and Zn. When their valency is zero, i.e., when they are in the form of neutral atoms, they each have two electrons in their outermost shell. Consequently, the atoms of Ca and Zn may be regarded with equal right as analogues of the Mg atom (if the structure of the second outermost shell is disregarded). It is different with the divalent state, when Mg and Ca each contain 8 electrons in their outermost shells, while Zn has 18 electrons in its outermost shell. Now, only Ca, and not Zn, is an analogue of Mg. The same is true of the elements Na, K and Cu. The difference lies merely in the fact that owing to the presence of only one electron in the outermost shell of their neutral atoms, the structure of the second outermost shell has a much greater effect than in any other part of the periodic table. Therefore, of all the *atomic* analogues, Na and Cu show the least resemblance.

By systematically carrying out this comparison of the atomic structures of the elements in their characteristic valency states, it is easy to see that there can be *two different cases of analogy* in the groups of the periodic table. In one case, the elements in question have the same type of structure in their outermost electronic shells with *any* given valency, and therefore may be called *complete analogues.* This applies to all the elements which are arranged below one another in

the long periods, e. g., V, Nb and Ta, on the one hand (the slight difference between the neutral atom of Nb and those of V and Ta is of minor importance), and As, Sb and Bi, on the other hand, as can be seen from their electronic structures:

V	Nb	Ta	Valency	As	Sb	Bi
—	—	—	—3	2, 8, 18, 8	2, 8, 18, 18, 8	2, 8, 18, 32, 18, 8
2, 8, 11, 2	2, 8, 18, 12, 1	2, 8, 18, 32, 11, 2	0	2, 8, 18, 5	2, 8, 18, 18, 5	2, 8, 18, 32, 18, 5
2, 8, 10	2, 8, 18, 10	2, 8, 18, 32, 10	+3	2, 8, 18, 2	2, 8, 18, 18, 2	2, 8, 18, 32, 18, 2
2, 8, 8	2, 8, 18, 8	2, 8, 18, 32, 8	+5	2, 8, 18	2, 8, 18, 18	2, 8, 18, 32, 18

In the other case, the uniformity of structures of the outermost shells applies only to certain *individual* valencies, and therefore the corresponding elements may be called *incomplete analogues*. An example of these is vanadium and arsenic with respect to phosphorus:

Valency	V	P	As
—3	—	2, 8, 8	2, 8, 18, 8
0	2, 8, 11, 2	2, 8, 5	2, 8, 18, 5
+3	2, 8, 10	2, 8, 2	2, 8, 18, 2
+5	2, 8, 8	2, 8	2, 8, 18

As can be seen from the above comparison, arsenic is a structural analogue of phosphorus for the valencies —3, 0 and +3, but ceases to be such when the valency is +5. On the other hand, vanadium which has no structural similarity with phosphorus at lower valencies *becomes its direct analogue when the valency is* +5. A similar relationship holds good for the elements of groups III, IV, VI and VII of the periodic table. Thus, the regularity of structure of its conventional (short) form is theoretically substantiated.

From the above it follows, that there is one series of analogous elements (a) for all valencies other than the positive valency corresponding to the number of the group (which may be called the *charac-*

teristic valency and which, as a rule, is the maximum possible valency), and another essentially different series (b) for the characteristic valency.

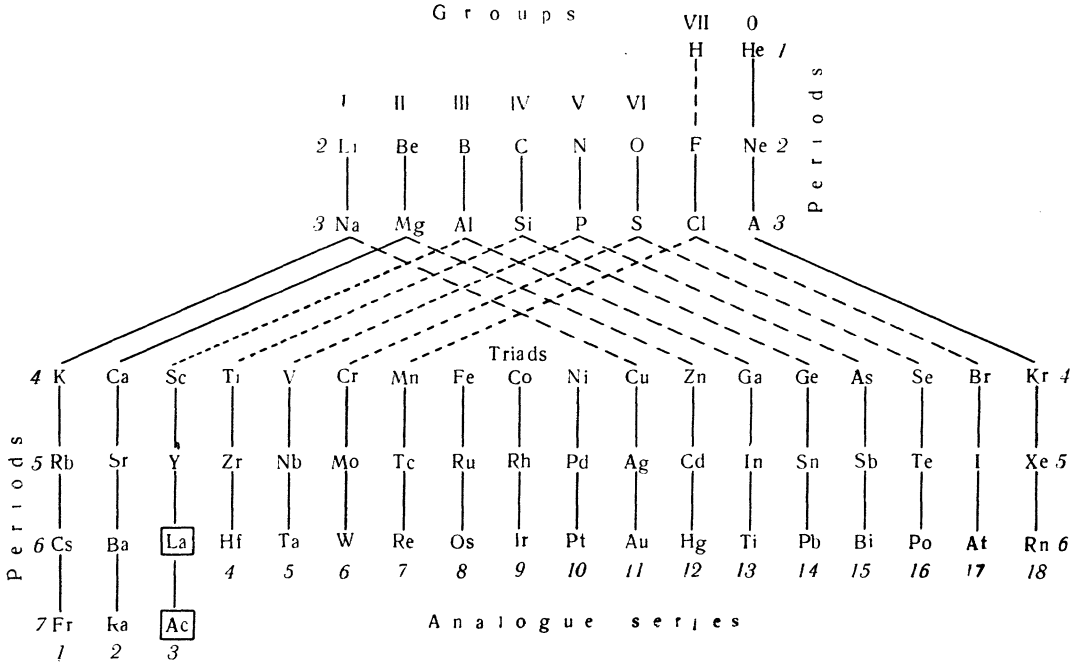
Groups	I	II	III	IV	V	VI	VII
a	Li Na K Cu	Be Mg Ca Zn	B Al Sc Ga	C Si Ti Ge	N P V As	O S Cr Se	F Cl Mn Br
b	Li Na K Cu	Be Mg Ca Zn	B Al Sc Ga	C Si Ti Ge	N P V As	(O) S Cr Se	(F) Cl Mn Br

Both distributions of analogues are clearly reflected in the modification of the periodic table shown on p. 171. Complete analogues are connected by continuous lines; elements similar in all except the characteristic valencies are connected by broken lines, and elements that are analogues in the characteristic valency (and only in this valency) are connected by dotted lines. The symbol |La| denotes lanthanum and the lanthanides, and the symbol |Ac| denotes actinium and the actinides.

For convenience in using the table, it will be useful to note that the number of each analogue series (except 9, 10 and 18) either corresponds direct to the group number, or does so when ten is subtracted from it. For example, in the third group, the left- and right-hand subgroups form series 3 and 13, and in the fourth group, they form series 4 and 14, respectively. Since this modification of the periodic system takes into account the electronic structure of the elements not only in the form of neutral atoms, but in all their valency states as well, it is the most suitable basis for the classification of chemical data.

The position of hydrogen in the periodic table warrants additional discussion. Formal approach to the structure of its atom would make hydrogen an analogue of lithium. However, the nature of the outermost electronic shell does not determine the similarity of the elements in itself, but only in the light of the general law of development of the structures. In accordance with this law, the transition in the periods 2 → 1 is accompanied in similar elements by a decrease of eight units in the positive nuclear charge and in the number

PERIODIC TABLE OF ELEMENTS (after Nekrasov)



of outer electrons (Ne → He). This makes the neutral hydrogen atom actually an analogue of the fluorine atom. In its negative valency hydrogen is related to fluorine in the same way as He is to Ne, Li^+ to Na^+, etc., but in its positive valency (being a bare proton) it cannot have analogues among the other elements, and stands completely alone. On the whole, therefore, hydrogen is an *incomplete analogue of fluorine*. The closeness to the halogen family is in keeping with the aggregate of physical properties of hydrogen, while the structural similarity of its atom to those of the first-group elements is of the same purely formal nature as the similarity of the helium atom to the atoms of the second-group elements.

VII. SEVENTH GROUP OF THE PERIODIC TABLE

Of the members of this group, hydrogen was considered earlier. The elements immediately following it—F, Cl, Br and I—are known as the *halogens*. Element No. 85—astatine (At)—also belongs to this group. The rest of the group consists of the *manganese subgroup* elements (Mn, Tc, Re).

As can be seen from their electronic structures, the atoms of the halogens have 7 electrons in their outermost shell. On this basis certain features of their chemical properties can be outlined. Since only one electron is lacking for a stable configuration of the outermost shell, the most typical halogen compounds should be those in which the halogens behave as *monovalent non-metals*. On the other hand, their maximum positive valency may be expected to be equal to seven.

It is different with the manganese subgroup. In this case, the two outer shells are incomplete. Since there are only 2 electrons in the shell farthest from the nucleus, there is no tendency towards the addition of any more electrons. On the contrary, when electrons are yielded, 5 of the electrons from the second last shell may take part in the formation of valency bonds besides the two from the outermost shell. Therefore, the maximum positive valency of the manganese subgroup elements may also be expected to be equal to seven.

Thus, the elements of both subgroups differ greatly from one another in their basic tendencies: whereas the halogens must, primarily, be clearly non-metallic, manganese and its analogues will behave like metals.

			1			
			H			
			1.00797			1
			9			
			F			7
			18.9984			2
			17			
			Cl			7
						8
			35.453			2
		25				
2		**Mn**				
13						
8						
2	54.9381					
			35			
			Br			7
						18
						8
			79.909			2
		43				
		Tc				
2						
13		[99]				
18						
8						
2						
				53		7
				I		18
						18
			126.9044			8
						2
		75				
2		**Re**				
13						
32						
18	186.22					
8						
2						
				85		7
				At		18
						32
						18
				[210]		8
						2

VII-1. Fluorine. Like the other halogens, fluorine occurs on the earth's surface exclusively in the form of salts. Its total content in

the earth's crust is 0.02%*. The bulk of fluorine is dispersed in various rocks. The most important of the individual forms of its natural accumulations, is the mineral *fluorite* or *fluorspar*, CaF_2.

Fluorine is prepared by the electrolysis of fluorine compounds, whereupon fluorine is liberated at the anode according to the equation:

$$2F^- \rightarrow 2\ominus + 2F \rightarrow 2\ominus + F_2 \uparrow$$

A low-melting mixture of the composition $KF \cdot 2HF$ usually serves as the electrolyte. The process is conducted at about 100° C in steel electrolytic cells with steel cathodes (at which hydrogen is liberated) and carbon anodes.

Free fluorine consists of diatomic molecules and is an almost colourless gas (thick layers being greenish yellow) with a pungent odour. It condenses into a yellowish liquid at—188° C and solidifies at —218° C.

Dissociation of an F_2 molecule into atoms takes place fairly readily, the dissociation energy being 38 kcal/mole.

Chemically, fluorine may be characterised as a *monovalent non-metal*, the most active of the non-metals. This is mainly due to the fact that the fluorine atom possesses a pronounced *electron affinity*, i.e., it strongly attracts the missing valency electron necessary to fill up its outer shell:

$$F + \ominus = F^- + 82 \text{ kcal}$$

This figure, 82 kcal/gram-atom, is the quantitative expression of the electron affinity of fluorine.

Most *metals* combine with fluorine under ordinary conditions. However, the reaction is often limited to the formation of a surface film of a fluorine compound which protects the metal from further attack.

Since the fluorine derivatives of *non-metallic* elements are usually highly volatile, their formation does not protect the surface of the non-metal from the further action of fluorine. Therefore, the reaction of the latter with non-metals is often considerably more vigorous than with many metals. For example, phosphorus and sulphur ignite in gaseous fluorine and burn according to the reactions:

$$2P + 5F_2 = 2PF_5 \uparrow$$

$$S + 3F_2 = 3F_6 \uparrow$$

Fluorine does not combine directly with hydrogen or oxygen.

Fluorine removes hydrogen from hydrogen compounds of other elements. It decomposes most oxides displacing oxygen. In particular, water is decomposed according to the equation

$$F_2 + H_2O \rightarrow 2HF + O$$

* Data concerning the abundance of the elements in the earth's crust are expressed throughout in atomic percentages (cf. II-3).

in which part of the displaced oxygen atoms combine with molecules of water and fluorine as well as with each other. Therefore, besides gaseous oxygen, hydrogen peroxide and *difluorine monoxide*, F_2O, are always formed in this reaction. The latter is a colourless gas with an odour similar to that of ozone.

1) Fluorine oxide (or oxygen fluoride, OF_2) can be prepared by the reaction: $2F_2 + 2NaOH = 2NaF + H_2O + F_2O\uparrow$. It is slightly soluble in water and is hardly decomposed by the latter, but strong reducing agents decompose Fe_2O (m. p. —224° C, b. p. —145° C) fairly rapidly. Fluorine oxide is highly toxic.

Fluorine has found practical application only in recent years. It is used mainly for the fluorination of organic compounds, i. e., the substitution of fluorine for hydrogen. This process has acquired great importance, since many fluororganic derivatives possess valuable properties.

Unlike free fluorine, *hydrogen fluoride*, HF, and many of its derivatives have been in use for a long time.

Direct combination of fluorine with hydrogen is accompanied by the evolution of a large amount of heat:

$$H_2 + F_2 = 2HF + 128 \text{ kcal}$$

The reaction is usually explosive, even in the dark and even if the gases are cooled to a very low temperature. This direct synthesis is of no practical value for the preparation of HF.

The industrial preparation of hydrogen fluoride is based on the reaction between CaF_2 and concentrated H_2SO_4, according to the equation:

$$CaF_2 + H_2SO_4 = 2HF\uparrow + CaSO_4$$

The process is carried out in steel furnaces at 120-300° C. The parts of the unit used for the absorption of HF, are made of lead.

Hydrogen fluoride is a colourless, highly volatile liquid (m. p. —83° C, b. p. +19.5° C), miscible with water. It has a pungent odour, fumes in air (owing to the formation of minute droplets of solution when in contact with water vapour), and vigorously attacks the walls of the respiratory tract.

2) The H—F bond has an extremely high polarity (0.45). For this reason, hydrogen fluoride has a pronounced tendency to associate by forming hydrogen bonds according to the scheme ...H—F... H— F... The energy of this bond is about 7 kcal/gram-atom, i. e., it is somewhat stronger than the hydrogen bond between water molecules.

The chemical properties of HF depend substantially on the presence or absence of water. Dry hydrogen fluoride does not act on the majority of metals. Neither does it react with metal oxides. However, once such a reaction is started, it will proceed for some time and accelerate

by itself, since the amount of water increases as a result of the reaction in accordance with the equation:

$$MO + 2HF = MF_2 + H_2O$$

Hydrogen fluoride acts on the oxides of certain non-metals in a similar manner. The reaction between HF and silicon dioxide, SiO_2 (sand, quartz), is of practical importance, since the latter is contained in glass. The reaction proceeds according to the equation:

$$SiO_2 + 4HF = SiF_4\uparrow + 2H_2O$$

That is why hydrogen fluoride must not be prepared or kept in glass vessels. Solutions are usually stored in bottles made of artificial plastics which are not affected by HF.

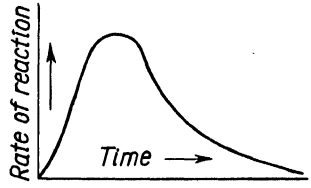


Fig. 95. Course of an autocatalytic reaction

The application of hydrogen fluoride for "etching" glass, is based on the reaction between HF and SiO_2. As a result of the removal of SiO_2 molecules, the surface of the glass becomes dull, and it is possible to make various inscriptions, etc., on it.

3) The above cases of the reactions between dry hydrogen fluoride and oxides of metals and non-metals, are typical examples of *autocatalytic reactions*, i. e., processes in which the catalyst (water in this case) is not introduced into the system from without, but is one of the reaction products. As shown in Fig. 95, the rate of these processes at first rises to a certain maximum as the quantity of catalyst in the system increases, after which it begins to fall off owing to the reduction in the concentration of the reacting substances.

In aqueous solutions HF behaves like a monobasic acid of medium strength. A commercial solution of *hydrofluoric* acid, as it is called, usually contains 40% HF.

Hydrofluoric acid reacts more or less vigorously with the majority of metals. However, in many cases, the reaction occurs only on the surface of the metal, after which the latter is protected from further attack by the coating of sparingly soluble salt formed. Lead, in particular, behaves in this way, and can therefore be employed for the manufacture of HF-resistant equipment parts.

4) Besides electrolytic dissociation according to the equation $HF \rightleftarrows H^+ + F'$ ($K = 7 \times 10^{-4}$), there is another equilibrium peculiar to hydrofluoric acid, $F' + HF \rightleftarrows HF_2'$. The value of the equilibrium constant $[HF_2']/[F'][HF] = 5$

shows that in solutions of HF there are more complex anions $(FHF)'$ (of linear structure with d (FF) = 2.3 Å) than the usual F' anions.

The salts of hydrofluoric acid are called *fluorides*. Most of them are sparingly soluble in water; of the derivatives of the common metals, only the fluorides of Na, K, Ag, Al, Sn and Hg are readily soluble. All the salts of hydrofluoric acid are poisonous. If HF contacts the skin, it causes painful burns which are difficult to heal (especially under the nails). Therefore, rubber gloves should be used when handling it.

The practical applications of hydrofluoric acid are fairly diverse. It is used in the oil industry (for the synthesis of high-grade petrols), for the removal of sand from metal castings, in the analysis of minerals, etc. Certain fluorides, which will be considered in greater detail under the corresponding elements, also find extensive practical application.

VII-2. Chlorine. Chlorine is approximately as abundant in nature as fluorine, and accounts for 0.02% of the total number of atoms in the earth's crust. The human organism contains 0.25% of chlorine by weight.

The original form of occurrence of chlorine in nature is in keeping with its extraordinary dispersion: the element is contained in small quantities in a great variety of mineral species in the earth's crust. The incessant action of water over millions of years eroded the rocks and washed out their soluble constituents so that chlorine compounds accumulated in seas. When the latter dried up huge deposits of NaCl were formed in many parts of the earth, and these are the basic raw material for the production of chlorine.

The total world consumption of chlorine is about 10 million tons a year. It is used mainly for bleaching cloth and paper pulp, disinfecting drinking water (approximately 1.5 g per cu m), and in the chemical industry.

The principal industrial method for the preparation of chlorine is the electrolysis of a concentrated solution of NaCl (Fig. 96). In this process, chlorine is liberated at the anode ($2Cl' - 2\ominus = Cl_2\uparrow$), while hydrogen ($2H^+ + 2\ominus = H_2\uparrow$) and NaOH are formed at the cathode.

In the laboratory chlorine is usually prepared by the cation of MnO_2 or $KMnO_4$ on hydrocloric acid:

$$MnO_2 + 4HCl = MnCl_2 + Cl_2\uparrow + 2H_2O$$

$$2KMnO_4 + 16HCl = 2KCl + 2MnCl_2 + 5Cl_2\uparrow + 8H_2O$$

The latter reaction is much more vigorous than the former (which requires heating).

Free chlorine is a yellowish-green gas (m. p. —101°C, b. p. —34°C) consisting of diatomic molecules. One volume of water dissolves about

two volumes of chlorine. The resulting solution is often called "chlorine water".

Like fluorine, chlorine has a pungent odour and causes inflammation of the respiratory tract. A first aid measure in case of acute poisoning by chlorine is inhalation of the vapour of an alcohol-ether mixture. Inhalation of spirits of ammonia is also beneficial.

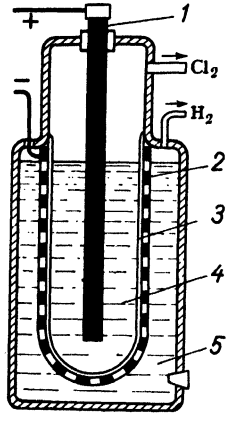


Fig. 96. Electrolytic cell for producing chlorine:
1—carbon anode; *2*—iron cathode; *3*—asbestos membrane; *4*—NaCl solution; *5*—NaOH solution

Chlorine is similar to fluorine in chemical properties; it is also an active *monovalent non-metal*. However, its activity is lower than that of fluorine. Therefore, the latter is able to displace it from its compounds.

Owing to its lower electron affinity, the non-metallic properties of chlorine are weaker than those of fluorine. Nevertheless, its chemical activity is very high—chlorine combines with almost all the common metals (sometimes only in the presence of traces of water or on heating) and with all the non-metallic elements except carbon, nitrogen and oxygen. It is important to note that in the absence of moisture, chlorine practically does not attack iron.

1) The reaction between chlorine and fluorine occurs only if a mixture of the gases is heated above 200° C. Under these conditions, colourless ClF (m. p. —154° C, b. p. —101° C) is formed, and if this is heated with an excess of fluorine, colourless ClF_3 (m. p. —83° C, b. p. +11° C) results. Both substances are highly reactive.

The reaction between chlorine and *hydrogen* in accordance with the equation

$$H_2 + Cl_2 = 2HCl + 44 \text{ kcal}$$

proceeds very slowly under ordinary conditions, but if a mixture of these gases is heated or exposed to strong light (direct sunlight, burning magnesium, etc.), the reaction takes place explosively.

A detailed study of this reaction cleared up the nature of its separate stages (its so-called *elementary processes*). First, owing to the energy ($h\nu$) of ultraviolet rays (or heating), the chlorine molecule dissociates into atoms, which then react with hydrogen molecules, forming HCl and an atom of hydrogen. The latter, in turn, reacts with

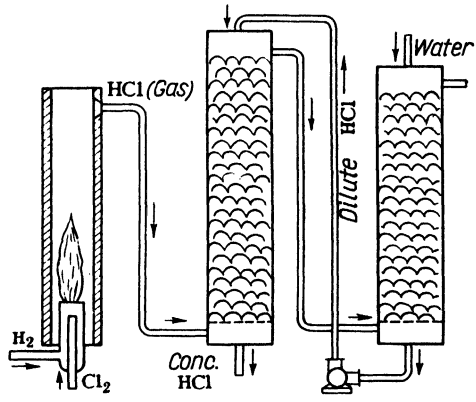


Fig. 97. HCl synthesis plant

a chlorine molecule, forming HCl and an atom of chlorine, etc. The whole process may be represented by the following scheme:

1) $Cl_2 + h\nu = Cl + Cl$ (initial excitation)

2) . . . . . $Cl + H_2 = HCl + H$

3) . . . . . $H + Cl_2 = HCl + Cl$, etc.

Thus, a *chain*, as it were, of consecutive reactions results, in which each initially excited molecule of Cl_2 produces up to a million HCl molecules. Such reactions are known as *chain reactions* and play an important part in many chemical processes.

At present, direct synthesis is the chief industrial method for the production of HCl. The raw materials are chlorine and hydrogen, which are simultaneously liberated during the electrolysis of NaCl solution. Smooth running of the process is ensured by mixing the two gases only at the moment of reaction.

2) A plant for the industrial synthesis of HCl is shown in Fig. 97. After ignition, the mixture of chlorine and hydrogen continues to burn with a quiet flame, and forms hydrogen chloride. The latter is passed through two absorption towers where it is absorbed by water. The system makes use of the counter-current principle, i. e., the gas and the liquid move in opposite directions thus ensuring complete absorption of the HCl and continuity of the entire process.

Another method for the industrial production of HCl is based on the reaction between NaCl and concentrated H_2SO_4, in accordance

with the equations:

$$NaCl + H_2SO_4 = NaHSO_4 + HCl\uparrow$$
$$NaCl + NaHSO_4 = Na_2SO_4 + HCl\uparrow$$

The first of these partially takes place under ordinary conditions, and will run practically to completion on slight heating; the second is brought about only at higher temperatures. High capacity furnaces are used for this process.

Hydrogen chloride is a colourless gas (m. p. —112° C, b. p. —84° C). In the absence of moisture at ordinary temperatures, it has no effect on the majority of metals and their oxides. It is oxidised by gaseous oxygen only on heating.

Hydrogen chloride fumes in air owing to the formation of droplets of mist on contact with water vapour. Its solubility is extremely high: under ordinary conditions 1 volume of water can dissolve up to 450 volumes of hydrogen chloride.

A solution of hydrogen chloride in water is called *hydrochloric* (or muriatic) acid and is one of the strongest acids. Concentrated hydrochloric acid has a specific gravity of 1.19 and contains about 37% hydrogen chloride.

Like other strong acids, HCl vigorously dissolves many metals. The majority of its salts, called *chlorides*, are readily soluble in water. Of the derivatives of the common metals, only the chlorides of silver and lead are sparingly soluble.

The annual world consumption of hydrochloric acid runs into the millions of tons. Many of its salts find wide practical application.

Since chlorine does not react with *oxygen*, its oxygen compounds can be obtained only by indirect methods. In considering the methods of their formation, it is reasonable to proceed from the following reversible reaction between chlorine and water:

$$Cl_2 + H_2O \rightleftarrows HCl + HOCl$$

Under ordinary conditions, about half of the dissolved chlorine in saturated solution is hydrolysed.

Of the two acids—hydrochloric and *hypochlorous* (HOCl)—which are formed during the hydrolysis of chlorine, the former is very strong, while the latter is very weak ($K = 3 \times 10^{-8}$). This wide difference between the strengths of the two acids can be utilised for their separation.

If powdered chalk, $CaCO_3$, is shaken up in water, and chlorine passed through the mixture, the hydrochloric acid reacts with the chalk (according to the equation $CaCO_3 + 2HCl = CaCl_2 + CO_2\uparrow + H_2O$), while hypochlorous acid accumulates in the solution. By distilling the reaction mixture a dilute solution of HOCl can be obtained in the receiver.

Since it is an unstable compound, HOCl slowly decomposes even in such a dilute solution. The salts of hypochlorous acid are called *hypochlorites*. HOCl and its salts are *very powerful oxidising agents*.

The preparation of hypochlorites is based on the above reversible reaction between chlorine and water. Since both the substances on the right-hand side of the equation—HCl and HOCl—produce H^+ ions in solution, while both the reactants—Cl_2 and H_2O—hardly form such ions, the equilibrium can be shifted to the right by linking the H^+ ions.

The simplest way to do this is by adding an alkali to the reaction mixture. Since the H^+ ions, as they are formed, will combine with the OH^- ions into undissociated water molecules, the equilibrium will shift to the right. In the case of NaOH, for example, we have:

$$Cl_2 + H_2O \rightleftarrows HOCl + HCl$$

$$HOCl + HCl + 2NaOH \longrightarrow NaOCl + NaCl + 2H_2O$$

or, when combined,

$$Cl_2 + 2NaOH = NaOCl + NaCl + H_2O$$

The reaction between chlorine and an alkali solution results in a mixture of salts of hypochlorous and hydrochloric acids. The resulting solution ("eau de Javel") is a powerful oxidant, and is widely employed for bleaching fabrics and paper.

The reaction between chlorine and a cheaper alkali, $Ca(OH)_2$, gives what is known as *bleaching powder*. The reaction may be approximately represented by the equation

$$Cl_2 + Ca(OH)_2 = Ca\begin{<}{Cl}{OCl}\end{} + H_2O$$

which shows that bleaching powder is a *mixed* salt of hydrochloric and hypochlorous acids.

Bleaching powder is a white powder which possesses powerful oxidising properties. It is used for bleaching and disinfection, and is also one of the principal *decontaminants*, i. e., means for destroying military toxic substances.

3) In air bleaching powder gradually decomposes, mainly in accordance with the equation: $2CaCl(OCl) + CO_2 = CaCl_2 + CaCO_3 + Cl_2O$. When bleaching powder is treated with hydrochloric acid, chlorine is liberated: $Ca(Cl)OCl + 2HCl = CaCl_2 + H_2O + Cl_2$. Good commercial-quality bleaching powder has the approximate composition $3Ca(Cl)OCl \cdot Ca(OH)_2 \cdot xH_2O$ and its content of "active chlorine", i. e., chlorine which can be liberated by hydrochloric acid, is about 35% by weight.

In solution, free hypochlorous acid undergoes three different types of transformation which are brought about independently of

each other, and are therefore called *parallel* reactions:

$$1)\ HOCl = HCl + O$$
$$2)\ 2HOCl = H_2O + Cl_2O$$
$$3)\ 3HOCl = 2HCl + HClO_3$$

All these processes may take place simultaneously, but their relative rates depend greatly upon the prevailing conditions. By altering the latter, it is possible to arrive at a point where the transformation will proceed practically entirely in one direction.

Under the action of direct sunlight, the decomposition of hypochlorous acid takes place according to the first of the above equations. It proceeds in the same way in the presence of substances that combine readily with oxygen, and certain catalysts, e. g., cobalt salts.

The second type of decomposition gives *chlorine oxide*, Cl_2O. This reaction takes place in the presence of dehydrating agents, e. g., $CaCl_2$. Chlorine oxide is an explosive, brownish-yellow gas (m. p. —121° C, b. p. + 2° C) with an odour similar to that of chlorine. Cl_2O reacts with water to form HOCl, i. e., chlorine oxide is the anhydride of hypochlorous acid.

The decomposition of HOCl in accordance with the third equation proceeds very readily on heating. Therefore, the action of chlorine on a *hot* solution of an alkali can be represented by the combined equation:

$$3Cl_2 + 6KOH = KClO_3 + 5KCl + 3H_2O$$

The products of the reaction are KCl and the potassium salt of *chloric* acid, $HClO_3$. As this salt is sparingly soluble in cold water, it precipitates when the solution is cooled.

Free $HClO_3$ is known to exist only in solution. It is a strong acid (dissociated to approximately the same degree as HCl and HNO_3) and is a *powerful oxidising agent*. Its corresponding anhydride is unknown.

In contrast to free $HClO_3$, its salts (*chlorates*) possess no oxidising properties in solution. The majority of chlorates are colourless (as is $HClO_3$ itself) and are readily soluble in water. They are all highly poisonous.

4) If a moistened mixture of $KClO_3$ and oxalic acid, $H_2C_2O_4$, is heated to 60°, greenish-yellow *chlorine dioxide* (m. p. —59° C, b. p. +10° C) is formed according to the reaction: $2KClO_3 + H_2C_2O_4 = K_2CO_3 + CO_2\uparrow + H_2O + 2ClO_2\uparrow$. Free ClO_2 is unstable and may decompose eruptively. It is readily soluble in water.

5) The reaction between ClO_2 and a solution of an alkali results in the formation of salts of two acids—chloric and chlorous: $2ClO_2 + 2KOH = KClO_3 + KClO_2 + H_2O$. Chlorous acid can be obtained separately from chloric acid by the following reactions: $BaO_2 + 2ClO_2 = Ba(ClO_2)_2 + O_2$ and $Ba(ClO_2)_2 + H_2SO_4 = BaSO_4\downarrow + 2HClO_2$. Chlorous acid, which is unstable ($K = 5 \times 10^{-3}$), is known to exist only in dilute solutions in which it decomposes rapidly if stored. Its salts (*chlorites*) are colourless as a rule, and are readily soluble in water.

Unlike hypochlorites, they have powerful oxidising properties only in an acid medium. Preparations containing $NaClO_2$ are employed in the textile industry for bleaching fabrics.

On heating, $KClO_3$ begins to decompose at about 400° C in two directions:

$$4KClO_3 = 4KCl + 6O_2 \quad \text{or} \quad 4KClO_3 = 3KClO_4 + KCl$$

The reaction proceeds chiefly in accordance with the first equation in the presence of a catalyst (MnO_2, etc.), and in accordance with the second reaction, without a catalyst. *Potassium perchlorate*, which is formed in the second type of decomposition, is very slightly soluble in water, and is therefore easily separated from potassium chlorite.

In industry, $KClO_4$ is usually prepared by electrolysis of a solution of $KClO_3$ [according to the equation: $H_2O + KClO_3 = H_2\uparrow$ (cathode) + $KClO_4$ (anode)]. Its thermal decomposition according to the equation $KClO_4 = KCl + 2O_2$ begins only above 600° C.

Free *perchloric acid*, $HClO_4$, a colourless liquid that fumes in air, can be obtained by the action of concentrated sulphuric acid on potassium perchlorate. Since $HClO_4$ is volatile and can be distilled under reduced pressure without decomposing, it is easily separated from the reaction mixture:

$$KClO_4 + H_2SO_4 \rightleftarrows KHSO_4 + HClO_4$$

Anhydrous $HClO_4$ (m. p. —112° C, b. p. +39° C) is unstable and sometimes explodes even when stored. It is usually marketed as a 72% solution, which is quite stable. $HClO_4$ is much less active as an oxidising agent than $HClO_3$, and practically does not display any oxidising properties in dilute solution. On the other hand, its acidic properties are exceptionally pronounced; in fact, it is the *strongest* of all known acids.

Salts of $HClO_4$ are, as a rule, readily soluble in water. Like the acid itself, the majority of perchlorates are colourless.

When a mixture of anhydrous perchloric acid and phosphorus pentoxide, P_2O_5, is slightly heated under reduced pressure, a colourless oily liquid, *chlorine heptoxide* or *perchloric anhydride*, can be distilled off, the reaction being:

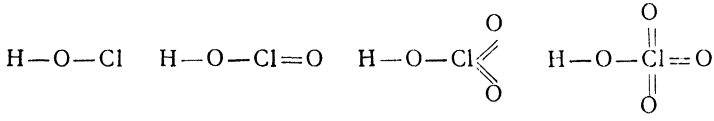
$$2HClO_4 + P_2O_5 = 2HPO_3 + Cl_2O_7$$

The structure of the chlorine heptoxide molecule (m. p. —91° C, b. p. +82° C) is represented by the formula $O_3Cl—O—ClO_3$. Cl_2O_7 explodes when strongly heated or upon impact. When it reacts with water perchloric acid is slowly formed.

Though the names of the oxyacids of chlorine and their salts have already been mentioned above, it will be useful to compare these names including the unstable acid $HClO_2$.

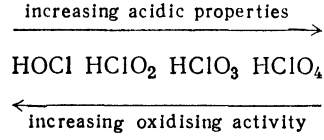
Acid	Formula	Names of salts
Hypochlorous	HOCl	Hypochlorites
Chlorous	$HClO_2$	Chlorites
Chloric	$HClO_3$	Chlorates
Perchloric	$HClO_4$	Perchlorates

The structural formulas of the four acids are:



As can be seen from the formulas, the valency of chlorine in these acids is respectively +1, +3, +5, +7.

If the oxyacids of chlorine are compared with regard to their most important chemical properties—acidity and oxidising activity—the following scheme is obtained:



Consequently, the acidity and oxidising activity grow in opposite directions. The latter is generally the greater, the less stable the acid. Indeed, whereas hypochlorous and chlorous acids are more or less stable only in dilute solution, the concentration of chloric acid may be as high as 40%, and perchloric acid is known to exist in the anhydrous state. The first three acids gradually decompose in solution, but perchloric acid may be kept for as long as may be required. The corresponding salts are usually much more stable than the free acids, but their relative stability is approximately the same as that of the acids.

VII-3. Adsorption. As far back as the end of the 18th century it was known that gases, vapours and solutes can be taken up by solid surfaces. This phenomenon now bears the general name of *adsorption*. The adsorption of water vapour which is taken up to a greater or lesser degree by the surfaces of all objects in contact with the air is a particularly frequent case. This adsorbed, or as it is sometimes called *hygroscopic*, water substantially affects certain properties of the substances that adsorb it, and, therefore, has to be taken into account in many production processes.

One of the substances with the most strongly developed ability for adsorption, i. e., *retention on the surface*, is charcoal. Treatment with superheated steam at high temperatures greatly increases its adsorptive properties, and such *activated* charcoal has become the most important component of the gas mask, which is the principal means for protecting the respiratory tract from toxic substances. On passing through the canister, the poisonous substances are retained by the charcoal surface, and thus the air entering the respiratory tract is freed from them.

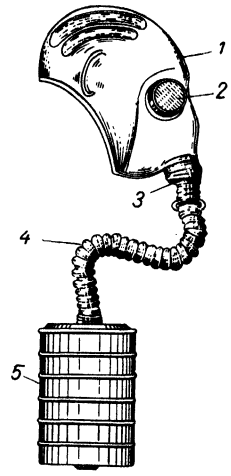


Fig. 98. A gas mask

1) One of the types of gas mask is shown in Fig. 98 where: *1*—rubber helmet; *2*—goggles; *3*—expiratory valve; *4*—flexible connecting tube made of rubber hose covered with a knitted fabric; *5*—absorption canister (kept in a special bag when the gas mask is in use). Besides charcoal, the absorbent includes certain chemicals which combine with the toxic substances, and a special packing for retaining poisonous fumes which are not absorbed by the charcoal.

The origin of adsorptive power may be made clear by referring to Fig. 99. In any solid, the individual particles (atoms, molecules or ions) are arranged in a definite order. The particles inside the body are under different conditions than those on the surface. Indeed, particle *A* is uniformly surrounded by others on all sides. Its external force field is, consequently, equally compensated on all sides by the similar fields of neighbouring particles.

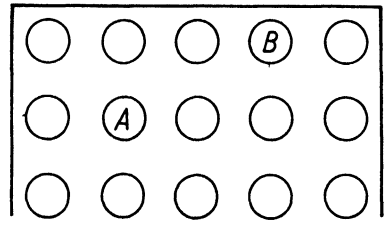


Fig. 99. Origin of an adsorption field

Particle *B* is in a different position, since its field is not compensated from without. This leaves an unsatisfied force field on the surface, by virtue of which it attracts the particles of various substances from the gas or solution in contact with it.

The intensity and nature of an adsorption field depend on the nature of the *adsorbent* and the arrangement of the particles on its surface.

Furthermore, the adsorptive capacity depends on the surface area. It is clear, therefore, that individual adsorbents may differ widely both quantitatively and qualitatively in adsorptive capacity.

2) Sometimes, adsorption may be followed by the adsorbed substance dissolving in the absorbent, i. e., passing from the surface into the bulk of the latter (*absorption*). This is apparently what happens when hydrogen is taken up by metallic palladium. Considered together, the processes of adsorption and absorption, are combined under the general heading of *sorption*, while the reverse release of adsorbed or absorbed substances into the surrounding medium is called *desorption*.

3) A special case of adsorption from solutions is the take-up of certain ions in preference to others by the surface of an ionic-type precipitate. In this case a general rule is observed, according to which *those ions are preferentially adsorbed which form sparingly soluble* (or slightly dissociated) *compounds with the oppositely charged ion of the precipitate.*

An especially frequent case is absorption by the precipitate surface of ions which form part of its own composition. If, for example, $AgNO_3$ is treated with an excess of HCl solution, mainly Cl' ions will be taken up by the AgCl precipitate. On the other hand, when HCl is treated with an excess of $AgNO_3$, the AgCl precipitate will preferentially adsorb $Ag^{\cdot}$ ions.

Adsorption phenomena are of great practical importance. Gas masks of various designs are widely used for work in different harmful industrial conditions. Adsorption is employed directly in the production of sugar (for refining), in the oil industry (for the recovery of petrol from natural gases), etc. The dyeing of fabrics, the tanning of hides and similar operations are based on adsorption processes.

Adsorption plays the principal role in many catalytic reactions and in the chemistry of colloidal solutions. Certain methods of analytical chemistry are also based on it. Thus, the best reaction for the detection of free iodine—the blue colour it imparts to starch—is due to the formation of an adsorption compound. The so-called chromatographic method for the separation substances, based on the difference in take-up by the adsorbent of the individual constituents in the initial mixture, has lately acquired great importance.

VII-4. The Bromine Subgroup. Among the elements which come under this heading, No. 85—*astatine*, At,—is not found in the earth's crust, and was obtained artificially. Since it has been investigated only in extremely small quantities, the properties of this element are practically unknown.

The content of *bromine* in the earth's crust is $3 \times 10^{-5}\%$, while that of *iodine* is $4 \times 10^{-6}\%$. Both elements are similar to chlorine with respect to occurrence in nature, but they do not, as a rule, form accumulations.

The principal sources for the industrial production of bromine are the waters of certain salt-water lakes (0.01 to 0.5% Br) and sea water (0.007% Br on the average). Some bromine is also extracted from its

compounds, which are usually contained as slight impurities in natural deposits of potassium salts, and from oil-well brines (0.01-0.1% Br).

Oil-well brines, which contain an average of 0.003% I, are also of primary importance for the industrial production of iodine. Another source of this element is seaweed, the ash of which usually contains up to 0.5% I.

Free bromine and iodine are generally prepared by displacement from their salts by chlorine according to reactions such as

$$MgBr_2 + Cl_2 = MgCl_2 + Br_2$$
$$2KI + Cl_2 = 2KCl + I_2$$

In these reactions, bromine is liberated in the form of a heavy brownish-red liquid, and iodine is evolved in the solid state. The annual world production of bromine runs into the tens of thousands, and of iodine, into the thousands of tons.

By physical properties, bromine and iodine naturally fall into the same series as chlorine and fluorine, as can be seen from the table below (in which hydrogen is also included).

The stability of the molecules (except for fluorine) from element to element of the series changes fairly regularly, the energy of dissociation generally being the higher, the smaller the distance between the nuclei:

Molecule	H_2	F_2	Cl_2	Br_2	I_2
Distance between the nuclei (Å)	0.74	1.44	1.98	2.28	2.66
Energy of dissociation (kcal/mole)	104	38	58	46	36

The specific gravity of bromine is 3.1, and that of iodine, 4.9. Since the vapour pressure of solid iodine is very high, it usually sublimes on heating. The sublimation of technical iodine is used for its purification.

Chemical formula	Molecular weight (approx.)	Under ordinary conditions		Melting point (°C)	Boiling point (°C)
		Physical state	Colour		
H_2	2	gas	colourless	—259	—253
F_2	38	gas	almost colourless	—218	—187
Cl_2	71	gas	yellowish-green	—101	—34
Br_2	160	liquid	reddish-brown	—6	59
I_2	254	solid	blackish-violet	113	184

The vapours of bromine and iodine have a pungent odour. Bromine is very similar to chlorine in its action on the organism. Its most important use is in the production of special additives for improving the quality of petrols. Iodine is used as a 5% solution in alcohol

(tincture of iodine) for sterilising wounds. Compounds of both heavy halogens are of great importance in photography, medicine, etc.

The solubilities of bromine and iodine in water are about 35 g and 0.3 g per litre, respectively. Both of these halogens (as well as astatine) dissolve much better in various organic solvents than in water.

1) When an aqueous solution of a halogen comes in contact with an organic solvent (which is immiscible with water) the halogen will be distributed between the solvent and the water in strictly definite proportions. If we take, for instance, bromine and carbon disulphide, CS_2, the ratio of the concentration of bromine in the carbon disulphide phase to its concentration in the aqueous phase remains constant (and approximately equal to 80) for different total amounts of dissolved bromine. The fact that the *concentration ratio* (or, more exactly, the *activity* ratio) of a substance distributed between two immiscible solvents is constant, is due to operation of the so-called *Distribution Law*. The ratio of the concentrations (in this case, 80) is called the partition coefficient. Its value (at constant temperature) is characteristic of the given system, viz.: solvent *A*—distributed substance—solvent *B*. This distribution is of great industrial importance, since it often enables a particular dissolved substance to be selectively extracted from a solution by means of another solvent.

Bromine and iodine are *monovalent non-metals* in their most characteristic chemical functions. As has already been pointed out (VII-1), the chemical activity of a monovalent non-metal is partly determined approximately by the value of its electron affinity, i. e., the energy which is evolved when a surplus electron is added to the corresponding neutral atom. It is obvious that exactly the same amount of energy must be expended to detach the electron from the negative ion.

The radii of the halogen ions X^- and the corresponding values of their electron affinity are compared below:

Halogen	F	Cl	Br	I
Radius of ion (Å)	1.33	1.81	1.96	2.20
Electron affinity (kcal)	82	85	77	72

Except for fluorine, the regularity that would be expected is observed, i. e., the further the electron being detached is from the nucleus, the less firmly is it retained, i. e., the lower the electron affinity of the neutral atom.

As the non-metal activity decreases in the order F—Cl—Br—I, each halogen in this series is able to displace all those to the right of it from their compounds. The displacement of chlorine by fluorine has already been discussed (VII-2). In a similar way, bromine is displaced from its compounds by chlorine, and iodine by bromine.

Nevertheless, bromine and iodine are very active non-metals. They are able to react at ordinary temperatures with many metals and some of the non-metals (e. g., phosphorus). In these reactions, bromine is not much less active than chlorine, but iodine is considerably less active.

2) The known compounds which bromine, iodine and the other halogens form with each other are compared in the table below.

Compound	ClF	ClF_3	BrF	BrF_3	BrF_5	IF_5	IF_7	BrCl	ICl	ICl_3	IBr
Physical state	gas	gas	liq.	liq.	liq.	liq.	gas	gas	solid	solid	solid
Colour	colourless	colourless	red	colourless	colourless	colourless	colourless	yellow	red	yellow	violet
M. p. (°C)	−154	−83	−33	+9	−61	+10	+6 (pressure)	−66	+27	+101 (pressure)	+42
B. p. (°C)	−101	+11	+23	+123	+41	+98	+5	+5	+97 (decomposes)	+64 (decomposes)	+59 (decomposes)

All these compounds are formed by direct interaction between the elements, and are unstable substances.

Bromine reacts with *hydrogen* only on heating, and iodine, only on intense heating and incompletely (since the reverse reaction—the decomposition of hydrogen iodide—sets in). Neither of the two hydrogen halides finds much application as such. They can be conveniently obtained by decomposing the corresponding phosphorus halides with water, according to the equation:

$$PX_3 + 3H_2O = H_3PO_3 + 3HX\uparrow$$

The reaction proceeds readily even at ordinary temperatures.

Like hydrogen chloride, HBr and HI are colourless gases which fume in air and are very soluble in water. Some of their properties are compared with the properties of HF and HCl in the table below and in Fig. 100. The latter also includes the X^- ionic radii, which approximately characterise the sizes of the corresponding hydrogen halide molecules.

Hydrogen halide	Heat of formation from elements (kcal/mole)	Length of molecular dipole (Å)	Nuclear separation (Å)	Polarity of H-X bond	Melting point (°C)	Boiling point (°C)	Degree of dissociation in 0.1 *N* solution (%)
HF	64	0.41	0.92	0.45	−83	+20	8.0
HCl	22	0.22	1.28	0.17	−112	−84	92.6
HBr	8	0.17	1.41	0.12	−88	−67	93.5
HI	−6	0.08	1.62	0.05	−51	−35	95.0

As can be seen from Fig. 100, in the series HI—HBr—HCl the properties change quite regularly whereas on passing to HF, a more or less abrupt change in properties is observed, sometimes even in a direction opposite to the general trend. This is due to the fact that contrary to its analogues hydrogen fluoride is highly associated.

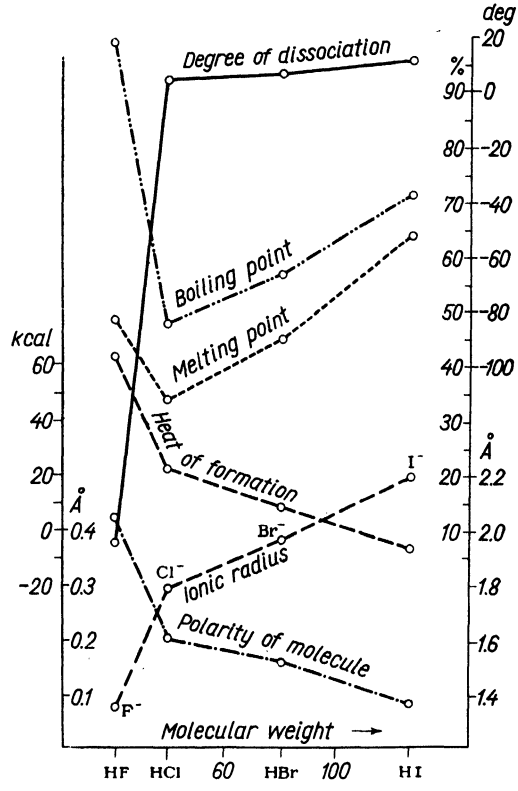


Fig. 100. Properties of the hydrogen halides

HBr and HI are very similar to hydrogen chloride in chemical properties. Like the latter, they do not attack the majority of metals in the anhydrous state, but in aqueous solution they form very strong acids, *hydrobromic* and *hydriodic*, respectively. Salts of the former are called *bromides*, and of the latter, *iodides* (the derivatives of the hydrohalic acids are, in general, known as *halides*). The solubility of bromides and iodides is, in most cases, similar to the solubility of the corresponding chlorides. In solution, astatine also exists in the form of negatively monovalent ions.

HI, HBr and HCl differ essentially in their behaviour towards oxidising agents. Molecular oxygen gradually oxidises hydriodic acid even at ordinary temperature (the reaction is greatly speeded up under the action of light):

$$O_2 + 4HI = 2H_2O + 2I_2$$

Hydrobromic acid reacts much more slowly with molecular oxygen, while hydrochloric acid is not oxidised by the latter at all. Since, however, hydrochloric acid can be oxidised by MnO_2, etc., it follows that the hydrogen halides (except HF) can be used as substances that remove oxygen, i. e., *as reducing agents*, the most active in this respect being HI. Derivatives of negatively monovalent astatine are also readily oxidised in solution.

3) The free iodine which separates out during partial oxidation of hydriodic acid is not precipitated, but remains in solution as a result of its reaction with the excess I' ions according to the equation: $I' + I_2 \rightleftarrows I_3'$. The formation of I_3' ion is not accompained by the transfer of electrons, but is due to the fact that the I' ion attracts the I_2 molecule (in the same way as it attracts molecules of water). The high solubility of iodine in aqueous solutions of iodine salts, such as potassium iodide, is due to such a formation. Certain compounds containing I_x^- ions—called *polyiodides*—are known to exist in the solid state. One example is the crystal hydrate $KI_3 \cdot H_2O$.

As in the case of chlorine, when considering the *oxygen* compounds of bromine and iodine, it is convenient to start with the reversible reaction

$$X_2 + H_2O \rightleftarrows HX + HOX$$

the equilibrium of which shifts progressively to the left as the place of the halogen is successively filled by chlorine, bromine and iodine.

Solutions of *hypobromous* acid, HOBr, and *hypoiodous* acid, HOI, can be obtained in a manner similar to the preparation of hypochlorous acid. Both acids are unstable compounds and *powerful oxidising agents*. Stability and oxidising power decrease in the order HOCl—HOBr—HOI.

The acidic nature of the compounds HOX becomes weaker in the same direction. Hypobromous acid is very weak, and hypoiodous acid possesses *amphoteric* properties. Both acids exist only in dilute solution.

4) Solutions of HOBr ($K = 2 \times 10^{-9}$) can be carried distilled only under greatly reduced pressure, whereas distillation cannot be used at all for the preparation of HOI. The constant of acidic dissociation of hypoiodous acid ($K = 2 \times 10^{-11}$) is even lower than its constant of basic dissociation (3×10^{-10}).

Besides oxidative decomposition, the following reactions are characteristic of HOBr and HOI:

$$3HOX = 2HX + HXO_3$$

These lead to the formation of *bromic* ($HBrO_3$) or *iodic* (HIO_3) acids, respectively. Of these, the former, like $HClO_3$, is known to exist only in solution, whereas the latter can be separated out in the form of readily soluble crystals. Both acids are colourless.

Bromic acid is very similar in its properties to $HClO_3$, whereas the oxidative and acidic properties of iodic acid are much weaker. The solubility of the salts decrease, as a rule, in the order $HClO_3$—$HBrO_3$—HIO_3. Like chlorates, *bromates* and *iodates*, are not oxidising agents in alkaline and neutral media.

There is no known anhydride corresponding to $HBrO_3$. If HIO_3 is heated to 230° C *iodine pentoxide*, I_2O_5, (a white powder) is formed; with water, this again produces iodic acid. Above 275° C it decomposes into iodine and oxygen.

5) Iodic acid can be formed, in particular, by the action of chlorine on iodine shaken up with water, according to the reaction: $I_2 + 5Cl_2 + 6H_2O = 2HIO_3 + 10HCl$. Therefore, if an excess of chlorine water is added to a solution of an iodine salt, the iodine colouring which appears at first will subsequently disappear. HIO_3 is usually prepared by the reaction between iodine and concentrated nitric acid, which takes place mainly in accordance with the equation: $I_2 + 10HNO_3 = 2HIO_3 + 10NO_2 + 4H_2O$.

Bromine compounds analogous to $HClO_4$ and Cl_2O_7 are unknown. On the other hand, *periodic* acid, HIO_4, and many of its salts (*periodates*) have been studied in detail. As a rule, they are sparingly soluble in water. The acid itself may be obtained by the electrolysis of an HIO_3 solution [according to the equation $H_2O + HIO_3 = H_2\uparrow$ (cathode) + HIO_4 (anode)]. It separates out as colourless crystals of the composition $HIO_4 \cdot 2H_2O$. The acidic properties of HIO_4 are much weaker than those of $HClO_4$, but its oxidising properties are, on the contrary, much more pronounced. No anhydride corresponding to it is known. When heated, HIO_4 decomposes in accordance with the equation:

$$2HIO_4 = H_2O + I_2O_5 + O_2$$

6) As an acid, HIO_4 ($K = 2 \times 10^{-2}$) is weaker than iodic acid ($K = 2 \times 10^{-1}$). On the other hand, as an oxidising agent, it is more active than HIO_3 but less active than HOI. In the crystal hydrate $HIO_4 \cdot 2H_2O$, the hydrogen atoms of the water can also be displaced by a metal, and such salts as Ag_5IO_6 and $Ba_5(IO_6)_2$ have been obtained. This shows that the crystal hydrate is actually the pentabasic *orthoiodic* acid, H_5IO_6.

It can be seen from the material considered above that the similarity of bromine and iodine to chlorine in their oxygen compounds is by no means as complete as in their hydrogen compounds: the resemblance is restricted mainly to acids of the HOX and HXO_3 types and their salts. As to the oxygen compounds of astatine, it is known only that they exist, the highest degree of oxidation corresponding to the ion AtO_3^-, i. e., to a valency of +5.

VII-5. Oxidation-reduction (Redox) Reactions. All processes of inorganic chemistry may be divided into two types: a) *not involving a change* in the valency of the reacting elements and b) *involving such a change* in the valency. The first type includes various cases of double decomposition, the equations for which are usually very simple. The second type covers displacement reactions and a number of other, often very complicated chemical processes. To be able to complete and balance their equations quickly and accurately, specially developed methods must be mastered.

Reactions of the second type are called *oxidation-reduction* reactions (redox, for short). Originally, oxidation meant only the addition of oxygen to a substance, while reduction meant only the removal of oxygen. The concepts "oxidation" and "reduction" can, however, be generalised, taking into consideration that oxygen almost always draws electrons away from the element with which it combines. Therefore, oxidation essentially consists in the *loss of electrons* by the substance being oxidised. On the other hand, when it is reduced, it recovers the electrons it had yielded earlier. Consequently, reduction essentially consists in the *addition of electrons* to the substance being reduced.

For further discussion, it is immaterial whether the electrons are completely transferred from one atom to the other (ionic bond) or whether they are only more or less drawn to (polar bond). Therefore, in this section, the yielding or gaining of electrons will be discussed irrespective of the actual type of valency bond. In general, therefore, oxidation-reduction reactions may be defined as processes associated with the *transfer of electrons* from one set of atoms to another.

Consider the following chlorine compounds:

$$HCl \quad Cl_2 \quad Cl_2O \quad Cl_2O_7$$

In HCl, chlorine is negatively monovalent. In the Cl_2 molecule, neither atom attracts electrons any more than the other; consequently, the charge of each of them is zero. In Cl_2O, chlorine is likewise monovalent, but positively so in this case. In Cl_2O_7, chlorine is positively heptavalent. Chemically, this can all be expressed thus:

$$\begin{array}{cccc} \overset{-1}{HCl} & \overset{0}{Cl_2} & \overset{+1}{Cl_2O} & \overset{+7}{Cl_2O_7} \\ A & B & C & D \end{array}$$

When referring to the conversion of chlorine from state *A* to state *D*, it may be said that it *yields* eight electrons; in the conversion from *C* to *D*, it yields six electrons; and from *B* to *D*, seven electrons. On the other hand, in the conversion from *D* to *C*, each chlorine atom *gains* six electrons; in the conversion from *D* to *B*, it gains seven electrons; and from *D* to *A*, eight electrons. A substance containing an

element that gains electrons is called an *oxidising agent*; a substance containing an element that yields them is called a *reducing agent*.

1) The relationship between the concepts "reducing agent" and "oxidising agent" can be vividly expressed by the scheme: reducing agent $\rightleftarrows$ electrons + + oxidising agent. The simplest oxidation-reduction system is an apparatus for electrolysis (Fig. 101). In this system, the cathode gives up electrons to ions, i. e., it is a reducing agent, while the anode removes them from the ions, i. e., behaves as an oxidising agent. It should be noted that of all the oxidation-reduction methods at the disposal of chemistry, electrolysis is the most powerful and universal.

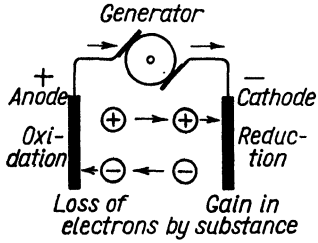


Fig. 101. Diagram of electrolytic oxidation and reduction

2) When working with oxidising and reducing agents, it is convenient to use them in normal concentrations. By a normal solution of an oxidising or reducing agent is meant a solution containing one oxidising equivalent per litre, i. e., the fraction of a gram-molecule corresponding to one electron gained or yielded by each molecule. For example, when $HClO_3$ is employed as an oxidising agent and is reduced to HCl, the valency of chlorine changes from + 5 to —1, i. e., one chlorine atom (and, consequently, one molecule of $HClO_3$) gains 6 electrons. Therefore, a normal solution of $HClO_3$, as an oxidising agent, will contain 1/6 gram-molecule per litre (while as an acid it will contain one gram-molecule per litre). All the designations for concentration remain the same as for normal solutions of acids and bases (V-5).

In order to complete equations for oxidation-reduction reactions, it is first of all necessary to know the chemical formulas of the reactants and the resultants. The former are, of course, known, while the latter must be determined either by special chemical analysis, or directly, from the known properties of the elements. Since, however, oxidation-reduction processes usually take place in aqueous solution, it is often impossible to determine directly whether water takes part in the reaction or whether, on the contrary, it results, and this is ascertained only in the course of drawing up the equation.

The simplest example of an oxidation-reduction process is any displacement reaction (V-8). A somewhat more complex reaction, viz., that between a solution of chloric acid and elementary phosphorus, is considered below.

An investigation of the products of this reaction shows that it results in the formation of H_3PO_4 and HCl. Consequently,

$$HClO_3 + P \rightarrow H_3PO_4 + HCl \qquad (I)$$

Determining the charges of the elements that change their valency and writing them above these elements, we have:

$$\overset{+5}{H}\overset{}{Cl}\overset{}{O_3} + \overset{0}{P} \rightarrow \overset{+5}{H_3}\overset{}{P}\overset{}{O_4} + \overset{-1}{H}\overset{}{Cl} \qquad (II)$$

From equation (II) it can be seen that the valency of chlorine has changed from +5 to —1. Consequently, $HClO_3$ is the *oxidising agent*, and one molecule (or, more exactly, the chlorine) of this compound gains six electrons in the course of the reaction. On the other hand, the valency of phosphorus changes from 0 to +5. Consequently, phosphorus is the *reducing agent*, and each of its atoms gives up five electrons. Putting this down under the corresponding substances, we have:

$$\underset{\boxed{6}}{\overset{+5}{HClO_3}} + \underset{\boxed{5}}{\overset{0}{P}} \rightarrow \overset{+5}{H_3PO_4} + \overset{-1}{HCl} \qquad \text{(III)}$$

But all the molecules of the reactants and resultants are electrically neutral. Therefore, *the total number of electrons given up by the reducing agent in the course of the reaction must be equal to the total number of electrons gained by the oxidising agent.* Hence, we can find the *principal coefficients* of the equation—the coefficients of the oxidising agent and the reducing agent:

$$\underset{\boxed{6}}{5HClO_3} + \underset{\boxed{5}}{6P} \rightarrow H_3PO_4 + HCl \qquad \text{(IV)}$$

We now check the number of atoms of each element on both sides of the equation and assign the corresponding coefficients (in checking, it is best to begin with the elements that change their valency in the course of the reaction; hydrogen and especially oxygen should usually be checked last, unless they participate in the equation in the free state). Balancing the number of atoms of Cl and P on both sides by means of the coefficients, we arrive at the following expression:

$$5HClO_3 + 6P \rightarrow 6H_3PO_4 + 5HCl \qquad \text{(V)}$$

On checking the hydrogen atoms, we find that there are more of them on the right-hand side than on the left. Since no free hydrogen was introduced into the system, this means that *water* participated in the reaction. Therefore, we finally have:

$$5HClO_3 + 6P + 9H_2O = 6H_3PO_4 + 5HCl \qquad \text{(VI)}$$

Checking the oxygen atoms, we see whether the equation has been completed correctly.

Briefly summarising the above discussion, we arrive at the following logical sequence of mental operations when drawing up equations for oxidation-reduction reactions (simultaneously considering a more complex example—the reaction between As_2S_3 and HNO_3):

I. Determine the formulas of the substances resulting from the reaction:

$$As_2S_3 + HNO_3 \rightarrow H_3AsO_4 + H_2SO_4 + NO$$

II. Determine the valency (before and after the reaction) of those elements that change their valency in the course of the reaction:

$$\overset{+3\ -2}{As_2S_3} + \overset{+5}{HNO_3} \rightarrow \overset{+5}{H_3AsO_4} + \overset{+6}{H_2SO_4} + \overset{+2}{NO}$$

III. Count up the number of electrons yielded by a molecule of the reducing agent and gained by a molecule of the oxidising agent:

$$\overset{+3\ -2}{As_2S_3} + \overset{+5}{HNO_3} \rightarrow \overset{+5}{H_3AsO_4} + \overset{+6}{H_2SO_4} + \overset{+2}{NO}$$

$2\times2+8\times3$ $\boxed{3}$

$\boxed{28}$

IV. Find the principal coefficients, i. e., the coefficients of the oxidising agent and the reducing agent:

$$3As_2S_3 + 28HNO_3 \rightarrow H_3AsO_4 + H_2SO_4 + NO$$

$\boxed{28}$ $\boxed{3}$

V. Check the number of atoms of each element (neglecting hydrogen and oxygen for the time being) in the reactants and resultants of the reaction, and balance the equation by assigning appropriate coefficients:

$$3As_2S_3 + 28HNO_3 \rightarrow 6H_3AsO_4 + 9H_2SO_4 + 28NO$$

VI. Check hydrogen and find the number of molecules of water participating in the reaction:

$$3As_2S_3 + 28HNO_3 + 4H_2O = 6H_3AsO_4 + 9H_2SO_4 + 28NO$$

VII. Check oxygen to see whether the equation is correctly completed.

Of course, there is no need to rewrite the reaction several times, and all the operations shown above are carried out in succession with the same equation (even mentally, with sufficient experience). The criterion of correctness of the coefficients assigned is the equality of the number of atoms of each element on both sides of the equation.

Exercises. Complete and balance the following skeleton equations:

1) $Sb_2S_5 + HNO_3 \rightarrow H_3SbO_4 + H_2SO_4 + NO$
2) $FeSO_4 + KClO_3 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + KCl$
3) $HOCl + Br_2 \rightarrow HBrO_3 + HCl$
4) $HClO_3 + HCl \rightarrow Cl_2$

The above method of balancing equations of oxidation-reduction reactions is directly applicable to the majority of processes encountered in practice. However, in some special cases, additional explanation is required. The most important of these cases are considered below.

a) If the number of electrons yielded by the reducing agent and the number of electrons gained by the oxidising agent have a *highest common factor*, both numbers are divided by this factor to find the principal coefficients. For example, in the reaction

$$\underset{\boxed{6}}{HClO_3} + \underset{\boxed{8}}{H_2S} \rightarrow H_2SO_4 + HCl$$

the principal coefficients will be 4 and 3, instead of 8 and 6. On the other hand, if the number of electrons gained and yielded by the reactants is odd, while the number of resultant atoms is even, the principal coefficients *must be doubled*. Thus, in the reaction

$$\underset{\boxed{1}}{FeSO_4} + \underset{\boxed{3}}{HNO_3} + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + NO$$

the principal coefficients will be 6 and 2, instead of 3 and 1.

Exercises. Complete and balance the following skeleton equations:

1) $HClO_3 + H_2S \rightarrow H_2SO_4 + HCl$

2) $FeSO_4 + HNO_3 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + NO$

3) $HClO_4 + SO_2 \rightarrow H_2SO_4 + HCl$

4) $FeCl_3 + HI \rightarrow I_2 + FeCl_2 + HCl$

b) The oxidising or reducing agent is expended partially for binding the resultants.

For example, reasoning as before we find that in the reaction (stages I-IV having been carried out):

$$\underset{\boxed{1}}{\overset{+2+5}{3Fe(NO_3)_2}} + \underset{\boxed{3}}{\overset{+5}{HNO_3}} \rightarrow \overset{+3+5}{Fe(NO_3)_3} + \overset{+2}{NO}$$

one molecule of the oxidising agent, HNO_3, is consumed for every 3 molecules of the reducing agent, $Fe(NO_3)_2$. However, on comparing the substances on the left- and right-hand sides of the equation, we see furthermore, that to convert $Fe(NO_3)_2$ into $Fe(NO_3)_3$ each molecule of the reducing agent requires one extra molecule of HNO_3 to bind the trivalent iron. Thus, altogether, the following amount of nitric acid is required: 1 molecule for oxidation plus 3 molecules for binding, i. e., a total of 4 molecules. The equation takes the form

$$3Fe(NO_3)_2 + \underset{\text{for oxidation}}{HNO_3} + \underset{\text{for binding}}{3HNO_3} \rightarrow Fe(NO_3)_3 + NO$$

and finally (after carrying out stages V and VI):

$$3Fe(NO_3)_2 + 4HNO_3 = 3Fe(NO_3)_3 + NO + 2H_2O$$

For a similar example involving the reducing agent consider the reaction:

$$\overset{\boxed{4}}{\overset{+6}{K_2Mn}O_4} + \overset{\boxed{1}}{4H\overset{-1}{Cl}} \rightarrow \overset{-1}{KCl} + \overset{+2-1}{MnCl_2} + \overset{0}{Cl_2}$$

Here we find that, besides the 4HCl molecules acting as the reducing agent, another 4 molecules are needed to bind the $2K^+$ and Mn^{2+}. Thus, the equation becomes

$$K_2MnO_4 + \underset{\text{reduction}}{4HCl} + \underset{\text{binding}}{4HCl} \rightarrow KCl + MnCl_2 + Cl_2$$

and finally:

$$K_2MnO_4 + 8HCl = 2KCl + MnCl_2 + 2Cl_2 + 4H_2O$$

Exercises. Complete and balance the following skeleton equations:

1) $CrO_3 + HCl \rightarrow CrCl_3 + Cl_2$

2) $Cu_2O + HNO_3 \rightarrow Cu(NO_3)_2 + NO$

3) $Ag + HNO_3 \rightarrow AgNO_3 + NO$

c) Both elements — the one yielding the electrons and the one gaining them — are *in the same molecule.* In particular, this includes cases where a substance is decomposed into compounds of one and the same element with a higher and a lower valency simultaneously. In order to find the principal coefficients, these processes should be ragarded as proceeding from right to left.

Exercises. Complete and balance the following skeleton equations:

1) $CuI_2 \rightarrow CuI + I_2$

2) $HNO_2 \rightarrow HNO_3 + NO$

3) $HClO_3 \rightarrow ClO_2 + HClO_4$

d) *Peroxide* compounds are oxidising (or reducing) agents. Derivatives of hydrogen peroxide, these compounds behave like the latter (IV-5). On oxidative decomposition, H_2O_2 liberates one atom of oxygen, hence in the capacity of an oxidising agent, one molecule of H_2O_2 is capable of gaining *two* electrons. On reductive decomposition, H_2O_2 liberates two atoms of hydrogen, which corresponds to the possibility of yielding two electrons.

Exercises. Complete and balance the following skeleton equations:

1) $Cr_2(SO_4)_3 + H_2O_2 + KOH \rightarrow K_2CrO_4 + K_2SO_4$

2) $HOCl + H_2O_2 \rightarrow HCl + O_2$

3) Since the bond between identical atoms is non-polar, it is neglected when calculating electrochemical valency. For example, in hydrogen peroxide H—O—O—H, oxygen, being essentially divalent, has a negative valency of —1.

4) Non-coincidence of electrochemical and general valency may be encountered in a number of other cases. For example, in H—C≡N, if a valency of +1 is attributed to hydrogen and a valency of —3 is attributed to nitrogen, then in view of the electrical neutrality of he molecule, the electrochemical valency of carbon must be +2.

It should be noted that the values of the coefficients in the oxidation-reduction equation are not affected by the character of the intramolecular distribution of charges. Thus, for the reaction of combustion of HCN in oxygen—$4HCN + 5O_2 = 2H_2O + 4CO_2 + 2N_2$—the principal coefficients 4 and 5 are calculated independently of whether the above electrochemical valencies or any others (e. g., zero) are adopted for the individual atoms of the HCN molecule. It goes without saying that irrespective of the distribution of charges, the molecule as a whole must be electrically neutral.

5) Owing to the low polarity of the bonds in organic molecules, it is often difficult to decide which of the atoms in the molecule are polarised positively and which negatively. Therefore, when writing equations for oxidation reactions of organic compounds, the principal coefficients are sometimes more conveniently found by first determining the number of oxygen atoms needed to convert the reactant molecule into the resultant, instead of directly calculating the number of electrons. Since it is known that each oxygen atom used for oxidation corresponds to the transfer of *two* electrons, it is easy to find the principal coefficients for the equation.

Example. Glucose can be completely oxidised by the action of $KMnO_4$ in acid solution, according to the equation: $C_6H_{12}O_6 \rightarrow 6CO_2 + 6H_2O$. By counting up the number of atoms of oxygen in glucose and in the products of its oxidation, we find that 12 atoms of oxygen must be used for each glucose molecule. This corresponds to a loss of 24 electrons, from which the principal coefficients for the equation are found:

$$5C_6H_{12}O_6 + 24KMnO_4 + 36H_2SO_4 = 12K_2SO_4 + 24MnSO_4 + 30CO_2 + 66H_2O$$

In conclusion, it is necessary to consider in brief the relationship between oxidation-reduction processes and the acidity or alkalinity of the solution in which they take place. Most frequently, an oxidising or reducing agent behaves as such only in definite solution (acid or alkaline). The process takes place more or less vigorously, depending on the acidity (alkalinity) of the solution. Sometimes the nature of the solution can have so great an influence that it causes the process to reverse its direction. For example, the reaction

$$3I_2 + 3H_2O \underset{\text{in acid solution}}{\overset{\text{in alkaline solution}}{\rightleftharpoons}} HIO_3 + 5HI$$

proceeds from left to right in alkaline solution, and from right to left in acid solution.

In practice, sulphuric acid is most commonly used to make solutions acid (HCl and HNO_3 are used less frequently, because the former is oxidisable, while the latter is an oxidising agent, and therefore, various by-reactions may occur in both cases). Solutions are made alkaline usually by adding NaOH or KOH.

The substance used to acidify a solution or to make it alkaline is not always included in the final equation for the reaction. Consider, for instance, the following cases of oxidation by $KMnO_4$ in alkaline solution:

$$\text{I. } SO_2 + KMnO_4 + KOH \rightarrow K_2SO_4 + MnO_2$$
$$\text{II. } S + KMnO_4 + KOH \rightarrow K_2SO_4 + MnO_2$$
$$\text{III. } H_2S + KMnO_4 + KOH \rightarrow K_2SO_4 + MnO_2$$

After finding the principal coefficients and balancing the number of atoms which change their valency during the reaction, we have

$$3SO_2 + 2KMnO_4 + KOH \rightarrow 3K_2SO_4 + 2MnO_2$$
$$S + 2KMnO_4 + KOH \rightarrow K_2SO_4 + 2MnO_2$$
$$3H_2S + 8KMnO_4 + KOH \rightarrow 3K_2SO_4 + 8MnO_2$$

Only after this do we start checking the atoms of the substance added to adjust the acidity or alkalinity of the solution (neglecting hydrogen and oxygen for the time being). Balancing the number of potassium atoms, we get

$$3SO_2 + 2KMnO_4 + 4KOH \rightarrow 3K_2SO_4 + 2MnO_2$$
$$S + 2KMnO_4 \rightarrow K_2SO_4 + 2MnO_2$$
$$3H_2S + 8KMnO_4 \rightarrow 3K_2SO_4 + 8MnO_2 + 2KOH$$

Finally, after balancing hydrogen and oxygen, we obtain

$$3SO_2 + 2KMnO_4 + 4KOH = 3K_2SO_4 + 2MnO_2 + 2H_2O$$
$$S + 2KMnO_4 = K_2SO_4 + 2MnO_2$$
$$3H_2S + 8KMnO_4 = 3K_2SO_4 + 8MnO_2 + 2KOH + 2H_2O$$

Thus, from the point of view of choosing the coefficients, the acid or alkali introduced to adjust the solution, behaves like water: it may be consumed during the reaction (case I), may take no part in the reaction (case II), or may even be produced additionally as a result of the reaction (case III).

VII-6. The Manganese Subgroup. Of the elements in this subgroup, No. 43—*technetium* (Tc)—is not contained in the earth's crust. Very small quantities of it have been obtained artificially, and it has been established that with respect to chemical properties it is, in general, much closer to *rhenium* than to *manganese*. However, no detailed study of this element and its compounds has been carried out so far.

Manganese is one of the abundant elements; it constitutes about 0.03% of the total number of atoms in the earth's crust. Small quantities of Mn are contained in many rocks. At the same time, accumulations of its oxygen compounds are found mainly in the form of *pyro-*

lusite, $MnO_2 \cdot xH_2O$. The annual world output of manganese ores is about 5 million tons.

Pure manganese can be obtained by electrolysing solutions of its salts. However, 90% of all the Mn extracted is used in the manufacture of various iron-base alloys. For this reason it is usually smelted directly from its ores as *ferromanganese*, a high-percentage alloy with iron (60 to 90% Mn), which is then used for introducing manganese into other alloys. Ferromanganese is smelted from a mixture of manganese and iron ores in electric furnaces, the manganese being reduced by carbon according to the reaction:

$$MnO_2 + 2C + 70 \text{ kcal} = 2CO + Mn$$

The content of rhenium in the earth's crust is extremely low (9×10^{-9}%). This element is highly dispersed: even the richest minerals with respect to rhenium (molybdenites) contain quantities which usually do not exceed 0.002% by weight. No extensive use for rhenium or any of its derivatives has, as yet, been found.

1) Metallic rhenium is usually obtained by heating ammonium perrhenate in a stream of hydrogen: $2NH_4ReO_4 + 4H_2 = 8H_2O + N_2 + 2Re$. The annual world output of rhenium and its derivatives is measured in hundreds of kilograms.

In powder form, manganese and rhenium are grey, while in the compact state they are white metals similar in appearance to iron and platinum, respectively. Their most important constants are compared below:

Element	Specific gravity	Melting point, °C	Boiling point, °C
Mn	7.4	1250	2150
Re	20.9	3170	5440

The mechanical properties of both metals depend greatly on the method of their separation and preliminary treatment.

2) The electrical conductivity of rhenium is approximately $^1/_4$ that of tungsten. Rhenium is an excellent material for the manufacture of electric lamp filaments which are more reliable and durable than the conventional tungsten filaments.

In air, compact metallic manganese becomes covered with a very thin layer of oxide which protects it from further oxidation even on heating. On the other hand, when finely ground, it is fairly readily oxidised. Its reactions with the halogens are extremely vigorous, and result in MnX_2 salts. On heating, manganese also combines with other typical non-metals such as sulphur, nitrogen, phosphorus, carbon, silicon and boron. It does not react with hydrogen.

The chemical activity of rhenium is somewhat lower. Thus, on heating, it reacts with oxygen, sulphur and the halogens, but does

not combine directly with nitrogen. Hydrogen is quite readily taken up by rhenium powder, but no chemical compounds are formed.

Manganese lies between Mg and Zn in the electromotive series. Accordingly, manganese powder decomposes water on heating. Manganese reacts vigorously with dilute acids, displacing hydrogen, e. g., in accordance with the reaction:

$$Mn + H_2SO_4 = MnSO_4 + H_2\uparrow$$

Rhenium lies a little to the right of copper in the electromotive series, and does not react with dilute HCl and H_2SO_4. Nitric acid dissolves rhenium in accordance with the equation:

$$3Re + 7HNO_3 = 3HReO_4 + 7NO + 2H_2O$$

The position of technetium in the electromotive series has not been established as yet. It is known, however, that it is displaced from solutions by zinc and can be deposited on the cathode by electrolysis.

Chemically, manganese is extremely interesting because it forms compounds through which the effect of valency changes on the properties of *one and the same element* can be traced. Derivatives corresponding to the following oxides have been well studied:

MnO	Mn_2O_3	MnO_2	(MnO_3)	Mn_2O_7
Manganous oxide	Manganic oxide	Manganese dioxide	Manganese trioxide	Manganese heptoxide

Since an increase in the positive valency of the atom is connected with an increase in charge and a decrease in radius, it can be expected (in accordance with Fig. 87) that the dissociation of manganese compounds of the type EOH will take place in different ways for the different valency states of manganese. As the scheme below shows, this does actually occur:

$$\underset{\text{increasing basic properties}}{\longleftarrow} \qquad \underset{\text{increasing acidic properties}}{\longrightarrow}$$

$$Mn(OH)_2 \quad Mn(OH)_3 \quad Mn(OH)_4 \quad (H_2MnO_4) \quad HMnO_4$$

A similar gradation of properties is observed for rhenium derivatives. The heptavalent state is the most characteristic for both Re and Tc.

The raw material usually employed for the preparation of manganese compounds is natural pyrolusite. By heating this mineral in a stream of hydrogen, *manganous oxide*, MnO, can de obtained as a green powder insoluble in water but quite soluble in acids. Salts corresponding to this oxide are also formed when pyrolusite is dissolved in acids, e. g., according to the reactions:

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O$$

$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + O_2 + 2H_2O$$

When solutions of these salts are treated with alkalis, manganous *hydroxide*, $Mn(OH)_2$, comes down as a white precipitate. It gradually turns brown in air owing to oxidation in accordance with the equation:

$$2Mn(OH)_2 + O_2 + 2H_2O = 2Mn(OH)_4$$

$Mn(OH)_2$, which is practically insoluble in water, is a base, and on reacting with acids it produces the corresponding salts of divalent manganese. The majority of the latter are pink ($Mn^{\cdot\cdot}$ ion) and are readily soluble in water. The salts of *divalent* manganese are the most stable derivatives of this element in *acid* solution.

Black *manganic oxide*, Mn_2O_3, can be obtained by heating pyrolusite to 800° C. The corresponding brownish-black hydroxide, $Mn(OH)_3$, is almost insoluble in water, and is a very weak base. Its salts are unstable, as a rule, and are not encountered in practice.

While MnO_2 is the most stable oxygen compound of manganese under ordinary conditions, ReO_2 can be obtained only from the highest oxide of rhenium, Re_2O_7, and is readily converted back to the latter on heating in air or under the action of an oxidising agent. Both dioxides are black substances insoluble in water. The corresponding dark brown hydroxides, $E(OH)_4$, are practically insoluble and possess *amphoteric* properties. However, both the basic and acidic properties of these oxides are extremely weak. Salts derived from them are, as a rule, unstable.

3) The salts corresponding to $Mn(OH)_4$ regarded as an acid are called *manganites*. They are very difficult to isolate in the pure state.

One of the salts corresponding to $Mn(OH)_4$ regarded as a base is the black sul hate, $Mn(SO_4)_2$. It is soluble in concentrated sulphuric acid, but hydrolyses completely if the solution is diluted with water.

4) Hausmanite, a dark red mineral which occurs in nature, can be obtained from manganous acid (with manganous hydroxide as the base): $2Mn(OH)_2 + H_4MnO_4 = Mn_2MnO_4 + 4H_2O$. Thus, chemically, hausmanite (Mn_3O_4) is manganese manganite.

If MnO_2 is fused with an alkali in the presence of oxidising agents, the corresponding salt of *manganic* acid, H_2MnO_4, is formed, in which manganese is *hexavalent*. Usually, finely ground pyrolusite is mixed with a 50% solution of KOH, and the oxidation is conducted at 250° C using atmospheric oxygen:

$$2MnO_2 + 4KOH + O_2 = 2K_2MnO_4 + 2H_2O$$

Salts of H_2MnO_4 (*manganates*) are dark green in colour. The manganates of Na and K are readily soluble in water, but the manganate of Ba is only sparingly soluble.

Free H_2MnO_4, which is liberated when solutions of manganates are acidified, is unstable and decomposes instantly according to the equation

$$3H_2MnO_4 = MnO_2 + 2HMnO_4 + 2H_2O$$

forming MnO_2 and free *permanganic* acid, $HMnO_4$. A similar spontaneous decomposition, for example, according to the equation

$$3K_2MnO_4 + 2H_2O = MnO_2 + 2KMnO_4 + 4KOH$$

is characteristic of manganates in solution too, but this takes place only as they are hydrolysed, i. e., much slower.

All the derivatives of hexavalent manganese are *powerful oxidising agents* and are readily reduced to MnO_2 (in alkaline solution) or the corresponding salts of Mn^{2+} (in acid solution). On the other hand, manganates can be oxidised to the corresponding salts of permanganic acid by still more powerful oxidants, such as free chlorine:

$$2K_2MnO_4 + Cl_2 = 2KCl + 2KMnO_4$$

The above reaction is sometimes used for the preparation of $KMnO_4$. This salt, potassium *permanganate*, is one of the most important compounds of manganese in practical work.

The oxides of the *heptavalent* elements differ greatly from one another in stability. Yellow *rhenium heptoxide*, Re_2O_7, may easily be obtained by heating rhenium powder in air. It melts at 297° C and boils at 363° C without decomposing. Decomposition sets in appreciably only at about 600° C.

Manganese heptoxide, Mn_2O_7, is evolved as a greenish-black oily liquid when ground $KMnO_4$ is treated with cold 90% H_2SO_4. It is stable only below 0° C, and may decompose explosively into MnO_2 and oxygen (containing a considerable amount of ozone) even at ordinary temperatures. In contrast to Re_2O_7, manganese heptoxide possesses very powerful oxidising properties. Thus, ether and alcohol flare up when brought into contact with it.

The reaction of the anhydrides E_2O_7 with water results in a colourless solution of *perrhenic* acid, $HReO_4$, or a violet-red solution of *permanganic* acid. The former may be boiled to dryness without decomposition of the acid. The latter withstands concentration only up to a 20% content of $HMnO_4$, after which it begins to decompose in accordance with the equation:

$$4HMnO_4 = 4MnO_2 + 3O_2 + 2H_2O$$

Permanganic acid is very strong, being dissociated to approximately the same degree as HCl and HNO_3. Rhenic acid is somewhat more weakly dissociated.

Salts of permanganic acid (*permanganates*), as a rule, possess the violet-red colour of the MnO_4' ion, while salts of perrhenic acid (*perrhenates*) are colourless like the ReO_4' ion. Both acids (like perchloric acid which is similar to them in structure) form sparingly soluble salts with Rb^+ and Cs^+ cations.

Perrhenates are very stable to heating. For example, $KReO_4$ can be distilled at 1370° C without decomposing. In contrast, $KMnO_4$ decomposes above 200° C, mainly according to the equation:

$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2$$

This reaction is suitable for the laboratory preparation of oxygen.

Oxidising properties, which are pronounced in permanganic acid and its salts, are not characteristic of perrhenic acid and perrhenates, and their conversion into derivatives in which rhenium has a lower valency takes place only under the action of very powerful reducing agents. Technetium occupies an intermediate position: $HTcO_4$, which forms a pink solution, can be reduced fairly easily.

The most frequently used salt of $HMnO_4$ is the potassium salt, $KMnO_4$, which forms dark violet crystals. In industry, it is usually prepared by electrolysis of a concentrated solution of K_2MnO_4, $KMnO_4$ being formed at the anode ($MnO_4'' - \ominus = MnO_4'$), and hydrogen being liberated at the cathode.

Potassium permanganate is a *very powerful oxidising agent* in both acid and alkaline solutions. For example, it oxidises ferrous sulphate according to the equations:

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

$$KMnO_4 + 3FeSO_4 + 5KOH + 2H_2O = 3K_2SO_4 + MnO_2 + 3Fe(OH)_3$$

The nature of the reduction of potassium permanganate in acid (to $Mn^{\cdot\cdot}$) and alkaline or neutral solution (to MnO_2) should be remembered, because oxidation of different substances by this salt is often encountered in chemical practice.

5) The course of the reduction of $KMnO_4$ in solution depends substantially on the acidity-alkalinity reaction of the solution. An example of this is the oxidation of potassium sulphite:

in acid solution — $5K_2SO_3 + 2KMnO_4 + 3H_2SO_4 = 6K_2SO_4 + 2MnSO_4 + 3H_2O$

in neutral solution — $3K_2SO_3 + 2KMnO_4 + H_2O = 3K_2SO_4 + 2MnO_2 + 2KOH$

in alkaline solution — $K_2SO_3 + 2KMnO_4 + 2KOH = K_2SO_4 + 2K_2MnO_4 + H_2O$

However, the process takes place according to the last equation only under definite conditions, viz.: deficiency of the reducing agent and high concentration of alkali. At the same time, it only reduces the system to a metastable state: although the excess alkali more or less inhibits hydrolysis of the manganate being formed, in the long run this hydrolysis and the attendant decomposition proceed to completion according to the scheme $3Mn^{VI} \rightarrow Mn^{IV} + 2Mn^{VII}$. Therefore, the stable end product of the reduction of $KMnO_4$ in alkaline solution is MnO_2, just as in neutral solution.

6) It is convenient to use an alkaline solution of $KMnO_4$ for the removal of organic substances from laboratory glassware. The MnO_2 deposited on the walls is then removed by washing with concentrated hydrochloric acid.

Potassium permanganate is also used in medicine. For example, in the case of burns it is recommended to moisten the burnt spot immediately with a 4% solution of $KMnO_4$; this dries the skin and prevents blistering.

7) A very characteristic reaction of manganese chemistry, in addition to those mentioned above, is the ready formation of an intermediate state of oxidation from a lower and a higher: $3MnSO_4 + 2KMnO_4 + 2H\,O = 5MnO_2 + K_2SO_4 + 2H_2SO_4$. This reaction is, in principle, the reverse of the decomposition of K_2MnO_4 into MnO_2 and $KMnO_4$.

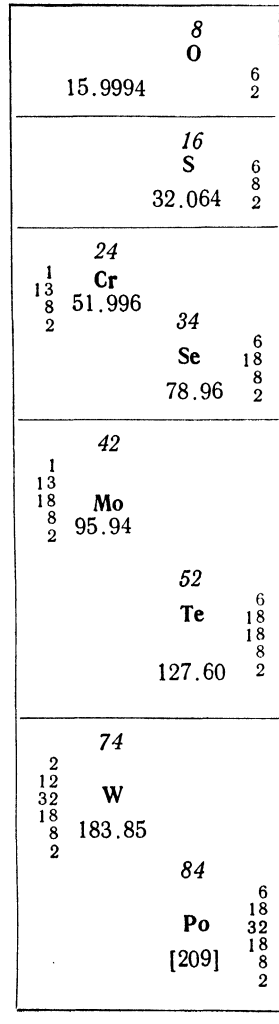
If we now, after our examination of the halogens and the manganese subgroup, compare the compounds of these elements, one of the most striking features we shall find is the sharp difference in properties in the lower valencies and the close similarity in higher valencies. As would be expected from the standpoint of the theory of electronic analogues, the elements of the manganese subgroup are analogues of chlorine in their *higher* valencies. Indeed, Re_2O_7 and Mn_2O_7 are analogous to perchloric acid, whereas no derivatives of heptavalent bromine are known.

VIII. SIXTH GROUP OF THE PERIODIC TABLE

The atoms of the elements of group VI may contain either six electrons in their outermost shell or one or two electrons. The first kind of structure is typical of sulphur and the elements of the selenium subgroup (Se, Te, Po), as well as oxygen, which was considered earlier, while the second kind of structure is typical of the elements of the chromium subgroup (Cr, Mo, W).

The structure of the outermost atomic shell of sulphur and of selenium and its analogues determines their predominantly *non-metallic* nature and their maximum negative valency of two. These elements must be less active non-metals than the halogens of the respective series (since the latter lack only one electron for a stable configuration). The maximum positive valency of sulphur and of selenium and its analogues may be expected to equal six, and they should yield electrons more readily than the halogens in the same horizontal series.

The presence of only one or two electrons in the outermost shell of the atoms determines the *metallic* nature of the chromium subgroup elements. At the same time, their maximum positive valency should also be equal to six.



VIII-1. Sulphur. Sulphur, which was known in ancient Egypt, played an important part in the theoretical concepts of the alchemists, since it was thought to be the most perfect expression of one of the "basic elements" of nature—combustibility. It forms 0.03% of the earth's crust, and is, therefore, among the very abundant elements.

In nature, sulphur occurs in various forms. Sometimes it is encountered in the native state, but most of it is combined with metals in various minerals which may be divided into two large groups, namely sulphides and sulphates. Of the minerals of the first type,

pyrite, FeS_2, is of particular importance in technology. One of the minerals of the second type is *gypsum*, $CaSO_4 \cdot 2H_2O$. Furthermore, sulphur compounds are usually present in volcanic gases and in the water of certain mineral springs. Sulphur also forms part of many proteins, and is, therefore, always found in the organisms of animals and plants.

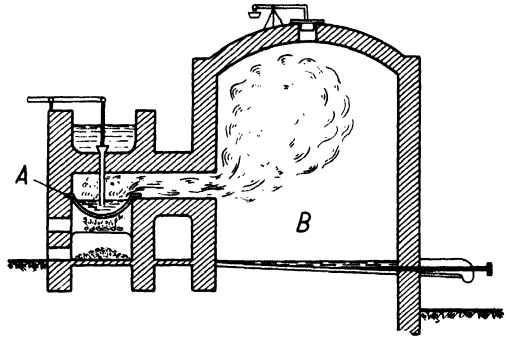


Fig. 102. Sulphur-distillation kiln

The world consumption of sulphur is about 4 million tons a year. A considerable part of this is used in combating agricultural pests. Industrially, sulphur is used in the production of sulphuric acid, paper, rubber, matches, etc. Sulphur is also used in pyrotechnics, and partly in medicine.

Free sulphur may be obtained either from native deposits or from its compounds. Almost the entire world production of sulphur is carried out by the first method, the technological process consisting essentially of separating the sulphur from the waste rock with which it is mixed (sand, clay, etc.). This is usually achieved by melting the sulphur out of the ores by heating them to 140 or 150° C with steam.

The sulphur obtained from natural deposits almost always contains impurities. It is purified by distillation in special kilns (Fig. 102). The vapour of sulphur which is heated in pot *A*, is admitted into chamber *B* where it rapidly cools off, and sulphur is deposited on the walls as a fine dust (*"flowers of sulphur"*). If chamber *B* is heated above 120° C liquid sulphur is obtained, which subsequently hardens. This fused sulphur is usually put on the market.

Pure sulphur is a yellow crystalline substance with a specific gravity of 2.1, which melts at 119° C and boils at 445° C. It is a very poor conductor of heat and electricity, and is insoluble in water. The best solvent for sulphur is carbon disulphide, CS_2.

1) There are two typical allotropic forms of solid elemental sulphur. Ordinary yellow sulphur with a specific gravity of 2.07 is stable below 95.6° C, and its m. p. is 112.8° C (if heated quickly). The almost colourless allotrope

with a specific gravity of 1.96 and a m. p. of 119.3° C is stable above 95.6° C. The difference between the two forms is due to their different crystalline structure.

2) The melting of sulphur is accompanied by an appreciable increase in volume (approximately 15%). Molten sulphur is a mobile yellow liquid which turns brown above 160° C and changes into a dark brown viscous mass at 190° C. Above 190° C, its viscosity begins to decrease, and at about 400° C it again becomes mobile but remains dark brown.

These changes in properties on heating are due to changes in the internal structure of sulphur. Under ordinary conditions, the latter is characterised

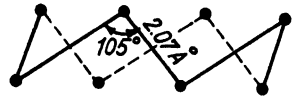


Fig. 103. The structure of the molecule of S_8

by octatomic ring molecules (Fig. 103). Above 160° C, the S_8 rings begin to break up into open chains, this being accompanied by an increase in viscosity (and a change in colour). Further heating above 190° C leads to a reduction in the average length of these chains, owing to which the viscosity decreases again.

3) Pure sulphur is not poisonous. Small quantities taken internally promote resolution of abscesses and are useful, in particular, for hemorrhoids. The human organism does not display any habituation to sulphur. Very fine (precipitated) sulphur is a component of a number of ointments intended for the care of the skin and the treatment of skin diseases.

Sulphur is fairly inert in the cold (combining vigorously only with fluorine), but on heating it becomes extremely active chemically and reacts with the other halogens (except iodine), oxygen, hydrogen and almost all the metals. Reactions with the latter result in *sulphides*, e. g., according to the equation:

$$Fe + S = FeS + 23 \text{ kcal}$$

Sulphur does not combine with hydrogen under ordinary conditions.

Only on heating does the reversible reaction

$$H_2 + S \rightleftarrows H_2S + 5 \text{ kcal}$$

take place, its equilibrium being shifted to the right at about 350° C, and to the left at higher temperatures. In practice, *hydrogen sulphide*, H_2S, is usually obtained by the action of dilute acids on metal sulphides, e. g., in accordance with the reaction:

$$FeS + 2HCl = FeCl_2 + H_2S\uparrow$$

4) A convenient method of preparing hydrogen sulphide is by heating a mixture of sulphur and paraffin (2 : 1 by weight) with crushed asbestos to approximately 300° C. On cooling the reaction ceases, but can be started again by reheating.

Hydrogen sulphide is a colourless gas (m. p. —86° C, b. p. —60° C). As little as one part of H_2S in 100,000 parts of air can be detected by its characteristic odour (rotten eggs). Hydrogen sulphide is highly toxic. When ignited in air, it burns according to one of the following equations:

$$2H_2S + 3O_2 = 2H_2O + 2SO_2 \text{ (in an excess of oxygen)}$$

$$2H_2S + O_2 = 2H_2O + 2S \text{ (in a limited supply of oxygen)}$$

One volume of water dissolves about 3 volumes of hydrogen sulphide under ordinary conditions (forming an approximately 0.1 *M* solution). On standing in air, an aqueous solution of H_2S gradually becomes turbid owing to the liberation of sulphur in accordance with the second of the above reactions. Iodine is readily reduced by hydrogen sulphide:

$$I_2 + H_2S = 2HI + S$$

Hydrogen sulphide acts similarly on many other substances. It is thus a *powerful reducing agent.*

In aqueous solution, H_2S behaves as an *extremely weak acid.* Neutral salts of *hydrosulphuric* acid (containing the S'' anion) are called *sulphides*, while acid salts (containing the HS' anion) are called *hydrosulphides.* In spite of the fact that S'' and HS' ions are colourless, many salts of hydrosulphuric acid possess characteristic colours. Most sulphides (except the derivatives of Na, K and a few other cations) are very sparingly soluble in water. On the other hand, the majority of hydrosulphides are readily soluble (and are known only in solution).

5) Hydrosulphuric acid ($K_1 = 9 \times 10^{-8}$ and $K_2 = 4 \times 10^{-13}$) is somewhat weaker than carbonic acid. Besides direct combination between metals and sulphur and neutralisation reactions, many of its salts may be obtained by double decomposition of salts of the corresponding metal and H_2S or $(NH_4)_2S$. A solution of the latter salt, which is often used in laboratories, is usually prepared by saturating a solution of NH_4OH with hydrogen sulphide (yielding NH_4SH), and then mixing it with an equal volume of NH_4OH.

6) The difference in solubilities of the metal sulphides is used as the basis for the conventional system of qualitative analysis of cations. Some metals ($Na^{\cdot}$, $K^{\cdot}$, $Ba^{\cdot\cdot}$, etc.) form sulphides that are soluble in water, others ($Fe^{\cdot\cdot}$, $Mn^{\cdot\cdot}$, $Zn^{\cdot\cdot}$, etc.) form sulphides that are insoluble in water but are soluble in dilute HCl, and, finally, the sulphides of still others ($Cu^{\cdot\cdot}$, $Pb^{\cdot\cdot}$, $Hg^{\cdot\cdot}$, etc.) are soluble neither in water nor in dilute acids. Therefore, by treating a dissolved mixture of cations with hydrogen sulphide, first in acid solution and then in slightly alkaline solution, these groups of cations can be separated from one another, after which the cations of each group can be dealt with separately.

7) If finely ground sulphur is added to a concentrated solution of a sulphide, the sulphur dissolves to form the corresponding *polysulphide*, e. g., $(NH_4)_2S + (x - 1)S = (NH_4)_2S_x$. Usually, a mixture of polysulphides containing different amounts of sulphur results. As x increases, the colour of the compound changes from yellow through orange to red. The highest compound of this type in sulphur $(NH_4)_2S_9$ has an intense red colour. Of the polysul-

phides occurring in nature, the best known is the mineral pyrite, FeS_2, which is the ferrous salt of hydrogen disulphide.

8) If a concentrated solution of a polysulphide is poured into an excess of HCl solution, a heavy oil consisting of a mixture of *hydrogen polysulphides* of the general formula H_2S_x, collects at the bottom of the vessel. All the members of the series up to H_2S_6 have been isolated. They are very unstable oily yellow liquids with a pungent odour.

The affinity of sulphur for the halogens decreases so rapidly in the order F—Cl—Br—I that its iodine derivative cannot be obtained at all. But it combines more or less readily with the rest of the halogens. The most interesting of the compounds which can be formed is sulphur hexafluoride, SF_6, a gas under ordinary conditions. It is colourless, odourless, and is not poisonous. SF_6 differs from the other sulphur halides in its exceptional chemical inertness. It is employed in high voltage installations as a gaseous insulator. Sulphur chloride, S_2Cl_2, which is a liquid under ordinary conditions, is used in the rubber industry.

9) Some of the properties of the halogen compounds of sulphur are listed below:

Compound	SF_6	S_2F_{10}	SF_4	S_2F_2	SCl_4	SCl_2	S_2Cl_2	S_2Br_2
Physical state	gas	liquid	gas	gas	unstable	liquid	liquid	liquid
Colour	colourless	colourless	colourless	colourless	pale yellow	red	colourless	red
Melting point (°C)	—51 (pressure)	—92	—124	—128	—31	—78	—80	—46
Boiling point (°C)	—64 (sublimes)	+29	—40	—30	—15 (decomposes)	59	138	154 (0.2 mm)

The majority of these compounds are formed by direct interaction of the elements, and are readily decomposed by water.

An appreciable reaction between sulphur and oxygen sets in only on heating. When ignited in air, sulphur burns with a blue flame, forming the *dioxide*:

$$S+O_2=SO_2+71 \text{ kcal}$$

The O=S=O molecule is polar (dipole length 0.33 Å). Its atoms are arranged at the corners of an isosceles triangle with S at the apex [d (SO) = 1.43 Å, α = 120°]. Sulphur dioxide is a colourless gas with a characteristic pungent odour (m. p. —73° C, b. p. —10° C). Its solubility is very high: about 40 volumes in 1 volume of water under ordinary conditions.

Sulphur dioxide is chemically very active. Its characteristic reactions fall into three groups: a) those involving *no* change in the valency of sulphur, b) those in which its valency decreases, and c) those in which it increases.

A typical process of the first group is the reaction between sulphur dioxide and water, which results in *sulphurous* acid, H_2SO_3. The latter, an acid of medium strength, is at the same time rather unstable. Thus, in an aqueous solution of sulphur dioxide, the following equilibria exist simultaneously:

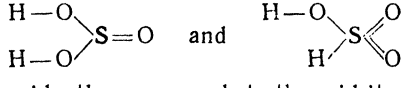
$$H_2O + SO_2 \rightleftarrows H_2SO_3 \rightleftarrows H^{\cdot} + HSO_3' \rightleftarrows 2H^{\cdot} + SO_3''$$

The pungent odour of sulphurous acid solutions is due to the invariable presence of a considerable amount of free sulphur dioxide. Sulphurous acid has not been isolated in the anhydrous state.

When solutions of sulphurous acid are heated, SO_2 escapes and the above equilibria shift to the left. By boiling the solution, therefore, the SO_2 can be removed completely. On the other hand, if an alkali is added, the equilibrium shifts to the right (due to binding of the $H^{\cdot}$ ions) and the solution, which now contains the corresponding salts of sulphurous acid (*sulphites*), loses its sulphur dioxide odour.

Being dibasic, sulphurous acid produces two series of salts: neutral salts (*sulphites*) and acid salts (*bisulphites* or *acid sulphites*). Like the SO_3'' and HSO_3' ions, both salts are colourless as a rule. Bisulphites are stable only in solution, and of the common metals, only the sulphites of sodium and potassium are soluble.

10) The equilibrium between the anhydrous and hydrated forms of sulphur dioxide in solution is determined by the relation: $[SO_2][H_2O]/[H_2SO_3] = 16$. For sulphurous acid ($K_1 = 2 \times 10^{-2}$ and $K_2 = 6 \times 10^{-8}$) two possible structures are assumed:



The first of these evidently corresponds to the acid itself and to the majority of its neutral salts, while the second corresponds to certain salts (of the less active metals) and many organic derivatives. The latter is also probable for acid salts.

11) Salts of H_2SO_3 are usually obtained by the reaction between SO_2 and the hydroxides or carbonates of metals in aqueous solution. The most important of these is calcium bisulphite, $Ca(HSO_3)_2$, which is known to exist only in solution and which is used in large quantities under the name of "sulphite liquor" in the cellulose industry for the extraction of lignin from wood pulp.

The sulphites of the active metals decompose when calcined at about 600° C to form the corresponding salts of sulphuric and hydrosulphuric acids, e. g.: $4K_2SO_3 = 3K_2SO_4 + K_2S$. This process is analogous to the formation of perchlorates and chlorides when chlorates are heated.

Chemical processes involving a *decrease* in the valency of the sulphur are not very characteristic of sulphur dioxide. The reduction of SO_2 by carbon monoxide at 500° C which takes place rapidly in the presence of a catalyst (bauxite), is one such case of practical importance:

$$SO_2 + 2CO = 2CO_2 + S$$

This process is used for the recovery of sulphur from waste gases at some metallurgical plants.

Another interesting case is the reaction between SO_2 and hydrogen sulphide in accordance with the equation:

$$SO_2 + 2H_2S = 2H_2O + 3S$$

This reaction takes place spontaneously even under ordinary conditions, but proceeds at an appreciable rate only in the presence of very small quantities of water.

12) In the presence of large quantities of water, the reaction between SO_2 and H_2S is very complex: in addition to free sulphur, a mixture of acids of the general formula $H_2S_xO_6$ (where $x = 3$ to 6), called *polythionic* acids, is formed. In these acids, the sulphur atoms are linked directly with one another in chain fashion. For example, tetrathionic acid, $H_2S_4O_6$, has the structure $HO—SO_2—S—S—SO_2—OH$. The polythionic acids are comparatively unstable and are known to exist only in aqueous solution (where they are rather strongly dissociated), but some of their salts have been isolated. They are all readily soluble in water.

13) When an aqueous suspension of zinc is treated with sulphur dioxide, the zinc salt of *hydrosulphurous* acid, $H_2S_2O_4$, results according to the equation $Zn + 2SO_2 = ZnS_2O_4$. Other *hydrosulphites* may be obtained from this salt by double decomposition. These are colourless, readily soluble in water (with the exception of CaS_2O_4), and possess powerful reducing properties. Free $H_2S_2O_4$ ($K_1 = 5 \times 10^{-1}$, $K_2 = 4 \times 10^{-3}$) is very unstable—it gradually decomposes even in dilute solutions, and is rapidly oxidised by atmospheric oxygen.

The reactions most characteristic of the derivatives of tetravalent sulphur are those involving an increase in its valency: both sulphurous acid and its salts are *powerful reducing agents*. When allowed to stand in air, solutions of these substances gradually (very slowly) combine with oxygen:

$$2Na_2SO_3 + O_2 = 2Na_2SO_4$$

Sulphurous acid and sulphites are oxidised much more rapidly (practically instantaneously) under the action of such oxidising agents as $KMnO_4$, Br_2 and I_2. Oxidation results in sulphuric acid or its salt, e. g.:

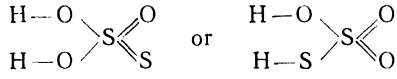
$$I_2 + H_2O + Na_2SO_3 = 2HI + Na_2SO_4$$

Sulphites are also able to combine with sulphur, in which case they are converted into salts of *thiosulphuric* acid, e. g.:

$$Na_2SO_3 + S = Na_2S_2O_3$$

As in the case of oxygen, the addition of sulphur takes place slowly, and to obtain *thiosulphates*, the reaction mixture must be boiled.

Thiosulphuric acid has the general structural formula:



Thus, in these structures, the sulphur atoms have *different* valencies (+6 and —2). This must be taken into consideration when writing the equations for reactions in which $H_2S_2O_3$ or its salts participate.

Thiosulphuric acid is about as strong as sulphuric acid, but it is quite unstable, decomposing into sulphurous acid and sulphur. In contrast, many of its salts (of which only the neutral ones are known) are perfectly stable. As a rule, they are colourless and readily soluble in water. The most important of them is $Na_2S_2O_3 \cdot 5H_2O$ (known as *sodium thiosulphate*). This salt is used mainly in photography and as an "antichlor". The latter application is based on the reducing properties of sodium thiosulphate, which is readily oxidised to sulphuric acid under the action of chlorine:

$$Na_2S_2O_3 + 4Cl_2 + 5H_2O = 2H_2SO_4 + 2NaCl + 6HCl$$

Sodium thiosulphate is also employed in medicine (for the treatment of scabies, etc.).

14) Like free chlorine, other powerful oxidising agents (HOCl, Br_2, etc.) oxidise sodium thiosulphate to *sulphuric* acid and its salts. With comparatively weak (or slow acting) oxidising agents, such as iodine, the oxidation of sodium thiosulphate takes place in a different way, namely, with the formation of a salt of *tetrathionic* acid: $I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6$. This reaction is of great importance in analytical chemistry.

Sulphur dioxide is much less apt to give reactions involving an increase in the valency of sulphur than sulphurous acid and its salts. The most important of these reactions are those of SO_2 with chlorine and oxygen.

Sulphur dioxide combines with chlorine only in direct sunlight or in the presence of a catalyst (camphor) according to the equation

$$SO_2 + Cl_2 = SO_2Cl_2$$

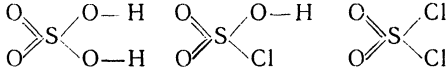
resulting in *sulphuryl chloride*, SO_2Cl_2. The latter is a colourless liquid with a pungent odour. It is decomposed by water (only slowly, if

the water is cold) into sulphuric and hydrochloric acids:

$$SO_2Cl_2 + 2H_2O = H_2SO_4 + 2HCl$$

A substance which on reacting with water produces a mixture of a hydrohalic and some other acid is called the *acid halide* of the latter. Sulphuryl chloride is, consequently, the *acid chloride* of sulphuric acid.

15) While sulphuryl chloride (m. p. —54° C, b. p. + 69° C) may be regarded as sulphuric acid in which both hydroxyl radicals are replaced by chlorine atoms, *chlorosulphonic acid* is the product of displacement of only one of them:



sulphuric acid | chlorosulphonic acid | sulphuryl chloride

Chlorosulphonic acid is a colourless, fuming liquid with a pungent odour (m. p. — 80° C, b. p. 155° C), which reacts violently with water in accordance with the equation: $SO_2(OH)Cl + H_2O = H_2SO_4 + HCl$. It is usually obtained by the action of gaseous HCl on a solution of SO_3 in sulphuric acid: $SO_3 + HCl = SO_2(OH)Cl$. Chlorosulphonic acid and sulphuryl chloride are used in organic syntheses.

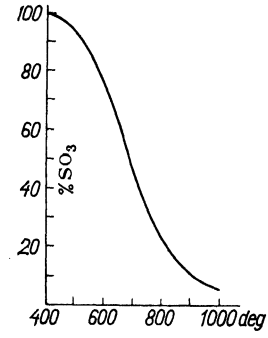


Fig. 104. Equilibrium of thermal dissociation of SO_3

SO_2 combines with oxygen even less readily than it does with chlorine, although the reaction is strongly exothermic:

$$2SO_2 + O_2 = 2SO_3 + 46 \text{ kcal}$$

The process takes place only in the presence of catalysts.

The SO_3 molecule has the structure of a plane triangle with the sulphur atom in the centre [$d(SO) = 1.43$ Å]. Condensation of *sulphur trioxide* vapour results in a colourless ice-like mass. When stored, this form of SO_3 passes slowly into another form consisting of white silky crystals which sublime at about 50° C. Both modifications are highly hygroscopic and fume in the air. The thermal dissociation of sulphur trioxide (into SO_2 and O_2) becomes appreciable at about 400° C, and the higher the temperature, the further it proceeds (Fig. 104).

Sulphur trioxide is a strong *oxidant*: phosphorus ignites in contact with it, free iodine is liberated from potassium iodide, etc. On the other hand, it is an *acid anhydride*, and the formation of H_2SO_4 from sulphur trioxide and water is accompanied by a considerable evolution of heat:

$$H_2O + SO_3 = H_2SO_4 + 19 \text{ kcal}$$

Pure 100% *sulphuric acid* (known as *monohydrate*) is a colourless, oily liquid which solidifies into a crystalline mass at +10° C. The

concentrated acid used as a reagent usually has a specific gravity of 1.84 and contains about 95% H_2SO_4. It solidifies only below —20°C. When concentrated sulphuric acid is dissolved in water a considerable amount of heat is evolved.

Concentrated sulphuric acid strongly attracts moisture, and is, therefore, often employed for drying gases. It removes water from many organic substances containing hydrogen and oxygen, and this property is often utilised in industry. This (as well as the oxidising properties of strong H_2SO_4) accounts for its destructive effect on plant and animal tissues. If sulphuric acid contacts the skin or clothes during work, it should immediately be washed off with a large quantity of water. The affected spot may then be treated with a dilute solution of ammonia and again washed with water.

Concentrated H_2SO_4 is a fairly strong oxidising agent, especially on heating (it is usually reduced to SO_2). For example, it oxidises HI and partially oxidises HBr (but not HCl) to free halogens. Many metals—Cu, Hg, etc.—are also oxidised by it (whereas gold and platinum are completely resistant to H_2SO_4). For example, the reaction with copper takes place according to the equation:

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O$$

The fact that very strong sulphuric acid (above 93%) does not attack iron, is of practical importance. This permits it to be transported in steel tanks. On the other hand, dilute H_2SO_4 dissolves iron readily, liberating hydrogen. Oxidative properties are not at all characteristic of sulphuric acid.

A strong dibasic acid, H_2SO_4 produces two series of salts: neutral (*sulphates*) and acid (acid sulphates or *bisulphates*); the latter have been isolated in the solid state only for a few monovalent metals (Na, K, etc.). Most sulphates are colourless, easily crystallised and readily soluble in water. Among the derivatives of the most common metals, $CaSO_4$ is slightly soluble, $PbSO_4$ is still less soluble, and $BaSO_4$ is practically insoluble.

In regard to their attitude towards heating, sulphates may be divided into two groups. Some of them, e. g., the salts of Na, K and Ba, do not decompose even at 1000° C, while others, e. g., the salts of Cu, Al and Fe, decompose into a metal oxide and SO_3 at much lower temperatures. Some sulphates containing crystallisation water are sometimes called *vitriols*, e. g., $CuSO_4 \cdot 5H_2O$—blue vitriol and $FeSO_4 \cdot 7H_2O$—green vitriol.

Many salts of H_2SO_4 find extensive technical application. This is particularly true of sulphuric acid itself, tremendous quantities of which are used in the chemical, oil, metallurgical and other industries. The annual world production of sulphuric acid (in terms of monohydrate) is more than 30 million tons. In 1963 production in the

U.S.S.R. was 6.9 million tons (exceeding the 1913 output by almost 58 times).

Two methods are now used for the industrial production of sulphuric acid: the *lead chamber* process and the *contact* process. The basic initial substance in both cases is sulphur dioxide which is obtained by burning sulphur in air (U.S.A.) or by burning pyrite, FeS_2, a mineral rich in sulphur (majority of European countries, among them the U.S.S.R.). SO_2 from the waste gases of copper and zinc smelters is also used for the production of sulphuric acid.

16) Pyrite is roasted at sulphuric acid plants in special burners. It burns in accordance with the equation: $4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2 + 815$ kcal. The temperature in the burner reaches 800-900° C.

17) The initial gas usually used in sulphuric acid production contains about 9% SO_2, 10% O_2 and 80% N_2. If the pyrite is burnt in oxygen-enriched air, the concentration of SO_2 is higher. Thus, if the air contains 45% oxygen, the SO_2 content in the product rises to 16%. The use of such an enriched gas in sulphuric acid production sharply increases the output.

The lead chamber process for the production of H_2SO_4 was first employed in the middle of the 18th century. Chemically, it may be represented by the following equations:

$$\text{I. } SO_2 + H_2O + NO_2 = H_2SO_4 + NO \qquad \text{II. } 2NO + O_2 = 2NO_2$$

From the first equation it is evident that nitrogen peroxide, NO_2, which is an oxidising agent, reduces to nitric oxide, NO, and the latter is reconverted into the peroxide on reacting with atmospheric oxygen, in accordance with the second equation. Thus, NO acts as an oxygen carrier, i. e., it is essentially a catalyst in the oxidation of SO_2 by atmospheric oxygen.

Up to the twenties of this century, the lead chamber process for the production of sulphuric acid was carried out in large lead chambers, whence the process got its name. Now it is carried out in special towers, and is often called the *tower* process. The acid produced by the tower process, as a rule, contains 76% H_2SO_4. It is usually slightly contaminated with various impurities. The principal consumer of this acid is the mineral fertiliser industry.

18) A schematic diagram of the tower process for the production of H_2SO_4 is shown in Fig. 105. The towers are lined with acid-resisting ceramic tiles and have an external casing of sheet steel. Inside, they are loosely packed with acid-resisting ceramics. The gas emerging from pyrite burner *A* is freed from dust in electrostatic precipitator *B*, and is then conveyed to the Glover towers *C* and *D*, where it meets a downward-trickling stream of "nitre acid" which is a solution of nitrogen oxides in concentrated sulphuric acid. The following equilibria exist in this solution:

$$NO + NO_2 + 2H_2SO_4 \rightleftarrows N_2O_3 + 2H_2SO_4 \rightleftarrows 2SO_2(OH)ONO + H_2O$$

Thus, nitre acid contains nitrogen oxides, both chemically combined (in the form of nitrosylsulphuric acid, $SO_2(OH)ONO$) and just dissolved. It should

be noted that SO_2 is oxidised only by the latter. The above equilibria are displaced to the left on heating, and to the right on cooling.

In the Glover towers, to which the hot gases are admitted (and to which water is also supplied), the nitrosylsulphuric acid decomposes completely, and practically all the incoming sulphur dioxide is oxidised. The final product is drawn off from the first tower, *C*. In the absorption (Gay-lussac) towers,

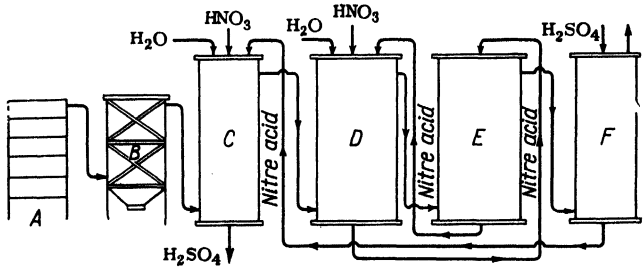


Fig. 105. Diagram of tower plant for manufacture of sulphuric acid

E and *F*, the nitrogen oxides are recovered and reconverted into nitre acid which is returned to the Glover towers. The waste gases (free nitrogen, etc.) are exhausted at the top of the last absorption tower, *F*. The movement of the gases in the system is maintained by means of a powerful blower. To make up for the slight losses of nitrogen oxides, nitric acid is fed to the Glover towers.

The other present-day method for the production of sulphuric acid, the contact process, began to be used in industry only at the end of the last century. It is based on the above-mentioned reaction:

$$2SO_2 + O_2 \rightleftarrows 2SO_3 + 46 \text{ kcal}$$

In the presence of a platinum catalyst, at 400° C the reaction proceeds from left to right practically to completion. The SO_3 formed is trapped by strong sulphuric acid (which is then diluted to the required concentration). The contact method is somewhat more costly than the lead chamber method, but contact sulphuric acid is much purer and can be obtained at any desired concentration. The high purity is due to careful preliminary purification of the gases formed on burning the pyrite, this being essential to normal functioning of the catalyst. The principal consumers of contact sulphuric acid are various chemical industries and the oil industry (for refining oil products).

19) A schematic diagram of the production of sulphuric acid by the contact method is shown in Fig. 106. The gases generated in burners *A* pass in succession through a dry electrostatic precipitator *B*, a humidifying tower *C*, a wet electrostatic precipitator *D*, a drying tower *E*, a contact apparatus *F*, containing the catalyst, and a absorption tower *G*. The resulting oleum is withdrawn at the bottom of the last tower, and waste gases (nitrogen, etc.) are expelled at the top. At present, the majority of contact plants operate with vanadium catalysts (V_2O_5 with various admixtures) which are cheaper than the formerly used platinum catalysts.

Solutions of SO_3 in sulphuric acid fume in air owing to the liberation of sulphur trioxide vapour. Therefore, sulphuric acid containing dissolved SO_3 is called *fuming* sulphuric acid (or "oleum"). Since sulphur trioxide is miscible with sulphuric acid, the composition of oleum, represented by the formula $H_2SO_4 \cdot xSO_3$, may vary. When

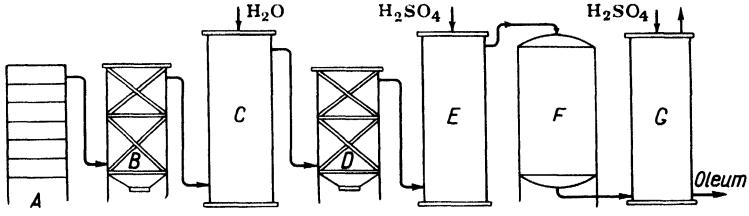


Fig. 106. Diagram of contact plant for manufacture of sulphuric acid

$x = 1$, colourless crystals of *pyrosulphuric* acid, $H_2S_2O_7$, are formed; the structure of the latter may be briefly represented by the formula HO—SO_2—O—SO_2—OH.

Pyrosulphuric acid (b. p. 35° C) is used for the preparation of various organic substances. Its salts (*pyrosulphates*) may be obtained by heating the corresponding bisulphates, e. g.:

$$2KHSO_4 = H_2O\uparrow + K_2S_2O_7$$

They are colourless crystalline substances, which change back into the bisulphates under the action of water.

If a concentrated solution of potassium bisulphate is electrolysed, hydrogen is released and KOH accumulates at the cathode, while *peroxydisulphuric* or *persulphuric* acid forms at the anode, according to the scheme: $2HSO_4' - 2\ominus = H_2S_2O_8$. Potassium *persulphate*, $K_2S_2O_8$, obtained as a result of its subsequent neutralisation, is sparingly soluble and, therefore, precipitates as colourless crystals. The majority of the other salts of peroxydisulphuric acid are readily soluble in water. All persulphates are *powerful oxidising agents*. For example, copper reacts slowly with $K_2S_2O_8$ in accordance with the equation:

$$Cu + K_2S_2O_8 = CuSO_4 + K_2SO_4$$

Free peroxydisulphuric acid forms colourless crystals which melt and decompose at 65° C. It possesses very powerful oxidising properties and, on contact, chars not only paper, sugar, etc., but paraffin as well. The structure of peroxydisulphuric acid is represented by the formula HO—SO_2—O—O—SO_2—OH, from which it is evident that it contains a peroxide chain. The spatial structure of its

corresponding ion, $S_2O_8^{2-}$, is shown in Fig. 107. Each half of the figure, taken separately, corresponds to the structure of a sulphate ion.

20) When $H_2S_2O_8$ reacts with concentrated hydrogen peroxide in accordance with the equation $H_2S_2O_8 + H_2O_2 = 2H_2SO_5$, *peroxymonosulphuric* acid is formed, which corresponds in structure to sulphuric acid in which one

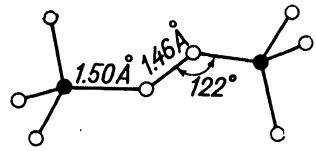


Fig. 107. Structure of the $S_2O_8^{2-}$ ion

hydroxyl radical is replaced by an OOH group. It consists of colourless crystals (m. p. 45° C, decomposes). Permonosulphuric acid is an even more powerful oxidising agent than persulphuric acid, and its reactions with many organic substances, e. g., benzene, are eruptive. The salts of H_2SO_5 are rather unstable. In its salts, H_2SO_5 is a monobasic acid.

VIII-2. Catalysis. In the previous section we saw that both methods for the production of sulphuric acid—one of the most important products of the chemical industry—are based on catalytic processes. The latter are so important that they must be considered in somewhat greater detail.

Although individual observations concerning the effect of "foreign" substances on the course of chemical processes were made as far back as the 18th century, the rapid development of the theory of catalysis began only in the present century. The definition of a catalyst may be given in the form already stated earlier (II-3): *a catalyst is a substance which speeds up a chemical reaction but which itself remains chemically unchanged.*

1) Sometimes a reaction is slowed down considerably when small quantities of foreign substances are added. A substance producing such an effect is called an *inhibitor* of the reaction in question. It either nullifies the effect of any catalysts present (by chemically combining with them or by being adsorbed on them) or converts the most active reactant molecules which determine the rapid course of the process to an inert state (deactivates them).

All the diverse catalytic processes can be divided into two broad categories, viz., *homogeneous* and *heterogeneous* catalysis. In the first case, the reacting substances and the catalyst are in the same phase, while in the second case, they are in different phases. For example, if the whole system is gaseous or is a solution, the case will be one of homogeneous catalysis. In particular, this includes the production of sulphuric acid by the lead chamber process. On the other hand, the contact process is a case of heterogeneous catalysis,

since here a solid catalyst speeds up the reaction between gaseous substances.

The chemical mechanism of homogeneous catalysis is usually considered on the basis of the *theory of intermediate compounds*. According to the latter, the reactions

$$A+B=AB \quad \text{or} \quad CD=C+D$$

which normally proceed slowly, may be considerably speeded up if conducted in a roundabout way, via more reactive intermediate compounds of the reactants with the catalyst. Denoting the catalyst by K, we obtain the exemplary equations:

$$A+K=AK \qquad CD+K=CDK$$

or

$$AK+B=AB+K \qquad CDK=C+D+K$$

As is evident from these equations, the catalyst remains chemically unchanged after the reaction. In many cases of homogeneous catalysis, the existence of intermediate compounds of the reacting substances with the catalyst has been proved experimentally.

The simplest example illustrating the theory of intermediate compounds is the lead chamber process of sulphuric acid production, for which we have

slow process:

$$O_2+2H_2SO_3=2H_2SO_4 \quad (A+B=AB)$$

rapid process:

$$O_2+2NO=2NO_2 \qquad (A+K=AK)$$

$$2NO_2+2H_2SO_3=2H_2SO_4+2NO \qquad (AK+B=AB+K)$$

Apart from its purely chemical importance, homogeneous catalysis is of enormous significance for biology. The organisms of animals and plants contain enzymes, complex organic substances which act as catalysts in various vital processes. They are highly specific in their action, each of them speeding up only one particular process without affecting any other. In this respect, enzymes are superior to inorganic catalysts, which can, for the most part, speed up several reactions of similar chemical mechanism.

Adsorption plays an important part in the chemical mechanism of heterogeneous catalysis. Adsorption increases the concentration of the reacting particles on the catalyst surface, and this in itself speeds up the reaction. However, a much more important factor is the *rise in chemical activity* of adsorbed molecules as compared with their usual state. This rise, as well as adsorption itself, is due to the effect of the strong field of the catalyst, which sharply increases the num-

ber of effective collisions between the reacting particles. The result is a corresponding increase in the reaction rate.

The specific action of a catalyst in heterogeneous catalysis is no less pronounced than in homogeneous catalysis. This is a great obstacle to the selection of a catalyst for a particular reaction. There being no theoretical guides as yet, such catalysts usually have to be chosen by making numerous trials of different substances.

2) When certain impurities—*catalyst poisons*—are present in the reacting substances, an originally good catalyst is more or less rapidly "poisoned", and ceases to speed up the reaction. Catalyst poisons act in a rather specific manner, poisoning some surfaces and having no effect on others. In the case of platinum, for instance, such poisons are HCN, H_2S, As compounds, etc.

On the other hand, other substances, known as *promoters*, do not in themselves affect a given reaction, but speed it up greatly when added to the primary catalyst in small quantities. Apparently, new active centres are created at the points of contact of the two solid phases. The effect of promoters is as specific as that of catalyst poisons. In particular, Fe, Al and SiO_2 often serve as promoters for platinum catalysts.

Besides obvious catalytic processes, there are others constantly encountered in chemistry, wherein the catalytic action is concealed. Typical of these are reactions taking place in solutions, the majority of which greatly depend on the nature of the solvent used.

The catalytic action of the latter mainly consists in weakening the bonds of the reactant molecules, making them more reactive. But the more polar the solvent molecules, the greater is their influence on the particles of the dissolved substances. Therefore, as a rule, reactions in solution proceed more rapidly with a more polar solvent.

Water is the most polar of the common solvents. As we know from the foregoing (V-4), its effect on intramolecular bonds is so great that many polar molecules dissociate into ions, exchange reactions between them taking place practically instantaneously. Even in traces, *water* is an extremely active and versatile catalyst. For example, in the complete absence of water, chlorine has no effect on metals, hydrogen fluoride does not attack glass, sodium and phosphorus do not oxidise in air, etc. Similarly, traces of water vapour greatly catalyse decomposition reactions of various substances (Cl_2O, etc.). It may be said that if water were suddenly to disappear from nature, our ideas about the chemical properties of many elements and compounds would have to undergo a radical change.

Another important factor, which often produces a catalytic effect in a concealed form, are the *walls of the vessels* in which chemical processes are carried out. Obviously, walls may act as heterogeneous catalysts in some cases. Therefore, the corresponding reactions will proceed at different rates, depending on the material of the reaction vessel. For example, hydrogen and oxygen begin to react perceptibly

in a glass vessel at 450° C, but in a platinum vessel they will react at ordinary temperatures. In the dark a mixture of hydrogen and chlorine in a glass container will explode even at the temperature of liquid air, while in a silver vessel it explodes only under ordinary conditions, and in vessels made of metallic magnesium (which have been first treated with fluorine) it explodes only on heating.

Catalytic phenomena play an exclusively important role in chemistry and biology. The above discussion shows that catalytic effects are present, in more or less obvious form, almost in every chemical reaction. Similarly, almost all processes occurring in living organisms are found, on closer examination, to involve catalytic effects. Today a number of important methods in the chemical industry are based on catalysis, and its scope of application keeps increasing from year to year. This will undoubtedly continue to be one of the principal trends in the development of the chemical industry.

VIII-3. The Selenium Subgroup. The content of *selenium* in the earth's crust is $1 \times 10^{-5}\%$, that of *tellurium* is $1 \times 10^{-7}\%$, and of *polonium*, only $2 \times 10^{-15}\%$. The latter is among the least abundant elements. It is radioactive, and has hardly been studied chemically.

Selenium and tellurium usually occur in combination with such metals as Pb, Cu, Hg, Ag and Au. However, minerals of Se and Te very rarely occur independently and are generally encountered in the form of impurities in analogous sulphur minerals.

The principal sources for the production of selenium and tellurium are sulphuric acid production wastes (dust from flues and dust traps, slime from washing towers) and the residues (anode mud) of the electrolytic refining of copper. The annual world production of selenium amounts to hundreds of tons, and that of tellurium, to a few score tons.

1) The recovery of Se and Te from industrial wastes is based on the conversion of both elements to the tetravalent state, and subsequent reduction by sulphur dioxide. They are first reduced in 10-12 *N* hydrochloric acid, where only selenium separates out. Then, the liquid is greatly diluted with water to separate out the tellurium.

2) Several allotropic modifications of selenium and tellurium are known, but these have been studied relatively little. The chief application of selenium is in the manufacture of a.c. rectifiers, and tellurium is used in the production of lead cables. Added to lead (up to 0.1%), it greatly increases its hardness, elasticity and resistance to various chemical influences.

When extracted from solutions of their compounds, selenium and tellurium are deposited as red and brown powders, respectively (*amorphous* Se and Te). But their most typical forms are the crystalline modifications, some properties of which are compared below with those of oxygen and sulphur.

Element	Under normal conditions		Melting point (°C)	Boiling point (°C)	Specific gravity in solid state
	Physical state	Colour			
O	gas	colourless	—218	—183	1.3
S	solid	yellow	119	445	2.1
Se	ditto	grey	220	680	4.8
Te	ditto	silver-grey	450	990	6.2

Both elements are stable in air and insoluble in water. All the compounds of selenium are poisonous.

Chemically, selenium and tellurium, in general, greatly resemble sulphur. Of the non-metals they react most vigorously with fluorine and chlorine, but combine with oxygen (and sulphur) only after heating. Only selenium partially reacts with gaseous hydrogen at elevated temperatures, whereas tellurium does not combine directly with hydrogen at all. With many metals, Se and Te yield the corresponding *selenides* and *tellurides* on heating, e. g., K_2Se, K_2Te which are generally analogous to sulphides.

When Se and Te are treated with dilute acids, *hydrogen selenide*, H_2Se, and *hydrogen telluride*, H_2Te result. Both are colourless gases

Compound	Heat of formation (kcal/mole)	Melting point (°C)	Boiling point (°C)	Dissociation constant (K_1)	Ionic radius E^{2-} (A)
H_2O	68.5	0	100	2×10^{-16}	1.32
H_2S	5	—86	—60	9×10^{-8}	1.74
H_2Se	—19	—66	—41	1×10^{-4}	1.91
H_2Te	—34	—51	—2	2×10^{-3}	2.11

with characteristic pungent odours. Their solubility in water is approximately the same as that of hydrogen sulphide, the solutions being distinctly acid. Some of the most important properties of these compounds are compared in the above table and in Fig. 108 with the respective properties of H_2O and H_2S. In order to give a rough idea of the sizes of the corresponding molecules, the radii of the E^{2-} ions are also given.

From the table it can be seen that H_2Se and H_2Te are stronger acids than acetic acid ($K = 2 \times 10^{-5}$). Both compounds (especially H_2Te) are extremely unstable and decompose readily. They are gradually oxidised by atmospheric oxygen, both in the gaseous state

and especially in solution even at ordinary temperatures. In general, reducing properties are even more characteristic of H_2Se and H_2Te than of hydrogen sulphide.

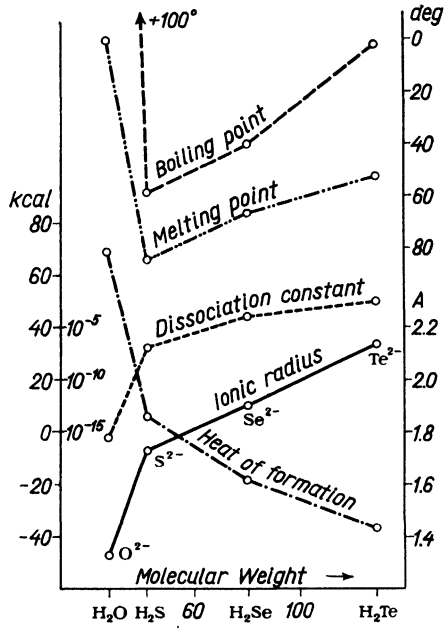


Fig. 108. Properties of hydrogen compounds of group VI elements

3) All the halogen compounds of selenium and tellurium can be obtained by reactions between the corresponding elements. The following halides are known:

Compound	SeF_6	SeF_4	$SeCl_4$	Se_2Cl_2	$SeBr_4$	Se_2B_2
Physical state	gas	liquid	solid	liquid	solid	liquid
Colour	colourless	colourless	colourless	yellow	yellow	red

Compound	TeF_6	TeF_4	$TeCl_4$	$TeCl_2$	$TeBr_4$	$TeBr_2$	TeI_4
Physical state	gas	solid	solid	solid	solid	solid	solid
Colour	colourless	colourless	colourless	green	orange	brown	grey-black

Selenium halides resemble the corresponding sulphur derivatives in character, the type E_2X_2 being, in this case, less stable and the type EX_4 more stable.

The properties of the tellurium halides are very different from those of the sulphur derivatives. For instance, TeF_6 is fairly easily decomposed by water, while TeI_4 is formed on triturating the elements together in the presence of water (whereas selenium and sulphur iodides have not been obtained at all).

When heated in a current of air, selenium and tellurium burn with the formation of the corresponding *dioxides*. The latter are colourless crystalline substances which greatly differ from each other in their solubility in water, that of SeO_2 being very high and that of TeO_2, very low.

Like SO_2, selenium and tellurium dioxides are *acid anhydrides*: on dissolving in water, they form *selenious*, H_2SeO_3, and *tellurous*, H_2TeO_3, acids, respectively. Both of them are somewhat more weakly dissociated than sulphuric acid.

Salts of selenious acid (*selenites*) can be obtained by neutralising solutions of H_2SeO_3, while salts of tellurous acid (*tellurites*) can be obtained by dissolving TeO_2 in alkalis. As a rule, both of these are similar in properties to the corresponding sulphites.

While reducing properties are more characteristic of tetravalent sulphur than oxidising properties, Se^{IV} and Te^{IV} are themselves fairly easily reduced to elementary Se and Te, e. g.:

$$H_2EO_3 + 2SO_2 + H_2O = 2H_2SO_4 + E$$

On the other hand, the conversion of selenium and tellurium into the hexavalent state can be accomplished only under the action of the most powerful oxidising agents.

4) *Selenious* acid ($K_1 = 2 \times 10^{-3}$, $K_2 = 5 \times 10^{-9}$) may be obtained by the reaction: $3Se + 4HNO_3 + H_2O = 3H_2SeO_3 + 4NO$. Its oxidising properties are not very pronounced. Thus, it oxidises I' but is incapable of oxidising Br'. Of the salts of H_2SeO_3, mention should be made of silver selenite, Ag_2SeO_3, which is sparingly soluble.

Tellurous acid ($K_1 = 2 \times 10^{-3}$, $K_2 = 1 \times 10^{-8}$) has never been isolated. Its oxidising properties are weaker than those of selenious acid. Thus, it oxidises SO_2 but not I'. The amphoteric character of tellurous acid is displayed when TeO_2 is dissolved in concentrated strong acids, in which case salts of tetravalent tellurium are formed, e. g.: $TeO_2 + 4HI \rightleftarrows TeI_4 + 2H_2O$.

When H_2SeO_3 and H_2TeO_3 are oxidised, as, for instance,

$$5H_2EO_3 + 2HClO_3 = 5H_2EO_4 + Cl_2 + H_2O$$

selenic, H_2SeO_4, or *telluric*, H_2TeO_4, acid, respectively, is formed. Both of them are colourless crystalline substances, readily soluble in water. Selenic acid is approximately equal in strength to sulphuric acid, but telluric acid is a very weak one.

Salts of selenic acid (*selenates*) are similar in properties to the corresponding sulphates. On the other hand, salts of telluric acid (*tellurates*) differ substantially from them. For example, $BaTeO_4$ separates out from solution with water of crystallisation and is readily soluble in hydrochloric acid. Only the tellurates of the most active monovalent metals are readily soluble in water.

Both of these acids are powerful oxidising agents, reacting with HCl, for example, in accordance with the equation:

$$H_2EO_4 + 2HCl \rightleftarrows H_2EO_3 + Cl_2 + H_2O$$

In acid solution, the equilibrium shifts to the right, and in alkaline solution, to the left.

5) Free *selenic* acid ($K_2 = 1 \times 10^{-2}$) is most easily prepared by treating a suspension of Ag_2SeO_3 with bromine water. The reaction takes place according to the equation: $Ag_2SeO_3 + Br_2 + H_2O = 2AgBr\downarrow + H_2SeO_4$. *Telluric* acid ($K_1 = 2 \times 10^{-8}$, $K_2 = 5 \times 10^{-11}$) may be obtained by means of reaction between amorphous tellurium and H_2O_2. It separates out as the colourless crystal hydrate, $H_2TeO_4 \cdot 2H_2O$. As in the case of periodic acid (VII-4, suppl. 6), the hydrogen atoms contained in the water of this crystal hydrate can be displaced by a metal. For example, salts of the composition Ag_6TeO_6 and Hg_3TeO_6 are known, which correspond to the hexabasic *orthotelluric* acid, H_6TeO_6.

When H_2TeO_4 is heated to 300° C, water is eliminated leaving a yellow powder, *tellurium trioxide*, TeO_3. On further heating, this oxide decomposes into TeO_2 and oxygen. Tellurium trioxide is practically insoluble in water, dilute acids and alkalis. However, it dissolves in concentrated alkali solutions, forming the corresponding tellurates.

Selenium trioxide, SeO_3, could not be obtained for a long time. It was prepared only recently (by means of the reaction between K_2SeO_4 and an excess of SO_3), and is a colourless crystalline substance (m. p. 118° C) which dissolves readily in water forming selenic acid.

VIII-4. The Chromium Subgroup. The high content in the earth's crust of *chromium* (6×10^{-3}%), *molybdenum* (3×10^{-4}%) and *tungsten* (6×10^{-4}%) places them among the fairly abundant elements. They occur solely in the form of compounds.

The principal ore of chromium is native *chromite* or *chrome ironstone*, $FeO \cdot Cr_2O_3$. The most important molybdenum ore is the mineral *molybdenite*, MoS_2, and the most important of the tungsten ores are the minerals *wolframite*, $xFeWO_4 \cdot yMnWO_4$, and *scheelite*, $CaWO_4$.

1) The annual world output of chromium is about 2 million tons. Approximately 30 thousand tons each of molybdenum and tungsten are mined annually.

2) The first task in producing the elements of the chromium subgroup is to separate their oxides. This is usually done as follows. Chromite is fused with soda in the presence of oxygen: $[4(FeO \cdot Cr_2O_3) + 8Na_2CO_3 + 7O_2 = 2Fe_2O_3 + 8Na_2CrO_4 + 8CO_2]$; then the Na_2CrO_4 extracted from the melt is converted into $Na_2Cr_2O_7$ (in accordance with the equation: $2Na_2CrO_4 + H_2SO_4 = Na_2SO_4 + Na_2Cr_2O_7$), which is reduced to Cr_2O_3 with carbon ($Na_2Cr_2O_7 + 2C = Cr_2O_3 + Na_2CO_3 + CO$).

Sodium tungstate, which is obtained from wolframite similarly by fusing with soda ($4FeWO_4 + 4Na_2CO_3 + O_2 = 4Na_2WO_4 + 2Fe_2O_3 + 4CO_2$ and $6MnWO_4 + 6Na_2CO_3 + O_2 = 6Na_2WO_4 + 2Mn_3O_4 + 6CO_2$), is decomposed by hydrochloric acid, and the resulting H_2WO_4 is heated to convert it to WO_3. Molybdenite is converted into MoO_3 by roasting in air: $2MoS_2 + 7O_2 = 4SO_2 + 2MoO_3$. As in the case of manganese, high percentage alloys with iron, and not the pure metals, are more frequently smelted from Cr, Mo and W ores.

Elementary chromium may be conveniently obtained from its oxide, Cr_2O_3, by mixing the latter with aluminium powder. The

reaction, which sets in on heating, takes place according to the equation:

$$Cr_2O_3 + 2Al = Al_2O_3 + 2Cr$$

Molybdenum and tungsten may be obtained by reducing their oxides with carbon or hydrogen at high temperatures.

In compact form, the elements of the chromium subgroup are lustrous greyish-white metals. Their most important constants are listed below:

Properties	Cr	Mo	W
Specific gravity	7.2	10.3	19.3
Melting point (°C)	1900	2625	3410
Boiling point (°C)	2500	4800	5370
Electrical conductivity (Hg = 1)	7	20	18

Ordinary commercial chromium is the hardest of all the metals. Molybdenum and tungsten are much softer. The very pure metals are quite machinable, but even traces of impurities make them brittle. Cr, Mo and W are highly resistant to air and water under normal conditions. Their principal consumer is the metallurgical industry where these metals are used as alloying elements for special steels.

3) Besides the manufacture of special steels, *chromium* is used for plating metal articles requiring wear-resistant surfaces (calipers, etc.). Chromium plating is usually carried out electrolytically, the thickness of the chromium layer deposited not exceeding 0.005 mm. *Molybdenum* is chiefly employed in the manufacture of supports for electric lamp filaments. Since *tungsten* is the most refractory and non-volatile of all the metals, it is particularly suitable for the manufacture of electric lamp filaments and the anticathodes of high-power X-ray tubes. Tungsten also plays an extremely important part in the production of extrahard alloys for tipping cutting tools, drills, etc.

Under ordinary conditions, all three metals interact markedly only with fluorine, but combine more or less vigorously with other typical non-metals when heated to a sufficient degree. A feature common to all of them is the lack of chemical interaction with hydrogen.

In the chromium subgroup, the chemical activity of the metals decreases downwards (Cr → Mo → W). This is particularly evident in their attitude toward the halogens. Fluorine reacts with all three metals, even in the cold. *Chromium* also combines vigorously with all the other halogens on heating. *Molybdenum* reacts with chlorine and bromine on heating, but not with iodine. *Tungsten* does not combine directly with either iodine or bromine.

Chromium and its analogues react with oxygen and a number of other non-metals (S, N, C, Si) only at sufficiently high temperatures. A feature common to all the elements of the subgroup is that they do not react with hydrogen.

Chromium is soluble in dilute HCl and H_2SO_4. The latter have no effect on molybdenum, but the metal dissolves in hot concentrated H_2SO_4. Tungsten is extremely resistant to all the common acids and mixtures of them (with the exception of a mixture of HF and HNO_3). Molybdenum and tungsten can easily be converted into the soluble state by fusing with saltpetre and soda:

$$E + 3NaNO_3 + Na_2CC_3 = Na_2EO_4 + 3NaNO_2 + CO_2\uparrow$$

Compounds corresponding to different valencies up to VI are known for the elements of the chromium subgroup. Of these, only the derivatives of the *hexavalent* elements and those of *trivalent chromium* find more or less extensive application, the chromium compounds being more important than the others. The most characteristic derivatives of the chromium subgroup elements are those in which they are *hexavalent*. Of the *trioxides*, EO_3, corresponding to this valency, only colourless MoO_3 and light yellow WO_3 can be formed by heating the metals in air. Dark red CrO_3 can be obtained only indirectly. All these trioxides are solid under ordinary conditions.

Being a typical acid anhydride, CrO_3 dissolves readily in water forming *chromic* acid, H_2CrO_4, an acid of medium strength. *Chromic anhydride* is poisonous, and is a very powerful *oxidising agent*. Even at about 200° C it decomposes in accordance with the equation:

$$4CrO_3 = 2Cr_2O_3 + 3O_2$$

In contrast, MoO_3 and WO_3 vaporise above 1000° C without decomposing.

The solubility of MoO_3 and WO_3 in water is very low, but they dissolve in alkalis to form *molybdic* and *tungstic* acids. In the free state, the latter are almost insoluble white (H_2MoO_4) or yellow (H_2WO_4) powders. On heating, both acids readily lose water and are converted into the corresponding trioxides.

The strengths of the acids H_2EO_4 rapidly decrease in the order Cr—Mo—W. The majority of their salts are sparingly soluble in water. Of the derivatives of the metals most frequently encountered, the readily soluble compounds are: the *chromates* of only Na^+, K^+, Mg^{2+} and Ca^{2+}, and the *molybdates* and *tungstates* of only Na^+ and K^+. As a rule, *chromates* have the light yellow colour of the CrO_4'' ion, while *molybdates* and *tungstates* are colourless.

When CrO_3 reacts with gaseous hydrogen chloride, *chromyl chloride*, CrO_2Cl_2, is formed, this being a reddish-brown liquid (b. p. 117° C). Compounds of the type EO_2Cl_2 (solids under ordinary conditions) are

known for Mo and W too. They all react with water according to the equation:

$$EO_2Cl_2 + 2H_2O \rightleftarrows EO_2(OH)_2 + 2HCl$$

In the case of chromium, the equilibrium is practically completely displaced to the right, i. e., chromyl chloride (like SO_2Cl_2) is a typical acid chloride. Derivatives of Mo and W are considerably less hydrolysed, and this indicates the pronounced amphoteric character of molybdic and tungstic acids.

4) Products of complete displacement of oxygen by a halogen from the trioxides EO_3 are known only for Mo and W. The fluorides of these elements—MoF_6 (m. p. 18° C, b. p. 35° C) and WF_6 (m. p. 2° C, b. p. 18° C)—are colourless, low-melting and highly volatile. Dark violet WCl_6 (m. p. 284° C, b. p. 337° C) has also been obtained.

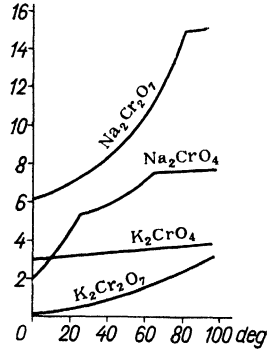


Fig. 109. Solubility of chromates and dichromates (moles/litre of H_2O)

In addition to acids of the H_2EO_4 type, chromium and its analogues also give acids corresponding to the general formula $H_2E_2O_7$, analogous in structure to pyrosulphuric acid. The most important of these is *dichromic* acid, $H_2Cr_2O_7$. The acid itself is known only in solution, but its salts (*dichromates*), especially $K_2Cr_2O_7$ and $Na_2Cr_2O_7 \cdot 2H_2O$, are the most common chromium compounds and the initial products for obtaining the other compounds of this element.

Like the Cr_2O_7'' ion, the majority of the dichromates have a reddish-orange colour. Their solubility is generally higher than that of the corresponding chromates. The data for sodium and potassium salts are given in Fig. 109.

Solutions of dichromates show an acid reaction owing to the following reaction between Cr_2O_7'' and water:

$$H_2O + Cr_2O_7'' \rightleftarrows 2HCrO_4' \rightleftarrows 2H^{\cdot} + 2CrO_4''$$

As can be seen from the equation, the addition of acids ($H^{\cdot}$ ions) to the solution should shift the equilibrium to the left, while the addition of alkalis (OH' ions) should shift it to the right. Therefore, chromates can easily be obtained from dichromates, and vice versa, e. g.:

$$K_2Cr_2O_7 + 2KOH = 2K_2CrO_4 + H_2O$$

$$2K_2CrO_4 + H_2SO_4 = K_2SO_4 + K_2Cr_2O_7 + H_2O$$

Salts of the chromic acids are powerful oxidising agents in *acid* solution (Cr^{VI} being reduced to Cr^{III}). For example, they will oxidise HI in the cold, and even HBr and HCl on heating. The reactions are:

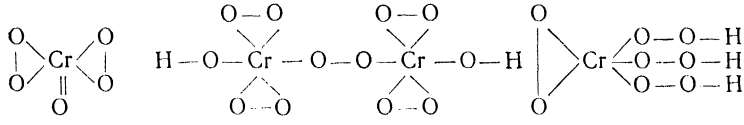
$$K_2Cr_2O_7 + 14HX = 2KX + 2CrX_3 + 3X_2 + 7H_2O$$

A mixture of equal volumes of a saturated solution of $K_2Cr_2O_7$ and concentrated H_2SO_4 (sometimes called "chromic acid mixture"), which possesses very powerful oxidising properties, is used in laboratories for washing chemical glassware.

5) Chromic acid ($K_1 = 2 \times 10^{-1}$ and $K_2 = 3 \times 10^{-7}$) is much weaker than dichromic acid ($K_2 = 2 \times 10^{-2}$). The latter is the simplest of the *isopolyacids* having the general formula $xH_2O \cdot yEO_3$ (where $y > x$) and known in the form of their salts. Besides dichromates ($x = 1$, $y = 2$), trichromates ($x = 1$, $y = 3$) and tetrachromates ($x = 1$, $y = 4$) have also been obtained. The formation of these and more complex *isopolysalts* is especially characteristic of molybdenum and tungsten.

6) The ultimate forms of the isopolyacids ($y = \infty$) are the corresponding free anhydrides. Of these, MoO_3 and WO_3 can be formed by heating the metals in air. CrO_3 crystals separate out when a mixture of a 10% solution of $K_2Cr_2O_7$ and concentrated H_2SO_4 (4 : 1 by volume) is allowed to stand.

7) All the members of the chromium subgroup form *peroxides* on reacting with H_2O_2. In the case of chromium, besides the blue *peroxide*, CrO_5, salts of the *peroxyacids*, $H_2Cr_2O_{12}$ and H_3CrO_8, are also known. The following structural formulas were deduced from the data of a study of these acids.



Thus, the valency of chromium differs in the two peroxyacids. The salts of the former are usually blue, while those of the latter are usually red.

8) The peroxycompounds of *molybdenum* and *tungsten* are chiefly of the type M_2EO_x, where x varies from 5 to 8. They are all derived from the hexavalent forms of the elements and contain from 1 o 4 peroxy-groups --O—O— in the acid radical, substituting oxygen atoms.

As has already been noted, among the derivatives of the lower valencies of these elements, only compounds of trivalent chromium are of any substantial practical importance. *Chromic oxide*, Cr_2O_3, results when chromium burns vigorously in oxygen, and is a dark green refractory substance, insoluble in acids as welll as in water. Both Cr_2O_3 and its corresponding salts are usually prepared from hexavalent chromium compounds rather than from the metal, e. g.:

$$K_2Cr_2O_7 + 3SO_2 + H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

9) In the laboratory, chromic oxide is conveniently prepared by the decomposition of ammonium dichromate. The reaction is initiated by heating after which it proceeds spontaneously in accordance with the equation: $(NH_4)_2Cr_2O_7 = Cr_2O_3 + N_2 + 4H_2O$. Chromic oxide may be converted into the soluble state by fusing with $NaNO_3$ and Na_2CO_3: $Cr_2O_3 + 3NaNO_3 + 2Na_2CO_3 = 2Na_2CrO_4 + 3NaNO_2 + 2CO_2\uparrow$.

Chrome alum, a dark violet crystalline compound of the composition $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$, is the most interesting salt of chromic oxide (having a Cr^{3+} cation). A greyish-blue precipitate of *chromic*

hydroxide, $Cr(OH)_3$, which is sparingly soluble in water, can be obtained by the action of NH_4OH on a solution of chrome alum. Chromic hydroxide is pronouncedly *amphoteric* in character. With acids, it yields salts of chromic oxide, and when treated with strong alkalis, it forms salts of *chromous* acid [$HCrO_2$, i. e., $Cr(OH)_3 - H_2O$] containing the anion CrO_2', which are called *chromites*. For example:

$$Cr(OH)_3 + 3HCl = CrCl_3 + 3H_2O$$
$$Cr(OH)_3 + KOH = KCrO_2 + 2H_2O$$

Thus for the dissolved portion of chromic hydroxide, the following equilibria exist simultaneously:

$$Cr^{\cdot\cdot\cdot} + 3OH' \rightleftarrows Cr(OH)_3 \equiv H_3CrO_3 \rightleftarrows H^{\cdot} + CrO_2' + H_2O$$

If acids ($H^{\cdot}$) are added, the equilibria shift to the left; if alkalis (OH'), they shift to the right. In itself, the electrolytic dissociation of $Cr(OH)_3$ is insignificant in either direction, since both the basic and especially the acidic properties of chromic hydroxide are fairly weak. Therefore, trivalent chromium salts are considerably hydrolysed in solution, while the soluble chromites are practically entirely hydrolysed in the absence of excess alkali. Natural chromite, $Fe(CrO_2)_2$, is an insoluble chromite.

While derivatives of hexavalent chromium are readily reduced in acid solution to Cr^{3+} salts, which are the most stable under these conditions, derivatives of trivalent chromium are fairly easily oxidised to chromates in *alkaline* solution by free halogens, hydrogen peroxide, etc., for example:

$$2KCrO_2 + 3Br_2 + 8KOH = 6KBr + 2K_2CrO_4 + 4H_2O$$
$$Cr_2(SO_4)_3 + 3H_2O_2 + 10NaOH = 3Na_2SO_4 + 2Na_2CrO_4 + 8H_2O$$

However, no oxidation takes place under the action of atmospheric oxygen.

10) *Chromous* chloride, $CrCl_2$, in which chromium is divalent, results when the metal reacts with hydrochloric acid in an atmosphere of hydrogen. It is a colourless crystalline substance, which dissolves in water to form a blue solution. Green CrF_2, yellowish $CrBr_2$ and red CrI_2 have also been obtained.

The $Cr^{\cdot\cdot}$ ion is such a powerful reducing agent that it is able to displace hydrogen according to the equation: $2Cr^{\cdot\cdot} + 2H^{\cdot} = 2Cr^{\cdot\cdot\cdot} + H_2\uparrow$. A hydrochloric acid solution of $CrCl_2$ is sometimes used to absorb oxygen. The following reaction ensues: $4CrCl_2 + O_2 + 4HCl = 4CrCl_3 + 2H_2O$.

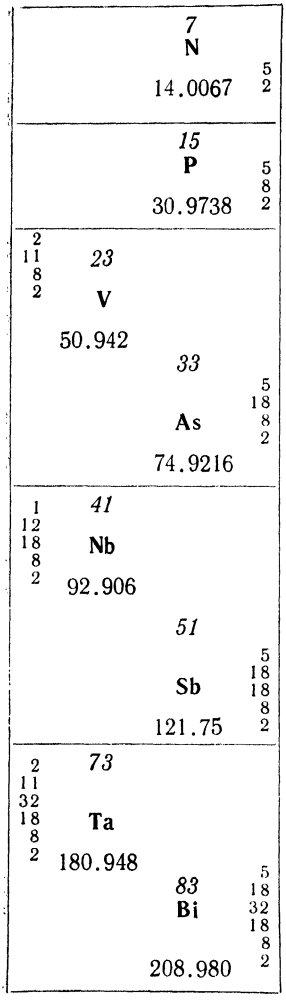
When sulphur is compared with the elements of the subgroups following it, complete agreement is observed between experimental data and the requirements of the theory of electronic analogues: in derivatives of *higher* valency sulphur displays similarity to the elements of the chromium subgroup; on the other hand, in compounds of *lower* valency, a similarity is observed in the series S—Se—Te,

whereas chromium and the other members of its subgroup lose their resemblance to sulphur.

Indeed, acids of the type H_2EO_4 are characteristic of all these elements, but a regular decrease in their strength is observed only in the series S—Cr—Mo—W (whereas selenic acid is not weaker than sulphuric acid). Compounds of the type EO_2Cl_2, characteristic of sulphur and the members of the chromium subgroup, do not exist for selenium and tellurium.

On the other hand, hydrogen compounds of the type EH_2, which are characteristic of S, Se and Te, have no counterparts in the chromium subgroup. In the case of S, Se and Te, the oxides of the type EO_2 and the acids H_2EO_3 derived from them, are similar, whereas the corresponding oxides are not very characteristic of the elements of the chromium subgroup (and have basic rather than acidic properties).

IX. FIFTH GROUP OF THE PERIODIC TABLE



The elements of this group may be divided into two subgroups according to the electronic structures of their *neutral atoms*. One of them includes nitrogen, phosphorus, arsenic and the analogues of the latter, while the other contains vanadium and its analogues.

Since the atoms of the elements from N to Bi each have five electrons in their outermost shell, they can be expected to have a tendency to build up this shell to an octet. However, this tendency should be weaker than in the corresponding elements of the sixth (O—Po) and seventh (F—At) groups, which are, respectively, short of only two or one electron for an eight-electron configuration. In connection with this, the non-metallic properties of phosphorus, for example, might be expected to be weaker than those of sulphur and chlorine. On the other hand, electrons should be given up by the neutral atoms more readily and the stability of the oxygen compounds should be greater in group V than those of the corresponding elements of groups VII and VI.

Like the elements of the chromium subgroup, vanadium and its analogues are characterised by the presence in their outermost shells of not more than two electrons, and therefore, there is no tendency to gain further electrons. At the same time, it can be expected that in the derivatives of higher valency vanadium and its analogues will display a marked similarity to phosphorus.

IX-1. Nitrogen. The total content of nitrogen in the earth's crust is estimated to be about 0.03%. Most of it is concentrated in the atmosphere, the bulk of which (75.5 wt.%) consists of *free* nitrogen, N_2. Complex organic derivatives of nitrogen form part of all living organisms. As a result of the death of the latter and the decay of their

remains, simpler nitrogen compounds are formed, which may accumulate under favourable conditions (mainly, in the absence of moisture). Such is probably the origin of $NaNO_3$ deposits in Chile, which are industrially valuable as one of the sources of *combined* nitrogen, i. e., nitrogen in compound form.

Since free nitrogen is contained in the atmosphere, it is obtained essentially by separation from oxygen and the other components of the air. This is accomplished by gradually evaporating liquid air in special plants, oxygen and the inert gases also being obtained simultaneously. In the laboratory, nitrogen may be obtained by various reactions, one of which is:

$$NH_4NO_2 = 2H_2O + N_2$$

which takes place readily when a concentrated solution of ammonium nitrite (or a mixture of $NaNO_2$ and NH_4Cl) is heated.

Nitrogen is a colourless, odourless gas (m. p. —210° C, b. p. —196° C). Its solubility in water is low—about 2% by volume. The nitrogen molecule is diatomic and does not decompose appreciably into atoms even at very high temperatures.

Chemically, free nitrogen is extremely inert. Under ordinary conditions it reacts neither with non-metals nor with metals (except Li). A rise in temperature increases its activity mainly in regard to metals, with some of which it combines on heating to form nitrides, e. g., Mg_3N_2

The applications of free nitrogen as such are fairly limited. Its most important use is for filling electric-light bulbs. Nitrogen compounds are of enormous importance in biology, and are employed in various branches of industry. Most of them are used as mineral fertilisers and in the production of explosives.

Free nitrogen from the air is the principal raw material for the industrial production of nitrogen compounds. It is converted into the combined state mainly by the *ammonia synthesis* method developed in 1913.

Application of Le Châtelier's principle to the reversible reaction

$$N_2 + 3H_2 \rightleftarrows 2NH_3 + 22 \text{ kcal}$$

shows that the most advantageous conditions for the formation of ammonia are the lowest temperature and the highest pressure possible. The curves in Fig. 110 characterise the position of the equilibrium of this system under various conditions. As can be seen from the diagram, a favourable relationship is established only at relatively low temperatures and high pressures. However, even at 700° C the reaction rate is so low (and consequently, equilibrium is established so slowly) that its practical application is out of the question. On the other hand, at higher temperatures, when the state of equilibrium

is established rapidly, the content of ammonia in the system becomes negligible. Thus, the technical implementation of this process appears to be impossible, since the speeding up of the attainment of equilibrium by heating, simultaneously shifts the position of equilibrium in a disadvantageous direction.

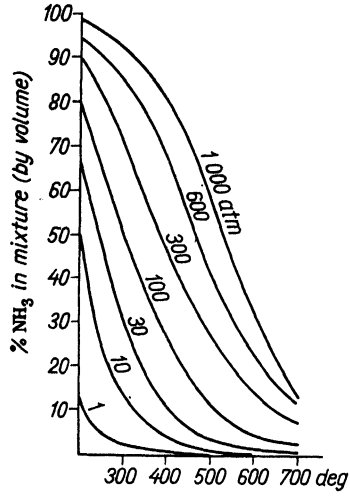


Fig. 110. Equilibrium of ammonia synthesis from its elements

There is, however, a way of speeding up the attainment of the equilibrium state without simultaneously displacing the equilibrium. A method which is often helpful is the use of a suitable catalyst. In this case, it was found that metallic iron (with admixtures of Al_2O_3 and K_2O) was highly effective.

A diagram of a commercial-size installation for the synthesis of ammonia is shown in Fig. 111. The process is conducted at 400 to 550°C (with a catalyst) and 100 to 1000 atm. Equilibrium sets in quite rapidly. After the ammonia has been separated from the gaseous mixture, the latter is returned to the cycle. During the quarter-century from 1913 to 1938, the annual world production of combined nitrogen by this method rose from 7

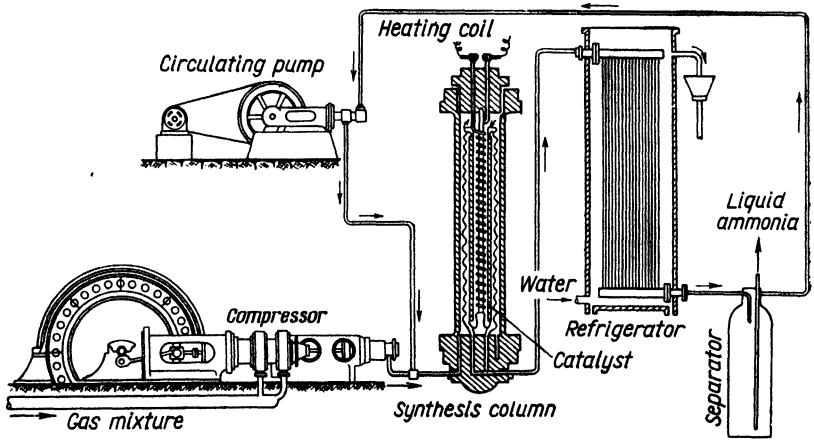


Fig. 111. Diagram of ammonia synthesis plant

to 1700 thousand tons. At present, the synthesis of ammonia is the *principal* industrial method for the production of combined nitrogen.

1) The *cyanamide* process, which was developed in 1901, is of considerably less industrial importance. This process is based on the fact that at high temperatures calcium carbide (obtained by heating a mixture of lime and carbon in an electric furnace) reacts with free nitrogen in accordance with the equation: $CaC_2 + N_2 = CaCN_2 + C + 70$ kcal. *Calcium cyanamide*, $Ca{=}N{-}C \equiv N$, which is obtained in this way, is a grey (owing to carbon impurities) powder. When treated with superheated steam, i. e., steam heated above 100° C, it decomposes with the liberation of ammonia: $CaCN_2 + 3H_2O = CaCO_3 + 2NH_3$.

A furnace for the production of calcium cyanamide is schematically shown in Fig. 112. It consists of a cylinder of refractory material, along the axis of which runs a tube containing a heating coil. After the furnace has been charged with crushed CaC_2, it is tightly sealed, and nitrogen is fed into it. Since the formation of cyanamide is accompanied by the evolution of heat, it is sufficient to heat the initial mixture to 800° C, after which the reaction continues of its own accord. From 1913 to 1938, the annual world production of combined nitrogen by the cyanamide process rose from 38 thousand to 300 thousand tons.

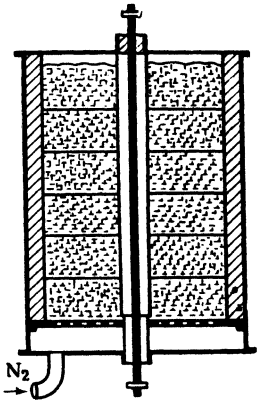


Fig. 112. Diagram of a cyanamide furnace

The NH_3 molecule has the form of a triangular pyramid (Fig. 113). Since the electrons of the H—N bond are rather strongly shifted from the hydrogen to the nitrogen ($p_{HN}=0.28$), the ammonia molecule as a whole is characterised by considerable polarity (dipole length 0.31 Å).

Ammonia is a colourless gas (m. p. —78° C, b. p. —33°C) with the characteristic pungent odour of ammonia water. Its solubility

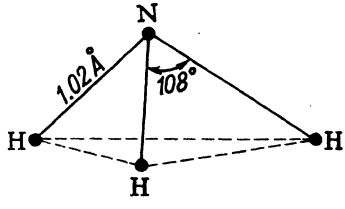


Fig. 113. Structure of the ammonia molecule

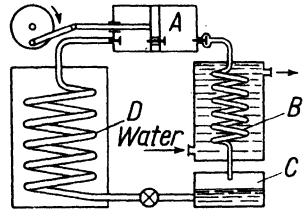


Fig. 114. Diagram of a refrigerator

in water is higher than that of any other gas: one volume of water absorbs about 1200 volumes of NH_3 at 0° C, and about 700 volumes at 20° C. A commercial concentrated solution usually has a specific gravity of 0.91 and contains 25% of NH_3 by weight.

2) Like water, liquid ammonia is associated chiefly owing to the formation of hydrogen bonds. It is a good solvent for many inorganic and organic compounds.

3) The high latent heat of vaporisation of ammonia (5.6 kcal/mole) is due to association of its molecules. Since the critical temperature of NH_3 is high (+133° C), and a great deal of heat is removed from the surrounding medium when NH_3 evaporates, liquid ammonia is a good and frequently employed working fluid for *refrigerating* machines.

Fig. 114 is a diagram of a refrigerating machine. When the piston *A* moves to the right, the NH_3, which is heated by compression, enters the spiral coil *B* which is cooled by water or air from the outside. The cooled ammonia, at a pressure of 7 or 8 atm which has already been established in the system, is condensed and flows into the receiver *C*. From here, the liquid ammonia enters the spiral coil *D* where it evaporates owing to rarefaction in this part of the system (caused by the movement of the piston *A*). The heat necessary for evaporation, is absorbed from the space surrounding the spiral coil *D*. Successive repetition of the entire cycle ensures continuous cooling of the space.

As far as the chemical properties of ammonia are concerned, three types of reactions are of basic importance: addition, hydrogen substitution and oxidation.

Most characteristic for ammonia are addition reactions. In particular, its action on many salts results in the formation of crystalline *ammines* of the composition $CaCl_2 \cdot 8NH_3$, $CuSO_4 \cdot 4NH_3$, etc., which are similar to crystal hydrates in stability and the nature of formation.

When dissolved in water, ammonia partially forms *ammonium hydroxide*:

$$NH_3 + H_2O \rightleftarrows NH_4OH$$

In this compound, the *ammonium* radical, NH_4, plays the part of a monovalent metal. Therefore, NH_4OH ionises like a base:

$$NH_4OH \rightleftarrows NH_4^+ + OH'$$

By combining the two equations we obtain a general representation of the equilibria existent in an aqueous solution of ammonia:

$$NH_3 + H_2O \rightleftarrows NH_4OH \rightleftarrows NH_4^+ + OH'$$

Owing to these equilibria, an aqueous solution of ammonia (often called simply "ammonia") has the pungent odour of the latter. As this solution contains comparatively few OH' ions, NH_4OH is regarded as a *weak* base.

The addition of acids shifts the above equilibria to the right (due to binding of the OH' ions) and leads to the formation of *ammonium salts*, e. g.:

$$NH_4OH + HCl = H_2O + NH_4Cl$$

These salts can also be formed by direct interaction of ammonia with acids, e. g., in accordance with the reaction:

$$NH_3 + HCl = NH_4Cl$$

Like the ammonium ion, NH_4^+, the majority of ammonium salts are colourless. Almost all of them are readily soluble in water (Fig. 115) and are highly dissociated in solution.

Ammonium salts decompose fairly readily on heating. The nature of the decomposition is determined by the properties of the acid forming the anion. If this acid is an oxidising agent, ammonia is oxidised, e. g., according to the reaction:

$$NH_4NO_2 = 2H_2O + N_2$$

If the acid is not an oxidising agent, the nature of decomposition depends on its volatility at the temperature of decomposition. Only ammonia is liberated from salts of non-volatile acids (e. g., H_3PO_4), while a volatile acid (e. g., HCl) will recombine with the NH_3 on cooling. Such decomposition and subsequent recombination is practically tantamount to sublimation of the given salt (e. g., NH_4Cl).

Strong alkalis liberate ammonia from ammonium salts, e. g.:

$$NH_4Cl + NaOH = NaCl + NH_4OH =$$
$$= NaCl + NH_3 + H_2O$$

This may be utilised for the laboratory preparation of ammonia, and also for the detection of NH_4^+ ions in solution: alkalis are added to the latter and the liberated ammonia is detected by its odour or by its action on moist litmus paper.

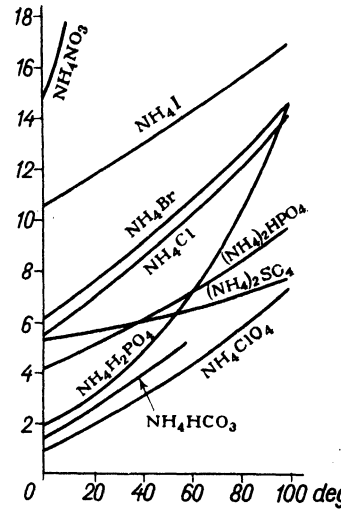


Fig. 115. Solubility of ammonium salts (moles/litre of H_2O)

Ammonia derivatives are of great practical importance. Its hydroxide, NH_4OH, is one of the most important chemical reagents, and dilute solutions (ammonia water) are sometimes used domestically for washing clothes and removing stains. Ammonium chloride (sal ammoniac) reacts with metal oxides at high temperatures, exposing the clean metal surface. Its use in soldering is based on this property. NH_4Cl is used in electrical engineering for the manufacture of "dry" cells. Ammonium nitrate, NH_4NO_3, serves as the basis for complex nitrogen fertilisers, and is also used in the production of certain explosive mixtures. Ammonium sulphate, $(NH_4)_2SO_4$, is used in large quantities in agriculture as a nitrogen fertiliser. Ammonium bicarbonate, NH_4HCO_3, is employed in baking (mainly in the production of pastry). This application is based on the fact that on heating, it readily decomposes in accordance with the equation $NH_4HCO_3 = NH_3 + H_2O + CO_2$, and the gases formed impart the necessary sponginess to the dough. Ammonium sulphide, $(NH_4)_2S$, is one of the principal reagents in analytical chemistry. Ammonium compounds play an important part in certain production

processes in the chemical industry, and are widely employed in laboratory practice.

4) The ammonia water usually on the market contains about 10% of ammonia. It also finds application in medicine. In particular, inhalation of its vapour or its intake (3-4 drops in a glass of water) relieves intoxication Application of ammonia water to the skin eases the effect of insect bites. In the removal of stains, the following compositions (by volume) give good results in many cases: a) 4 parts of ammonia water, 5 parts of ether and 7 parts of ethyl alcohol; b) 10 parts of ammonia water, 7 parts of ethyl alcohol, 3 parts of chloroform and 80 parts of petrol.

5) Ammonium nitrate decomposes explosively in accordance with the equation: $2NH_4NO_3 = 4H_2O + N_2 + O_2 + 57$ kcal. *Ammonal*, which is sometimes used for blasting, is an intimate mixture of NH_4NO_3 (72%), aluminium powder (25%) and carbon (3%). This mixture can be exploded only by detonation.

Reactions involving *hydrogen displacement* are less characteristic of ammonia than the addition reactions considered above. However, at high temperatures its hydrogen atoms can be substituted by a metal, according to the reaction:

$$2Al + 2NH_3 = 2AlN + 3H_2$$

Nitrides are mostly prepared in this way by heating metals in an atmosphere of ammonia. They are solid substances unaffected for the most part by heating. The nitrides of active metals are more or less easily decomposed by water with the liberation of ammonia, e. g.:

$$Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3$$

The nitrides of slightly active metals are, as a rule, quite stable to water.

Owing to the non-volatile nature of nitrides and their insolubility in any known solvent, there is, as yet, no suitable method for determining their molecular weights. Therefore, only the simplest formulas of the nitrides are known. In many of them, the apparent valency of the metal is consistent with its usual values. In other cases, the simplest formula indicates complexity of the molecular structure. Mn_3N_2 is an example of the first type, and Cr_2N, of the second type.

When only two hydrogen atoms are displaced in the ammonia molecule the resulting compounds are metal *imides*, and when only one is displaced, metal *amides*. The former contain a divalent radical, =NH (the *imino* group), while the latter contain a monovalent radical, $—NH_2$ (the *amino* group). For example, when dry NH_3 is passed over heated metallic sodium, colourless *sodamide* is formed according to the reaction:

$$2Na + 2NH_3 = 2NaNH_2 + H_2$$

this being a typical salt containing the NH_2^- anion. It is decomposed by water in accordance with the equation:

$$NaNH_2 + H_2O = NH_3 + NaOH$$

Sodamide is used in organic syntheses.

In addition to derivatives of metals, products of displacement of the hydrogen atoms of ammonia by *halogens* are known. An example of this is *nitrogen trichloride*, NCl_3, which is formed as yellow oily drops when a concentrated solution of ammonium chloride is treated with chlorine:

$$NH_4Cl + 3Cl_2 = 4HCl + NCl_3$$

The vapour of NCl_3 (m. p. —27° C, b. p. 71° C) has a pungent odour. On heating above 90° C (or on percussion), nitrogen trichloride decomposes into its elements with a violent explosion.

If a concentrated solution of NH_3 is treated with iodine, a dark brown precipitate of *nitrogen iodide* separates out, this being a mixture of NI_3 with NHI_2 and NH_2I. Nitrogen iodide is extremely unstable, and in the dry form explodes at the slightest touch.

Hydroxylamine, NH_2OH, is the product of displacement of one of the hydrogen atoms of ammonia by a *hydroxyl* radical. It is formed by the electrolysis of nitric acid (with a mercury or lead cathode) as a result of the reduction of HNO_3:

$$HNO_3 + 6H \rightarrow 2H_2O + NH_2OH$$

Hydroxylamine forms colourless crystals. It is chiefly used as a reducing agent.

6) With acids, hydroxylamine (m. p. 33° C) yields salts, of which the hydrochloride, $NH_2OH \cdot HCl$, is the most common compound. All the compounds of hydroxylamine are poisonous and, as a rule, readily soluble in water. Oxidising agents usually convert hydroxylamine either into N_2 or into N_2O, e. g.: $2NH_2OH + HOCl = N_2 + HCl + 3H_2O$ and $6NH_2OH + 4HNO_3 = 3N_2O + 4NO + 11H_2O$.

Like the displacement of hydrogen, oxidation reactions are hardly characteristic of ammonia. It does not burn in air, but when ignited in an atmosphere of oxygen, combustion takes place in accordance with the equation:

$$4NH_3 + 3O_2 = 6H_2O + 2N_2$$

Chlorine and bromine vigorously react with ammonia according to the reaction:

$$2NH_3 + 3X_2 = 6HX + N_2$$

They also oxidise ammonia in solution. Under ordinary conditions NH_3 is unaffected by most other oxidising agents.

The most important product of the partial oxidation of ammonia is *hydrazine*, N_2H_4, which is formed by the reaction:

$$2NH_3 + NaOCl = H_2O + N_2H_4 + NaCl$$

As can be seen from the equation, in this case each molecule of ammonia loses one atom of hydrogen under the action of the oxidising agent, and the remaining NH_2 radicals combine with each other. The structural formula of hydrazine will, consequently, be $H_2N—NH_2$.

Hydrazine melts at 20° C forming a colourless liquid which is miscible with water. It is used as a reducing agent.

7) Hydrazine (b. p. 114° C) can form two series of salts by the addition of acids, e. g., $N_2H_4 \cdot HCl$ and $N_2H_4 \cdot 2HCl$. It is usually oxidised to free nitrogen, e. g.: $2K_2Cr_2O_7 + 3N_2H_4 + 8H_2SO_4 = 2K_2SO_4 + 2Cr_2(SO_4)_3 + 3N_2 + 14H_2O$. Hydrazine vapour, when mixed with air, can burn in accordance with the reaction: $N_2H_4 + O_2 = 2H_2O + N_2 + 149$ kcal. Hence the use of hydrazine as a rocket fuel. Hydrazine and all its derivatives are poisonous.

Hydrazine reacts with nitrous acid,

$$N_2H_4 + HNO_2 = 2H_2O + HN_3$$

to form *hydrazoic acid*, H—N=N≡N, a colourless, volatile liquid with a pungent odour.

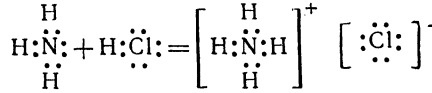
Hydrazoic acid is similar to acetic acid in strength, and resembles hydrochloric acid in the solubility of its salts (*azides*). HN_3 itself and some of the azides explode violently on heating or when struck. For this reason lead azide, $Pb(N_3)_2$, is employed as a *detonator*, i. e., a substance whose explosion brings about the eruptive decomposition of other explosives.

8) The acidic behaviour of HN_3 (m. p. —80° C, b .p. + 36° C) is characterised by the value $K = 3 \times 10^{-5}$. Its eruptive decomposition occurs according to the reaction: $2HN_3 = H_2 + 3N_2 + 142$ kcal. Anhydrous hydrazoic acid may explode even on jarring of its container. On the other hand, it does not decompose when stored in dilute aqueous solution. The vapour of HN_3 is very toxic, and its aqueous solutions cause inflammation of the skin. Salts of hydrazoic acid are colourless as a rule.

IX-2. Complex Formation. The addition reactions of ammonia considered in the previous section, clash with the usual concepts of valency bonds. Indeed, the molecules of both ammonia and of the substances that react with it, e. g., HCl, are electrically neutral and are formed in keeping with the requirements of the theory of valency. Consequently, none of the substances which enter into the reaction contain unpaired electrons capable of forming a valency bond. At the same time, experiment shows that addition does take place.

The inherent nature of reactions between ammonia and acids is revealed by the properties of the resulting products, i. e., ammonium

salts. Since NH_4^+ ion always splits off from the latter in solution, their formation must involve combination of the ammonia molecule with a hydrogen ion. In the case of the reaction, e. g., between NH_3 and HCl, this may be clearly represented by the following scheme:



From the scheme it follows that the nitrogen in the ammonia draws the hydrogen ion away from the chlorine. In contrast to chemical reactions leading to the formation of ordinary valency bonds (III-4), this process is not accompanied by the formation of new electron pairs (or by the transfer of electrons after Kossel).

Molecular compounds of a definite composition, such as NH_4Cl, *whose formation from simpler molecules does not entail the emergence of new electron pairs* are called *complex compounds*. It is often advisable to single out for separate consideration the *complex ion* contained in a series of similar complex compounds. For example, the complex ion NH_4^+ is contained in all ammonium salts, which are themselves complex compounds.

1) There are two fundamental approaches to the theory of the formation of complex compounds. From the point of view of the *electrostatic* approach, the formation of a complex compound is due to the coulomb attraction between particles and their mutual polarisation. For example, when ammonia reacts with HCl, the hydrogen ion is simultaneously attracted by both chlorine ion and the nitrogen ion of ammonia. Since the attraction by nitrogen is stronger, an ammonium salt is formed containing an NH_4^+ cation and a Cl^- anion, into which it dissociates on dissolving in water.

The other approach is based upon the assumption that there exist so-called *donor-acceptor* (or coordinate) bonds. According to these ideas, atoms possessing free electron pairs have a tendency to use them for linking with other particles. At the same time, atoms that do not possess a complete electronic configuration display a tendency to fill up their outermost electronic shell by using electron pairs of other atoms. Atoms of the first type are known as *donors*, and those of the second type are known as *acceptors*. If both tendencies are sufficiently strong, a bond forms between the atoms by means of the electron pair of the donor. For example, the formation of the NH_4^+ ion is accomplished by means of the free electron pair of the N atom, and takes place because the nitrogen of ammonia is a better donor than the chloride ion.

If we compare the processes of the formation of ordinaty valency bonds and coordinate bonds, we get the following schemes:

$$A^{\cdot} + {}^{\cdot}B = A:B \quad \text{and} \quad \underset{\text{donor}}{A:} + \underset{\text{acceptor}}{B} = A:B$$

From these schemes, it can be seen that the processes differ in the origin of the binding electron pair, but the bonds finally formed are of the same type and have a more or less clearly expressed covalent nature.

In the structural formulas of compounds, coordinate bonds are denoted by an arrow pointing from the donor to the acceptor atom, instead of by an ordinary line (as in the case of the ordinary valency bond). The above schemes

could, therefore, be rewritten in the following way:

$$A^{\cdot} + {}^{\cdot}B = A - B \quad \text{and} \quad A: + B = A \rightarrow B$$

2) The two points of view considered above do not exclude but complement each other. This becomes clear if it is taken into account that the range of the different forces substantially depends on their nature:

Decrease in the distance between the reacting molecules ⟶

beginning of electrostatic interaction:	formation of
ion-ion ion-molecule molecule-molecule	covalent bonds

As can be seen from the diagram, the particles which are gradually drawn together initially interact only electrostatically. If, for any reason, further approach is not possible, this practically terminates the process. If, on the other hand, the particles can approach each other close enough (to a distance not greatly exceeding the sum of the radii of the atoms which are being directly drawn together), the formation of ordinary covalent and coordinate bonds becomes possible. The stability of the latter and their relative value in the total energy of the complex bond continuously increase as the particles draw closer together.

From the above it follows that in general case a complex bond may be regarded as a combination of an electrostatic and a coordinate bond. Only when one of these types of interaction predominates to such a degree that the other can practically be neglected, does one of the above interpretations become approximately correct.

The above scheme of the formation of NH_4Cl clearly shows that the *central* position in this complex compound is occupied by nitrogen. This central atom (or ion) is called the *complexing agent*. The other constituents of the complex compound are arranged differently with respect to the complexing agent: while the hydrogen atoms are linked to it *directly* (they are in the *inner sphere* of the complex), the chlorine ion is further away (in the *outer sphere*) and, consequently, is linked much more loosely. The difference between the inner and the outer sphere is usually indicated in formulas by enclosing the former (together with the complexing agent) in square brackets. For example, the complex symbol for ammonium chloride is $[NH_4]Cl$. Both this formula and the above scheme emphasise the *complete equality* of all the four hydrogen atoms located around the nitrogen, no matter which of them was contained in the original ammonia molecule and which was added subsequently.

3) Obviously, the more loosely the hydrogen ion is retained by the acid radical of the corresponding acid, i. e., the stronger the latter, the more readily it will be drawn to the nitrogen of the ammonia molecule. Therefore, the heats of formation for ammonium salts of strong acids are greater than for those of weak acids. For example, in the cases of HCl and H_2O (regarding the latter as a weak acid), we have:

$$NH_3 + HCl = NH_4Cl + 42 \text{ kcal} \quad \text{and} \quad NH_3 + HOH = NH_4OH + 8 \text{ kcal}$$

Contrariwise, the ammonium salts will decompose into ammonia and an acid the more readily, the more strongly the acid radical attracts the hydrogen ion,

i. e., the weaker the acid. Therefore, NH_4Cl, for example, decomposes only at about 300° C, whereas free NH_4OH is unstable even at ordinary temperature.

The formation of complex compounds was discussed above, using the example of ammonium salts, where the complexing agent is the nitrogen in ammonia. However, a much more frequent case is complex formation around free ions.

To begin with, in examining this case, consider the interaction between ions and water molecules. As has already been pointed out (V-4), under the influence of the electric field due to the ion, the water molecules are oriented in a definite manner, and are then attracted towards the ion by the opositely charged end of the dipole. Owing to this attraction, a hydrated ion is formed in the solution. Now, suppose the solution becomes more and more concentrated. At a certain stage, crystals of the solute, which also contain this ion, will begin to separate out of the solution. If the water molecules immediately surrounding the ion in the solution are not firmly bound to it, water will not form part of the crystal. Conversely, if the bond between the ion and the water molecules is sufficiently strong, the ion will be included in the crystal together with a certain number of molecules of water of crystallisation. The result will be the crystal hydrate of the substance, which is essentially a complex compound. For example, the violet crystal hydrate, $CrCl_3 \cdot 6H_2O$, is, actually, the complex compound $[Cr(OH_2)_6]Cl_3$ in which six molecules of water are retained in the inner sphere around the complexing agent (Cr^{3+}). Other crystal hydrates of salts should similarly be regarded as complex compounds.

It is clear that a complex compound may be formed when the ion reacts with neutral molecules other than water. For example, if an aqueous solution of $CuCl_2$ is treated with ammonia, the complex compound $[Cu(NH_3)_4]Cl_2$ results, dissociating into $[Cu(NH_3)_4]^{\cdot\cdot}$ and $2Cl'$ ions. On the other hand, complex formation does not necessarily occur only in solution — complex compounds often result when solids react with gaseous substances. For instance, in an atmosphere of ammonia, anhydrous $CaCl_2$ yields the complex compound $[Ca(NH_3)_8]Cl_2$. The nature of the process remains the same and consists of the addition of neutral molecules to one of the ions of the salt owing to the mutual attraction arising between them.

This attraction may operate not only between an ion and a neutral molecule, but even more readily between oppositely charged ions. Suppose, for example, that several negative ions are simultaneously attracted towards a positive ion. If the mutual repulsion between the former is weaker than their attraction towards the complexing agent, the resultant grouping may prove so stable that it will exist as such both in the solid state and in solution. This is the case, for example, in $Na_2[SiF_6]$ where the fluoride ions are attracted to the Si^{4+} ion more strongly than they are repelled by each other (Fig. 116). This

compound dissociates in an aqueous solution as follows:

$$Na_2[SiF_6] \rightleftarrows 2Na^{\cdot} + [SiF_6]''$$

Finally, it is quite possible for both ions of opposite sign and neutral molecules to be attracted simultaneously to a given ion. If they are all held sufficiently firmly by the complexing agent, the resulting complex compound, e. g., $[Pt(NH_3)_4Cl_2]Cl_2$, will also be stable in solution, and will yield $[Pt(NH_3)_4Cl_2]^{\cdot\cdot}$ cations and chloride anions.

4) The fact that in $[Pt(NH_3)_4Cl_2]Cl_2$ only two chloride ions dissociate readily, while the two others are held more firmly in the inner sphere of the complex, has been established experimentally. Thus, if $AgNO_3$ is added to a solution of this compound, AgCl is immediately precipitated. By weighing this precipitate and carrying out the appropriate calculations, it can be shown that of the four chlorine ions contained in the molecule, only two are precipitated at once in the form of AgCl. Consequently, only two Cl^- ions out of four are in the external sphere. This, together with the results of complete chemical analysis, substantiates the formula.

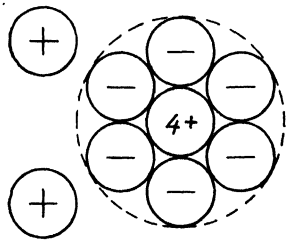


Fig. 116. Structure of Na_2SiF_6

From the above discussion it follows that complex compounds may be extremely diverse, since ions and/or neutral molecules may be included in the inner sphere. The total number of such particles forming the inner sphere around the complexing agent, is called its *coordination number*. Thus, in the examples considered above, the coordination numbers had the values: 4 for nitrogen, 6 for Cr^{3+}, 4 for Cu^{2+}, 8 for Ca^{2+} and 6 for Si^{4+}.

In determining the *charge* on the complex ion formed, the important factors are, on the one hand, the charge of the complexing agent and, on the other, the charges and number of ions of opposite sign included in the inner sphere (molecules in the inner sphere are disregarded when determining the charge, because they are electrically neutral). For example, in the case of $[Cu(NH_3)_4]Cl_2$, the double positive charge of the complexing agent (Cu^{2+}) is also that of the complex cation as a whole. In the case of $K_2[PtCl_6]$ and $[Pt(NH_3)_4Cl_2]Cl_2$, the complexing agent (Pt^{4+}) has four positive charges (more accurately, it is positively tetravalent), while the complex ions, $[PtCl_6]''$ and $[Pt(NH_3)_4Cl_2]^{\cdot\cdot}$, carry two negative or two positive charges, respectively.

On the other hand, the charge of the complex ion must be numerically equal to the total charge of the ions in the outer sphere and opposite to it in sign. Hence, it is again easy to determine the charge on the complex ion. For example, in the case of $K_2[PtCl_6]$, there are two positively charged ions of potassium in the outer sphere. Therefore, the complex ion has two negative charges.

If the composition of a complex compound is known, it is easy to find the charge of its complexing agent. Obviously, it must be numerically equal and opposite in sign to the algebraic sum of the charges of all the other ions contained in the formula. For example, in $K_2[PtCl_6]$, this sum is equal to (2+) + (6—) = (4—). Consequently, in this compound, the complexing agent, Pt, is positively tetravalent.

Complex compounds vary as widely with regard to stability of their inner spheres as they do in composition. Although during the dissociation of $K_2[PtCl_4]$, for example, besides the equilibrium

$$K_2[PtCl_4] \rightleftarrows 2K^{\cdot} + [PtCl_4]''$$

there is another equilibrium in accordance with the overall equation

$$[PtCl_4]'' \rightleftarrows Pt^{\cdot\cdot\cdot\cdot} + 4Cl'$$

the latter is displaced so far *to the left* that there are almost no $Pt^{\cdot\cdot\cdot\cdot}$ and Cl' ions in the solution. In contrast, for the complex $K_2[CuCl_4]$, the analogous equilibrium

$$[CuCl_4]'' \rightleftarrows Cu^{\cdot\cdot} + 4Cl'$$

is displaced so far *to the right* that dilute solutions contain hardly any complex $[CuCl_4]''$ ions. Between these extreme cases, there are numerous intermediate cases where the solution simultaneously contains considerable quantities of both complex ions and products of their dissociation.

5) The quantitative measure of stability of the inner sphere of a complex compound in aqueous solution is the value of its dissociation constant (the so-called *instability constant* of the complex). The smaller its value, the more stable the inner sphere (for a given coordination number). For example, the corresponding expressions for the complex ions $[Ag(NH_3)_2]^{\cdot}$ and $[Ag(CN)_2]'$ are:

$$\frac{[Ag^{\cdot}]\,[NH_3]^2}{[Ag(NH_3)_2^{\cdot}]} = 6 \times 10^{-8} \qquad \frac{[Ag^{\cdot}]\,[CN']^2}{[Ag(CN)_2^{\cdot}]} = 2 \times 10^{-21}$$

whence it can be seen that the second complex is far more stable than the first.

Both $K_2[PtCl_4]$ and $K_2[CuCl_4]$ are formed from the neutral salts, $PtCl_2 + 2KCl$ and $CuCl_2 + 2KCl$, respectively. Although both of these compounds equally fit the definition of complex compounds, substances like $K_2[CuCl_4]$ with a rather unstable inner sphere, are often called *double salts*, and are denoted in the following way: $CuCl_2 \cdot 2KCl$. The same method of designation is also usually employed with respect to crystal hydrates.

IX-3. The Oxygen Compounds of Nitrogen. Nitrogen forms oxides corresponding formally in composition to all valencies from

one to five:

N_2O	NO	N_2O_3	NO_2	N_2O_5
nitrous oxide	nitric oxide	nitrogen trioxide (nitrous anhydride)	nitrogen dioxide (or peroxide)	nitrogen pentoxide (nitric anhydride)

Nitric anhydride is a solid; the other oxides are gases under ordinary conditions.

1) Except for N_2O, all the oxides of nitrogen are toxic. On reacting with red-hot copper, they completely decompose to form CuO and N_2. The formula of the original oxide can be determined from the quantity of cupric oxide and nitrogen formed.

Nitrous oxide can be prepared by heating ammonium nitrate, which decomposes at about 200° C:

$$NH_4NO_3 = 2H_2O + N_2O$$

The structural formula of the N_2O molecule is $N \equiv N - O$. Nitrous oxide is a colourless gas (m. p. —91° C, b. p. —89° C) with a faint pleasant odour. It dissolves fairly well in water without reacting chemically.

Above 500° C, nitrous oxide decomposes according to the reaction:

$$2N_2O = 2N_2 + O_2$$

Therefore, at elevated temperatures it is a powerful oxidising agent. For example, a glowing splint bursts into flame in it.

Since the temperature of the human body is far from sufficient to decompose N_2O, this gas, which supports combustion, is not suitable for respiration. Inhalation of nitrous oxide together with air brings about a peculiar state of intoxication, which is accompanied by considerable deadening of sensibility to pain. This accounts for the use of N_2O as an anaesthetic during operations.

2) The N_2O molecule is linear [d(NN) = 1.13 Å, d(NO) = 1.19Å]. Nitrous oxide is a permanent component of air (0.00005% by volume). One volume of water absorbs about 1.3 volumes of N_2O at 0° C and about 0.6 volumes at 25° C.

Nitric oxide cannot be formed from its elements under ordinary conditions. Only at about 1200° C does the reversible reaction

$$N_2 + O_2 + 43 \text{ kcal} \rightleftarrows 2NO$$

begin to take place perceptibly. As can be seen from Fig. 117, at about 1500° C the reaction goes almost entirely from right to left. Equilibrium is established very slowly under these conditions: 30 hours are required to reach the equilibrium state. On the other hand, at a higher temperature, not only is the percentage of NO in the gas mixture higher, but equilibrium is attained much more rapidly, e. g.,

at 3000° C it is established in millionths of a second. For this reason, NO always forms in the atmosphere during lightning discharges.

Though endothermic in nature, nitric oxide is quite stable under ordinary conditions. In the laboratory, it is mostly prepared by the reaction:

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O$$

Nitric oxide is a colourless gas (m. p. —164° C, b. p. —151° C), is relatively sparingly soluble in water, and does not react with it chemically. Nitric oxide gives up its oxygen only with difficulty. Therefore, a burning splint is extinguished in an atmosphere of NO.

Addition reactions are the most characteristic of nitric oxide. Thus, when it reacts with chlorine according to the reaction

$$2NO + Cl_2 = 2NOCl$$

nitrosyl chloride, Cl—N=O, results, this being a yellow gas (m. p. —61° C, b. p. —6° C). NO also combines directly with oxygen. A number of complex compounds containing NO in their inner sphere are also known.

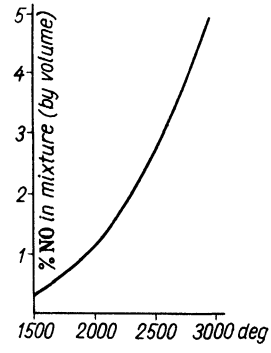


Fig. 117. Equilibrium of synthesis of nitric oxide

3) The NO molecule is characterised by the distance $d(NO) = 1.15$ Å and very low polarity (dipole length, 0.03 Å). One hundred volumes of water dissolve about 7 volumes of nitric oxide at 0° C. It has a blue colour in the liquid and solid states.

4) The number of outer electrons in the NO molecule totals 11 (5 for the nitrogen and 6 for the oxygen). Valency bonds are formed by electron pairs which must therefore be more stable systems than an unpaired electron. Hence, it might be expected that molecules with an odd number of electrons ("odd" molecules) would show a tendency to *dimerise*, i. e., to unite in pairs. As a rule, this is observed even under ordinary conditions. Nitric oxide is a rare exception, dimerising only at low temperatures, in accordance with the equation: $NO + NO \rightleftarrows N_2O_2$. In the liquid state at —163° C, the content of $(NO)_2$ molecules is 95%, and solid nitric oxide apparently consists entirely of these molecules.

NO combines quietly with atmospheric oxygen to form *nitrogen dioxide* in accordance with the equation:

$$2NO + O_2 = 2NO_2 + 27 \text{ kcal}$$

Nitrogen dioxide is a brown gas which readily condenses to a liquid boiling at +21° C. When cooled to —11° C, this liquid solidifies into a colourless crystalline mass. The molecular weight determined by the vapour density lies between its simplest value ($14 + 2 \times 16 = 46$) and twice this value (92), and depends on the temperature of

the experiment, decreasing when it is raised and increasing when it is lowered.

These results are due to the equilibrium between the molecules of nitrogen dioxide, NO_2, and *nitrogen tetroxide*, N_2O_4. The results of molecular weight determination at about 140° C show that under these conditions only nitrogen dioxide molecules are contained in the gas, whereas at lower temperatures, they partially pair off to form molecules of N_2O_4. Since the combination of neutral molecules of the same substance with each other to form larger molecules with twice, three times, etc., the original molecular weight is called *polymerisation*, it may be said that below 140° C, NO_2 partially *polymerises* into N_2O_4. This process is the more complete, the lower the temperature, and near the freezing point (—11° C), the substance consists exclusively of N_2O_4 molecules. On the other hand, on heating, nitrogen tetroxide dissociates into simple molecules.

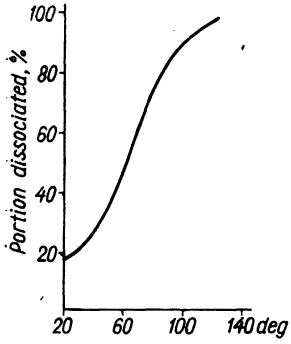


Fig. 118. Equilibrium of the system $N_2O_4 \rightleftarrows 2NO_2$

At each intermediate temperature between —11° C and + 140 C°, there is a definite state of equilibrium of the reversible reaction:

$$NO_2 + NO_2 \underset{\text{dissociation}}{\overset{\text{polymerisation}}{\rightleftarrows}} N_2O_4 + 13 \text{ kcal}$$

The position of this equilibrium at different temperatures is shown in Fig. 118. Since N_2O_4 is colourless, while NO_2 is reddish-brown, the shift of the equilibrium on heating or cooling of the gas mixture can easily be observed by the change in its colour.

The tendency of O=N=O molecules to react with each other is due to the presence in each of an unpaired electron (in the nitrogen atom). The pairing of two such electrons creates an N—N bond in the N_2O_4 molecule. The instability of the latter is due to the instability of this bond. The spatial structure of the NO_2 and N_2O_4 molecules is shown in Fig. 119.

Nitrogen peroxide is a very powerful oxidising agent. Carbon, sulphur, phosphorus and other elements burn vigorously in NO_2. It produces explosive mixtures with the vapours of many organic substances.

5) The reaction of oxygen addition to NO is particularly interesting in that it is one of the very few known cases where an increase in temperature does not speed up the reaction, but somewhat slows it down. The same is true of the reaction between NO and chlorine. The explanation of this reaction rate anomaly ensues from the fact that only the dimeric N_2O_2 molecules actually react, and the probability of formation of these molecules decreases very rapidly with rising temperature.

6) The NO_2 molecule has a low larity (dipole length, 0.08 Å). Above 140° C, the reaction of formation of nitrogen dioxide from NO and oxygen

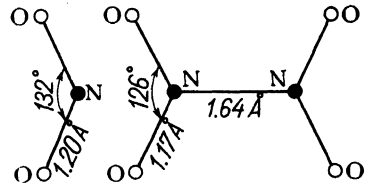


Fig. 119. Spatial structure of NO_2 and N_2O_4

becomes perceptibly reversible. The positions of its equilibrium at different temperatures are shown in Fig. 120. It is evident from the latter that nitrogen dioxide cannot exist under ordinary pressure above 620° C.

The interaction of NO_2 with NO in the reversible reaction

$$NO_2 + NO \rightleftarrows N_2O_3 + 10 \text{ kcal}$$

results in partial formation of *nitrogen trioxide*, N_2O_3, which can be obtained as a blue liquid (m. p. —102° C, b. p. +4° C) if the system is cooled. The structure of nitrogen trioxide is represented by the formula O=N—O—N=O. It is unstable under ordinary conditions, and the equilibrium in the above reaction is greatly displaced to the left.

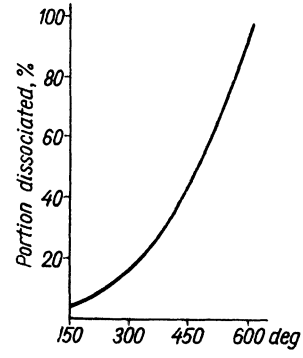


Fig. 120. Equilibrium of thermal dissociation of NO_2

Dissolving NO_2 (or N_2O_4) in water results in the formation of *nitric*, HNO_3, and *nitrous*, HNO_2, acids:

$$2NO_2 + H_2O = HNO_3 + HNO_2$$

Nitric acid is quite stable in solution, but nitrous acid decomposes readily in accordance with the reversible reaction

$$2H \rightleftarrows H_2O + N_2O_3 \rightleftarrows H_2O + NO + NO_2$$

and therefore, practically, the reaction between NO_2 and water proceeds according to the equation:

$$3NO_2 + H_2O = 2HNO_3 + NO$$

If nitrogen dioxide is dissolved in the presence of excess oxygen, the NO liberated is oxidised by the oxygen to NO_2. Under these conditions, all the nitrogen peroxide can be converted into nitric acid in accordance with the overall equation:

$$4NO_2 + 2H_2O + O_2 = 4HNO_3$$

NO_2 dissolves in alkalis in the presence of excess oxygen in a similar manner (forming salts of HNO_3). In the absence of oxygen, a mixture of salts of nitric and nitrous acids results (the salts of HNO_2, unlike the acid, are stable in solution), e. g.:

$$2NO_2 + 2NaOH = NaNO_3 + NaNO_2 + H_2O$$

Salts of nitrous acid are called *nitrites*. Like the NO_2^- anion, the majority of them are colourless. Almost all nitrites are readily soluble in water ($AgNO_2$ less so than the others). The nitrite most frequently encountered in practice is $NaNO_2$, which is usually prepared from nitrogen oxides in accordance with the reaction:

$$NO + NO_2 + 2NaOH = 2NaNO_2 + H_2O$$

All the salts of nitrous acid are very poisonous.

HNO_2 is known only in dilute aqueous solution. It is only slightly stronger than acetic acid.

Strong oxidising properties are most characteristic of nitrous acid, and in most cases it is reduced to NO. On the other hand, nitrous acid can be oxidised to nitric acid by the action of powerful oxidising agents. Typical examples of characteristic oxidation-reduction reactions are given below:

$$2HNO_2 + 2HI = I_2 + 2NO + 2H_2O$$

$$2HMnO_4 + 5HNO_2 = 2Mn(NO_3)_2 + HNO_3 + 3H_2O$$

Both of these reactions take place in acid solution.

7) Nitrous acid ($K = 5 \times 10^{-4}$), probably has two structures which are convertible into each other:

$$H-O-N=O \quad \text{and} \quad H-N\begin{matrix}=O\\ \diagdown O\end{matrix}$$

The nitrites of the active metals, e. g., $NaNO_2$, apparently have the structure corresponding to the first of these, while nitrites of the less active metals, e. g., $AgNO_2$, have the structure corresponding to the second. Organic derivatives are known for both forms of HNO_2.

The chief product of the reaction between NO_2 and water—*nitric acid*—is one of the most important chemical compounds. It is used in the manufacture of explosives, organic dyes, plastics and a number of other products. Three industrial methods are used for the production of nitric acid, the raw materials being, respectively: a) ammonia, b) air and c) potassium nitrate.

The first method consists essentially in the catalytic oxidation of ammonia by atmospheric oxygen. As far back as in 1900, it was found that if a mixture of NH_3 and an excess of air is passed rapidly over a platinum catalyst (heated to 800° C), nitric oxide is formed

according to the reaction:

$$4NH_3 + 5O_2 = 6H_2O + 4NO + 216 \text{ kcal}$$

The latter is then converted into NO_2 and HNO_3. The catalytic oxidation of ammonia is now the principal method for the production of nitric acid.

8) A diagram of a plant for the oxidation of ammonia is shown in Fig. 121 (*A* is a heat exchanger). A mixture of the initial gases is blown through a platinum alloy catalyst containing 5-10% rhodium, in the form of a fine screen. In practice, a mixture of ammonia and air containing not more than 12% of NH_3 by volume, is used. The maximum yield of nitric oxide is about 98% of the theoretical.

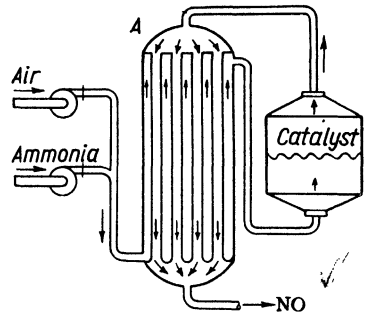


Fig. 121. Diagram of a plant for the catalytic oxidation of ammonia

The second (so-called *arc*) method for the production of nitric acid "by the combustion of air" was developed in 1905. As can be seen from Fig. 117, a more or less favourable position of equilibrium for the synthesis of NO from its elements is reached only at very high temperatures. On the other hand, under these conditions it is established practically instantaneously. In this connection, the problem of the technical realisation of the synthesis of NO was formulated as follows: it was necessary to find a way of heating air to the highest possible temperature, and then to cool the gas mixture *very rapidly* below 1200° C to keep the nitric oxide formed from decomposing back into nitrogen and oxygen.

This problem was solved by using an electric arc which produces a temperature of about 4000° C. If such an arc is struck between the poles of a powerful electromagnet, its flame forms a disc of fire. When a stream of air is passed rapidly through it, the air becomes very hot at the moment it comes in contact with the flame, after which its temperature drops instantly below 1200° C. On further cooling of the gas mixture, the NO combines with oxygen to form NO_2, from which nitric acid may be produced.

Though the yield of NO in the arc method as thus realised is only about 2% by volume, this is of no particular importance, because the initial raw material—air—costs nothing. A much more serious disadvantage of the method is the high consumption of electric power, owing to which its industrial importance is not great at present.

Finally, the third method for the production of nitric acid—from sodium nitrate—which was formerly the only one used, now has hardly any industrial value. This method is based on the follow-

ing reaction between sodium nitrate and concentrated sulphuric acid:

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$$

This reaction takes place readily on heating.

9) Highly concentrated (98%) HNO_3 can be prepared by the reaction between water or the dilute acid, liquid N_2O_4 and oxygen under a pressure of 50 atm. This "direct synthesis" is usually carried out at 70° C. The acid obtained is used in rocketry.

10) The structure of the nitric acid molecule may be represented briefly by the formula $HONO_2$. The value of d(NO) is 1.41 Å for the bond with the hydroxyl oxygen, and 1.22 Å for the bond with the two other oxygen atoms. The ONO angle in the NO_2 group is equal to 130° C. The NO_3^- ion has the structure of a plane equilateral triangle with nitrogen at the centre [d(NO) = 1.21 Å].

Anhydrous nitric acid is a colourless liquid (rapidly turning yellow when stored), which boils at 86° C. Boiling is accompanied by partial decomposition:

$$4HNO_3 = 2H_2O + 4NO_2 + O_2$$

The nitrogen dioxide dissolves in the distilled acid and imparts to it a yellow or red colour (depending on the quantity of NO_2). Since NO_2 gradually escapes from the solution, this is called *fuming* nitric acid. Concentrated HNO_3 decomposes slowly in the light even at ordinary temperatures.

HNO_3 is miscible with water. Concentrated nitric acid used in laboratory practice is about 65% HNO_3, and has a specific gravity of 1.40. In composition, it approximately corresponds to the formula $HNO_3 \cdot 2H_2O$.

Chemically, nitric acid features, primarily, powerful *oxidising* properties. The principal final product of the reduction of not very strong HNO_3 is NO, while that of concentrated HNO_3 is NO_2.

11) *Nitrous acid* appears to be the principal initial product of reduction of concentrated HNO_3. If the reaction is conducted in not very strong solutions, then of the gases into which HNO_2 decomposes, only NO is evolved (NO_2 reacts with water to form HNO_3 and NO). However, if the concentration is increased, the back reaction $3NO_2 + H_2O \rightleftarrows 2HNO_3 + NO + 33$ kcal acquires great importance. With equivalent proportions of the reactants, its equilibrium shifts to the right, but a gradual rise in the concentration of HNO_3 shifts it progressively to the left. That is why the principal final product of reduction of concentrated HNO_3 is NO_2, and not NO.

Except for Au and Pt, all the metals frequently encountered in practical work are converted by concentrated nitric acid into oxides. If the latter are soluble in HNO_3, nitrates result. Nitric acid likewise dissolves metals located to the right of hydrogen in the electromotive series, such as Cu, Hg and Ag.

Some metals that react vigorously with dilute nitric acid, e. g., Fe, hardly react at all with concentrated (especially fuming) nitric

acid. This is due to the fact that a thin but dense protective layer of oxides which are insoluble in the acid forms on their surfaces. Owing to this "passivity" of iron, concentrated HNO_3 can be transported in steel tanks.

Concentrated (especially fuming) nitric acid vigorously attacks certain non-metals. Thus, sulphur is oxidised by it on boiling to H_2SO_4, carbon to CO_2, etc. Animal and vegetable tissues are destroyed when attacked by HNO_3.

To distinguish between nitric and nitrous acids, it is important to know the difference in their behaviour towards hydrogen iodide. While HNO_2 instantly oxidises it to iodine, *dilute* nitric acid has no effect on HI. In contrast, *concentrated* HNO_3 oxidises both HI and HCl. However, in the latter case, the reaction is reversible:

$$HNO_3 + 3HCl \rightleftarrows 2H_2O + NOCl + Cl_2$$

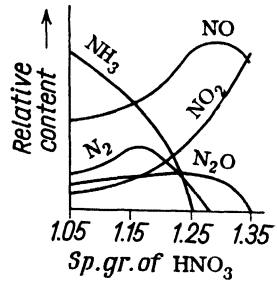


Fig. 122. Products[12] of reduction of HNO_3 with iron

A mixture of concentrated HNO_3 and concentrated HCl is usually called *aqua regia*. It reacts considerably more vigorously than either of these acids taken separately. Thus, even Au and Pt dissolve readily in aqua regia forming the corresponding *chlorides*:

$$Au + HNO_3 + 3HCl = AuCl_3 + NO + 2H_2O$$

$$3Pt + 4HNO_3 + 12HCl = 3PtCl_4 + 4NO + 8H_2O$$

The source of the activity of aqua regia is, on the one hand, chlorine at the moment of formation, and on the other hand, nitrosyl chloride which readily gives off chlorine.

Like its oxidising properties, the acidic properties of HNO_3 are very pronounced. Since diluting the solution weakens the former and enhances the latter, many metals react with dilute HNO_3 after the general pattern, i. e., displacing hydrogen. However, the latter is not given off, but reduces the excess HNO_3 to derivatives with a lower valency of nitrogen, down to NH_3. As a rule, a mixture of different reduction products results.

12) The nature of the final reduction products of HNO_3 greatly depends on a number of factors, viz., the concentration of the acid, the nature of the reducing agent, the temperature, etc. The effect of the acid concentration (other conditions being equal) can be seen from the example shown in Fig. 122. Nitrates can be reduced quantitatively to ammonia by boiling in alkaline solution with aluminium powder. The reaction proceeds, for example, as follows: $8Al + 3NaNO_3 + 5NaOH + 2H_2O = 8NaAlO_2 + 3NH_3$.

Being a *very strong* monobasic acid, HNO_3 forms salts which are quite stable under ordinary conditions. Like the NO_3^- ion, the majority

of *nitrates* are colourless. Almost all nitrates are readily soluble in water. Many of them have found various practical applications.

If heated sufficiently, nitrates decompose in various ways, depending on the nature of the cation. The salts of the most active metals (those to the left of Mg in the electromotive series) are converted into the corresponding *nitrites* upon elimination of oxygen, the salts of less active metals (Mg—Cu) decompose with the formation of *oxides*, and the salts of still less active metals (those to the right of Cu) yield the *free metals*. Examples of this are the reactions:

$$2NaNO_3 = 2NaNO_2 + O_2 \qquad 2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$$

$$2AgNO_3 = 2Ag + 2NO_2 + O_2$$

The dissimilar character of these reactions is due to the different stabilities of the corresponding nitrites and oxides at the temperatures of decomposition: under these conditions, the nitrite of Na is stable, while in the case of Pb, the nitrite is unstable but the oxide is stable, and in the case of Ag, both compounds are unstable, owing to which the free metal is liberated.

Because nitrates give up oxygen easily at high temperatures, they burn very rapidly when mixed with combustible substances. The use of nitrates in pyrotechnics and in the manufacture of black gunpowder is based on this property.

13) *Black gunpowder* is an intimate mixture of KNO_3 with sulphur and charcoal, "normal" gunpowder (68% KNO_3, 15% S and 17% C) having the approximate composition $2KNO_3 + 3C + S$. It burns mainly in accordance with the equation: $2KNO_3 + 3C + S = N_2 + 3CO_2 + K_2S + 169$ kcal.

The anhydride corresponding to nitric acid can be obtained by the reaction between NO_2 and ozone:

$$2NO_2 + O_3 = O_2 + N_2O_5$$

Nitrogen pentoxide or *nitric anhydride*, N_2O_5, forms colourless, highly volatile crystals (sublimation temp. 32° C). The latter are built up of NO_2^+ and NO_3^- ions, while in the vapour state nitrogen pentoxide consists of separate molecules whose structure corresponds to the formula $O_2N—O—NO_2$. It is extremely unstable, and decomposes slowly even under ordinary conditions into nitrogen dioxide and oxygen (sometimes this decomposition is speeded up so that it becomes explosive). Being a powerful oxidising agent, N_2O_5 reacts vigorously with many substances. It forms nitric acid with water.

IX-4. Phosphorus. Phosphorus is one of the abundant elements; it accounts for about 0.04% of the total number of atoms in the earth's crust. It is of exceptional importance to life, since it enters into the composition of certain proteins (particularly, nerve and brain tissues), as well as of bones and teeth. Accumulations of phosphorus are en-

countered mainly as the mineral *apatite*, $Ca_5X(PO_4)_3$, where X = F, or less frequently Cl or OH, and as *phosphorite* beds which consist of $Ca_3(PO_4)_2$ with various impurities.

Free phosphorus is obtained from natural calcium phosphate by heating it with sand (SiO_2) and carbon in an electric furnace. The process takes place in accordance with the overall equation:

$$Ca_3(PO_4)_2 + 3SiO_2 + 5C = 3CaSiO_3 + 5CO + 2P$$

A diagram of an electric furnace for producing phosphorus is shown in Fig. 123 (*A*—massive carbon electrodes, *B*—charge mixture of phosphate with sand and carbon, *C*—liquid slag outlet, *D*—phosphorus vapour outlet). The phosphorus vapour formed is put through water-spray condensers and collected in a receiver where the molten phosphorus accumulates under water.

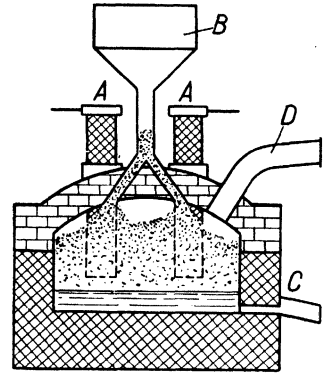


Fig. 123. Diagram of electric furnace for phosphorus production

As a vapour (below 800° C) and in the liquid state, phosphorus is tetratomic, the molecule P_4 having the structure of a regular tetrahedron (Fig. 124). Several allotropic modifications of solid phosphorus are known, of which two are encountered in practice: red and white.

When phosphorus vapour is cooled it condenses into the white form, which has a specific gravity of 1.8, a melting point of 44° C and a boiling point of 281° C. White phosphorus is practically insoluble in water, but dissolves readily in carbon disulphide, CS_2. It is stored under water and in the dark whenever possible.

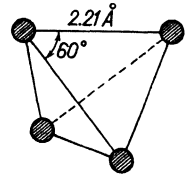


Fig. 124. Structure of P_4 molecule

When stored, white phosphorus gradually (very slowly) changes into the more stable red form. The transformation is accompanied by the evolution of heat (*heat of transition*):

$$P_{white} = P_{red} + 4 \text{ kcal}$$

The process is considerably accelerated by heating and under the influence of light. In practice, red phosphorus is obtained by pro-

longed heating of white phosphorus to 280-340° C (in an air-tight vessel). Most of it is used in the production of matches.

Red phosphorus, a powder with a specific gravity of 2.3, is insoluble in carbon disulphide and sublimes on heating (sublimation temp. 416° C). The vapour condenses into white phosphorus. The latter, in contrast to the red form, is *highly poisonous*.

The chemical activity of phosphorus is considerably higher than that of nitrogen. Thus, it combines readily with oxygen, the halogens, sulphur and many metals. In the latter case, *phosphides* (Mg_3P_2, Ca_3P_2, etc.) analogous to nitrides are formed.

White phosphorus is considerably more reactive than the red modification. For example, white phosphorus slowly oxidises in air even at low temperatures and ignites even at about 50° C, whereas red phosphorus hardly oxidises in air and ignites only at 250° C. Similarly, other reactions proceed much more vigorously with white phosphorus than with the red modification. This difference in reactivity is typical of allotropic modifications: of two modifications of the same substance, the less stable is usually the more active.

1) If white phosphorus is heated to 220° C at 12,000 atm it passes into *black* phosphorus which has a specific gravity of 2.7. This modification resembles graphite in outward appearance, is a fairly good conductor of electricity and is chemically slightly less active than red phosphorus.

Phosphorus practically does not combine with hydrogen. However, the decomposition of certain phosphides with water, e. g., according to the reaction

$$Ca_3P_2 + 6H_2O = 3Ca(OH)_2 + 2PH_3$$

yields *hydrogen phosphide* (phosphine), PH_3, which is analogous to ammonia. Phosphine is a colourless, very poisonous gas (m. p. —134° C, b. p.—88° C). It has an unpleasant odour (of rotten fish), readily ignites in air and is a very strong reducing agent. In contrast to ammonia, addition reactions are not characteristic of phosphine: *phosphonium* (PH_4^+) salts are known only for a few acids ($HClO_4$, HCl, HBr, HI) and are very unstable; phosphine does not react chemically with water (although it dissolves in it fairly readily).

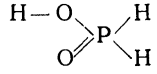
2) When phosphides are decomposed by water, small quantities of *liquid diphosphine*, P_2H_4, analogous in composition to hydrazine, are always formed together with PH_3. Diphosphine is a colourless liquid (m. p. — 99° C, b. p.+ 52° C) which spontaneously ignites in air.

One of the methods employed for preparing PH_3, is to heat white phosphorus with a concentrated aqueous solution of an alkali. The reaction proceeds, for example, as follows:

$$8P + 3Ba(OH)_2 + 6H_2O = 2PH_3\uparrow + 3Ba(H_2PO_2)_2$$

The other resultant is a salt of *hypophosphorous* acid.

Free hypophosphorous acid, H_3PO_2, may be obtained by the action of H_2SO_4 on this salt. In spite of the presence of three hydrogen atoms in its molecule, this acid is only monobasic (and fairly strong), which is in keeping with its structural formula:



The salts of hypophosphorous acid (*hypophosphites*) are colourless, as a rule, and readily soluble in water.

3) Hypophosphorous acid ($K = 9 \times 10^{-2}$) forms colourless crystals (m. p. 27° C) which are readily soluble in water. It is a vigorous reducing agent in strongly acid solution (especially on heating). For example, it reduces mercury salts to the metal: $HgCl_2 + H_3PO_2 + H_2O = H_3PO_3 + Hg + 2HCl$. On the other hand, in the cold, H_3PO_2 is not oxidised in dilute solution either by atmospheric oxygen or by free iodine.

The reaction between phosphorus and oxygen results in different products, depending on the conditions. When phosphorus is burnt in excess oxygen (or air), it forms its higher oxide, *phosphoric anhydride* or *phosphorus pentoxide*, P_2O_5. On the other hand, burning phosphorus in a limited supply of air, or slow oxidation results mainly in *phosphorous anhydride* or *phosphorus trioxide*, P_2O_3.

The latter is a white, wax-like crystalline mass (m. p. 24° C, b. p. 175° C). Determinations of its molecular weight give the doubled formula, P_4O_6, the spatial structure of which is shown in Fig. 125.

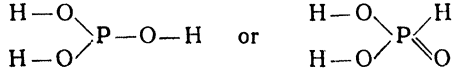
When heated in air, phosphorus trioxide changes to P_2O_5. This reaction takes place gradually even under ordinary conditions, and is accompanied by a glow which may be observed in the dark. On reacting with water, P_2O_3 slowly forms phosphorous acid:

$$P_2O_3 + 3H_2O = 2H_3PO_3$$

Like white phosphorus, phosphorus trioxide is highly poisonous.

Free *phosphorous acid*, H_3PO_3, forms colourless crystals which are readily soluble in water. It is a strong (but in most cases slowly acting) reducing agent. Though there are three hydrogen atoms in its molecule, H_3PO_3 is only a *dibasic* acid of medium strength. Its salts (*phosphites*) are, as a rule, colourless and sparingly soluble in water. Of the derivatives of the more common metals, only the salts of Na, K and Ca are readily soluble.

The structure of phosphorous acid may be represented by the following structural formulas:



The second formula corresponds to the acid itself, while its derivatives are known to have both structures.

4) Phosphorous acid (m. p. 74° C, $K_1 = 2 \times 10^{-2}$, $K_2 = 2 \times 10^{-7}$) is conveniently obtained by the hydrolysis of PCl_3 and subsequent concentration of the liquid by evaporation until crystallisation sets in. Its solutions are not appreciably oxidised by atmospheric oxygen under ordinary conditions. The reaction between phosphorous acid and mercuric chloride proceeds slowly in accordance with the equation: $H_3PO_3 + 2HgCl_2 + H_2O = H_3PO_4 + Hg_2Cl_2 + 2HCl$.

The more characteristic oxide of phosphorus, *phosphorus pentoxide*, P_2O_5, is a white amorphous, odourless powder which sublimes when strongly heated. Determination of its molecular weight in the vapour state, indicates that it has the doubled formula, P_4O_{10}, the

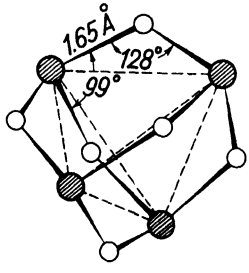


Fig. 125. Spatial structure of P_4O_6

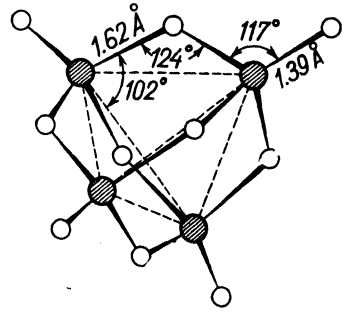


Fig. 126 Spatial structure of P_4O_{10}

spatial structure of which is shown in Fig. 126. Phosphorus pentoxide attracts moisture vigorously, and is therefore often employed as a *drying agent* for gases.

The reaction between P_2O_5 and water results in addition of the latter, and, depending on the number of molecules of H_2O added, the following principal hydrated forms may result:

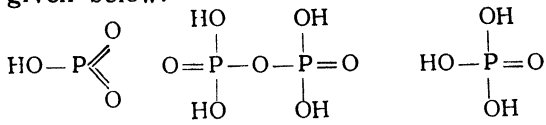
$$P_2O_5 + H_2O = 2HPO_3 \text{ (metaphosphoric acid)}$$
$$P_2O_5 + 2H_2O = H_4P_2O_7 \text{ (pyrophosphoric acid)}$$
$$P_2O_5 + 3H_2O = 2H_3PO_4 \text{ (orthophosphoric acid)}$$

As can be seen from the above, orthophosphoric acid, which is usually simply called *phosphoric* acid, has the highest water content. When this acid is heated, the water splits off, to form *pyro-* and *meta*phosphoric acids successively:

$$2H_3PO_4 = H_2O\uparrow + H_4P_2O_7 \quad \text{and} \quad H_4P_2O_7 = H_2O\uparrow + 2HPO_3$$

Conversely, when metaphosphoric acid reacts with water, it is converted into the pyro- and then into the ortho-modification. However, in the cold this conversion takes place very slowly. Therefore, each acid reacts as an individual substance. Their structural

formulas are given below:



5) Orthophosphoric acid ($K_1 = 7 \times 10^{-3}$, $K_2 = 6 \times 10^{-8}$, $K_3 = 3 \times 10^{-12}$) can be distinguished from meta- and pyrophosphoric acids by taking advantage of the reaction with $AgNO_3$, which forms a *yellow* precipitate (Ag_3PO_4) with the PO_4''' ion, and a *white* precipitate in the presence of P_2O_7'''' and PO_3' ions. The two latter acids are distinguished from one another by their different effects on egg albumin: pyrophosphoric acid does not coagulate it, while metaphosphoric acid does.

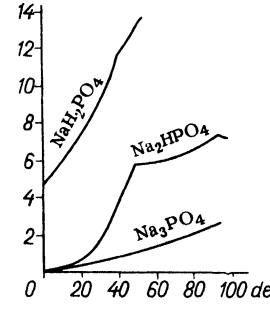


Fig. 127. Solubility of sodium phosphates (moles/litre of H_2O)

Of the acids of pentavalent phosphorus, the orthohydrate, H_3PO_4, is the most important practically. It is conveniently obtained by the oxidation of phosphorus with nitric acid:

$$3P + 5HNO_3 + 2H_2O = 3H_3PO_4 + 5NO$$

On an industrial scale, H_3PO_4 is produced from P_2O_5 obtained by burning phosphorus (or its vapour) in air.

Phosphoric acid forms colourless, deliquescent crystals (m. p. 42° C). It is usually sold as an 85% aqueous solution which has the consistency of thick syrup. Unlike other derivatives of phosphorus, H_3PO_4 is not poisonous. Oxidising properties are not at all characteristic of it.

Being a tribasic acid of medium strength, H_3PO_4 is able to form three series of salts, e. g.:

acid salts $\begin{cases} NaH_2PO_4 — \textit{primary} \text{ salt, sodium dihydrogen phosphate} \\ Na_2HPO_4 — \textit{secondary} \text{ salt, disodium hydrogen phosphate} \end{cases}$

neutral salt Na_3PO_4 — *tertiary* salt, trisodium phosphate

All the primary phosphates are readily soluble in water, but only very few of the secondary and tertiary phosphates are soluble, in particular, the salts of Na (Fig. 127). As a rule, phosphates are colourless.

The derivatives of phosphoric acid find various applications in different branches of industry. However, they are especially important in agriculture. This applies, in particular, to primary calcium phosphate of the composition $Ca(H_2PO_4)_2 \cdot H_2O$, which is the basis of *superphosphate*, the most important phosphate fertiliser. The production of superphosphate in the U. S. S. R. has increased by more than 100 times as compared with 1913.

6) Superphosphate is produced by treating crushed natural phosphorites (or apatite concentrates) with sulphuric acid. After thorough mixing, the wet

mass is "matured" for a certain period. The reaction $Ca_3(PO_4)_2 + 2H_2SO_4 = 2CaSO_4 + Ca(H_2PO_4)_2$ results in a mixture of calcium sulphate and primary calcium phosphate, which after grinding is used as a fertiliser (under the name of *ordinary* superphosphate). The phosphorus contained in readily soluble $Ca(H_2PO_4)_2$ is assimilated well by crops.

A serious disadvantage of this fertiliser is the presence in it of $CaSO_4$ which is a useless component. What is known as *double* superphosphate is obtained from natural phosphorite by first separating phosphoric acid by the reaction: $Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 \downarrow + 2H_3PO_4$. After removing the $CaSO_4$ precipitate, the acid obtained is used to treat a fresh batch of phosphorite: $Ca_3(PO_4)_2 + 4H_3PO_4 = 3Ca(H_2PO_4)_2$. Sometimes, the H_3PO_4 is neutralised, instead, with calcium hydroxide to form $CaHPO_4 \cdot 2H_2O$ (called *precipitate*) which is also a good fertiliser. In many soils (of acidic properties) phosphorus is fairly well assimilated by crops directly from finely ground phosphorite (*phosphate meal*).

7) The production of *mixed* fertilisers is acquiring great importance for the further concentration of the elements essential to crops. The most important of these is *ammophos*, a mixture of $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$, obtained by direct reaction between ammonia and phosphoric acid. A ton of ammophos replaces three tons of ordinary superphosphate and one ton of $(NH_4)_2SO_4$. A mixture of ammophos and KNO_3 (known as *azophoska*) is especially useful since it contains all the "fertilising" elements most essential to crops—N, P and K.

The extent to which the latter are consumed by cultivated crops can be seen from the typical data given below (in kg per ton):

Element	Winter rye		Spring wheat		Potatoes		Sugar beet	
	grain	chaff	grain	chaff	tubers	leaves	roots	leaves
N	14.0	4.5	20.5	6.0	3.0	3.0	2.0	3.0
P	3.7	1.1	3.7	0.9	0.7	0.7	0.4	0.4
K	5.0	8.3	5.0	6.2	5.0	7.0	2.1	4.1

As a result, crops annually remove enormous quantities of each of these elements from the fields, and they must be compensated by introducing fertilisers into the soil. The total production of mineral fertilisers in the U.S.S.R. in 1962 was 17.3 million tons (as against 3.0 million tons in 1940, and 0.07 million tons in 1913).

8) Phosphorus reacts with sulphur only when a mixture of the elements is heated (in an atmosphere of CO_2). Yellow *phosphorus sulphides* may be obtained in this way, the most important of them being those corresponding to the formulas P_4S_3, P_4S_7 and P_4S_{10}. The particular sulphide that will form in each case depends on the relative quantities of the elements. In dry air, all three sulphides are quite stable at ordinary temperatures, but flare up when heated and burn, e. g., according to the reaction: $P_4S_3 + 8O_2 = 2P_2O_5 + 3SO_2$

Phosphorus *halides* are formed by reactions between the elements which are, as a rule, very vigorous. Halides of the types PX_3 and PX_5 are known for all the halogens (except PI_5), but the chlorine derivatives are almost the only ones that have any practical value.

Phosphorus trichloride, PCl_3, is obtained by the action of dry chlorine on excess phosphorus. The latter ignites and burns in accordance with the reaction:

$$2P + 3Cl_2 = 2PCl_3$$

Phosphorus trichloride is a colourless liquid which fumes intensely in moist air, and reacts vigorously with water:

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl$$

Thus, PCl_3 is the acid chloride of phosphorous acid.

When PCl_3 is treated with excess chlorine, colourless crystals of *phosphorus pentachloride* result:

$$PCl_3 + Cl_2 \rightleftarrows PCl_5$$

As can be seen from the equation, this reaction is reversible. Under ordinary conditions, its equilibrium is displaced to the right, and above 300° C, to the left.

Since it is the acid chloride of phosphoric acid, PCl_5 is completely decomposed by water to form H_3PO_4 and HCl. The reaction takes place in two stages (the second being slower than the first):

$$PCl_5 + H_2O = POCl_3 + 2HCl$$

and

$$POCl_3 + 3H_2O = H_3PO_4 + 3HCl$$

Phosphorus oxychloride, $POCl_3$, obtained in the first of these reactions, is a colourless liquid. Like both phosphorus chlorides, phosphorus oxychloride is used for the synthesis of organic substances. The vapours of all three compounds are poisonous.

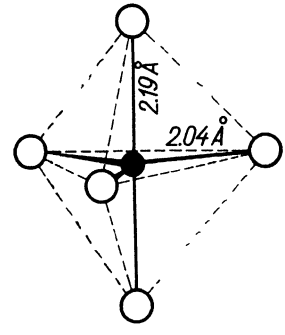


Fig. 128. Structure of PCl_5 molecule

9) The spatial structure of the phosphorus trihalides (PX_3) is that of a triangular pyramid with the P atom at the apex. Their principal constants are compared below:

Substance	PF_3	PCl_3	PBr_3	PI_3
Melting point (°C)	−152	−94	−40	+61
Boiling point (C°)	−101	+75	173	

Phosphorus tri-iodide is red, and all the other trihalides are colourless.

No iodine derivatives are known among the pentahalides. Phosphorus pentafluoride is a colourless gas (m. p. −94° C, b. p. −85° C), the pentachloride sublimes at 159° C, and the pentabromide (m. p. 106° C) is known in two forms: red and light yellow. In the vapour state, these halides have structures of the trigonal bipyramid type (Fig. 128). The lattice of crystalline PCl_5 consists of $[PCl_4]^+$ and $[PCl_6]^-$ ions, while that of crystalline PBr_5 consists of $[PBr_4]^+$ and Br^- ions.

A pronounced tendency towards addition reactions is characteristic of all the phosphorus halides. The gradual (very slow) oxidation of PCl_3 to $POCl_3$

(m. p. 1° C, b. p. 107° C) by atmospheric oxygen may be regarded as one of the manifestations of the unsaturated nature of PCl_3. All the phosphorus halides are easily decomposed by water.

IX-5. The Arsenic Subgroup. The content of the elements of this subgroup in the earth's crust is relatively small, and decreases in the order *arsenic* (1×10^{-4}%), *antimony* (5×10^{-6}%), *bismuth* (2×10^{-6}%). They are chiefly encountered in the form of the *sulphide* minerals, *realgar*, As_4S_4, *orpiment*, As_2S_3, *stibnite* (*antimony glance*), Sb_2S_3, and *bismuthinite* (*bismuth glance*), Bi_2S_3. All three elements are often contained as impurities in the ores of different metals, and may be separated out as by-products during their extraction.

To obtain As, Sb and Bi from their sulphide ores, the latter are roasted in air to convert the sulphides into oxides which are then reduced with carbon. The following reactions are involved:

$$2E_2S_3 + 9O_2 = 6SO_2 + 2E_2O_3 \quad \text{and} \quad E_2O_3 + 3C = 3CO + 2E$$

In the free state, the elements of the arsenic subgroup have a metallic appearance and are fairly good conductors of heat and electricity. However, they are very brittle and are easily pulverised. The most important of their constants are listed below together with the corresponding data for nitrogen and phosphorus:

Element	Under ordinary conditions		Melting point (°C)	Boiling point (°C)	Specific gravity in the solid state
	Physical state	Colour			
N	gas	colourless	—240	—196	1.0
P	solid	white	44	280	1.8
As	ditto	grey	814 (36 atm)	610	5.7
Sb	ditto	silvery	631	1635	6.6
Bi	ditto	reddish	271	1430	9.8

Sb remains unchanged in air under ordinary conditions, while As and Bi are slightly oxidised on the surface. Neither arsenic nor its analogues are soluble in water or organic solvents. They readily form alloys with many metals.

1) Like phosphorus, arsenic can exist in several allotropic modifications, of which the common *grey* form is the most stable. When As vapour is cooled very rapidly, *yellow* arsenic with a specific gravity of 2.0 is obtained, and when As sublimes in a current of hydrogen, amorphous *black* arsenic with a specific gravity of 4.7 results. Antimony is very similar to arsenic with regard to allotropy, but as to bismuth, only one form is known under ordinary conditions.

2) *Arsenic* is chiefly used as an additive to lead (about 0.5%) in the manufacture of shot. This addition increases the hardness of the metal and enables it to solidify as drops strictly spherical in shape.

Arsenic compounds are employed in medicine, in the dressing of leather and furs, in the production of glass and porcelain, etc. The most important field of application is, however, agriculture, where various As derivatives are employed as the principal means for combating pests that damage cultivated crops. The annual world production of As is about 50 thousand tons.

Antimony is an important constituent of certain special-purpose alloys (printing type, bearing alloys, etc.). Its compounds are used in the manufacture of rubber, glass, dyes, matches, etc. The world production of Sb is about 50 thousand tons annually.

Bismuth is used chiefly in the manufacture of various alloys to which it usually imparts fusibility. These alloys are important for fire-fighting equipment, signalling apparatus, etc. Bi compounds are employed mainly in medicine, cosmetics and the glass industry. The annual world production of Bi is about 2 thousand tons.

As, Sb and Bi are located between hydrogen and copper in the electromotive series. Therefore, they do not displace hydrogen from acids, but can be transferred into solution by the action of oxidising agents, e. g.:

$$2As + 5Cl_2 + 8H_2O = 2H_3AsO_4 + 10HCl$$

$$Bi + 4HNO_3 = Bi(NO_3)_3 + NO + 2H_2O$$

The soluble derivatives of all three elements are extremely poisonous.

On heating in air, As, Sb and Bi burn forming oxides of the general formula E_2O_3. They also combine readily with the halogens and with sulphur. The formation of definite compounds with metals is less characteristic of these elements than of nitrogen and phosphorus, but still, some *arsenides*, *antimonides* and *bismuthides* analogous to nitrides and phosphides are known, such as Mg_3As_2, Mg_3Sb_2 and Mg_3Bi_2.

The action of dilute acids on these compounds gives hydrogen *arsenide* (arsine), hydrogen *antimonide* (stibine) and hydrogen *bismuthide* (bismuthine) which have the general formula EH_3 and are analogous to ammonia and phosphine. The reactions proceed according to the equation:

$$Mg_3E_2 + 6HCl = 3MgCl_2 + 2EH_3$$

These compounds are rather unstable and decompose to a greater or lesser degree into their elements at the moment of formation. For this reason in practice they always come off in mixture with hydrogen. This applies particularly to BiH_3, which has hardly been studied so far on account of its extreme instability.

Arsine and stibine are colourless, highly poisonous gases with the odour of garlic (AsH_3) or hydrogen sulphide (SbH_3). Their melting and boiling points are compared below with the corresponding data for ammonia and phosphine:

	NH_3	PH_3	AsH_3	SbH_3
Melting point (°C)	—78	—134	—116	—88
Boiling point (°C)	—33	—88	—62	—17

The reducing power of the hydrides increases in the order NH_3—PH_3—AsH_3—SbH_3. Addition reactions, so characteristic of ammonia, are not observed at all in the case of arsine and stibine. Both of these are fairly soluble in water but do not react with it chemically. On heating, AsH_3 and SbH_3 decompose readily into their elements, and when ignited in air, burn with the formation of water and the corresponding oxides.

3) Besides the decomposition of arsenides and antimonides with acids, arsine and stibine can also be obtained by the action of nascent hydrogen on various soluble compounds of arsenic and antimony, for example, in accordance with the reaction: $As_2O_3 + 6Zn + 12HCl = 6ZnCl_2 + 2AsH_3 + 3H_2O$. One of the methods for the detection of arsenic is based on this reaction in conjunction with the subsequent thermal decomposition of AsH_3.

The *oxides* of As, Sb and Bi correspond to the formula E_2O_3. They form readily when the elements are heated in air, and are white (As_2O_3 and Sb_2O_3) or yellowish (Bi_2O_3) solids. Arsenious oxide, As_2O_3, is fairly soluble in water, but the other two oxides are almost insoluble.

The chemical properties of the corresponding *hydroxides*, $E(OH)_3$, change very regularly in the order As—Sb—Bi. They are all *amphoteric*, acidic properties predominating in $As(OH)_3$ and basic properties, in $Sb(OH)_3$; in $Bi(OH)_3$ the acid function is so weak that it is evident only from the insignificant solubility of this hydroxide in concentrated solutions of strong alkalis. Thus, the *acidic* properties of the hydroxides $E(OH)_3$ rapidly diminish in the order As—Sb—Bi.

Arsenious acid, H_3AsO_3, is known only in solution. Antimony hydroxide (or *antimonious acid*) and $Bi(OH)_3$ are white precipitates. Both elements give products of partial dehydration of the hydroxides, viz., SbO(OH) and BiO(OH). The radicals SbO (*antimonyl*) and BiO (*bismuthyl*) forming these hydroxides are often contained as such in salts, in which they play the part of monovalent metals.

The dissolved part of the hydroxides of As and Sb can dissociate simultaneously after the overall patterns:

$$E''' + 3OH' \leftrightarrows E(OH)_3 \equiv H_3EO_3 \rightleftarrows 3H^{\cdot} + EO_3'''$$

If acids are added to the solution, the equilibria shift to the left, and salts of E^{3+} cations are formed, while if alkalis are added, the equilibria shift to the right, and salts of arsenious acid (*arsenites*) or antimonious acid (*antimonites*) containing the EO_3^{3-} anion are obtained, respectively. Acidic dissociation may also occur with the elimination of a molecule of water in accordance with the equation $H_3EO_3 \rightleftarrows H^{\cdot} + EO_2' + H_2O$ yielding salts of *meta*-arsenious acid, $HAsO_2$, and *meta*-antimonious acid, $HSbO_2$. Both of these are very weak.

4) The values $K_1 = 4 \times 10^{-10}$, $K_2 = 7 \times 10^{-13}$ and $K_3 = 4 \times 10^{-14}$ correspond to the acidic dissociation of H_3AsO_3, while for the basic dissociation of $As(OH)_3$, only the value $K_1 = 5 \times 10^{-15}$ is known. Thus, both func-

tions are extremely weak, but the acidic function is considerably stronger than the basic. Yellow silver arsenite, Ag_3AsO_3, which is practically insoluble in water, is a particularly characteristic compound of arsenious acid, while colourless and sparingly soluble sodium meta-antimonite, which usually separates out as the crystal hydrate $NaSbO_2 \cdot 3H_2O$, is particularly characteristic of antimonious acid ($K_1 = 10^{-11}$).

Since the basic properties of the hydroxides $E(OH)_3$ increase in the order As—Sb—Bi, so does the stability of salts containing the E^{3+} cation. In particular, whereas salts of the oxyacids of As^{3+} have not been isolated at all and only rare examples of those for Sb^{3+} are known, colourless $Bi(NO_3)_3 \cdot 5H_2O$ is the most common compound of bismuth. The soluble derivatives of Sb^{3+} and Bi^{3+} are readily decomposed by water with the formation of basic salts.

Parallel with the decline in acidic properties and the growth in basic properties of the hydroxides $E(OH)_3$, their reducing properties, i. e., the tendency of the elements to pass into compounds in which they have a higher valency, also decrease in the order As^{III}—Sb^{III}—Bi^{III}. Arsenious acid, a strong reducing agent in alkaline solution, is much more difficult to oxidise in acid solution. In general, antimonious acid is not a typical reducing agent, although it is oxidised fairly readily in alkaline solution. Finally, bismuth hydroxide can be oxidised only in strongly alkaline solution and by the most powerful oxidising agents.

The higher oxides of As and Sb—*arsenic pentoxide*, As_2O_5, and *antimony pentoxide*, Sb_2O_5, may be obtained by heating the hydroxides formed when As and Sb are oxidised by concentrated nitric acid. Arsenic pentoxide is a white, vitreous, deliquescent substance. The yellowish powder of antimony pentoxide is very sparingly soluble in water.

Orthoarsenic acid, H_3AsO_4, which corresponds to As_2O_5, can be obtained by the reaction:

$$3As + 5HNO_3 + 2H_2O = 3H_3AsO_4 + 5NO$$

It is readily soluble in water, and about as strong as phosphoric acid. Definite hydrated forms are not characteristic of Sb_2O_5, and the white precipitate $xSb_2O_5 \cdot yH_2O$ varies in composition depending on the conditions of formation. It is almost insoluble in water. The acidic properties of antimonic acid are fairly weak.

Salts of orthoarsenic acid (*arsenates*) are mainly derived from the *orthohydrate*, H_3AsO_4. Salts of antimonic acid (*antimonates*) are usually derived from *hexahydroxyantimonic* acid, $H[Sb(OH)_6]$, which corresponds to the hydrated *meta*-form, $HSbO_3 \cdot 3H_2O$. Like phosphates, arsenates and antimonates are, as a rule, colourless and sparingly soluble in water.

5) The chocolate-brown, practically insoluble silver salt is characteristic of orthoarsenic acid ($K_1 = 6 \times 10^{-3}$, $K_2 = 2 \times 10^{-7}$, $K_3 = 3 \times 10^{-12}$).

The difference in colour between Ag_3AsO_3 and Ag_3AsO_4 is often used to determine the valency of arsenic in solution. As to the salts of antimonic acid ($K_1 = 4 \times 10^{-5}$), the formation of sparingly soluble $Na[Sb(OH)_6]$ is used in analytical chemistry for the detection of sodium.

Insoluble derivatives of pentavalent bismuth, varying in colour from violet to yellow, are obtained by the action of certain strong oxidising agents (Cl_2, etc.) on bismuth hydroxide suspended in a concentrated solution of NaOH or KOH. Their composition more or less approaches the formulas $NaBiO_3$ and $KBiO_3$. These *bismuthates* are very strong oxidising agents. Thus, in acid solution they readily oxidise divalent manganese to the heptavalent form, e. g.:

$$10NaBiO_3 + 4MnSO_4 + 16H_2SO_4 = 5Bi_2(SO_4)_3 + 4HMnO_4 + 5Na_2SO_4 + 14H_2O$$

The relative oxidation-reduction activity of the arsenic subgroup elements in their characteristic tri- or pentavalent states, can be represented by the following scheme:

As^{III} Sb^{III} Bi^{III} ← Increasing reducing properties

As^{V} Sb^{V} Bi^{V} → Increasing oxidising properties

The oxidising properties of orthoarsenic and antimonic acids are displayed only in acid solution, the former being capable of oxidising HI to I_2, and the latter, of oxidising even HCl to Cl_2, in accordance with the reversible reactions:

$$H_3AsO_4 + 2HI \rightleftarrows H_3AsO_3 + I_2 + H_2O$$
$$H_3SbO_4 + 5HCl \rightleftarrows SbCl_3 + Cl_2 + 4H_2O$$

The derivatives of pentavalent bismuth are oxidising agents in alkaline as well as acid solution.

Sulphides, which are very characteristic of As, Sb and Bi, can be obtained both by the reactions between these elements and sulphur on heating, and by double decomposition in solution. Bi_2S_3 and Sb_2S_3 obtained by the dry method (as well as the naturally occurring compounds) are grey-black crystalline substances. Bi_2S_3 precipitates from solution as a brown-black powder, while Sb_2S_3 and Sb_2S_5 separate out as orange-red powders, and As_2S_3 and As_2S_5 as bright yellow powders. All these sulphides are insoluble in water and dilute acids (which are not simultaneously oxidising agents). Arsenic sulphides are also insoluble in concentrated HCl, but concentrated nitric acid (and aqua regia) dissolve them, e. g., in accordance with the reaction:

$$3As_2S_5 + 40HNO_3 + 4H_2O = 6H_3AsO_4 + 15H_2SO_4 + 40NO$$

The sulphides of As, Sb and Bi exhibit a certain similarity in properties to the oxides of these elements. Just as the oxides of As and Sb yield salts of the acids H_3EO_3 and H_3EO_4 on reacting with alkalis, their sulphides form salts of the corresponding *thioacids*, i. e., acids, in which the oxygen is replaced by sulphur, with soluble

metal sulphides, for example according to the reactions:

$$3(NH_4)_2S + As_2S_3 = 2(NH_4)_3AsS_3 \quad \text{and} \quad 3(NH_4)_2S + As_2S_5 = 2(NH_4)_3AsS_4$$

The reaction in the case of antimony sulphides is exactly the same. In contrast, Bi_2S_3 hardly reacts with the soluble sulphides. Consequently, this sulphide behaves like the oxide Bi_2O_3 which is almost insoluble in alkalis.

Salts of *thioarsenious* acid, H_3AsS_3, *thioarsenic* acid, H_3AsS_4, and the corresponding thioacids of antimony are quite stable. As a rule, they are yellow or red, and are sparingly soluble. Certain *thioarsenites* and *thioarsenates* are used to combat agricultural pests.

Unlike their salts, the free thioacids are unstable and decompose into the corresponding sulphide and hydrogen sulphide:

$$2H_3AsS_3 = As_2S_3\downarrow + 3H_2S \quad \text{and} \quad 2H_3AsS_4 = As_2S_5\downarrow + 3H_2S$$

Therefore, when a solution of a thiosalt is acidified, its corresponding sulphide precipitates out, e. g.:

$$2(NH_4)_3AsS_4 + 6HCl = 6NH_4Cl + As_2S_5\downarrow + 3H_2S$$

The formation and decomposition of thiosalts of As and Sb is of great importance in qualitative chemical analysis.

Halides of As, Sb and Bi are formed readily by the reaction between the elements and the halogens. Trihalides are known for all these compounds and for all the halogens, whereas of the pentahalides only the fluorine derivatives and $SbCl_5$ are more or less stable.

In practice, one has to do almost exclusively with the chlorides. Under ordinary conditions, $AsCl_3$ and $SbCl_5$ are liquids, while $SbCl_3$ and $BiCl_3$ are solids. All four chlorides are colourless and readily soluble in water, but are strongly hydrolysed. They are capable of forming complex compounds, mainly of the type $M[ECl_4]$ and $M[SbCl_6]$, with chlorides of some monovalent metals.

6) Being the acid chloride of arsenious acid, $AsCl_3$ (m. p. —18° C, b. p. 130° C) is decomposed by water according to the equation: $AsCl_3 + 3H_2O \rightleftarrows As(OH)_3 + 3HCl$. Unlike the hydrolysis of PCl_3, this reaction is reversible, and its equilibrium can be shifted to the left by adding an excess of concentrated HCl.

Since the basic properties of $Sb(OH)_3$ and $Bi(OH)_3$ are considerably stronger than those of $As(OH)_3$, the hydrolysis of $SbCl_3$ (m. p. 73° C, b. p. 223 °C) and $BiCl_3$ (m.p. 232° C, b. p. 447° C) results in basic salts (instead of the free bases) in accordance with the equations: $ECl_3 + H_2O \rightleftarrows E(OH)Cl_2 + HCl$ and $E(OH)Cl_2 + H_2O \rightleftarrows E(OH)_2Cl + HCl$. The basic salts of the type $E(OH)_2Cl$ readily give up a molecule of water, and are converted into insoluble antimonyl or bismuthyl chlorides (otherwise known as the *oxychlorides* of Sb and Bi). Therefore, in practice, the reactions between either $SbCl_3$ or $BiCl_3$ and water proceed after the pattern: $ECl_3 + H_2O \rightleftarrows EOCl\downarrow + 2HCl$.

7) Being the acid chloride of antimonic acid, $SbCl_5$ (m. p. 4° C, b. p. 140° C) is readily decomposed by water: $SbCl_5 + 4H_2O = H_3SbO_4 + 5HCl$. This reaction (which is carried out with chlorine-saturated water to avoid reduction of the antimony) is a convenient method for preparing antimonic acid.

IX-6. The Vanadium Subgroup. The members of this subgroup—*vanadium*, *niobium* and *tantalum*—are as similar to each other as Cr, Mo and W.

Vanadium is fairly abundant in nature, accounting for about 0.005% of the total number of atoms in the earth's crust. However, rich deposits of its minerals are encountered very rarely. Apart from such deposits, an important source of raw material for the industrial preparation of vanadium are certain iron ores containing compounds of this element.

The content of niobium ($2 \times 10^{-4}\%$) and tantalum ($2 \times 10^{-5}\%$) in the earth's crust is much smaller than that of vanadium. They are chiefly encountered in the form of the minerals *columbite* or *niobite*, $Fe(NbO_3)_2$, and *tantalite*, $Fe(TaO_3)_2$, which are usually intermixed with each other.

The metallurgy of V, Nb and Ta is rather complicated. The free elements are obtained by taking advantage of the reaction between their oxides, E_2O_5, and aluminium:

$$3E_2O_5 + 10Al = 5Al_2O_3 + 6E$$

The reaction sets in when the original mixture is heated and is accompanied by a considerable evolution of heat.

Vanadium, niobium and tantalum are grey, lustrous metals, which remain unchanged in air and are readily machinable. Some of their constants are listed below:

Properties	V	Nb	Ta
Specific gravity	6.0	8.6	16.6
Melting point (°C)	1920	2500	3000
Boiling point (°C)	3400	4800	5300
Electrical conductivity (Hg = 1)	4	5	6

In the compact state, all three metals are highly resistant to different chemical effects. This is especially characteristic of Nb and Ta, which are insoluble in all the common acids and their mixtures. An exception is a mixture of $HF + HNO_3$, which dissolves both metals in accordance with the equation:

$$3E + 5HNO_3 + 21HF = 3H_2[EF_7] + 5NO + 10H_2O$$

Vanadium dissolves only in acids which are simultaneously powerful oxidising agents, for example, nitric acid:

$$3V + 5HNO_3 = 3HVO_3 + 5NO + H_2O$$

Solutions of alkalis have no effect on these metals.

In powder form, V, Nb and Ta combine with oxygen, the halogens, sulphur and nitrogen on heating. All three metals are capable of absorbing considerable quantities of hydrogen, but no definite compounds are formed.

Vanadium is of the greatest industrial value, its principal field of application being the production of special steels. Niobium and tantalum are used to a limited extent as yet, but there is a tendency towards an increase in their use.

1) The annual world production of *vanadium* is about 5 thousand tons. Vanadium steel is widely employed in the manufacture of automobile and aircraft motors, axles, springs, etc. Vanadium compounds are used chiefly in the rubber, glass and ceramic industries. They also often serve successfully as catalysts (principally in oxidation reactions).

The principal use of *niobium* is in the production of special steels intended for the manufacture of welded structures. Its annual world production amounts to several hundred tons.

The extraordinary resistance of *tantalum* to different chemical effects, together with its hardness, ductility and malleability, makes this metal (as well as niobium) especially suitable for the manufacture of various important components of factory chemical equipment. Extensive development of this application is impeded only by the high cost of tantalum. Its annual world production amounts to a few score of tons.

Most typical of vanadium and its analogues are derivatives of the *pentavalent* elements. Besides these, compounds are known corresponding to valencies of IV, III and II. The number of these compounds and their stability decrease in the order V — Nb — Ta. None of the derivatives of the lower valencies of these elements have any practical value as yet.

The *oxides* of the pentavalent elements, E_2O_5, result when the finely crushed metals are heated in a current of hydrogen. Of these, V_2O_5 has pronounced *acidic* properties, but in the case of Nb_2O_5 and Ta_2O_5 they are much weaker.

Although red *vanadium pentoxide*, V_2O_5, is poorly soluble in water, its yellow solution contains the fairly weak *vanadic acid*, HVO_3. V_2O_5 readily dissolves in alkalis to form the corresponding *vanadates*. Of greatest practical importance among the latter is ammonium vanadate, NH_4VO_3, a relatively poorly soluble salt, which is the usual commercial vanadium compound. Compounds of this element are poisonous.

2) Vanadium pentoxide is prepared conveniently by heating NH_4VO_3 in air. In the finely ground state, V_2O_5 (m. p. 675° C) has an orange or yellow colour. For vanadic acid ($K = 1 \times 10^{-4}$), both possible courses of electrolytic dissociation $VO_3^- + H^+ \rightleftarrows VO_2OH \rightleftarrows VO_2^+ + OH^-$ are equally probable. Only the vanadates of a few monovalent metals are readily soluble in water.

Colourless Nb_2O_5 and Ta_2O_5 are refractory and are almost insoluble in water. The corresponding salts—*niobates* and *tantalates*—can be prepared by fusing the corresponding pentoxide with an alkali

(or a metal oxide). They are strongly hydrolysed in aqueous solutions. When these solutions are acidified, white gelatinous precipitates of varying composition, $E_2O_5 \cdot xH_2O$, separate out. Both hydroxides are soluble in strong acids as well as in concentrated alkali solutions, which shows their amphoteric character.

3) The dehydration of the precipitated hydroxides $E_2O_5 \cdot xH_2O$ of niobium and tantalum by heating is accompanied (on loss of the water of hydration by the latter) by intense incandescence of the substance due to the considerable evolution of heat during the transition of the oxide from the amorphous to the crystalline state (heat of crystallisation). Both oxides melt only at about 1500° C, and are non-volatile. The formation of various *peroxide* compounds is very characteristic of all three elements of this subgroup.

The halogen derivatives of the pentavalent elements are not characteristic of vanadium (only VF_5 is known). All the possible pentahalides of Nb and Ta can be obtained. They are low-melting, highly volatile crystalline substances. The fluorides and chlorides are colourless, whereas the bromides and iodides vary in colour from yellow to black. All the pentahalides are decomposed by water with the formation of a precipitate of niobic or tantalic acid, $E_2O_5 \cdot xH_2O$, respectively. A tendency towards complex formation is characteristic of the fluorides, the majority of the complex compounds formed being of the type $M_2[EF_7]$, where M is a monovalent metal.

4) Derivatives of the lower valencies of these elements are more or less characteristic only of vanadium. Its bluish-black dioxide, VO_2, is amphoteric. The salts formed when it is dissolved in strong alkalis (*vanadites*) are usually derived from an acid of the composition $H_2V_4O_9$, i. e., $H_3O \cdot 4VO_2$, and when VO_2 reacts with acids, salts of the cation VO^{2+} (*vanadyl*) result. Both lower oxides of vanadium—V_2O_3 and VO (both of them black)—possess only basic properties. The derivatives of all three oxides and different acids have characteristic colours in solution: VO_2 salts are mostly light blue, those of V_2O_3 are largely green and those of VO are chiefly violet. The alkaline derivatives of VO_2 are usually brown or black. Under the action of oxidising agents (in many cases, atmospheric oxygen) all the derivatives of the lower valencies are more or less readily converted into V_2O_5 or salts of vanadic acid.

A comparison between the elements of the vanadium subgroup and phosphorus and nitrogen shows a drastic difference in the properties of the derivatives of the *lower* valencies, and a regular change in the character of the higher oxides. Indeed, the acidic nature of the oxides decreases very consistently in the order N_2O_5, P_2O_5, V_2O_5, Nb_2O_5, Ta_2O_5. In contrast, the derivatives of the lower valencies of the arsenic subgroup elements which are similar to those of N and P, exhibit no regular change from N to Bi in the chemical character of the higher oxides. A good illustration of the above is the following comparison of the heats of formation of the oxides E_2O_5 from the elements (kcal/mole):

Sb	As	P	N	P	V	Nb	Ta
230	218	360	13	360	437	463	499

X. FOURTH GROUP OF THE PERIODIC TABLE

Like in the previous group, with respect to electronic structure of the neutral atoms, the members of the right-hand subgroup, i.e., germanium and its analogues should be classed with carbon and silicon. The maximum valency of all these elements, as regards both gaining and yielding electrons, should be equal to four. Bearing in mind the increase in atomic volume from carbon to lead, it may be supposed that the tendency for the outermost shell to complete its octet will decline in this particular series, while the ease with which electrons are given up will increase. Accordingly, there should be a decrease in the non-metallic nature and an increase in the metallic nature of the elements from C to Pb. The most essential difference between the members of the titanium subgroup, on the one hand, and carbon and silicon, on the other, from the point of view of electronic structures, is probably the fact that titanium and its analogues have no tendency to complete their outermost shell octet. At the same time, by analogy with the vanadium, chromium and manganese subgroups, it can be expected that derivatives of the elements of the titanium subgroup having the highest positive valency will exhibit a close resemblance to silicon.

	6 **C** 12.01115		4 2
	14 **Si** 28.086		4 8 2
2 10 8 2	*22* **Ti** 47.90		
	32 **Ge** 72.59		4 18 8 2
2 10 18 8 2	*40* **Zr** 91.22		
	50 **Sn** 118.69		4 18 18 8 2
2 10 32 18 8 2	*72* **Hf** 178.49		
	82 **Pb** 207.19		4 18 32 18 8 2

X-1. Carbon. Carbon is not among the most abundant elements—it only accounts for 0.14% of the total number of atoms in the earth's crust. Nevertheless, its importance is exceptionally great, since its compounds are the basis of all living organisms.

Carbon occurs in nature in various forms. Besides the tissues of living organisms and the products of their decay (coal, oil, etc.), it is contained in many minerals, which for the most part have the general formula MCO_3, where M is a divalent metal. The most abundant

of these minerals is *calcite*, $CaCO_3$, which sometimes forms vast deposits in various parts of the earth's surface. The atmosphere contains carbon as carbon dioxide, CO_2, which is also present in all natural waters in the dissolved state.

Free carbon occurs in the form of two simple substances—*diamond* and *graphite*. With some reservation (owing to the presence of impurities), a third form may be added to these two—what is known as *amorphous* carbon, the most important examples of which are carbon black and charcoal. Outwardly, diamond differs sharply form the other two modifications. It is colourless and transparent, has a specific gravity of 3.5 and is the hardest of all minerals. Graphite is a grey, opaque substance, greasy to the touch, with a specific gravity of 2.2. In contrast to diamond, it is very soft, can easily be scratched with the fingernail and leaves grey streaks on paper. "Amorphous" carbon is rather similar to graphite in its properties. Its specific gravity usually varies from 1.8 to 2.1. Certain varieties of "amorphous" carbon display a great ability to adsorb gases, vapours and dissolved substances.

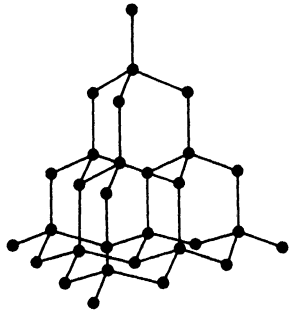


Fig. 129. Arrangement of carbon atoms in diamond

1) As can be seen from Fig. 129, in diamond each atom of carbon is linked with four others, the distance from its centre to the centre of any of its neighbours being the same (1.54 Å). In relation to each C atom, the four neighbouring atoms are arranged at the corners of a regular tetrahedron which encloses it (Fig. 124).

The diamond lattice is atomic in nature (III-7). This accounts for a number of its properties: though very hard, diamond is brittle, practically does not conduct electricity and has a low thermal conductivity.

Diamonds occur in alluvial beds formed as a result of the disintegration of rocks. The annual world output of diamonds is about 4 tons. Recently diamonds were produced artificially for the first time.

The exceptional hardness of diamond makes it a valuable industrial material. Diamonds are employed in drilling operations ("diamond drilling"), glass cutting, drawing fine wire, etc. The most beautiful crystals are polished and used as ornaments (Fig. 130). The unit of weight used to evaluate them is the *carat* (0.2 g) generally applied to precious stones.

2) Like in diamond, each atom of carbon in graphite (Fig. 131) is linked with four others, and the distances from it to three of the others are approximately equal (1.42 Å), but it is considerably more distant from the fourth of its neighbours (3.35 Å). As a result, the bond in the latter direction is much weaker than the others. Outwardly, this is expressed in the easy cleavage of graphite into thin scales along the line *AB* shown in Fig. 131, known as the *cleavage plane* of the crystal.

The bonds between atoms in the same plane of the graphite lattice are covalent, while those between atoms in different planes are metallic in nature. The presence of the latter explains the high electrical conductivity of graphite

(0.1 of the electrical conductivity of mercury) and its good thermal conductivity (three times that of mercury). At the same time, the structure of graphite possesses certain molecular features, since the presence of cleavage planes in the crystal allows it to be regarded as a number of huge flat particles, relatively weakly bound to one another by intermolecular forces.

In all cases investigated, the crystalline structure of "amorphous" carbon proved to be identical with the structure of graphite. It may, therefore, be assumed that "amorphous" carbon consists essentially of very small and randomly disposed graphite crystals.

Deposits of the latter are often very huge and run into the millions of tons. The usual initial material for its formation were the remains of vegetation of very ancient times. Graphite may be obtained artificially by the crystallisation of "amorphous" carbon at very high temperatures. It is used in many branches of industry.

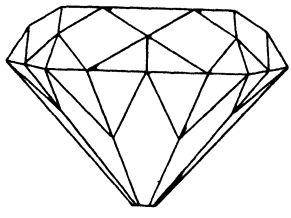


Fig. 130. Diamond facets

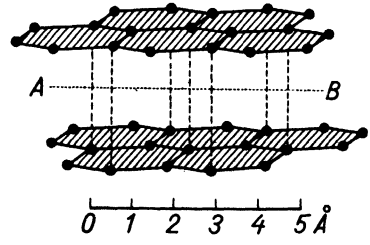


Fig. 131. Arrangement of carbon atoms in graphite

The triple point in the phase diagram of carbon corresponds to a temperature of about 3700° C and a pressure of about 100 atm. For this reason carbon does not melt on heating under normal pressure (in the absence of air), but sublimes at about 3500° C.

Under ordinary conditions, carbon is very inert. On the other hand, at sufficiently high temperatures it becomes chemically active with respect to the majority of metals and many non-metals. "Amorphous" carbon is considerably more reactive than both of the principal forms of the element.

On heating in air "amorphous" carbon reacts vigorously with oxygen, forming *carbon dioxide* according to the reaction:

$$C + O_2 = CO_2 + 94 \text{ kcal}$$

Diamond and graphite burn only in oxygen (on heating to 700 or 800° C). In the laboratory, CO_2 can be prepared conveniently by the reaction:

$$CaCO_3 + 2HCl = CaCl_2 + CO_2\uparrow + H_2O$$

The O=C=O molecule is linear [d(CO) = 1.15 Å]. Carbon dioxide is a colourless gas with a slightly sourish odour and taste. At a pressure of about 60 atm it condenses even at ordinary tempera-

tures to a colourless liquid which is stored and transported in steel cylinders. When intensely cooled, CO_2 solidifies into a white snow-like mass which sublimes at —78° C under normal pressure. Precompressed solid carbon dioxide evaporates comparatively slowly, the surrounding space being intensely cooled. This makes possible its use as "dry ice".

Carbon dioxide (or carbonic acid gas) does not support the combustion of ordinary fuels, such as carbon and its compounds. Only substances whose affinity to oxygen is considerably greater than that of carbon, burn in carbon dioxide. An example of this is metallic magnesium, which ignites in carbon dioxide at 600° C and burns in accordance with the equation:

$$CO_2 + 2Mg = 2MgO + C$$

The atmosphere contains, on the average, 0.03% CO_2 by volume.

Carbon dioxide dissolves fairly readily in water (approximately 1 : 1 by volume). Its solution is accompanied by its partial reaction with the water to form *carbonic acid*, H_2CO_3:

$$H_2O + CO_2 \rightleftarrows H_2CO_3$$

Although the equilibrium of this reaction is greatly displaced to the left, carbon dioxide should be regarded as the anhydride of carbonic acid. The latter is very weak, and dissociates but negligibly into H^+ and HCO_3^-; its further dissociation to CO_3^{2-} ions hardly takes place by itself. However, taking into account the possibility of this dissociation, the following simultaneous equilibria exist in an aqueous solution of CO_2:

$$H_2O + CO_2 \rightleftarrows H_2CO_3 \rightleftarrows H^+ + HCO_3^- \rightleftarrows 2H^+ + CO_3^{2-}$$

On heating, CO_2 escapes, and the equilibria shift to the left; on the other hand, if an alkali is added, the hydrogen ions are bound, and the equilibria shift to the right.

3) An aqueous solution saturated under ordinary conditions is approximately 0.04 *M* with regard to CO_2, and its pH is equal to 4. The carbonic acid, H_2CO_3, contained in it, has the dissociation constant values $K_1 = 4 \times 10^{-7}$, $K_2 = 5 \times 10^{-11}$.

4) The high solubility of carbon dioxide is utilised in the production of artificial mineral waters. Of these, ordinary carbonated water is simply a saturated solution of CO_2, while other waters contain additions of certain salts. Soft drinks such as lemonade are prepared similarly, the only difference being that a small quantity of sugar and various flavourings are added instead of salts.

Being a dibasic acid, H_2CO_3 yields two series of salts: neutral salts (containing the CO_3^{2-} anion) and acid salts (containing the HCO_3^- anion). The former are called *carbonates*, and the latter, *bicarbonates*. Like the anions of carbonic acid, most of its salts are colourless.

Among the carbonates of the most common cations, only the salts of Na^+, K^+ and NH_4^+ are soluble. Owing to considerable hydrolysis their solutions are alkaline. The first two salts can be melted without decomposition, but most other carbonates decompose on heating into the metal oxide and CO_2. Under the action of strong acids, all carbonates decompose readily forming a salt of the strong acid, water and carbon dioxide. The most important carbonates are Na_2CO_3 (soda), K_2CO_3 (potash), $CaCO_3$ (limestone, chalk, marble).

In contrast to the majority of carbonates all bicarbonates are soluble in water. The acid salt of carbonic acid of greatest practical importance is $NaHCO_3$ (baking soda). Its hydrolysis is negligible under ordinary conditions but increases markedly on heating. Bicarbonates are decomposed by strong acids in a manner similar to carbonates, e. g.:

$$2NaHCO_3 + H_2SO_4 = Na_2SO_4 + 2CO_2\uparrow + 2H_2O$$

5) The CO_3^{2-} ion contained in carbonates has the structure of an equilateral triangle with the C atom at the centre [d(CO) = 1.23 Å]. The pH values for 0.1 N and 1.0 N solutions of Na_2CO_3 are 10.9 and 12.3, respectively.

6) $NaHCO_3$ solutions have a pH value of about 8.4. One of the important applications of this salt is connected with the manufacture of *fire extinguishers*.

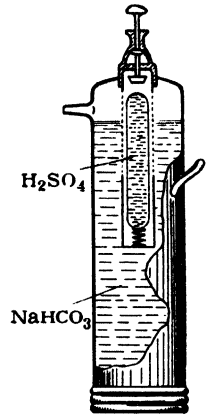


Fig. 132. A fire extinguisher (cut-away view)

Generally speaking, a fire may be put out by one of the following methods (or by a combination of them): 1) removal of the inflammable material, 2) cutting off access of oxygen and 3) cooling the burning substance below its ignition temperature. Fire extinguishers containing $NaHCO_3$ operate in accordance with the second and partly the third method. A diagram of such a fire extinguisher is shown in Fig. 132. Almost the whole cylinder is filled with a concentrated solution of $NaHCO_3$ (with foam forming admixtures). At the top of the cylinder, there is a glass ampoule containing sulphuric acid. In order to set the fire extinguisher off, it is inverted and the ampoule is smashed by a plunger mounted in the cap. The acid comes in contact with the $NaHCO_3$ solution, and a large quantity of carbon dioxide is immediately formed. The liquid saturated with it is discharged in a powerful jet, and blankets the burning area with a thick foam. The latter cools it (by evaporation of water) and above all isolates it from atmospheric oxygen, thus putting out the fire.

Sometimes, small cylinders containing liquid CO_2 are used for this purpose. On evaporating, the carbon dioxide simultaneously cools and isolates the burning substance from atmospheric oxygen by forming a blanket on it. The chief advantage of this type of fire extinguisher is that the CO_2 evaporates completely without damaging objects surrounding the burning area.

Besides carbon dioxide, carbon forms another typical oxide, *carbon monoxide*, CO. It results whenever carbon or its compounds are burnt in a limited supply of oxygen. It is mostly obtained as a result of the following reaction between carbon dioxide and

red-hot coal:

$$CO_2 + C + 41 \text{ kcal} = 2CO$$

This reaction is reversible, the equilibrium below 400° C being practically wholly displaced to the left, while above 1000° C it is completely shifted to the right (Fig. 133). However, it is established at an appreciable rate only at high temperatures. Therefore, CO is quite stable under ordinary conditions.

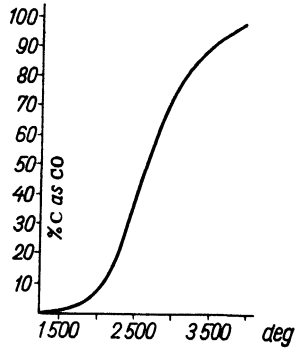


Fig. 133. Equilibrium of the system $CO_2 + C \rightleftarrows 2CO$

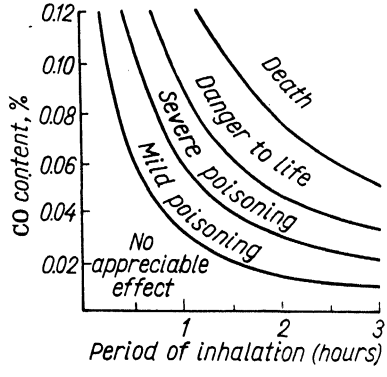


Fig. 134. Effect of carbon monoxide on a human being

Small quantities of carbon monoxide are conveniently prepared by the decomposition of formic acid in accordance with the equation:

$$HCOOH = H_2O + CO$$

This reaction takes place readily when HCOOH interacts with hot concentrated sulphuric acid.

Carbon monoxide is a colourless, odourless gas (m. p. —205° C, b. p. —192° C), is sparingly soluble in water (2.5 : 100 by volume) and does not react with it chemically. Nor does it react with acids or alkalis. It is very poisonous.

7) The electronic structure of the carbon monoxide molecule (d = 1.13 Å) may be represented by two formulas: according to one of these (: C = Ö) both atoms are linked by an ordinary double bond, while according to the other (: C ⇆ O :), the molecule also contains a donor-acceptor bond, the oxygen being the donor and the carbon being the acceptor (IX-2, suppl. 1). The second formula is in better agreement with the properties of carbon monoxide than the first (which is the classical one). For example, according to the classical formula, the polarity of the molecule should be fairly high, whereas, actually, it is very low (dipole length 0.02 Å).

8) As has been pointed out above, carbon monoxide reacts neither with water nor with alkalis under ordinary conditions. On the other hand, at elevated temperatures and high pressures, this reaction does take place: free formic acid can be obtained from CO and H_2O, and sodium formate, HCOONa, from

CO and NaOH. The latter reaction, which takes place at 120° C and 4 atm, has found industrial application.

9) The first symptoms of acute poisoning by carbon monoxide are headache and dizziness, followed by loss of consciousness. Fig. 134 shows the relationship between the physiological effect of CO, its percentage in the air and the period of inhalation of the latter. The principal antidote for carbon monoxide poisoning is fresh air. Inhalation of ammonia vapour for a short period is also beneficial.

Chemically, carbon monoxide is characterised mainly by a tendency towards *addition reactions* and by its *reducing properties*. However, both these tendencies are usually exhibited only at elevated temperatures. Under these conditions, CO combines with oxygen, chlorine, sulphur, certain metals, etc. At the same time, on heating, carbon monoxide reduces many oxides to the metals, this being of great importance in metallurgy.

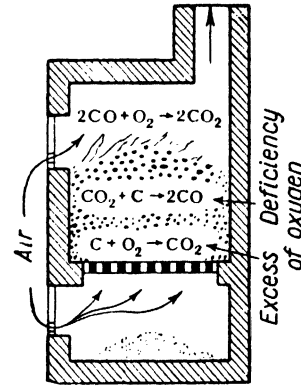


Fig. 135. Formation and combustion of CO in a furnace

Besides heating, the chemical activity of carbon monoxide can often be increased by dissolving it. Thus, in solution, it is capable of reducing salts of Au, Pt and certain other elements to the free metals even at ordinary temperatures.

CO ignites in air at about 700° C and burns with a blue flame in accordance with the equation:

$$2CO+O_2=2CO_2+135 \text{ kcal}$$

The large amount of heat evolved during this reaction makes carbon monoxide a valuable gaseous fuel. Moreover, from year to year it finds wider application as a starting material for the synthesis of various organic substances.

From the above it follows that the combustion of thick layers of coal in furnace takes place essentially in three stages, as schematically shown in Fig. 135. Premature closing of the flue, which causes a deficiency of oxygen in the furnace, may result in the CO spreading throughout the heated space and lead to poisoning. It should be pointed out that the odour of carbon monoxide fumes is due to certain organic impurities.

10) Large quantities of carbon monoxide are obtained by incomplete combustion of coal in special furnaces called gas producers. *Producer gas* contains, on the average, 25% CO, 70% N_2 (including the inert gases) and 5% CO_2 by volume. When it is burnt, each cubic metre provides 800-1000 kcal.

11) Still more CO is contained in what is known as *water gas*, which consists (in the ideal case) of a mixture of equal volumes of CO and H_2 and which

on combustion yields 2800 kcal per cu m. This gas is produced by blowing steam through a layer of red-hot coal, whereupon, at about 1000° C, the following reaction takes place: $H_2O+C+31$ kcal$=CO+H_2$. The reaction of water gas formation is endothermic, and the coal gradually cools off; therefore, to keep it red-hot, the steam is alternated with air. For this reason, water gas contains approximately 44% CO, 45% H_2, 5% CO_2 and 6% N_2.

12) *Mixed gas* is also often employed in practice. The process of its production consists essentially in blowing air and steam simultaneously through a bed of red-hot coal. Hence, this is a combination of both the above methods, and the composition of the mixed gas is intermediate between that of producer and water gas. On the average, it contains 30% CO, 15% H_2, 5% CO_2 and 50% N_2. One cubic metre of the gas yields about 1300 kcal on combustion.

13) Producer and water gases are extremely important as one of the principal sources for obtaining a nitrogen-hydrogen mixture for ammonia synthesis. When they are passed together with steam over a catalyst (chiefly Fe_2O_3) heated to 500° C, the carbon monoxide reacts with the water in accordance with the reversible reaction: $H_2O + CO \rightleftarrows CO_2 + H_2 + 10$ kcal, the equilibrium of which is greatly displaced to the right. The carbon dioxide formed is then removed by scrubbing the mixture with water (under pressure), and the small remaining amount of CO is taken up by an ammoniacal solution of copper salts. By suitably regulating the initial amounts of producer and water gas, N_2 and H_2 may be obtained in the required proportions. Before being fed to the synthesis column, the gas mixture is thoroughly dried and impurities liable to poison the catalyst are carefully removed.

The reaction between CO and *chlorine*

$$CO+Cl_2 \rightleftarrows COCl_2+27 \text{ kcal}$$

proceeds fairly rapidly even at room temperature in the presence of a catalyst (activated carbon). The resultant *phosgene*, is a colourless gas (m. p. —128° C, b. p. + 8° C) with a characteristic odour, sparingly soluble in water, but gradually decomposed by the latter according to the equation:

$$COCl_2+2H_2O=H_2CO_3+2HCl$$

It is, consequently, the acid chloride of carbonic acid.

Due to its extreme toxicity, high density, low cost and simplicity of production, phosgene was used in chemical warfare during World War I. In view of the high reactivity of phosgene, it is widely used in organic syntheses.

Carbon monoxide is capable of combining directly with certain *metals*. Such reactions usually take place only at an elevated temperature and under pressure. The resulting compounds are *metal carbonyls* [$Fe(CO)_5$, $Ni(CO)_4$, $Cr(CO)_6$, etc.], which should be regarded as complex compounds.

Metal carbonyls are, as a rule, highly volatile liquid or solid substances, insoluble in water, but readily soluble in many organic solvents. They are all very poisonous, and decompose readily on heating into the corresponding metal and carbon monoxide.

14) Of the metals already considered, the formation of carbonyl derivatives is most characteristic of the members of the chromium subgroup. They correspond to the formula $E(CO)_6$, and are colourless crystals which sublime readily and begin to decompose already above 120° C.

In contrast to the strongly exothermic process of the formation of CO_2 from its elements, the combination of carbon with *sulphur* is endothermic:

$$C + 2S + 15 \text{ kcal} = CS_2$$

Industrially, *carbon disulphide*, CS_2, is produced by passing sulphur vapour through a bed of red-hot coal.

Pure carbon disulphide is a highly volatile (b. p. 46° C), colourless liquid with a fairly pleasant odour, but usually it contains slight impurities which make its colour yellow and its odour disgusting. Carbon disulphide is almost insoluble in water. Its vapour is poisonous and ignites very readily, burning according to the equation:

$$CS_2 + 3O_2 = CO_2 + 2SO_2$$

Carbon disulphide is an excellent solvent for fats, oils, tars, etc., and is used for the extraction of these substances from various natural materials. It is also used to combat agricultural pests.

15) The S=C=S molecule is linear [d(CS) = 1.54 Å]. Hydrolysis of carbon disulphide (m. p. —109° C) in accordance with the equation $CS_2 + 2H_2O = CO_2 + 2H_2S$ takes place only above 150° C.

Like carbon dioxide, CS_2 is an acid anhydride, and on reacting with certain sulphides, can form salts of *thiocarbonic acid*, H_2CS_3. Only a few *thiocarbonates*, in particular, those of Na, K and NH_4, are readily soluble in water.

16) *Carbon oxysulphide*, S=C=O, intermediate in composition between CO_2 and CS_2, is a colourless, odourless gas (m. p. —139° C, b. p. —48° C). It is fairly readily soluble in water and hydrolyses gradually according to the equation: $COS + H_2O = CO_2 + H_2S$.

The reaction of direct combination between carbon and *nitrogen* is strongly endothermic and takes place partially only at very high temperatures. The most important of the simplest nitrogen derivatives of carbon is *hydrocyanic acid*, H—C≡N, which can be obtained from CO and ammonia by the reaction

$$CO + NH_3 = H_2O + HCN$$

which takes place sufficiently rapidly at about 500° C in the presence of ThO_2.

Hydrocyanic (or *prussic*) acid is a very volatile colourless liquid with a peculiar faint odour (m. p.—13° C, b. p. 26° C). HCN is miscible with water. Its acidic properties are very weak and, therefore, it can be easily liberated from its salts (*cyanides*) by the action of stronger acids.

Prussic acid is employed chiefly in the synthesis of organic substances, and its salts (NaCN, KCN) are used mainly in the extraction

of gold, etc. Both the acid itself and its salts are highly poisonous. Like the CN^- ion, the majority of cyanides are colourless. The salts of the most active metals are readily soluble in water, while those of the less active metals are, as a rule, sparingly soluble.

The CN^- ion very often forms part of the inner sphere of complex compounds. The usual method of obtaining *complex cyanides* is by the action of excess KCN (or NaCN) on the salts of the corresponding metals. The precipitates of simple cyanides initially separating out dissolve subsequently in the excess of precipitating agent owing to the formation of soluble complex cyanides; the reactions take place, for example, in accordance with the equations:

$$CrCl_3 + 3KCN = Cr(CN)_3\downarrow + 3KCl \quad \text{and} \quad Cr(CN)_3 + 3KCN = K_3[Cr(CN)_6]$$

The stability of these complexes greatly depends on the nature of the complexing agent.

17) The HCN molecule has a linear structure [d(HC) = 1.06 Å, d(CN) = =1.16 Å] and a pronounced polar character (dipole length 0.61 Å). As an acid, it is characterised by the value $K = 7 \times 10^{-10}$.

18) Prussic acid consists of a mixture of the molecules H—C≡N (normal form) and H—N⇄C (isoform). Both forms are able to change into one another (by a proton jump). Therefore, they are in dynamic equilibrium, the position of which depends on the temperature. Under ordinary conditions, prussic acid is almost entirely in the normal form, but on intensive heating, the equilibrium shifts in favour of the isoform. Organic derivatives—nitriles (RCN) and isonitriles (RNC) are known for both forms of prussic acid.

The presence in substances of two (or more) forms which differ in atomic structure and are in dynamic equilibrium with each other is known as *tautomerism* of the given substance, while its different modifications are called *tautomeric*.

It has now been established that tautomerism is a considerably more widespread phenomenon than was thought formerly. This especially refers to those compounds in which tautomerism is based on *proton migration*, i. e., intramolecular transfer of the hydrogen nucleus from one of the atoms to another.

On heating mercuric cyanide, *cyanogen*, N≡C—C≡N, is formed according to the reaction:

$$Hg(CN)_2 = Hg + (CN)_2$$

It is a colourless, poisonous gas with a peculiar odour (m. p. —28° C, b. p. —21° C), which burns to CO_2 and N_2 if ignited in air. Cyanogen displays great similarity to the halides in a number of chemical properties, the role of the halogen atom being played by the CN radical.

19) The reaction between cyanogen and alkalis is analogous to the corresponding reactions of the halides—with the simultaneous formation of salts of prussic and *cyanic* (H—N=C=O) *acids*: $(CN)_2 + 2KOH = KCN + KNCO + H_2O$. Potassium *cyanate* is also formed if KCN is heated in air. This salt is readily soluble in water, which gradually decomposes it in accordance with the equation: $KNCO + 2H_2O = NH_3 + KHCO_3$.

Fulminic acid, H—O—N⇄C, has the same elementary composition as cyanic acid, but differs from the latter in the arrangement of atoms in the

molecule. Both acids are very unstable. The most important of their salts is *mercury fulminate*, $Hg(ONC)_2$. It explodes on impact and is used as a detonator. It decomposes according to the equation: $Hg(ONC)_2 = Hg + 2CO + N_2 + 118$ kcal.

If a solution of potassium cyanide is boiled with sulphur (or the two substances are fused) a salt of *thiocyanic acid*, H—N=C=S, will result, in accordance with the equation:

$$KCN + S = KNCS$$

Free HNCS is stable only in dilute solution. It is fairly strongly dissociated. The majority of its salts, called *thiocyanates*, are colourless and readily soluble in water. The most common are those of ammonium and potassium. Unlike cyanides, they are not poisonous.

20) Free *thiocyanogen*, $(SCN)_2$, consists of colourless crystals (m. p. —2° C) which are stable only at low temperatures. It is readily soluble in water, but is rapidly decomposed by the latter. Thiocyanogen resembles halogens (bromine and iodine) in chemical properties.

The simplest *halogen* compounds of carbon correspond to the formula CX_4. Only the fluorine derivative can be obtained by interaction of the elements; the rest are obtained by indirect means.

Of greatest practical importance among these compounds is *carbon tetrachloride*, CCl_4. It is a heavy, colourless liquid with a characteristic faint odour, which boils at 77° C. CCl_4 is almost insoluble in water. Chemically, it is characterised chiefly by its inertness. Thus, under ordinary conditions, CCl_4 reacts neither with acids nor alkalis.

Carbon tetrachloride is an excellent solvent for fats, oils, tars, many paints, etc., and can therefore serve as a good stain remover. Being incombustible, it does not involve any fire hazard when handled and this gives CCl_4 a considerable advantage over the cheaper solvent, carbon disulphide, referred to above.

21) Carbon tetrachloride (m. p. —24° C) is usually obtained by the equation: $CS_2 + 2Cl_2 = CCl_4 + 2S$, while analogous derivatives of other halogens are usually obtained by the double decomposition of CCl_4 on heating with AgF, $AlBr_3$ or AlI_3, respectively. Mixtures of chlorofluoromethane and ethane under the general commercial name of "freon" are good working fluids for refrigerators. An example is "freon-12", the formula of which is CF_2Cl_2 (b. p. —30° C).

Direct combination of carbon (amorphous) and *hydrogen* to form *methane*, CH_4, in accordance with the reaction

$$C + 2H_2 \rightleftarrows CH_4 + 18 \text{ kcal}$$

practically does not occur under ordinary conditions. On heating and in the presence of a catalyst (finely divided Ni), an equilibrium is established, the position of which depends greatly on the temperature (Fig. 136). Besides this synthetic method, methane can be prepared

by a number of other methods, starting from more complex carbon compounds. It is constantly formed in nature by the decomposition of organic substances in the absence of air (for example, in marshes). It is also often contained in natural gases and usually in coal gas.

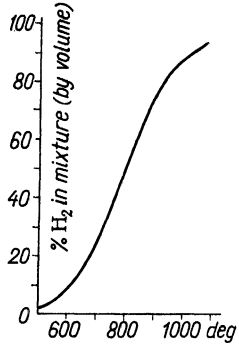


Fig. 136. Equilibrium of methane synthesis

Methane is the simplest of the numerous compounds of carbon and hydrogen called *hydrocarbons* and studied in organic chemistry. It is a colourless, odourless gas (m. p. —184° C, b. p. —162° C), sparingly soluble in water. Chemically, methane is very inert. In particular, neither alkalis nor acids have any effect upon it. It does not react with hydrogen under ordinary conditions, but on ignition, burns according to the reaction:

$$CH_4 + 2O_2 = CO_2 + 2H_2O + 192 \text{ kcal}$$

22) Under laboratory conditions, methane may be prepared in accordance with the following reaction which takes place on heating:

$$CH_3COONa + NaOH = Na_2CO_3 + CH_4$$

The solubility of methane in water is about 4 : 100 by volume.

23) Natural gases rich in methane, are very good fuels, one cu m providing 8 to 9 thousand kcal. At the same time, they are an excellent raw material for obtaining hydrogen. The usual method employed (*methane conversion*) consists of the reaction between CH_4 and steam which takes place at 1000° C : $H_2O + CH_4 + 49$ kcal $= CO + 3H_2$. The gas obtained is then again treated with steam (suppl. 13).

Numerous deposits of natural gases often containing more than 90% methane have been found in all parts of the U.S.S.R. In 1962, 75.2 thousand million m^3 of gas was produced (as against 3.4 thousand million m^3 in 1940, and 0.017 thousand million m^3 in 1913).

24) Coal gas is produced by strongly heating coal without access of air (destructive distillation). This gas usually contains about 50% H_2, 30% CH_4, 4% other hydrocarbons, 9% CO, 2% CO_2 and 5% N_2. Owing to its considerable content of carbon monoxide, coal gas is highly toxic. Combustion of gas of the composition indicated yields 5500 kcal per cu m.

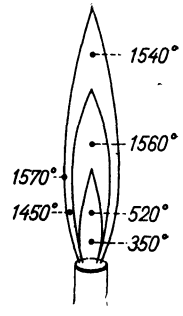


Fig. 137. Flame of a gas burner

The principal by-products of coal gas production are coal tar (used for the production of a number of organic substances), ammonia and coke.

25) When coal gas is burnt in ordinary gas burners, the non-luminous flame consists of three cones (Fig. 137). The innermost cone consists of a jet of gas mixed with air, and no combustion occurs inside this cone. The next cone contains an excess of combustible material and a lack of oxygen. Therefore, combustion in this cone is incomplete, and the flame in this zone is "reductive". Finally, in the outermost cone, complete combustion is accomplished in an excess of atmospheric oxygen, owing to which the flame here is "oxidative". The approximate distribution of temperatures at different points in the flame

is shown in Fig. 137. The figures indicated can be regarded only as tentative (because they greatly depend on the composition of the gas).

Carbon reacts with *metals* only at high temperatures. Of the compounds formed (called *carbides*), *calcium carbide*, CaC_2 is of the greatest practical importance. The derivatives of tungsten (W_2C and WC) are also very important, as their extraordinary hardness makes it possible to use them, in many cases, as substitutes for diamond. Carbides are, in general, similar in properties to nitrides. They are refractory, non-volatile and insoluble in all solvents.

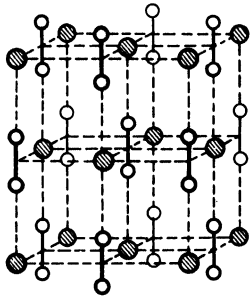


Fig. 138. Structure of a CaC_2 crystal

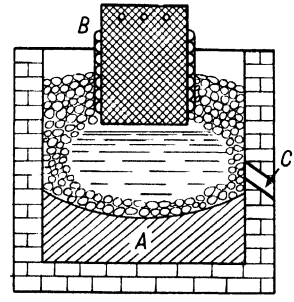


Fig. 139. Calcium carbide furnace

26) In their attitude towards water and dilute acids, the carbides can be divided into two major groups: those decomposed and those not decomposed by these substances. The latter are usually also very resistant to other chemical influences. However, they can all be broken down by fusing with alkalis in the presence of air, for example:

$$2WC + 8NaOH + 5O_2 = 2Na_2WO_4 + 2Na_2CO_3 + 4H_2O$$

The majority of carbides are more conveniently prepared by heating the metal oxides with carbon instead of the metals. At high temperatures, the oxide is reduced and the metal combines with the carbon. Calcium carbide is prepared by strongly heating a mixture of carbon and calcium oxide in an electric furnace:

$$CaO + 3C = CO\uparrow + CaC_2$$

The commercial product is grey in colour due to an admixture of free carbon. Pure CaC_2 forms colourless crystals consisting of Ca^{2+} and C^{2-} ions (Fig. 138).

27) The electrodes in the electric furnace for the production of CaC_2, shown schematically in Fig. 139, are the thick layer of graphite *A* lining the bottom of the furnace, and a massive carbon block *B* which is lowered from above.

An incrustation of the original mixture remains around the walls of an operating furnace; this incrustation is pierced at the opening *C* to let the molten carbide out. The production of each ton of CaC_2 requires 3 thousand kilowatt-hours. Its annual world production is about 5 million tons.

Calcium carbide reacts vigorously with water (even traces) to form *acetylene*, H—C≡C—H:

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$$

Acetylene obtained from commercial CaC_2 has an unpleasant odour owing to a number of impurities (NH_3, PH_3, H_2S, etc.). In the pure form, it is a colourless gas with a faint characteristic odour, and is fairly readily soluble in water.

Acetylene is the starting product for the synthesis of quite a number of more complex organic compounds. At present, this is its widest field of application. Another important application of acetylene is based on its combustion reaction, which is accompanied by an intensive evolution of heat:

$$2C_2H_2 + 5O_2 = 4CO_2 + 2H_2O + 601 \text{ kcal}$$

The high temperature (3000° C) which develops when acetylene is burnt with oxygen, is used for autogenous welding and cutting of metals. Acetylene burns in air with a white flame which is very smoky, owing to the incomplete combustion of carbon.

28) The formation of acetylene (sublimation temp. —84° C) from its elements takes place only above 2000° C. Being highly endothermic, acetylene may decompose explosively. This decomposition does not occur under ordinary conditions, but under pressure (especially when acetylene is in the liquid or solid state) it may result from the slightest influence.

From the above discussion it follows that carbon is tetravalent in all its more or less stable compounds. The sole exception is carbon monoxide, but as has already been noted, it also tends towards addition reactions which are accompanied by the conversion of carbon into the tetravalent state. Besides CO, only a very few derivatives of carbon with a valency other than four (namely, 2 and 3) are known, but all these compounds are rather unstable under ordinary conditions. Thus, the characteristic valency of carbon is *four*.

X-2. Organic Compounds. In wealth and variety of derivatives, carbon leaves all the other elements far behind: while only some tens of thousands of chemical compounds containing no C are known, the number of carbon compounds studied has topped two million. For this reason the detailed study of the chemistry of carbon had to be singled out as an independent field which is usually called *organic* chemistry.

The great variety of compounds of carbon as compared with the other elements is due to certain specific features of carbon atoms. The most important of these is their ability to form stable bonds with each other. Owing to this, molecules containing *chains of carbon atoms* are quite stable under ordinary conditions, whereas molecules of other elements with similar chain-like accumulations of atoms are mostly very unstable. Thus, for oxygen, the maximum known chain

length is two atoms, and compounds containing it (hydrogen peroxide and its derivatives) are rather unstable, whereas in the case of carbon, a perfectly stable compound containing a chain of 100 carbon atoms has been obtained.

X-ray studies of molecules containing carbon chains have shown that the carbon atoms in these chains are arranged in a zigzag manner rather than in a straight line (Fig. 140). This is due to the fact that the four valencies of the carbon atom are oriented in a definite way

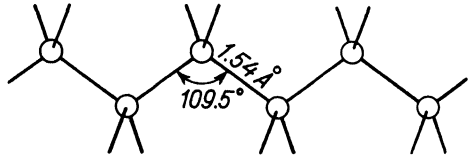


Fig. 140. Structure of a carbon chain

relative to one another: the angle between the lines connecting any three carbon atoms equals that between the lines drawn from the centre of a tetrahedron to its corners (Fig. 124).

The chains of carbon atoms in the molecules of organic substances may be closed or open. Derivatives of the first type are called *cyclic* compounds, and those of the second type, *open-chain* compounds.

Owing to the formation of stable chains, carbon forms tens and hundreds of compounds of the same type while other elements can form only a few. Thus, only two hydrogen compounds, H_2O and H_2O_2, are known for oxygen, whereas in the case of carbon, besides methane, CH_4, we have ethane, C_2H_6, propane, C_3H_8, butane, C_4H_{10}, and many others.

It is evident from the formulas of these hydrocarbons that they all form *a series in which each subsequent member may be derived from the preceding member by adding a CH_2 group*. Such series are called *homologous*, and are distinguished from one another by the first member. Thus, the above hydrocarbons belong to the methane homologous series, or are *homologues* of methane. Each homologous series may be represented by a *generic formula*. In this particular case, the generic formula is C_nH_{2n+2}. Knowing the formula, it is easy to find the chemical composition of any member of the given series. For example, the homologue of methane with 7 carbon atoms has the composition $C_7H_{7\times2+2}$ or C_7H_{16}.

Homologous series are a vivid example of the change of quantity into quality. In fact, "by adding a CH_2 group each time, a substance qualitatively different from the one preceding it is obtained" (Engels)*.

* "...durch Zusatz von je CH_2 jedesmal ein von dem früheren qualitativ verschiedner Körper gebildet wird".

(F. Engels, Op. cit., S. 58).

The Methane Homologous Series

Name	Formula	Melting point (°C)	Boiling point (°C)	Specific gravity in liquid state	Name	Formula	Melting point (°C)
Methane	CH_4	—184	—162	0.42	Eicosane	$C_{20}H_{42}$	36
Ethane	C_2H_6	—183	—88	0.45			
Propane	C_3H_8	—188	—42	0.54	Triacontane	$C_{30}H_{62}$	66
Butane	C_4H_{10}	—138	0	0.60			
Pentane	C_5H_{12}	—130	36	0.63	Tetracontane	$C_{40}H_{82}$	81
Hexane	C_6H_{14}	—95	69	0.66			
Heptane	C_7H_{16}	—91	98	0.68	Pentacontane	$C_{50}H_{102}$	92
Octane	C_8H_{18}	—57	126	0.70			
Nonane	C_9H_{20}	—54	151	0.72	Hexacontane	$C_{60}H_{122}$	99
Decane	$C_{10}H_{22}$	—30	174	0.73			
Pentadecane	$C_{15}H_{32}$	+10	270	0.77	Hectane	$C_{100}H_{202}$	115

The data given in the above table show that the first four members of the methane homologous series are gases under ordinary conditions, those following are liquids and the subsequent ones are solids. Throughout the series, the physical constants of the homologues change fairly regularly. With regard to melting and boiling points, the same regularity, i. e., an increase in both constants with increasing molecular weight, is observed, as a rule, in other homologous series as well, but with respect to specific gravities, it is sometimes reversed, i. e., specific gravities decrease with increasing molecular weight.

Members of the same homologous series resemble one another in chemical behaviour. In particular, the same reactions are characteristic of the methane homologues as of CH_4 itself, a difference appearing only in the degree of ease with which they take place. This similarity of chemical properties (including, of course, some elements of difference, too), together with the more or less regular change in physical constants within a homologous series, greatly facilitates the study of organic chemistry, since a knowledge of the properties of one of the members of a series provides a sufficiently clear idea of the properties of all the others.

Apart from the existence of stable chains, carbon is characterised by the fact that its valency bonds with hydrogen and different nonmetals are relatively close to one another in stability. This can be seen from the data given below for bond energies.

Bond	C—C	C—H	C—O	C—S	C—N	C—F	C—Cl	C—Br	C—I
Bond energy (kcal/g-atom)	85	99	82	67	61	115	78	66	58

The fact that the energy of the C—H bond is close to the arithmetical mean of the known values for the non-polar bonds C—C and H—H (104 kcal) indicates its low polarity. This conclusion is confirmed by experiment. Most other bonds in organic compounds have a similarly low polarity.

An important conclusion concerning the course of organic reactions follows from the above. Since low polarity of the bonds does not favour the dissociation of molecules into ions, the overwhelming majority of carbon compounds practically do not undergo electrolytic dissociation. But exchange reactions between electrolytes occur almost instantaneously only because they essentially amount to different combinations of already available ions. In contrast, a chemical reaction between *neutral molecules* necessarily involves partial splitting of those molecules, and therefore it proceeds much more slowly. On the other hand, the absence of sharp differences between the energies of formation of the individual bonds also contributes to the slowness and incompleteness of the processes. As a result, completion of a particular reaction between organic compounds takes hours, as a rule, instead of seconds or minutes; the reactions often take place at an appreciable rate only at elevated temperatures and usually do not proceed to completion.

The low polarity of the individual bonds is the most important factor determining the low polarity of the majority of organic molecules. Externally, this is manifested in the comparatively low melting and boiling points of the substances which they form. Whereas NaCl, for example, melts at 800° C and boils at 1454° C, almost all organic compounds melt and boil below 300° C and decompose on heating to higher temperatures.

Hydrocarbons are the simplest organic compounds. Besides the single bonds, C—H and C—C, their molecules may also contain the *double* bond, C=C, and the *triple* bond, C≡C. The chemical properties of hydrocarbons possessing no *multiple* (double or triple) bonds, in general approximately repeat the properties of methane. The introduction of a multiple bond into the molecule usually imparts to it a tendency towards addition reactions. This is indicated by referring to the *unsaturated* nature of a substance containing multiple bonds. For example, the simplest unsaturated hydrocarbons—*ethylene*, $H_2C{=}CH_2$, and *acetylene*, HC≡CH, readily add halogens. Addition reactions involve conversion of the multiple bonds between carbon atoms into single bonds. The comparative ease of this conversion determines the unsaturated nature of the compounds.

1) The distances d(CC) in single, double and triple bonds are 1.54 Å 1.35 Å and 1.20 Å, respectively. The distance d(CH) also varies somewhat, depending on the character of the C atom. Thus, for methane, ethylene and

acetylene, d (CH) is 1.093 Å, 1.071 Å and 1.057 Å, respectively. The acetylene molecule is linear. In the case of ethylene, all the atomic nuclei are arranged in one plane, and $< HCH = 120°$.

2) *Ethylene* is usually prepared by dehydration of ethyl alcohol, i. e., by the elimination of water from the latter in accordance with the equation: $C_2H_5OH - H_2O = C_2H_4$. It is a colourless gas (m. p. —169° C, b. p. —104° C), and is fairly readily soluble in water (1 : 4 by volume). Under high pressure, ethylene polymerises forming very long chains of CH_2 groups. The solid polymer obtained (polythene) has found various practical applications.

3) The most important cyclic hydrocarbon in organic chemistry is the *benzene*, C_6H_6. The structure of its molecule corresponds to a flat hexagon [d(CC) = 1.39 Å and d(CH) = 1.08 Å], a very stable "aromatic" bond being formed between the carbon atoms, the nature of which is not entirely clear as yet. Structurally, benzene is usually represented in the form of an equilateral hexagon.

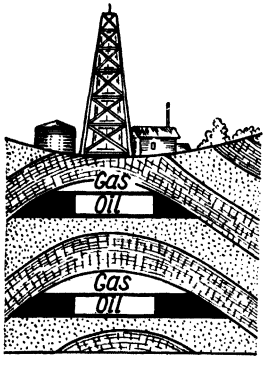


Fig. 141. Section through an oil field

Benzene is a colourless liquid (m. p. 5° C, b. p. 80° C), almost insoluble in water. It is the parent of a vast number of diverse derivatives. The closest homologue of benzene—*toluene*, $C_6H_5CH_3$, a colourless liquid (m. p. —95° C, b. p. 111° C), is also of great practical importance. Both benzene and toluene are produced mainly as by-products during the coking of coal.

4) *Petroleum* or mineral oil is a natural accumulation of hydrocarbons. Petroleum deposits are encountered in sedimentary rocks of different ages. As can be seen from Fig. 141, oil is located under domes of a layer of clay or other rock impervious to gas. Above the petroleum layer is usually a cushion of gas, and below it, a shelf of sand saturated with salt water.

Although the chemical mechanism of the formation of petroleum is still not quite understood, there is almost no doubt that the remains of life in shallow sea basins served as the principal initial material for them. The vigorous development in these sea basins of primitive algae, which may be likened to the "flowering" of our lakes, led to just as vigorous a development of animal life. Bearing in mind the collosal rate of reproduction of primitive organisms under favourable conditions, it is not surprising that enormous quantities of remains of these organisms could accumulate in the depressions at the bottom of ancient seas and lakes. As they slowly decayed without access of air in the stagnant water at the bottom, these remains were, at the same time, gradually covered over with clay and sand. In the course of millions of years, they were converted into petroleum.

Crude petroleum is a brown or black oily liquid of specific gravity 0.75-0.95, which is insoluble in water. Usually it contains 83 to 87% carbon, 11 to 14% hydrogen and small quantities of nitrogen, oxygen and sulphur. Hydrocarbons of the methane homologous series predominate in some kinds of petroleum, while cyclic hydrocarbons predominate in others.

Petroleum is an excellent fuel: 1 kg of petroleum yields 11,000 kcal. In oil refineries, a number of products are separated from it: petroleum ether, petrol, ligroin, kerosene, various lubricating oils, vaseline, paraffin wax and some others. All these substances are mixtures of hydrocarbons, ranging from those which are highly volatile (in petroleum ether) to those that are solids under ordinary conditions (in paraffin wax). Petroleum gas (better known as casing-head gas) consists, in the main, of gaseous hydrocarbons. It can be employed both as a fuel

and for the catalytic production of various substances (hydrogen, alcohol, formaldehyde, etc.). The waters in petroleum deposits often contain iodine and bromine.

The widespread use of internal combustion engines has brought about an enormous growth in the consumption of petroleum. During the period from 1860 to 1960, its annual world production rose from 67 thousand tons to 1051 million tons, i. e., approximately 16,000 times. The U.S.S.R. is one of the biggest producers of petroleum (206 million tons in 1963, as against 31.1 million tons in 1940 and 9.2 million tons in 1913).

Organic *halogen derivatives* are formed by substitution of a halogen for hydrogen in a C—H bond (or by direct addition of a halogen to unsaturated hydrocarbons). Thus, substitution of chlorine for a hydrogen in methane yields methyl chloride, CH_3Cl, and substitution of chlorine for a hydrogen in ethane yields ethyl chloride, C_2H_5Cl, etc. As can be seen from the examples quoted, the names of the halides are derived from the names of the *hydrocarbon radicals* or *alkyl radicals* they contain (in this case, these radicals are *methyl*—CH_3, and *ethyl* — C_2H_5). Denoting the hydrocarbon radical in the general form by R, the equation for the reaction between a saturated hydrocarbon and a halogen may be represented in the following way:

$$RH + X_2 = HX + RX$$

Like the rest of the simplest derivatives of the saturated hydrocarbons, the alkyl halides, RX, are mostly colourless liquids. They are almost insoluble in water. The stability of the bond between the carbon and the halogen decreases in the order F—Cl—Br—I, while the chemical activity of the alkyl halides increases in the same order. The most characteristic reactions of the alkyl halides are those in which a halogen is exchanged for other radicals (NH_2, OH, etc.); this accounts for the wide use of alkyl halides in syntheses.

5) The best known of the simplest organic halogen derivatives is *chloroform*, $CHCl_3$. It is a colourless liquid (m. p. —63° C, b. p. +61° C) with a sweetish smell, and is used in surgical operations as an anaesthetic.

In recent years, organic fluorine compounds have acquired great importance. In particular, a solid plastic (*teflon*) which is unusually resistant to all kinds of chemical influences, can be obtained by polymerisation of tetrafluoroethylene, $F_2C = CF_2$.

When alkyl halides react with ammonia (in alcoholic solution), *amines*, RNH_2, which are organic derivatives of ammonia, result in accordance with the equation:

$$RX + NH_3 = HX + RNH_2$$

The lower members of the homologous series of amines are readily soluble in water, but their solubility decreases with growing R. This decrease of solubility when ascending a homologous series is characteristic of other types of organic compounds as well as of amines.

Aqueous solutions of amines are alkaline owing to complex formation according to the equation:

$$RNH_2 + H{\cdot}OH' \rightleftarrows [RNH_3]^{\cdot} + OH'$$

With acids, amines (like NH_3) combine directly to form salts, e. g.:

$$RNH_2 + HCl = [RNH_3]Cl$$

Thus, introduction of an amino-group ($—NH_2$) into an organic compound imparts basic properties to the latter.

6) Products of the replacement of only one hydrogen atom in ammonia by an alkyl radical are called *primary* amines (RNH_2). On further replacement, *secondary* (R_2NH) and *tertiary* (NR_3) amines are formed. The properties of the latter two are, in the main, similar to those of primary amines.

The most important representative of the amine class is *aniline*, $C_6H_5NH_2$, which is a colourless liquid (m. p. —6° C, b. p. 184° C) having a peculiar odour and gradually turning brown in the air. The basic properties of aniline are very weak.

Under the influence of water alkyl halides gradually hydrolise (the alkyl iodides being hydrolised most readily):

$$RX + HOH \rightleftarrows ROH + HX$$

This reaction can be greatly speeded up and its equilibrium shifted to the right by the addition of an alkali. The resultants are *alcohols*, ROH, which may be regarded as products of the replacement of one of the hydrogen atoms in water by alkyl radicals.

The introduction of a hydroxyl group imparts the character of an *amphoteric* compound to an organic molecule. However, the dissociation of alcohols is still lower than that of water, and therefore, alcohols themselves and their aqueous solutions do not conduct electricity. The amphoteric character of alcohols is demonstrated, on the one hand, by the reversibility of the above reaction of their formation (where the alcohol behaves as a base), and on the other, by the reaction with metallic sodium which takes place in accordance with the equation

$$2ROH + 2Na = 2RONa + H_2\uparrow$$

(where the alcohol behaves as an acid).

7) *Ethyl alcohol*, C_2H_5OH, often called just *alcohol*, is the most important compound of this class. It is usually obtained by fermentation of natural products containing starch or sugar. Ethyl alcohol (m. p. —117° C, b. p. +78° C) is miscible with water.

Another important representative of the alcohol class is *glycerol*, $C_3H_5(OH)_3$, the molecule of which contains three hydroxyl groups. Glycerol is a colourless, viscous liquid (m. p. 20° C, b. p. 290° C) which solidifies only at about 0° C, and is miscible with water.

While alcohols may be regarded as the products of the replacement of *one* of the hydrogen atoms in water by an alkyl radical,

ethers (ROR) are the products of replacement of *both* the hydrogen atoms. Their reaction with water results in the equilibrium

$$ROR + HOH \rightleftarrows 2ROH$$

which is established at an appreciable rate, however, only at elevated temperatures. By using substances which combine with water (P_2O_5, etc.), it is possible under these conditions to displace the equilibrium completely to the left, and thus obtain an ether from an alcohol.

Ethers are chemically fairly inert substances. For example, metallic sodium has no effect on them at ordinary temperatures. The volatility of ethers is greater, i. e., their boiling points are lower, than those of the alcohols from which they are derived, but their solubility in water is much lower.

8) *Diethyl ether*, $C_2H_5OC_2H_5$, practically the most frequently encountered ether, is usually obtained by the action of ethyl alcohol on sulphuric acid (dehydrating agent) at an elevated temperature. In connection with this method of preparation, diethyl ether is sometimes incorrectly called "sulphuric" ether. Diethyl (loosely called ethyl) ether is a colourless, volatile liquid (m. p. —116° C, b. p. +35° C). Its vapour readily ignites in air, and its inhalation results in intoxication and subsequent narcosis.

The presence of a hydroxyl group (—OH) in the molecule of an alcohol appreciably decreases the stability of the neighbouring C—H bonds. That is why alcohols are oxidised much more readily than the corresponding hydrocarbons, for example, according to the equation:

$$CH_3CH_2OH + O(\text{from an oxidising agent}) = H_2O + CH_3CHO$$

Compounds containing a —CHO radical in their molecule are called *aldehydes* (generic formula, RCHO).

The double bond C=O in aldehydes fairly readily changes to a single bond C—O with the release of one valency of carbon and one of hydrogen. For this reason addition reactions are characteristic of aldehydes. At the same time, the oxygen in the *carbonyl* group (=CO) activates the neighbouring C—H bond, so that the hydrogen of the latter is easily replaced by an OH group. Since this substitution involves introduction of an oxygen atom into the molecule, it amounts to oxidation of the aldehyde. Therefore, aldehydes are reducing agents and, moreover, fairly strong ones: many of them are gradually oxidised even by atmospheric oxygen.

Ketones (generic formula R_2CO) are closely related to aldehydes. Owing to the presence of the carbonyl group, ketones, like aldehydes, possess a tendency towards addition reactions, but reducing properties are not characteristic of them.

9) The first member of the homologous series of aldehydes—*formaldehyde*, HCHO, a colourless gas (m. p. —92° C, b. p. —21° C) with a characteristic pungent odour, is the most frequently encountered in practice. Its 40% aqueous solution is used as a disinfectant under the name of *formalin*.

10) Formaldehyde is used in incomparably larger quantities for the production of *plastics*, which find new fields of application every year. Structurally, plastics are usually products of the successive combination with each other of a very large number of structural units of the same type, e. g.:

$-CH_2-C(CH_3)(COOCH_3)-$	for plexiglas
$-NH(CH_2)_5CO-$	for capron
$-CO(CH_2)_4CO-NH(CH_2)_6NH-$	for nylon

The annual world production of various plastics runs into millions of tons and is rapidly growing.

So-called *ion-exchange resins* featuring pronounced adsorptive capacity in relation to cations (*cation exchange*) or anions (*anion resins*) are of particular importance. The use of such plastics makes it possible to extract certain elements selectively from solution.

11) *Acetone*, CH_3COCH_3, an important representative of the ketone class is widely employed as a solvent for many substances. It is a colourless liquid with a characteristic odour (m. p. —94° C, b. p. +57° C), and is miscible with water.

The oxidation products of aldehydes contain the *carboxyl* group (—COOH) and are called organic *acids* (generic formula RCOOH). For example, oxidation of acetaldehyde results in acetic acid:

$$CH_3CHO + O \text{ (from an oxidising agent)} = CH_3COOH$$

The fact that the C=O and C—OH bonds stem from the same carbon atom greatly affects their character. The OH group strengthens the double bond, so that addition reactions become uncharacteristic of acids (in contrast to aldehydes and ketones). On the other hand, the C=O bond imparts acidic properties to the hydrogen atom in the hydroxyl group. Though organic acids are much more dissociated than alcohols or water, their dissociation is low compared to the typical "mineral" acids (HCl, H_2SO_4, etc.). Therefore, it may be said that organic compounds of the type RCOOH are, as a rule, *weak* acids.

12) The first member of the homologous series of acids is *formic* acid, HCOOH, a colourless liquid (m. p. +8° C, b. p. 101° C) with a pungent odour. The presence of the bonds C—H and C=O stemming from the same carbon atom in the molecule of formic acid ($K = 2 \times 10^{-4}$) makes this acid (like the aldehydes) a strong reducing agent. Its salts (called *formates*) are, as a rule, readily soluble. A dilute (1 or 1.5%) aqueous solution of HCOOH is used for embrocation in the treatment of rheumatism.

13) *Acetic acid*, CH_3COOH, a colourless substance with a characteristic odour (m. p. 17° C, b. p. 118° C), is commercially the most common organic acid. It is miscible with water and in solution behaves as a weak acid ($K = 2 \times 10^{-5}$). The majority of its salts (*acetates*) are readily soluble. An 80% solution of CH_3COOH, sold under the name of "vinegar essence" is used for the preparation

of vinegar, i. e., a dilute (5-7%) solution of CH_3COOH, which is used for flavouring.

14) The simplest of the *dibasic* organic acids is *oxalic* acid, $H_2C_2O_4$, the molecule of which is composed of two carboxyl groups (HOOC—COOH). Oxalic acid is a white, crystalline substance, fairly readily soluble in water. It is one of the few organic acids of medium strength ($K_1 = 7 \times 10^{-2}$, $K_2 = 6 \times 10^{-5}$). The majority of its salts (called *oxalates*) are sparingly soluble in water. Of the derivatives of the common cations, only the salts of Na^+, K^+ and NH_4^+ are readily soluble. Under the action of powerful oxidising agents ($KMnO_4$, etc.), oxalic acid is readily oxidised to CO_2 and H_2O.

When acids react with alcohols, the following reversible reaction of *esterification*, formally analogous to neutralisation, slowly takes place:

$$RCOOH + HOR = H_2O + RCOOR$$

The resulting *esters* (generic formula RCOOR) are, consequently, substances which are analogous to salts in their method of formation. However, the latter differ very sharply in properties from esters, which, in the majority of cases, are colourless, highly volatile liquids sparingly soluble in water. The main reason for this divergence in properties between salts and esters is the wide difference in the polarity of the bonds O—M (M standing for a metal) on the one hand, and O—R on the other.

Esters include widely used organic solvents, perfumes, etc., as well as *fats*, that form part of almost all living organisms and are one of principal foodstuffs.

Owing to the reversibility of the esterification reaction, the resulting ester partially hydrolyses on reacting with water, forming an acid and an alcohol. Under the influence of water alone the hydrolysis (or *saponification* as it is called) of esters proceeds extremely slowly, but is considerably accelerated in the presence of acids and especially alkalis. Boiling with NaOH solution results in rapid saponification of an ester in accordance with the equation:

$$RCOOR + NaOH = ROH + RCOONa$$

In particular, soap is obtained in this way from natural fats, the former being a mixture of sodium (less often, potassium) salts of the organic acids contained in the initial fat.

15) *Fats* are esters of glycerol and various organic acids, chiefly *palmitic*, $C_{15}H_{31}COOH$, *stearic*, $C_{17}H_{35}COOH$ and *oleic*, $C_{17}H_{33}COOH$. The first two acids are saturated, while the latter contains one double bond in the molecule. Their relative amounts determine the properties of the fats: solid fats, e. g., mutton tallow, contain more esters of stearic and palmitic acids, while liquid fats such as sunflower oil, contain more esters of oleic acid.

16) Ordinary *soap* is essentially a mixture of sodium salts of stearic and palmitic acids. In addition, soap usually contains a number of admixtures, in particular, colouring substances and perfumes. An important by-product of soap production is glycerol.

The washing action of soap is due to its partial hydrolytic dissociation into a free alkali and fatty acids. The alkali removes the fatty substances in perspiration, which hold the dirt on the hands, linen, etc., while the colloidal particles of the fatty acid adsorb the dirt. The annual production of soap in the U. S. S. R. amounts to about 2 million tons.

Besides fats, animal and plant organisms contain substances that come under the headings of *carbohydrates* and *proteins*. In contrast to the derivatives considered above the molecules of which contain a hydrocarbon radical and a characteristic group (OH, CHO, etc.) of only one type, carbohydrates and proteins are *complex-function* compounds.

Molecules of carbohydrates usually contain a CHO group as well as several OH groups. Hence, carbohydrates possess the properties of both alcohols and aldehydes simultaneously. This class of substances, which includes such important foodstuffs as ordinary *sugar*, $C_{12}H_{22}O_{11}$, and *starch*, $(C_6H_{10}O_5)_x$, owes its name to the fact that in these compounds, hydrogen and oxygen are usually in the same proportions as in water, i. e., there are twice as many atoms of hydrogen as there are of oxygen. Therefore, the composition of the vast majority of carbohydrates may be expressed in the form $nC + mH_2O$, as though it were a compound of carbon and water.

Animal organisms contain relatively small amounts of carbohydrates. In plants, on the contrary, they form the bulk of the tissue. The latter consists mainly of cellulose, which has the same composition as starch but a larger molecular weight. While starch (in the form of flour, cereals, potatoes, etc.) is one of man's principal foodstuffs, cellulose provides him with the raw material for clothes (cotton, etc.), fuel (wood) and for his cultural needs (paper), not to mention a number of other products which are obtained by processing various vegetable fibres and wood.

17) The principal constituents of wood (as well as of the tissue of grasses, mosses, etc.) are *cellulose* $(C_6H_{10}O_5)_x$, and *lignin*—an organic substance of as yet undetermined structure, richer in carbon than cellulose. When dead plant organisms decay without access of air (at the bottom of marshes or under layers of rocks), volatile decomposition products are given off, and the residue is gradually enriched in carbon. This affects the chemical composition and the fuel value or calorific power of the decomposition product which, depending on its specific features, is called peat, brown coal, coal or anthracite. A table is given below comparing the chemical composition and calorific power of the organic substance of wood and various products of its decomposition.

Peat is a relatively young product, and it retains the structure of the plant (most frequently, moss) fibres of which it was formed. Although the age of brown coal runs into the millions of years, the structure of the original species of wood can also be seen in it. In older coals, this structure can be discerned only in rare cases. Finally, anthracite, formed from the vegetation of still more ancient epochs, is a grey-black dense mass, in which no traces of plant structure are perceptible.

Mineral coal is the principal industrial fuel. Between 1800 and 1900, its annual world production rose from 10 to 760 million tons. In 1950, it was about

Product	Moisture content in air-dry product (%)	Organic substance				
		Elementary composition (%)			Volatiles (%)	Calorific power (kcal/kg)
		C	H	O+N+S		
Wood	60	50	6	44	85	4500
Peat	50	57	6	37	67	5400
Brown coal	25	72	5	23	53	6700
Coal: long-flame	5	80	5	15	35	8100
Coal: gas	3	83	5	12	30	8400
Coal: rich	2	87	5	8	23	8700
Coal: lean	1	91	4	5	10	8650
Anthracite	0.5	96	2	2	5	8400

1.8 thousand million tons. The output of coal in the U.S.S.R. in 1963 was 532 million tons (as against 166 million tons in 1940, and 29 million tons in 1913).

18) Since, in spite of mechanisation, the mining of coal is highly labour-consuming, practical realisation of the idea of *underground gasification* of coal, originally put forward by Mendeleyev in 1888, is of great importance. Essentially, this consists of the production of combustible gas through incomplete combustion of the coal underground without bringing it to the surface.

The world's first industrial plant for underground gasification of coal was commissioned on the 1st of December, 1937 in the U.S.S.R. At present, the underground gasification of coal has become a conventional process.

19) Besides the direct use of coal as a fuel, a large amount of it is consumed in the production of *coke*, which is indispensible in metallurgy. This is produced by strongly heating coal without access of air. As a result, various volatile products are given off from the coal, and a grey-black sintered mass of coke remains in the ovens. Owing to the preliminary expulsion of volatiles, coke burns with hardly any flame, and this makes it particularly suitable for the smelting of metals from their ores. The calorific power of coke is about 8000 kcal/kg.

Important by-products of coking are coal tar (from which, in particular, benzene and toluene are obtained), ammonia and coke oven gas. The latter chiefly consists of approximately 60% H_2, 25% CH_4, 2% other hydrocarbons, 5% CO, 2% CO_2 and 5 or 6% N_2 (by volume).

Coke oven gas is a good initial product for the industrial production of hydrogen. For this purpose, the gas mixture is very strongly cooled, so that all its constituents, except H_2, are liquefied, while hydrogen remains in the gaseous state and can therefore be easily separated.

The organic compounds most important to life are proteins. In addition to carbon (50-55%), hydrogen (6.5-7.5%), oxygen (19-24%) and nitrogen (15-19%), proteins usually contain sulphur (up to 2.5%) and sometimes certain other elements (P, Fe, Cu, etc.). The structural formulas of natural proteins are, as yet, unknown. The study of their decomposition products has shown that the principal part in the formation of protein molecules is played by organic

compounds containing NH_2 and COOH groups, known as *amino-acids*. These compounds, which simultaneously possess both basic and acidic functions (owing to the NH_2 and COOH groups, respectively), are capable of combining with each other to form complex particles which are close in properties to the molecules of the simplest proteins. Thus, although the artificial synthesis of proteins has not yet been accomplished, some important steps have already been made in this direction.

20) The simplest aminoacid is *aminoacetic acid*, NH_2CH_2COOH, called *glycocoll* or *glycine*. It is a colourless crystalline substance, readily soluble in water. The acidic properties of glycine are very weak ($K = 2 \times 10^{-11}$). Its basic properties show up when it reacts with water: $OH_2 + NH_2CH_2COOH \rightleftarrows OH' + {}^{\cdot}HNH_2CH_2COOH$. These properties are even weaker than its acidic properties ($K = 3 \times 10^{-12}$). The joining of a number of molecules of glycine to each other with the elimination of water in accordance with the

$$\cdots\cdots \overline{H} \quad NHCH_2CO \quad \overline{OH+H} \quad NHCH_2CO \quad \overline{OH} \cdots\cdots$$

equation can serve as a simplified model of the process of formation of protein molecules.

21) Plant, and especially animal, organisms as a whole contain a much greater variety of chemical elements than proteins taken separately. As an example, the average chemical composition of a human being (according to Vernadsky) is given below, the elements being grouped in the descending order of their percentage by weight:

I. more than	10	O (65.04), C (18.25), H (10.05)
II. ditto	1	N (2.65), Ca (1.4)
III. ditto	0.1	P (0.8), K (0.27), Na (0.26), Cl (0.25), S (0.21)
IV. ditto	0.01	Mg, Fe
V. ditto	0.001	Zn, Si
VI. ditto	0.0001	Al, Br, Cu, F, I, Mn
VII. ditto	0.00001	As, B, Pb, Ti

22) The *food* consumed by man consists mainly of proteins, fats and carbohydrates. It is expended in two ways:

a) to build up and restore tissues, and regulate metabolism,

b) to cover the work performed by the organism and to maintain body heat.

In the former function *proteins* and various minor constituents of food (vitamins, mineral salts, etc.) are of fundamental importance. The function of a "fuel" in the organism is mainly performed by *fats* and *carbohydrates*. As a rough estimate of the heat supplied to the organism, it may be reckoned that, on the average, each gram of food protein provides 5 kcal, fats—9 kcal and carbohydrates —4 kcal.

The amount of energy which should be supplied to the human organism by food depends greatly on the climate, type of employment, weight of the body, sex, age, etc. A very rough average would be 3000 kcal per day. From the point of view of the best assimilation by the organism, it is advisable to apportion the average daily ration approximately in the following way: 100 g of proteins, 60 g of fats and 500 g of carbohydrates. Fats and carbohydrates may be partially substituted for one auother without any harm. But fats or carbohy-

drates should not be substituted for proteins to any considerable extent, because their principal function is essentially different.

For the proper functioning of the organism, it is very important that it receives a sufficient quantity of mineral salts and vitamins. The latter are complex organic substances, the content of which varies a great deal in different kinds of food. An insufficiency of vitamins in the organism results in unbalanced metabolism and various diseases.

As we have seen in the case of carbohydrates and proteins, the molecule of an organic compound need not necessarily contain only one characteristic group, but may contain two or more of them, each imparting its properties (usually somewhat modified owing to the proximity of other groups) to the whole molecule. This is one of the facts that account for the extraordinary diversity of organic substances.

A still more important factor in this respect is the possibility of *different arrangements of the atoms* within an organic molecule. To say nothing of substances of more or less complex composition, even one of the simplest hydrocarbons—butane, C_4H_{10},—has two possible structures:

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

normal butane isobutane

Indeed, two hydrocarbons are known, both corresponding to the general formula C_4H_{10}, but differing in properties. For example, normal butane boils at 0° C, while isobutane boils at —10° C. *Compounds that have the same composition and molecular weight, but different arrangements of atoms within the molecule, are called isomeric*, and the phenomenon of the existence of isomeric compounds (*isomers*) is called *isomerism*.

The number of possible isomers for a substance of a given composition can be established on the basis of the *theory of chemical structure* developed by Butlerov in 1861, according to which "the chemical nature of a complex particle is determined by the nature of the elementary constituents, by their quantity and chemical structure". Hence, each compound must have a definite structural formula corresponding to its composition and properties.

One of the most important elements of the theory of chemical structure is the *principle of the mutual influence of atoms*. This principle states, essentially, that the properties of each atom forming part of a chemical compound depend not only on its own nature, but also on the nature of the other atoms forming the compound. The atom in question is affected, not only by the atoms directly linked with it, but also by those farther off. Thus, in CH_3COOH, the only acidic hydrogen is that linked with the oxygen. A good example of

the clear-cut influence of atoms not directly linked with the one in question is the change in the dissociation constants in the series of acids: CH_3COOH (2×10^{-5})—$CH_2ClCOOH$ (1×10^{-3})—$CHCl_2COOH$ (5×10^{-2})—CCl_3COOH (1×10^{-1}). As can be seen from these data, the substitution of hydrogen by chlorine in the *methyl* radical of acetic acid causes a rapid increase in the acidity of the *carboxyl* hydrogen.

Chemical structure theory is the principal theoretical basis of organic chemistry. It asserts, in particular, that a substance of given composition can have as many isomers as there are different structural formulas which can be theoretically constructed for the substance. The conclusions of structure theory are fully confirmed by experiment: in all cases when they were tested, all the predicted isomers were actually obtained. The number of isomers rapidly increases with the number of atoms in the molecule. For example, whereas 75 isomers are possible for the hydrocarbon $C_{10}H_{22}$, 115 thousand are possible for $C_{20}H_{42}$, and more than 62 thousand million for $C_{40}H_{82}$.

The above shows the enormous importance of *structural* formulas in organic chemistry. Indeed, only structural formulas represent quite definite substances, whereas a simple formula provides a representation only of a more or less large group of substances, similar in composition but differing from one another in properties. At the same time, by indicating the arrangement of the individual bonds between the atoms in the molecule, the structural formula makes it possible to draw important conclusions concerning the properties of the compound. It consequently represents, as it were, a shorthand note of the chemical characteristics of the compound, which can easily be understood by an experienced chemist.

23) While the *general* formula for a particular substance is derived simply from the data of chemical analysis and the molecular weight determination (which present no difficulties in most cases), derivation of its *structural* formula often requires long and painstaking work, the starting point being the method of preparation of the compound, its chemical and physical properties, etc. As a very simple example, let us consider the reasoning involved in the study of a substance of the composition, C_2H_6O. In this case, structure theory provides for two isomers with the structural formulas given below:

$$A)\ CH_3—O—CH_3 \quad \text{and} \quad B)\ CH_3—CH_2—OH$$

Two compounds of the composition C_2H_6O are actually known. One of them boils at —24° C, and the other, at +78° C. One of them does not react with metallic sodium, while the other reacts with it, giving off hydrogen and only one hydrogen atom for each molecule of C_2H_6O. This last fact provides the key to the solution of the problem: it is obvious that the hydrogen which is displaced by sodium must be bound in the molecule in some way that is different from the others. Since such a hydrogen atom is present only in structure *B*, this structure must be assigned to the isomer of the composition C_2H_6O that reacts with Na, and which is called *ethyl alcohol*. Structure *A* must be assigned to the other isomer (*dimethyl ether*) on which sodium has no effect.

Organic compounds are of such unusual diversity that substances with an extraordinary wide range of properties are to be found among them. On the other hand, the finest transitions and variations in properties can be brought about. Owing to both these possibilities, organic compounds find the most varied applications in literally every walk of modern life, and are constantly acquiring new fields of application.

X-3. Silicon. The closest analogue to carbon—silicon—is the third most abundant element (after oxygen and hydrogen); it accounts for 16.7% of the total number of atoms in the earth's crust. While carbon may be regarded as the basic element for organic life, silicon plays a similar role with respect to the solid crust of the earth, since the bulk of the latter consists of various silicate rocks which are compounds of silicon, oxygen and a number of other elements.

The simplest method of preparing elementary silicon is by the reduction of its dioxide (SiO_2) with magnesium. The reaction is started by igniting a mixture of the finely ground substances, and takes place according to the equation:

$$SiO_2 + 2Mg = 2MgO + Si$$

To remove the MgO and excess SiO_2, the product of the reaction is treated successively with hydrochloric and hydrofluoric acids.

1) In practice, silicon is usually obtained in the form of an alloy with iron (*ferrosilicon*) by strongly heating a mixture of SiO_2, iron ore and carbon. Ferrosilicon finds its most important application in metallurgy, where it is employed as an additive for introducing silicon into various special steels and cast irons.

The properties of silicon greatly depend on the size of its particles. Amorphous silicon obtained by reducing SiO_2 with magnesium is a brown powder. By recrystallising it from certain molten metals, e. g., Zn, silicon can be obtained in the form of hard, but fairly brittle, grey crystals of sp. gr. 2.4. Silicon melts at 1415° C and boils at 2360° C.

Crystalline silicon is chemically inert, whereas amorphous silicon is considerably more reactive. The latter reacts with fluorine under ordinary conditions, and with oxygen, chlorine and sulphur at about 500° C. At very high temperatures, silicon is also able to combine with nitrogen and carbon. It is soluble in many molten metals, and with some of them forms compounds, e. g., Mg_2Si, called *silicides*.

Acids have no effect on silicon under ordinary conditions (with the exception of the mixture $HF + HNO_3$). Alkalis convert it into salts of silicic acid, with the liberation of hydrogen:

$$Si + 2NaOH + H_2O = Na_2SiO_3 + 2H_2$$

The most characteristic and stable compound of silicon is its *dioxide*, SiO_2, the formation of which from its elements takes place with a very large evolution of heat:

$$Si + O_2 = SiO_2 + 203 \text{ kcal}$$

Silicon dioxide is a colourless, solid substance melting only at 1713° C.

Free silicon dioxide (or silicic anhydride) is found in nature mainly in the form of the mineral *quartz*, which is the chief constituent of common sand. The latter is one of the main products of disintegration of rocks, and is at the same time, one of the most important building materials, the world consumption of which is about 500 million tons a year. Free silicon dioxide accounts for approximately 12% of the weight of the whole of the earth's crust. A much larger quantity of SiO_2 (about 43% of the weight of the earth's crust) is chemically combined in various rocks. All in all, consequently, over half of the earth's crust consists of silicon dioxide.

2) Large transparent crystals of quartz (sp. gr. 2.65) are often called *rock crystal*, the violet coloured variety is called *amethyst*, etc. Among the finely crystalline modifications of silicon (mixed with some other substances), are *agate*, *jasper*, and others.

3) An important refractory material, *dinas*, is manufactured from SiO_2. Dinas is obtained by roasting finely ground quartz, to which 2 or 2.5% of lime has been added, at 1500° C. Dinas brick softens only at about 1700° C, and is used, in particular, for lining the roofs of open-hearth furnaces.

SiO_2 is practically insoluble in water. Acids also have no effect on it, with the exception of HF, which reacts in accordance with the equation:

$$SiO_2 + 4HF = SiF_4 + 2H_2O$$

Alkalis gradually dissolve SiO_2, forming the corresponding salts of silicic acid (which are called *silicates*), e. g.:

$$SiO_2 + 2NaOH = Na_2SiO_3 + H_2O$$

In practice, silicates are usually prepared by fusing SiO_2 with the corresponding carbonates, from which CO_2 is liberated at a high temperature, e. g.:

$$SiO_2 + Na_2CO_3 = Na_2SiO_3 + CO_2$$

The net result of the reaction is that carbon dioxide is liberated by silicic acid.

Silicates are, as a rule, colourless, refractory and practically insoluble in water. One of the very few that are soluble is Na_2SiO_3. In practice, this salt is often called "soluble glass" and its aqueous solution "water glass".

4) Sodium silicate is produced in very considerable amounts (of the order of hundreds of thousands of tons annually), because "water glass" is used for the

reinforcement of foundation soils in building work and in a number of other industries. Its solutions must be kept in containers with rubber stoppers (since glass stoppers and corks tend to stick).

As silicic acid is very weak, "water glass" is very alkaline owing to hydrolysis, and silicates of weak bases are practically completely hydrolysed in solution. For the same reason, silicic acid is liberated from solutions of its salts by many other acids, among them carbonic acid.

While carbonic acid *in solution* displaces silicic acid from its salts, *strong heating*, as was pointed out above, causes the reverse displacement. The first process is due to the lower strength (degree of dissociation) of silicic acid, while the second is due to its lower volatility on heating. Since the order of volatilities of a series of acids may differ sharply from the order of strengths of the same acids, the sequence in which they displace one another in solution will also differ greatly from that in which they displace one another on heating. This is exemplified by the following scheme:

$$\xrightarrow[\text{displaced in solution}]{} \quad \text{HCl} \quad \text{H}_2\text{SO}_4 \quad \text{H}_3\text{PO}_4 \quad \text{H}_2\text{SiO}_3 \quad \xleftarrow[\text{displaced on heating}]{}$$

Free *silicic acid* is practically insoluble in water (as a true solution). However, it readily forms colloidal solutions, and therefore, usually precipitates only partially. The precipitate has the appearance of a colourless jelly, the composition of which corresponds not to the simple formula H_2SiO_3 (*meta*silicic acid) or H_4SiO_4 (*ortho*silicic acid), but to the more general formula, $xSiO_2 \cdot yH_2O$ with varying values of x and y, depending on the conditions of precipitation. When $x > 1$, the result is various *polysilicic* acids, and from the point of view of chemical composition, many minerals may be regarded as derivatives of these acids.

5) The dissolved part of silicic acid is but slightly dissociated ($K_1 = 3 \times \times 10^{-10}$, $K_2 = 2 \times 10^{-12}$). Natural hydrated forms of silica with $x \gg y$ are encountered as inorganic formations—*flint*, *opal*, *tripoli*, etc., and also as the remains of the shells of ancient minute marine organisms—*diatomite* ("infusorial earth"). The formation of peroxide compounds is not characteristic of silicon, nor have derivatives of peracids of this element been obtained.

Salts are known for the hydrated forms of silicic acids with a great variety of values of x and y. Products of complete or partial replacement of the hydrogen in them by different metals are called *simple* silicates. An example is the mineral *asbestos*, $Mg_3H_4Si_2O_9$ or $3MgO \cdot 2H_2O \cdot 2SiO_2$.

Complex silicates which, from the point view of chemical composition, are mainly derived from acids of the general formula $xE_2O_3 \cdot$

$\cdot y SiO_2 \cdot z H_2O$, are much more abundant. The most important compounds of this type are the *alumosilicates* (E=Al), especially those that fall within the group of *feldspars* which account for more than half of the weight of the earth's crust. The minerals

orthoclase	$K_2Al_2Si_6O_{16}$	or	$K_2O \cdot Al_2O_3 \cdot 6SiO_2$
albite	$Na_2Al_2Si_6O_{16}$	"	$Na_2O \cdot Al_2O_3 \cdot 6SiO_2$
anorthite	$CaAl_2Si_2O_8$	"	$CaO \cdot Al_2O_3 \cdot 2SiO_2$

may be quoted as their principal representatives.

6) The spatial structure of a number of silicates has been studied by means of X-rays. These studies have shown that the structures examined may be classified into a few types differing from one another in the way the tetrahedral ions, SiO_4^{4-}, are combined.

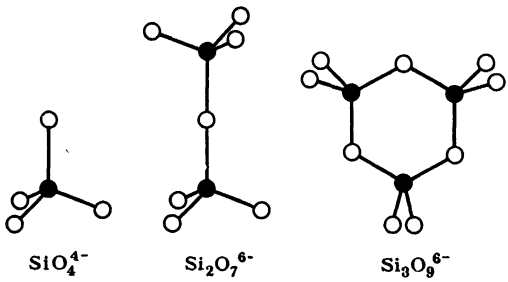


Fig. 142. Simplest silicate anions

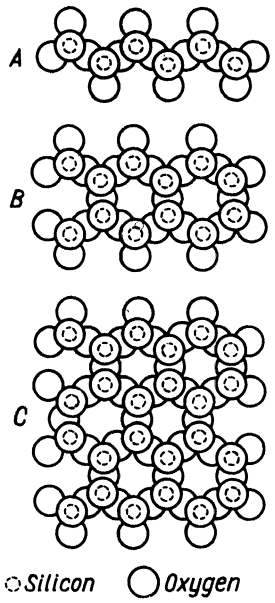


Fig. 143. Group silicate structures

Some of these types correspond to the simplest silicate anions. As can be seen from Fig. 142, this applies primarily to those cases where the space lattice nodes are filled by individual SiO_4^{4-} ions.

The lattice nodes of the second type are filled by $Si_2O_7^{6-}$ ions (consisting of two tetrahedral SiO_4^{4-} ions with a common corner), and those of the third type, by cyclic $Si_3O_9^{6-}$ ions (consisting of three tetrahedral SiO_4^{4-} ions with two corners common to each of them).

The other types of silicate structures may be called *group* structures, since they are composed of a theoretically infinite number of SiO_4^{4-} tetrahedra. These combinations (Fig. 143) may have the form of a single chain (*A*), a double chain (*B*) or a sheet (*C*). Finally, there are types with three-dimensional structures. In all such lattices, part of the Si^{4+} ions may be substituted by Al^{3+} ions, etc., and part of the O^{2-} ions may be substituted by OH^- ions, etc. At the same time, part of the ions contained in the silicate (K^+, Na^+, etc.) may be located between the chains or planes, as well as in the spaces of the three-dimensional structure.

Under the combined action of various natural factors, chiefly carbonic acid and water, mineral silicates, aluminosilicates, etc., are gradually decomposed (*weathered*), the soluble products being carried

away by rivers into the ocean, while the insoluble products are partially deposited on the spot, partially settle on the river beds or are carried out into the sea. The principal insoluble weathering products of the most abundant aluminosilicates are *silica*, SiO_2, which is deposited as *sand*, and *kaolin*, $H_4Al_2Si_2O_9$ or $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, which is the basis of common *clays* (coloured brown by impurities of ferric oxide) and which in a purer state sometimes forms deposits of white clay. The process of their formation on decomposition of an aluminosilicate may be represented by the following exemplary equation:

$$K_2Al_2Si_6O_{16} + CO_2 + 2H_2O =$$
orthoclase
$$= K_2CO_3 + H_4Al_2Si_2O_9 + 4SiO_2$$
kaolin silica

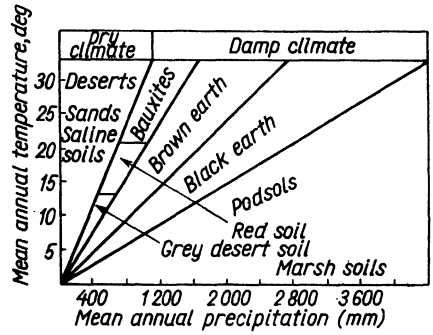


Fig. 144. Diagram of soil-type formation

Sand and clay are the principal mineral constituents of all types of soils. The nature of the latter depends chiefly on the temperature and humidity in the particular locality (Fig. 144).

The most important of man-made insoluble silicates is *glass*, which has been known to mankind since ancient times. The composition of "normal" glass is represented by the formula, $Na_2CaSi_6O_{14}$ or $Na_2O \cdot CaO \cdot 6SiO_2$ and approaches that of ordinary window glass. By suitably varying this basic composition, different special kinds of glass can be obtained, possessing the properties required for different applications.

The principal raw materials for glass manufacture are soda, limestone and sand. The formation of "normal" glass may be represented by the equation:

$$Na_2CO_3 + CaCO_3 + 6SiO_2 = 2CO_2\uparrow + Na_2O \cdot CaO \cdot 6SiO_2$$

The mixture of initial materials is heated to approximately 1400° C and is maintained in the molten state until the gases are completely expelled, after which it is subjected to further processing.

Although glass is on the whole practically insoluble, water partially decomposes its surface, washing out mainly sodium. The action of acids (except hydrofluoric acid) is similar to that of water—glass which has been in contact for some time with water or acids is practically not decomposed by them any further. On the other hand, owing to the considerable predominance of SiO_2 in the composition of glass, the effect of alkalis upon it is of a lasting nature. For this

reason, alkaline solutions stored in glass vessels usually contain dissolved silicates as impurities.

7) In the manufacture of glass, soda is often replaced by a cheaper mixture of sodium sulphate and carbon. In this case, the reaction proceeds as follows: $Na_2SO_4 + C + CaCO_3 + 6SiO_2 = Na_2O \cdot CaO \cdot 6SiO_2 + CO\uparrow + SO_2\uparrow + CO_2\uparrow$.

8) X-ray investigations have shown that the vitreous state of a substance (like the liquid state) is distinguished from the crystalline state by incomplete orderliness in the relative position of the elements of the space lattice. Fig. 145 shows diagrams of the structures of Al_2O_3 in the crystalline (*A*) and vitreous (*B*) states. As can be seen from these diagrams, the hexagons characteristic of the Al_2O_3 lattice are not strictly maintained in the vitreous state, but the general arrangement of the particles is similar to that in the crystal.

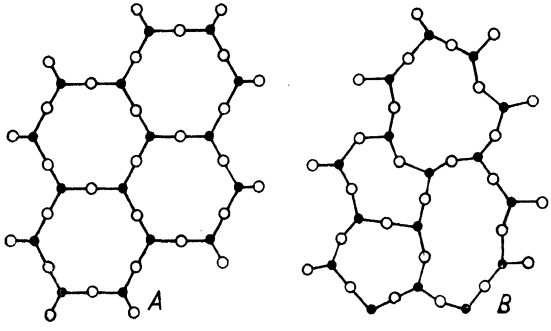


Fig. 145. Arrangement of atoms in Al_2O_3 in the crystalline and vitreous states

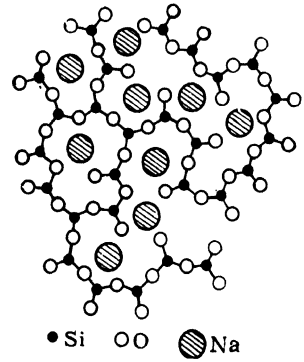


Fig. 146. Arrangement of atoms in sodium silicate glass

The diagram of the structure of sodium-silicate glass shown in Fig. 146 gives an idea of the arrangement of the metallic ions in the lattice: these ions are located in the vacancies of the silicate lattice without any definite system. Since this lattice exhibits no strictly regular repetition of structural elements, the stability of the individual bonds in the lattice is unequal. Therefore, glass, in contrast to a crystal, has no definite melting point, and softens gradually when heated.

9) The production of *quartz* glass, which in chemical composition is almost pure silica, SiO_2, began comparatively recently. Its most valuable advantage over ordinary glass is that its coefficient of thermal expansion is approximately 1/15 of the latter. Owing to this, a quartz vessel withstands very sharp changes in temperature without cracking: it may, for example, be heated to red heat and immediately plunged into water. On the other hand, quartz glass is almost completely transparent to ultraviolet rays which are strongly absorbed by ordinary glass. The disadvantage of quartz glass is its great brittleness compared to ordinary glass.

Halogen derivatives of silicon of the general formula SiX_4 can be prepared by direct synthesis in accordance with the equation: $Si + 2X_2 = SiX_4$. All the halogens of the SiX_4 type are colourless. Under ordinary conditions, SiF_4 is a gas, $SiCl_4$ and $SiBr_4$ are liquids and SiI_4 is a solid.

The most characteristic chemical property of the silicon halides is their vigorous interaction with water according to the equation:

$$SiX_4 + 2H_2O \rightleftarrows SiO_2 + 4HX$$

In the case of Cl, Br and I, the equilibrium is practically completely displaced to the right, whereas in the case of F, the reaction is reversible. Owing to the formation of solid particles of SiO_2 (more accurately $xSiO_2 \cdot yH_2O$) on hydrolysis, the vapours of the silicon halides fume in moist air.

10) Some constants of the silicon halides are compared below:

Substance	SiF_4	$SiCl_4$	$SiBr_4$	SiI_4
Melting point (°C)	—77 (pressure)	—68	+5	124
Boiling point (°C)	—90 (sublimes)	+57	155	290

Considerable amounts of SiF_4 are obtained as a by-product of superphosphate production. Silicon tetrafluoride is highly poisonous.

SiF_4 reacts with HF to form *hydrofluorosilicic acid*, a complex compound:

$$2HF + SiF_4 = H_2[SiF_6]$$

In the vapour state this reaction is perceptibly reversible, but in an aqueous solution its equilibrium is displaced to the right. No analogous complex acids of the type H_2SiX_6 are formed with the other halogens.

Free H_2SiF_6 is a strong dibasic acid. The majority of its salts (called *silicofluorides*) are colourless and readily soluble in water.

11) Owing to the formation of H_2SiF_6, the equation for the hydrolysis of SiF_4 is more accurately expressed in the following way: $3SiF_4 + 2H_2O = 2H_2SiF_6 + SiO_2$. Hydrofluorosilicic acid is usually obtained in this way.

Free H_2SiF_6 is used in beer brewing (as a disinfectant), and the slightly soluble silicofluorides of Na and Ba are used to combat agricultural pests. Under the commercial name of "fluates" the readily soluble silicofluorides of Mg, Zn and Al are used in building work (for waterproofing cemented surfaces).

12) White *silicon sulphide*, SiS_2, is formed by fusing "amorphous" silicon with sulphur. It is slowly decomposed by water into SiO_2 and H_2S.

13) Silicon combines with nitrogen only above 1300° C. The resulting *silicon nitride* Si_3N_4 is a white powder. On boiling with water it hydrolyses slowly to SiO_2 and NH_3.

14) If a mixture of SiO_2 and carbon is heated to 2000° C in an electric furnace, *silicon carbide*, SiC, commonly known as *carborundum*, is formed. The reaction proceeds in accordance with the equation: $SiO_2 + 3C = 2CO + SiC$. Pure carborundum forms colourless crystals, but the commercial product usually has a dark colour owing to impurities. The most important property of carborundum practically is its hardness, which is only slightly less than that of diamond. Therefore carborundum is widely employed for processing hard materials. In particular, grinding wheels are usually made of it.

15) Carborundum is a fairly good electrical conductor, and is employed in the manufacture of electric furnaces. A material more frequently employed for this purpose known as *silit*, is obtained by roasting a mixture of carborundum,

silicon and glycerol at 1500° C in an atmosphere of CO and N_2. Silit is characterised by mechanical strength, chemical stability and good thermal conductivity which increases with increasing temperature.

Hydrogen compounds of silicon (*silicon hydrides* or *silanes*) are obtained mixed with each other and with hydrogen by the action of dilute HCl on magnesium silicide, Mg_2Si. In composition and structural formulas, the silicon hydrides (SiH_4, Si_2H_6, etc., up to the last known member, Si_6H_{14}) are analogous to the hydrocarbons of the methane series. The two series are also very similar in *physical* properties. On the other hand, the overall *chemical* nature of the two classes of compounds differs greatly: in contrast to the very inert hydrocarbons, the silanes are extremely reactive. They readily ignite in air and burn to SiO_2 and water with a large evolution of heat, e. g., in accordance with the reaction:

$$SiH_4 + 2O_2 = SiO_2 + 2H_2O + 308 \text{ kcal}$$

16) As the number of silicon atoms in the molecule increases, the stability of silanes rapidly decreases. The constants of the first members of the series are given below:

Substance	SiH_4	Si_2H_6	Si_3H_8	Si_4H_{10}
Melting point (°C)	—185	—129	—117	—91
Boiling point (°C)	—112	—14	+53	107

All the silanes are colourless, they have a characteristic odour and are highly poisonous. They are slowly decomposed by water with the liberation of hydrogen, e. g.: $SiH_4 + 4H_2O = 4H_2 + Si(OH)_4$.

17) A large number of different *organosilicon* compounds are known for silicon, these being analogous in many respects to the corresponding derivatives of carbon. As a rule, they are stable in air and insoluble in water. Synthesis of high molecular derivatives of this type made possible their wide practical application for the manufacture of varnishes and resins featuring high thermal stability and a number of other valuable properties.

X-4. Colloids. Silicic acid, which was considered in the previous section, is a typical representative of substances that exhibit a pronounced tendency towards the formation of colloidal solutions. Therefore, when it is liberated from its salts, only part of the resulting silica hydrate usually precipitates. By suitably altering the concentrations of the solutions, it is possible to choose conditions in which no precipitate is formed, and the whole of the silicic acid remains in the colloidal-dissolved state.

As has already been noted (V-1), with regard to the sizes of the dispersed particles, colloidal solutions fall between suspensions, on the one hand, and molecular solutions, on the other. Roughly speaking, particle sizes from 1 to 100 mμ may be regarded as the range of the colloidal state of a substance. Magnified a million times, molecules would appear as more or less large dots, particles of fine suspensions would acquire the size of a large apple, and the whole inter-

mediate range of sizes would provide various gradations of the colloidal comminution of a substance.

A disperse system containing particles of colloidal sizes dispersed in a medium is known as a *colloidal solution* or *sol*. In practice, the most important of the various sols are *hydrosols*, i. e., colloidal systems in which the medium is water.

Like the molecules of a true solution, the colloidal particles of sols are in continuous random motion. Although the intensity of this motion rapidly decreases with increasing particle size, it is still sufficient to counteract the force of gravity in the case of colloidal solutions. Therefore, colloidal particles do not separate out spontaneously from the medium in which they are dispersed. On the other hand, such spontaneous separation due to gravity is characteristic of the coarser particles in suspensions, and this outwardly distinguishes the latter from colloidal solutions.

In most cases colloidal solutions can be distinguished from molecular solutions by their different *optical* properties. If an intense beam of light is passed through a beaker containing a colloidal solution, a luminous cone, quite visible in a darkened room, will be formed as a result of scattering of the light by the colloidal particles in the solution. In contrast, a true solution placed in the same conditions appears to be "optically void", since the particles of molecular dimensions it contains do not scatter light to an appreciable extent. The opalescence frequently observed in colloidal solutions, i. e., their cloudy appearance in reflected light, is also due to the scattering of light.

Apart from their optical properties, colloidal and molecular solutions also differ in many other respects. Since colloidal particles are much larger than individual molecules, the number of such particles in unit volume is much smaller at the same total concentration of the dispersed substance. Owing to this, the variations in the properties of solutions, related to the number of dissolved particles (osmotic pressure, freezing point depression, etc.), are quite negligible in colloidal solutions.

The essential peculiarity of the colloidal state of a substance, directly connected with the small size of its particles, is the enormous increase in total *surface area*. Consider a cube with edges 1 cm long: its volume will be 1 cm^3, and its total surface area 6 cm^2. If we divide this cube into smaller cubes, the total volume remains the same, but the total surface area will increase very rapidly, as can be seen from the table on page 310.

In the size range of colloidal particles (100 mμ-1 mμ), the *dispersion* of a substance, i. e., the ratio of its surface area to its volume, is enormous. In connection with this, all processes taking place at the interface between two phases, in particular, adsorption, are especially characteristic of colloids.

Length of edge of cube	Number of cubes in 1 cm³	Total surface area	Length of edge of cube	Number of cubes in 1 cm³	Total surface area
1 cm	1	6 cm²	1 μ	10^{12}	6 m²
1 mm	10^3	60	100 mμ	10^{15}	60
100 μ	10^6	600	10 mμ	10^{18}	600
10 μ	10^9	6000	1 mμ	10^{21}	6000

1) The pore diameter of ordinary filter paper is 10,000-3000 mμ, and therefore the particles of fine suspensions, as well as those of all colloidal solutions, readily pass through it. The same applies to "close" filters with pore diameters down to 1000 mμ. Glass filters usually have pores ranging in diameter from 100,000 to 10,000 mμ, while the pores of special porcelain and clay filters are down to 100 mμ in diameter. The latter fully retain suspended particles, but allow particles of colloidal solutions to pass through. These particles may be retained by films of certain substances, e. g., collodion, which serve for the manufacture of *ultrafilters*. The closest ultrafilters have pores with diameters down to 1 mμ, and retain not only all colloidal particles, but certain particularly bulky molecules of true solutions as well.

Since the sizes of colloidal particles are intermediate between suspended particles and molecules, a substance in the colloidal state may be prepared in two ways: either by breaking down larger particles, or, by the formation of aggregates from separate molecules. Methods of the first type are known as *dispersion* methods, and those of the second, as *condensation* methods. The simplest dispersion method in principle is mechanical grinding of the original substance. In this way, particles with diameters down to 10 mμ may be obtained by using a special colloid mill.

More frequently employed are condensation methods based on various chemical reactions leading to the formation of substances that are practically insoluble in the chosen medium. By adjusting the conditions of the process, the substances can be precipitated as colloidal particles of the desired dimensions.

In regard to the liquid phase in which they are dispersed, colloidal particles fall into two large groups. The members of one of these groups adsorb molecules of the medium on their surfaces, and form with them more or less stable complexes of the solvate type. These are called *lyophilic* colloids (in the special case of water, *hydrophilic* colloids). Each particle of a lyophilic colloid is surrounded by a liquid film which is bound to it and which does not completely collapse even when the particles adhere to one another. Owing to this, when larger aggregates are formed, the liquid phase is also included in their composition.

The members of the other group of colloids do not adsorb molecules of the liquid phase. These are known as *lyophobic* colloids (in

the particular case of water, *hydrophobic* colloids). In their sols, the individual particles are not surrounded by a film of the liquid phase, and when larger aggregates are formed they include no liquid phase. An example of a hydrophobic colloid is arsenic pentasulphide, and examples of hydrophilic colloids are silicic acid and ferric oxide.

Besides the medium in which they are dispersed, colloidal particles can adsorb other molecules present in the liquid phase, and, what is particularly important, they can also adsorb ions. In the latter case, they themselves become electrically charged. Since the properties of the surfaces of identical colloidal particles are the same, they all become similarly charged: those preferentially adsorbing cations become positively charged (*electropositive* colloids), and those mainly adsorbing anions become negatively charged (*electronegative* colloids). In particular, under ordinary conditions of preparation, the hydrosols of metal oxides are electropositive, and hydrosols of sulphides (as well as of silicic acid) are electronegative.

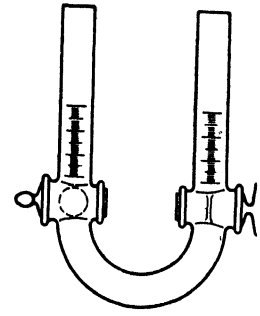


Fig. 147. Apparatus for electrophoresis

The sign of the charge of colloidal particles can be determined by experiment, since under the influence of a direct electric current electropositive colloids move towards the cathode, and electronegative colloids, towards the anode. To study this phenomenon (which is called *electrophoresis*), the hydrosol under examination is placed in the lower part of a U-tube provided with cocks (Fig. 147), after which both cocks are closed, the upper part of the apparatus is washed out, filled with water, and electrodes are immersed in the latter. After both cocks have been opened and a direct current applied, electrophoresis begins. The movement of the colloidal particles from one electrode to the other is particularly easy to observe in the case of coloured sols, by the change in level of the coloured layer of the liquid in the limbs of the tube.

Electrophoresis has a number of industrial applications. For example, in the production of porcelain it helps to remove ferric oxide impurities from the clay. The method is based on the fact that particles of clay suspended in water are negatively charged, whereas the particles of ferric oxide are positively charged. When an electric current is passed through the suspension, very pure clay collects at the anode.

It follows from the above that in addition to the original substance from which it was derived, a colloidal particle may include in its composition solvent molecules closely associated with it and adsorbed ions. Moreover, there inevitably must be ions of opposite sign in the surrounding medium near the particle. The colloidal particle

together with all these additions is known as a *micelle*, while the part of the latter containing only the molecules and ions *directly* associated with the colloidal particle, is known as a *granule*.

For example, besides Fe_2O_3, the hydrosol of ferric oxide resulting on hydrolysis of $FeCl_3$, contains water, $Fe^{\cdot\cdot\cdot}$ ions adsorbed by the colloidal particle, and Cl' ions surrounding it in the liquid phase. The general formula of a micelle of this hydrosol is $x Fe_2O_3 \cdot y H_2O \cdot z Fe^{\cdot\cdot\cdot} + 3z Cl'$, while the formula of the granule is $x Fe_2O_3 \cdot y H_2O \cdot z Fe^{\cdot\cdot\cdot}$. Similarly, the general formula of a micelle of the hydrophobic sol of As_2S_3 is $x As_2S_3 \cdot z SH' + z H^{\cdot}$, while that of the granule is $x As_2S_3 \cdot z SH'$. Schematically, this is often represented thus:

$$\left[\begin{array}{|c|}\hline Fe_2O_3 \\ \\ H_2O \\ \hline\end{array}\right] Fe^{\cdot\cdot\cdot} + 3Cl' \quad \text{and} \quad \underline{\overline{|As_2S_3|}\, SH' + H^{\cdot}}$$

Such schematic formulas for micelles and granules represent their composition only qualitatively, i. e., indicate their constituents, but give no idea of the relative amounts of these constituents.

Although there is mutual attraction between the particles of each sol in accordance with the law of gravitation, the forces arising in this way are very weak. Of much greater importance for the mutual attraction between the particles is the interaction of their surface layers (cf. Fig. 99). However, this is appreciable only on sufficiently close contact due to collisions between the randomly moving sol particles.

The result of operation of the attraction forces is *coagulation* of the sol, i. e., the adherence of the particles to one another, and the formation of more complex aggregates. Having reached a certain size, the particles can no longer remain in the suspended state, and settle out from the dispersion medium, the result being *sedimentation* of the colloid. It follows, therefore, that coagulation is the process of enlargement of the sol particles, and sedimentation is the result of this process. However, the term coagulation is often understood to cover both.

The most important factor impeding coagulation is the presence of electrical charges on the colloidal particles. Owing to the similarity of charges, it is only in very rare cases that particles moving towards one another succeed in coming together close enough for the forces of attraction to become sufficiently effective. As a result, a sol containing highly charged colloidal particles will not coagulate appreciably even on standing for a long time, i. e., it is very stable.

It is evident that removal of the electrical charge (even partial) from the colloidal particles should lower the stability of the sol and promote its coagulation. In the case of hydrosols, the simplest way to remove the charges is by adding an electrolyte to the colloidal

solution. Although an equal number of positive and negative charges is thus introduced, ions of opposite charge always slightly predominate in the "ionic atmosphere" immediately surrounding the colloidal particle, and are preferentially adsorbed by the particle. Since the introduction of an electrolyte greatly increases the total concentration of ions in the solution, the conditions for their adsorption become very favourable and the initial charge of the particles is rapidly neutralised, causing coagulation of the sol. Natural coagulation by electrolytes is a common occurrence in river estuaries, where colloids and suspensions carried down by the river settle out under the influence of the salts in sea water.

Coagulation of hydrophobic colloids by electrolytes usually takes place readily, and relatively small quantities of ions are sufficient to cause sedimentation. On the other hand, the coagulation of hydrophilic colloids, the particles of which are covered with a layer of adsorbed molecules of water, is often much more difficult, and sedimentation sometimes sets in only at very high concentrations of the electrolyte.

Colloid precipitates (*coagulums*) have a varied structure. Lyophobic colloids do not entrain the liquid phase during sedimentation, and separate out in the form of fine powders or flakes. On the other hand, lyophilic colloids entrain more or less considerable quantities of the liquid phase, and this accounts for the *gelatinous* nature of their precipitates. Sols of certain lyophilic colloids, such as gelatin, even congeal into a gelatinous mass (jelly). Such coagulums, which contain entrained liquid phase, are usually called *gels* (or *hydrogels* when the liquid phase is water).

2) Depending on the behaviour of the precipitates towards water (or any other liquid phase), colloids may be *reversible* or *irreversible*. Precipitates of the former, on coming in contact with pure water, pass back into it to form a sol. Gum arabic, for example, behaves in this way. On the other hand, precipitates of irreversible colloids will not pass spontaneously into the liquid phase on mere contact with it. Examples of irreversible colloids are silicic acid, ferric oxide and As_2S_3.

3) Sols that do not form on mere contact of the precipitates of irreversible colloids with pure water, may sometimes be obtained if a small amount of electrolyte is added to the water. The electrolyte ions are adsorbed by the precipitate particles, which thus acquire like charges; as a result, the particles begin to repell one another and are dispersed throughout the liquid phase. The formation of a sol by the action of very small concentrations of electrolytes on the precipitates of irreversible colloids is called *peptisation*, which is one of the most important dispersion methods for obtaining sols.

Another type of disperse systems of ever growing importance are those formed in a gaseous medium by particles of solid substances (*smokes*) or droplets of liquids (*fogs*). If the medium is air, these systems are called *aerosols*. An example of an aerosol is tobacco smoke (mean diameter of particles 0.25 μ).

In a high-intensity electric field, the particles of an aerosol undergo electrophoresis; on reaching the electrodes, they lose their charge and are precipitated. The electrophoresis of aerosols has a number of very important practical applications connected with removal of suspended solid and liquid particles from gases. This is essential for certain production processes (e. g., the purification of SO_2 in the contact process for H_2SO_4), while in others, it helps to collect various valuable products carried away in the form of dust by waste gases. Finally, the electrophoresis of aerosols is very important from the sanitary and hygienic point of view, since it permits removal of harmful industrial waste products from exhaust gases discharged into the atmosphere.

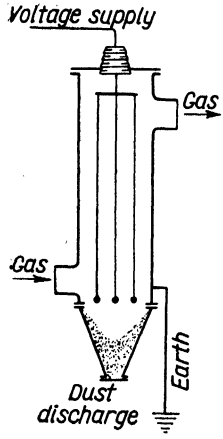


Fig. 148. Electrostatic precipitator

4) A diagram of an electrostatic precipitator for the removal of dust from waste gases is shown in Fig. 148. Its principal working part is a metallic cylinder with wires running along its axis; the wires are insulated from the walls and are stretched by loads. The latter are connected to the negative pole of a direct current source, which sets up a potential difference of about 100 thousand volts between the wires and the earthed walls of the cylinder. Under these conditions, the wires emit a continuous stream of electrons, which impart a negative charge to the dust particles suspended in the gas. The charged particles are attracted to the cylinder walls where they give up their charge and fall into the bottom chamber, from which the dust is periodically discharged. Besides the tubular electrostatic precipitators described above, screen precipitators are also employed. In these, the earthed electrodes are flat metal screens with wires under tension stretched between them.

The rapid development of the chemistry of colloids is due to the great importance of the phenomena studied by this science in human practice. Such apparently entirely different problems as the vital processes in organisms, the formation of certain minerals in nature and the texture and productivity of soils are actually closely connected with the colloidal state of a substance. Colloid chemistry is also the scientific basis of many industrial processes (artificial fibres, plastics, etc.).

X-5. The Germanium Subgroup. The content of the elements of this subgroup in the earth's crust varies only slightly in the order: *germanium* (2×10^{-4}%)—*tin* (6×10^{-4}%)—*lead* (1×10^{-4}%). Germanium is one of the greatly dispersed elements. The principal form of naturally occurring tin is the mineral *cassiterite* or *tinstone*, SnO_2, while that of lead is *galena*, PbS.

Germanium is not extracted on any considerable scale as yet. Small quantities are obtained as a by-product in the processing of

certain zinc ores. Tin is smelted by the reduction of cassiterite with coal. The usual method for processing galena is to convert it into PbO by heating in air, and reducing the resulting lead oxide to the metal with coal:

$$2PbS + 3O_2 = 2SO_2 + 2PbO \quad \text{and} \quad PbO + C = CO + Pb$$

With respect to physical properties, Ge, Sn and Pb are typical metals. Some of their constants are compared below:

Properties	Ge	Sn	Pb
Colour	greyish-white	silvery-white	bluish
Specific gravity	5.4	7.3	11.3
Melting point (°C)	937	232	327
Boiling point (°C)	2850	2720	1740
Electrical conductivity (Hg = 1)	0.001	8	5

The hardness and brittleness of these elements rapidly decrease in the order Ge—Sn—Pb: while germanium is fairly hard and very brittle, lead can be scratched with the fingernail and rolled into thin sheets. Tin occupies an intermediate position. All the elements of the germanium subgroup readily form alloys with one another and with many other metals. In some cases, chemical compounds (of the type Mg_2E, for example) are formed on fusion.

1) Metallic *germanium* has an important, though restricted, application in radio engineering. *Tin* is chiefly used for plating iron to protect it from corrosion ("tin plate" in the canning industry). *Lead* is employed in the manufacture of storage battery plates, electric cable sheathing, bullets and shot, for protection against X-radiation and γ-rays, and as a corrosion-resisting material in the chemical industry (pipelines, etc.). Major amounts of tin and lead are used in the manufacture of a number of industrially important alloys. At present the annual world production of tin is about 200 thousand tons, while that of lead is about 2 million tons.

2) Besides ordinary tin (sp. gr. 7.3), two other allotropic modifications of this element are known. The grey powdery form of sp. gr. 5.8 is stable below +13° C. The rate at which ordinary tin changes into the powdery variety is very slow. Therefore, this conversion, resulting in the transformation of a tin object into a grey powder, does not usually take place on cooling. However, it is observed on some ancient tin vessels and medals.

Above 161° C, tin changes (fairly rapidly from 200° C upwards) into a modification of sp. gr. 6.6, which is very brittle. Therefore, tin which has been heated above 200° C can be easily ground into a fine powder.

Under the influence of atmospheric oxygen, germanium and tin do not change, but lead oxidises. That is why lead objects do not have a lustrous metallic appearance. A film of oxide protects the

metal from further oxidation very well under ordinary conditions, but oxidation proceeds further on heating, and the lead is gradually completely oxidised. On heating in air, tin is also oxidised. Germanium reacts with oxygen only above 700° C. All three elements can combine with the halogens and with sulphur.

Water has no effect on germanium and tin, but it gradually removes the oxide film from lead, and this promotes further oxidation of the latter. In the electromotive series Ge lies between copper and silver, while Sn and Pb come before hydrogen. The best solvent for lead is dilute nitric acid, while for germanium and tin it is aqua regia. The reactions of both elements with the latter take place according to the equation:

$$3E + 4HNO_3 + 12HCl = 3ECl_4 + 4NO + 8H_2O$$

All the derivatives of lead are highly poisonous.

3) The behaviour of the elements of the germanium subgroup towards individual acids is substantially different. *Hydrochloric* acid has no effect on germanium. Tin is only very slowly dissolved in dilute HCl, whereas with the concentrated acid, a reaction readily takes place (especially on heating) in accordance with the equation: $Sn + 2HCl = SnCl_2 + H_2$. On reacting with HCl, lead is covered with a layer of sparingly soluble $PbCl_2$ which prevents further solution of the metal. The reaction between lead and *sulphuric* acid proceeds in a similar manner, provided the strength of the latter does not exceed 80%. At higher concentrations of H_2SO_4, the soluble acid salt $Pb(HSO_4)_2$ is formed, which does not protect the lead from the further action of the acid. Dilute sulphuric acid has no effect on germanium and has hardly any on tin. Both elements dissolve in hot concentrated H_2SO_4 in accordance with the equation: $E + 4H_2SO_4 = E(SO_4)_2 + 2SO_2 + 4H_2O$. When Ge reacts with *nitric* acid, a precipitate of the hydrated dioxide, $xGeO_2 \cdot yH_2O$, is formed. Concentrated nitric acid reacts with tin in a similar manner: $Sn + 4HNO_3 = SnO_2 + 4NO_2 + 2H_2O$. On the other hand, tin dissolves slowly in very dilute cold HNO_3 with the formation of $Sn(NO_3)_2$. Hydrogen is not liberated in this reaction, being used up in reducing the nitric acid. When HNO_3 reacts with lead, $Pb(NO_3)_2$ is formed in accordance with the reaction: $3Pb + 8HNO_3 = 3Pb(NO_3)_2 + 2NO + 4H_2O$. This salt is insoluble in concentrated HNO_3, and protects the metal from the further action of the acid. On the other hand, it is readily soluble in water, and therefore, lead dissolves well in dilute nitric acid.

Solutions of *alkalis* have hardly any effect on germanium. Tin and lead are slowly dissolved in strong alkalis according to the equation: $E + 2NaOH = Na_2EO_2 + H_2$. The solubility of tin in alkalis is taken advantage of for removing it from old tin cans, after which the metal is electrolytically extracted from the solution. Owing to the high cost of tin, its reclamation is of great economic importance.

The positive valencies characteristic of germanium and its analogues are 4 and 2. Therefore, two series of derivatives are known for these elements. For germanium, those compounds in which it is tetravalent are far more typical. In tin, the difference is not so sharp although under ordinary conditions the derivatives of tetravalent Sn are more stable. For lead, however, those compounds in which

it is divalent are much more typical. Accordingly, the derivatives of divalent Ge and Sn are reducing agents (very strong ones), while the compounds of tetravalent Pb are oxidising agents (also very strong ones). But the conversion from a lower to a higher positive valency, as a rule, takes place more readily in alkaline solution, while the reverse conversion takes place more readily in acid solution. Therefore, the reducing properties of divalent Ge and Sn are stronger in alkaline solution than in acid solution, while tetravalent Pb, which is a very strong oxidising agent in acid solution, does not behave as such in alkaline solution.

For the elements of the germanium subgroup, oxides of the types EO and EO_2 are known. The former are usually called *oxides*, and the latter, *dioxides*. On heating in air, Ge and Sn form their *highest oxides*, while Pb forms its *lowest* oxide. The others can be obtained only by indirect methods. For example, PbO_2 is usually obtained by the reaction between lead acetate and bleaching powder:

$$Pb(CH_3COO)_2 + Ca(Cl)OCl + H_2O = PbO_2\downarrow + CaCl_2 + 2CH_3COOH$$

All these oxides are solids, GeO and SnO being black, PbO yellowish-red, GeO_2 and SnO_2 white and PbO_2 dark brown.

Since these oxides hardly combine with water, their corresponding *hydroxides* are usually obtained by the action of strong alkalis on solutions of the corresponding salts, for example, in accordance with the reactions:

$$SnCl_4 + 4NaOH = 4NaCl + Sn(OH)_4$$
$$Pb(NO_3)_2 + 2NaOH = 2NaNO_3 + Pb(OH)_2$$

They separate out as white amorphous precipitates [except for brown $Ge(OH)_2$ and dark brown $Pb(OH)_4$]. The hydroxides of germanium are appreciably soluble in water, whereas the solubilities of the others are very low.

4) The hydrate of stannic oxide has the pronounced character of a *gel*. On standing in solution or on heating it gradually *ages*. The process apparently consists of polymerisation of the $xSnO_2 \cdot yH_2O$ molecules with the elimination of water. The difference in properties between a freshly precipitated and a greatly aged gel is so wide that they have to be considered separately. The form which has been freshly precipitated from salts is usually called α-stannic acid, and that which is greatly aged (or has been obtained by the action of concentrated HNO_3 on tin) is usually called β-stannic acid.

As regards chemical properties, all these hydroxides are *amphoteric* compounds. Their dissolved part dissociates, in the long run (neglecting its gradual nature), in accordance with the equations:

$$E^{\cdot\cdot} + 2OH' \leftrightarrows E(OH)_2 \equiv H_2EO_2 \rightleftarrows 2H^{\cdot} + EO_2''$$
$$E^{\cdot\cdot\cdot\cdot} + 4OH' \leftrightarrows E(OH)_4 \equiv H_4EO_4 \rightleftarrows 2H^{\cdot} + EO_3'' + H_2O$$

The directions of dissociation of the individual representatives are illustrated by the following scheme:

increasing acidic properties

$$\begin{array}{lll} Ge(OH)_4 & Sn(OH)_4 & Pb(OH)_4 \\ & Ge(OH)_2 & Sn(OH)_2 \quad Pb(OH)_2 \end{array}$$

increasing basic properties

Acidic properties are expressed most distinctly in the case of germanic hydroxide, which is, at the same time, a very weak acid. Basic properties are most pronounced in the case of $Pb(OH)_2$ which is markedly alkaline in solution.

Owing to their amphoteric nature, these hydroxides dissolve both in strong alkalis and in acids. When they are treated with alkalis, salts of acids of the type H_2EO_3 or H_2EO_2 are formed which contain Ge, Sn or Pb as part of the anion, and when they are treated with acids, salts of these elements are formed, containing the cations E^{2+} or E^{4+}.

From the hydrate of PbO_2, as the acid, and $Pb(OH)_2$, as the base, two *mixed* oxides of lead are derived: orange Pb_2O_3 (*lead sesquioxide*), and bright-red Pb_3O_4 (*red lead* or *minium*). The former is the plumbous salt of *meta*plumbic acid, H_2PbO_3, and the latter is the plumbous salt of *ortho*plumbic acid, H_4PbO_4. Thus, both oxides—$PbPbO_3$ and Pb_2PbO_4—contain lead atoms of different valencies. They are practically insoluble in water.

5) The structures of both intermediate oxides of lead can be verified by the results of their reactions with dilute nitric acid. For example, in the case of red lead, two-thirds of all the lead dissolves and is converted into $Pb(NO_3)_2$, whereas the remaining third is left in the form of PbO_2. This proves that the red-lead molecule contains two atoms of divalent lead and one of tetravalent lead. The structural formula of the sesquioxide can be verified in the same way.

The salts of the H_2EO_3 acids are known as *germanates*, *stannates* and *plumbates*, respectively. Most of them are colourless and sparingly soluble in water. The few soluble salts (of Na, K, etc.) are strongly hydrolysed in solution.

The salts of the H_2EO_2 acids are known as *germanites*, *stannites* and *plumbites*, respectively. They are generally similar to germanates, stannates and plumbates in their properties, but are considerably less stable and are still more strongly hydrolysed in solution. When treated with oxidising agents, they are readily converted into salts of the corresponding H_2EO_3 acids. This applies particularly to germanites and stannites, which are *very strong* oxidising agents. For example, the hydroxide of trivalent bismuth is reduced by a stannite to the metal:

$$2Bi(OH)_3 + 3Na_2SnO_2 = 3Na_2SnO_3 + 2Bi + 3H_2O$$

This reaction is used in analytical chemistry.

Owing to the weakness of the basic properties of the higher hydroxides of Ge, Sn and Pb, their derivatives containing E^{4+} cations are strongly hydrolysed in solution. The EX_4 *halides*, which are known for all these elements and for all the halogens (except $PbBr_4$ and PbI_4), are the most important.

With respect to physical properties, these compounds (except for SnF_4 and PbF_4) resemble the analogous compounds of Si and C rather than typical salts. For example, $SnCl_4$ is a colourless liquid (m. p. —32° C, b. p. 114° C).

The most characteristic chemical property of the EX_4 halides is their inclination towards *addition* reactions. Thus, $SnCl_4$ forms complexes with H_2O, NH_3, nitrogen oxides, PCl_5, etc., as well as with many organic substances. The complexes of most of the EX_4 halides with halogen hydracids (chiefly of the type $H_2[EX_6]$) and derivatives of similar complex acid salts are very stable. For example, a solution of $(NH_4)_2[SnCl_6]$ shows a neutral reaction to litmus.

Oxyacid salts are not characteristic of tetravalent Ge, Sn and Pb. Among those which have been obtained are the sulphates $E(SO_4)_2$ and the acetates $E(CH_3COO)_4$. All of them hydrolyse readily.

The derivatives of tetravalent lead are very powerful oxidising agents. Thus, on boiling with 30% sulphuric acid, PbO_2 oxidises divalent manganese to permanganic acid, in spite of the fact that the latter is itself a powerful oxidising agent. The reaction takes place in accordance with the equation:

$$5PbO_2 + 2MnSO_4 + 3H_2SO_4 = 5PbSO_4 + 2HMnO_4 + 2H_2O$$

In particular, the operation of a lead storage battery is based on the oxidising properties of tetravalent lead.

6) A *lead storage battery* consists of lead grid plates filled with a paste of PbO and water, and immersed in 30% sulphuric acid (sp. gr. 1.2). In accordance with the reaction: $PbO + H_2SO_4 = PbSO_4 + H_2O$, a layer of sparingly soluble plumbous sulphate is formed on the surface of the plates. If a direct electric current is now passed through the whole system in the direction shown by the arrow (Fig. 149, *A*), the following reactions take place at the plates (*charging*):

Negative electrode	*Positive electrode*
$PbSO_4 + 2\ominus + 2H^{\bullet} = Pb + H_2SO_4$	$PbSO_4 + SO_4'' - 2\ominus = Pb(SO_4)_2$
$(Pb^{\bullet\bullet} + 2\ominus = Pb)$	$(Pb^{\bullet\bullet} - 2\ominus = Pb^{\bullet\bullet\bullet\bullet})$
	$Pb(SO_4)_2 + 2H_2O \rightleftarrows PbO_2 + 2H_2SO_4$

Thus, on charging the negative plates are transformed into a spongy mass of metallic lead, the positive plates are converted into PbO_2, and the concentration of the sulphuric acid increases.

If the two electrodes are not connected by a wire, the battery can remain charged for a long time. On the other hand, if the electrodes are cut into a circuit, an electric current begins to flow through the latter in the direction shown by the

arrow (Fig. 149, *B*). The origin of the current is due to the following reactions at the electrodes (*discharging*):

Negative electrode

$$Pb + SO_4'' = PbSO_4 + 2\ominus$$
$$(Pb = Pb^{\bullet\bullet} + 2\ominus)$$

Positive electrode

$$PbO_2 + 2H_2SO_4 \rightleftarrows Pb(SO_4)_2 + 2H_2O$$
$$Pb(SO_4)_2 + 2\ominus + 2H^{\bullet} = PbSO_4 + H_2SO_4$$
$$(Pb^{\bullet\bullet} + 2\ominus = Pb^{\bullet\bullet})$$

These processes are the opposite of what takes place on charging the battery. While the latter is based on the transfer of electrons from one Pb^{2+} ion to another with the absorption of energy, discharging consists of the spontaneous drawing

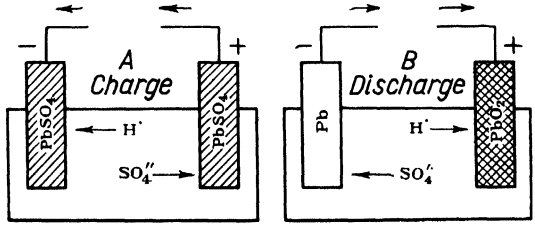


Fig. 149. Operation of a lead storage battery

off of electrons by the Pb^{4+} ion from the neutral lead atom. The electric current obtained on discharging a lead storage battery has an e. m. f. of about 2 volts. By connecting a number of these cells with one another, a battery can be made powerful enough to drive electric locomotives, etc.

In contrast to the EX_4 halides, the halogen derivatives of divalent Sn and Pb are pronouncedly salts by nature. All of them crystallise readily, melt only at relatively high temperatures and are considerably less hydrolysed in solution than the corresponding EX_4 halides. The fairly unstable halides of divalent germanium are somewhat closer to the latter in properties.

In connection with the decrease in basic properties of the hydroxides in the order $Pb(OH)_2$—$Sn(OH)_2$—$Ge(OH)_2$, the hydrolysis of the salts derived from them increases in the same order: while the salts of divalent Pb are negligibly hydrolysed, the derivatives of divalent Ge are almost completely decomposed by water in dilute solution. Sn^{2+} salts are intermediate in this respect.

The majority of Sn^{2+} salts are colourless and readily soluble in water. Owing to the tendency of Sn^{2+} to pass into Sn^{4+}, the derivatives of divalent tin (and also—to an even greater degree—of germanium) are powerful reducing agents. Their solutions are gradually oxidised by atmospheric oxygen.

The most important of the Sn^{2+} salts is *stannous chloride*, $SnCl_2$. It is chiefly employed as a reducing agent. For example, it reduces mercury salts to the metal:

$$HgCl_2 + SnCl_2 = SnCl_4 + Hg$$

Oxyacid salts are not very characteristic of divalent tin (and germanium). Of these, $SnSO_4$ is used in electroplating, i. e., the tinning of other metals. Like the other derivatives of Sn^{2+}, this salt is poisonous.

In contrast to the analogous compounds of tin, the salts of divalent lead are not reducing agents. The majority of them are colourless and sparingly soluble in water. Of those frequently encountered in practice, only the nitrate, $Pb(NO_3)_2$, and the acetate, $Pb(CH_3COO)_2$ are readily soluble.

Type ES and ES_2 sulphides of these elements may be obtained (with the exception of PbS_2) both by the dry method (from the elements) and by the action of hydrogen sulphide on solutions of the corresponding salts containing $E^{\cdot\cdot}$ and $E^{\cdot\cdot\cdot\cdot}$ ions. In the latter case, they form precipitates of the following colours:

GeS_2	SnS_2	GeS	SnS	PbS
white	yellow	brownish-red	brown	black

These sulphides are practically insoluble in water and dilute acids. GeS_2 is an exception, being slightly soluble in water and hydrolytically decomposed by the latter.

ES and ES_2 sulphides differ substantially in their behaviour towards ammonium sulphide. While it has no effect on the former, the latter are transferred into solution by it with the formation of ammonium salts of *thiogermanic*, H_2GeS_3, and *thiostannic*, H_2SnS_3, acids according to the equation:

$$(NH_4)_2S + ES_2 = (NH_4)_2ES_3$$

Owing to the instability of these thioacids in the free state, when solutions of their salts are acidified, H_2S is given off and the corresponding sulphide ES_2 is precipitated:

$$(NH_4)_2ES_3 + 2HCl = 2NH_4Cl + H_2S\uparrow + ES_2\downarrow$$

The *hydrogen* compounds of Ge, Sn and Pb stand somewhat apart in chemistry. These compounds are not characteristic of the divalent elements, while in the case of the tetravalent elements their stability diminishes so rapidly in the order Ge—Sn—Pb that the existence of PbH_4 could only be proved (by the volatility of lead when in contact with atomic hydrogen), but it has not been obtained in the isolated state. The hydrides of germanium and tin are formed as slight impurities in hydrogen when alloys of these elements with magnesium are decomposed by acids. They can be separated from the hydrogen by cooling the mixture of gases with liquid air.

As regards physical properties, GeH_4 and SnH_4 are similar to the analogous compounds of Si and C. They are also colourless gases

with low melting and boiling points, as can be seen from the comparison below.

Substance	CH_4	SiH_4	GeH_4	SnH_4
Melting point (°C)	—184	—185	—166	—150
Boiling point (°C)	—162	—112	—88	—52

The hydrides of germanium and tin gradually decompose into their elements on storing. Both are highly poisonous.

X-6. The Titanium Subgroup. *Titanium* accounts for about 0.2% of the total number of atoms in the earth's crust, i. e., it is one of the abundant elements. The proportion of *zirconium* is 3×10^{-3}%, and that of *hafnium*, 5×10^{-5}%.

Although the percentage of even hafnium in the earth's crust is greater than that of I or Hg, for example, both titanium and its analogues are relatively poorly utilised in practice and are sometimes regarded as "rare" elements. This is due, above all, to their dispersion, owing to which deposits suitable for commercial development are encountered only in a few parts of the earth. Another important reason is the difficulty of isolating these elements from their natural compounds.

1) Accumulations of *titanium* are encountered in the form of the minerals *ilmenite*, $FeTiO_3$, and *rutile*, TiO_2. Considerable quantities of titanium are also contained in certain iron ores, in particular, Ural titanomagnetites. *Zirconium* is mainly encountered in the form of the minerals *zircon*, $ZrSiO_4$, and *baddeleyite*, ZrO_2. No separate minerals have been found for *hafnium* as yet. It is always contained in Zr ores as an impurity (about 2% of the Zr content).

The elements of the titanium subgroup are usually obtained in the free state by the reduction of their chlorides with magnesium in accordance with the equation:

$$ECl_4 + 2Mg = 2MgCl_2 + E$$

The reaction is carried out by heating the initial substances to 900° in an atmosphere of an inert gas (under pressure).

In physical properties, the elements of the titanium subgroup are typical metals resembling steel in appearance.

Their characteristic constants are listed below.

Properties	Ti	Zr	Hf
Specific gravity	4.5	6.5	13.3
Melting point (°C)	1725	1850	1980
Boiling point (°C)	3170	4300	5700
Electrical conductivity (Hg = 1)	1	2	3

The pure metals are readily machinable. However, even traces of absorbed gases make them brittle.

Under ordinary conditions, the elements of the titanium subgroup are quite resistant to air and water. Only titanium reacts with hydrochloric, sulphuric and nitric acids, whereas HF and aqua regia dissolve all the three metals, e. g., in accordance with the reactions:

$$Zr + 6HF = H_2[ZrF_6] + 2H_2$$
$$3Zr + 12HCl + 4HNO_3 = 3ZrCl_4 + 4NO + 8H_2O$$

At high temperatures, Ti, Zr and Hf are chemically very active. Under these conditions, they combine vigorously not only with the halogens, oxygen and sulphur, but also with carbon and nitrogen. In powder form they are able to absorb very large amounts of hydrogen.

The practical importance of Ti and Zr is particularly great in metallurgy. The addition of titanium lends hardness and elasticity to steel, and the addition of zirconium greatly increases its hardness and ductility. Recently, the use of titanium in aircraft construction, and the use of zirconium in the building of nuclear reactors have greatly increased. Compounds of both elements find application in various branches of industry. Hafnium and its compounds are, as yet, hardly used at all.

In all their most important and most characteristic derivatives, the elements of the titanium subgroup are tetravalent. Titanium itself relatively easily forms rather unstable compounds in which it is trivalent. The derivatives of divalent titanium are few in number and are very unstable. The same applies to the derivatives of tri- and divalent zirconium, and also to hafnium, the compounds of which are very close to the corresponding compounds of zirconium as far as their chemical properties are concerned. Thus, the stability of the lower valencies decreases in the order Ti—Zr—Hf, i. e., a phenomenon opposite to what we saw in the case of the germanium subgroup.

When the elements of the titanium subgroup are heated in an atmosphere of oxygen, they burn to form white *dioxides* EO_2. The latter are very refractory and practically insoluble in water and in dilute solutions of acids and alkalis. Of these dioxides, TiO_2 serves as the base for a very good white oil paint ("titanium white"), and ZrO_2 is chiefly employed in the manufacture of refractories.

The *hydroxides* corresponding to the dioxides EO_2 (which may be obtained by the action of alkalis on compounds of the type ECl_4) are white gelatinous precipitates almost insoluble in water. The hydroxide of tetravalent titanium is amphoteric, its basic and especially its acidic properties being very weak. The acidic properties of Zr and Hf are even weaker, but their basic properties are stronger.

Since the $E(OH)_4$ hydroxides exhibit predominantly basic properties, they are all soluble in strong acids, whereas alkalis have almost no effect even on $Ti(OH)_4$.

2) *Peroxide* compounds are characteristic of the elements of the titanium subgroup, being readily formed by the action of H_2O_2 and alkalis on solutions of the corresponding salts. In the free state, the peroxide hydrates are gelatinous precipitates, that of Ti being yellowish-brown and that of Zr, white. In composition, they correspond to the respective hydroxides of the tetravalent elements, in which one or more hydroxyl groups are replaced by an —OOH group. This substitution makes the acidic properties of the hydroxides of Ti and Zr so much stronger that the salts of the peroxide hydrates are stable in solution and are hardly hydrolysed. The hydroperoxides of Ti and Zr are, consequently, typical *peracids*. Some salts of the latter have also been obtained in the solid state.

The metal salts of the hydrous dioxides of Ti and Zr *titanates* and *zirconates*—are usually prepared by fusing TiO_2 or ZrO_2 with the metal oxides or with alkalis. The types M_2EO_3 and M_4EO_4 (where M is a monovalent metal) are characteristic of the salts formed. The majority of titanates and zirconates are insoluble in water, and those that are soluble are completely hydrolysed.

Since the basic properties of the hydrous dioxides of Ti and Zr are more pronounced than their acidic properties, salts of the colourless cations Ti^{4+} and Zr^{4+} are more resistant to water than titanates and zirconates. Still, the hydrolysis of these salts is quite considerable, and even in concentrated solution results in the formation of the divalent radicals *titanyl*, TiO^{2+}, and *zirconyl*, ZrO^{2+}, according to the equation:

$$E^{\cdot\cdot}_{\cdot\cdot} + H_2O = EO^{\cdot\cdot} + 2H^{\cdot}$$

Many titanium and zirconium salts are derivatives of these radicals, and not of E^{4+} ions. Examples are $(TiO)SO_4 \cdot 2H_2O$ and $(ZrO)Cl_2 \cdot 8H_2O$. Their subsequent hydrolysis proceeds on a lesser, though rather considerable scale (particularly in the case of the titanium derivatives).

3) Highly refractory *sulphides* of the type ES_2 may be obtained by the reaction between the elements on heating. Titanium disulphide forms yellow crystals, and ZrS_2 is a dark brown powder.

4) The elements of the titanium subgroup combine readily with nitrogen at high temperatures. The resulting *nitrides* of Ti, Zr and Hf have compositions corresponding to the general formula EN. They are very hard, refractory and chemically inert substances.

5) On being strongly heated, the elements of the titanium subgroup combine with carbon to form *carbides* of the general formula EC. The latter are crystals of a metallic appearance; they are very hard and highly refractory.

The most important of the other derivatives of Ti, Zr and Hf are the halides of the type EX_4. They are usually obtained by heating a mixture of the dioxide and carbon in an atmosphere of the

halogen. The reaction takes place as follows:

$$EO_2 + 2C + 2X_2 = 2CO + EX_4$$

The character of the halides changes substantially in the order Ti—Hf. For example, under ordinary conditions, $TiCl_4$ is a liquid (m. p. —23° C, b. p. 136° C), while $HfCl_4$ is a typical salt. With the exception of ZrF_4 and HfF_4, the EX_4 halides are readily soluble in water.

Complex formation with the corresponding halogen hydracids and especially their salts is very characteristic of all of these compounds. The most typical are the complex derivatives of the general formula $M_2[EX_6]$ (where M is a monovalent metal). They are easily crystallised, and are much less hydrolysed than the original EX_4 halides.

6) As has already been noted above, derivatives of the *trivalent* elements are more or less characteristic only of titanium. In particular, on reduction in accordance with the equation $Zn + 2TiCl_4 = ZnCl_2 + 2TiCl_3$, the colourless solution of $TiCl_4$ assumes the violet colour characteristic of the $Ti^{\cdots}$ ions, and the crystal hydrate $TiCl_3 \cdot 6H_2O$ can be separated from it. When left standing in an open vessel, a solution of $TiCl_3$ is gradually discoloured owing to oxidation of $Ti^{\cdots}$ to $TiO^{\cdot\cdot}$ by atmospheric oxygen: $4TiCl_3 + O_2 + 2H_2O = 4TiOCl_2 + 4HCl$.

Though the elements of the titanium subgroup are not analogues of silicon in atomic structure, the derivatives of their characteristic valencies fit well in the same series as the corresponding silicon derivatives. In particular, the properties of the higher oxides vary quite regularly from Si to Hf. On the other hand, no such regularity is observed in the series Si—Pb, as is evident, for example, from the comparison of the heats of formation of EO_2 (kcal/mole) given below:

Pb	Sn	Ge	Si	C	Si	Ti	Zr	Hf
65	138	127	203	94	203	219	258	272

XI. THIRD GROUP OF THE PERIODIC TABLE

	5		
	B		3
	10.811		2
	13		
	Al		3
			8
	26.9815		2
2	*21*		
9			
8	**Sc**		
2			
	44.956		
		31	
			3
		Ga	
			18
			8
		69.72	2
2	*39*		
9			
18	**Y**		
8			
2	88.905		
		49	3
		In	18
			18
			8
		114.82	2
2	*57*		
9			
18	**La**		
18	138.91	*81*	3
8	and	**Tl**	18
2	lantha-		32
	nides		18
			8
		204.37	2
2	*89*		
9			
18	**Ac**		
32	[227]		
18	and		
8			
2	actinides		

The atoms of the elements of this group each contain a maximum of three electrons in their outermost shell. Therefore, the tendency towards the further addition of electrons (to complete the octet in the outermost shell) cannot be characteristic of them. On the contrary, the metallic properties of boron and its analogues should be more pronounced than those of the corresponding elements of the fourth group.

By analogy with the titanium subgroup, one would expect to find in the elements of the scandium subgroup a tendency to give up not only the two electrons from the outermost shell, but also the electron in excess of the octet in the next shell, i. e., they should behave largely as *trivalent* metals. On the other hand, by analogy with the germanium subgroup, Ga, In and Tl should also be expected to exhibit a lower valency in compounds.

Boron has approximately the same relation to its closest analogue, aluminium, as carbon has to silicon. The resemblance between the two elements is restricted chiefly to their identical valencies and the properties directly dependent upon the latter. In many respect, boron greatly differs from aluminium, and, on the whole, its chemistry rather resembles that of silicon.

XI-1. Boron. This element is fairly abundant: its content in the earth's crust is about $5 \times 10^{-4}\%$. Accumulations of boron are encountered in the form of its oxygen compounds—*boric acid*, H_3BO_3, *borax*, $Na_2B_4O_7 \cdot 10H_2O$, *ascharite*, $MgHBO_3$, and a number of more complex minerals. The annual world production of boron compounds amounts to about 300 thousand tons. The most important of these are borax and boric acid.

1) Boric acid is used for enameling iron vessels (forms part of the enamel) and in medicine (as an antiseptic mouth wash, etc.), and also serves as the usual starting material for obtaining other compounds of boron. Borax is used in a number of branches of industry—glass, ceramic, tanning, etc., and in medicine.

Boron can be prepared in the free state from boric acid. It is converted by heating into boric oxide, B_2O_3, which is then heated to redness with metallic magnesium:

$$B_2O_3 + 3Mg = 3MgO + 2B$$

On treatment of the resultants with hydrochloric acid MgO dissolves and elementary boron remains. In the very pure state it is black, has a specific gravity of 2.3, melts at 2075° C and boils at 2550° C.

Under ordinary conditions, boron is very inert. At high temperatures, however, it combines not only with oxygen, chlorine and bromine, but also with sulphur and nitrogen. When heated very strongly boron liberates the free elements even from such stable oxides as P_2O_5, CO_2 and SiO_2, and from many metal oxides. Fusion of boron with some of the latter yields *borides* of these metals, e. g., magnesium boride, Mg_3B_2.

Boron is quite resistant to air and water. It does not dissolve in the common acids, but hot concentrated HNO_3 gradually oxidises it to boric acid:

$$B + 3HNO_3 = H_3BO_3 + 3NO_2$$

In all its stable compounds, boron is *trivalent*.

Oxygen compounds are most characteristic of boron. On heating in air to 700° C, it burns in accordance with the equation:

$$4B + 3O_2 = 2B_2O_3$$

The resulting *boric oxide* is a colourless, fairly refractory vitreous mass.

B_2O_3 is hygroscopic, and dissolves in water to form *boric acid*:

$$B_2O_3 + 3H_2O = 2H_3BO_3$$

Boric (more accurately, *orthoboric*) acid forms colourless crystals. On heating, it loses water and passes first into *metaboric* acid, HBO_2, then into pyroboric or *tetraboric* acid, $H_2B_4O_7$, and, finally, into boric oxide. When dissolved in water these substances pass into H_3BO_3.

The hydrate $B(OH)_3$ dissociates like an acid in solution. However, boric acid is very weak, and therefore, it is easily liberated from solutions of its salts by most other acids. Its salts (*borates*) are usually derived from various *polyboric* acids having the general formula $xB_2O_3 \cdot yH_2O$, most frequently from *pyroboric* acid ($x = 2$, $y = 1$). The latter is considerably stronger than orthoboric acid.

Salts of $H_2B_4O_7$ are formed by neutralising H_3BO_3 with alkalis, for example, according to the equation:

$$2NaOH + 4H_3BO_3 = Na_2B_4O_7 + 7H_2O$$

They can be converted into metaborates by adding an excess of alkali:

$$2NaOH + Na_2B_4O_7 = 4NaBO_2 + H_2O$$

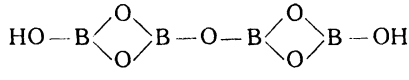
On the other hand, when pyroborates (or metaborates) are treated with strong acids, free orthoboric acid is liberated:

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O = Na_2SO_4 + 4H_3BO_3$$

Only the borates of the most active monovalent metals are soluble in water. Owing to hydrolysis, their solutions are strongly alkaline. Practically, the most important borate, is borax.

Since anhydrous borates are very heat-resistant, at high temperatures boric acid liberates most other acids from their salts. In this respect (as well as in its weakness), it resembles silicic acid.

2) Boric acid ($K_1 = 6 \times 10^{-10}$, $K_2 = 2 \times 10^{-13}$, $K_3 = 2 \times 10^{-14}$) imparts a green colour to a flame and is slightly volatile with water vapour. Pyroboric acid ($K_1 = 2 \times 10^{-4}$, $K_2 = 2 \times 10^{-5}$) probably has the structural formula:



Many of the salts of various polyboric acids are found in nature and serve as initial products for the preparation of boron compounds.

3) Boron *sulphide*, B_2S_3, is formed as a colourless, vitreous mass when boron is heated in sulphur vapour. It is completely decomposed by water into boric acid and H_2S. Boron combines with nitrogen only above 1200° C. Boron *nitride*, BN, is a white powder which melts only at about 3000° C (under pressure). It resembles graphite in crystalline structure.

Boron *carbide*, B_4C, is formed as black shiny crystals when a mixture of boron (or B_2O_3) and carbon is heated in an electric furnace. It is distinguished by its refractoriness (m. p. 2550° C) and extreme hardness (close to that of diamond). Both the nitride and the carbide are highly resistant to different chemical influences.

Halides of boron having the general formula BX_3 can be obtained by the reactions between the elements on heating. They are colourless substances. Under ordinary conditions, BF_3 is a gas, BCl_3 boils at +18° C, BBr_3 is a liquid and BI_3 is a solid. All of them hydrolyse in aqueous solutions in accordance with the equation:

$$BX_3 + 3H_2O = B(OH)_3 + 3HX$$

Reactions of *addition* of molecules of various other substances are very characteristic of boron halides. In particular, boron trifluoride forms an addition product with HF:

$$HF + BF_3 = H[BF_4]$$

Complex *fluoboric* acid, HBF_4, is stable only in solution, its acidic properties being considerably stronger than those of HF. Most of the salts of HBF_4 (*fluoborates*) are colourless and readily soluble in water. As in the case of silicon, analogous derivatives are not formed with other halogens.

4) The structure of the molecules of the BX_3 halides corresponds to a flat triangle with the B atom at the centre. Some of their properties are compared below:

Substance	BF_3	BCl_3	BBr_3	BI_3
Melting point (°C)	−129	−108	−47	+43
Boiling point (°C)	−101	+18	91	210

When boron halides form complexes with other substances, the B atom behaves as the *acceptor* (IX-2, suppl. 1). Therefore, only molecules containing an atom with clearly defined *donor* functions are able to combine with BX_3 molecules.

The tendency of BX_3 molecules to complex formation decreases fairly rapidly in the order F—Cl—Br—I. Boron trifluoride is a good catalyst for various organic reactions. Owing to the formation of HBF_4, the hydrolysis of BF_3 proceeds somewhat differently than in the case of the other boron halides, viz., in accordance with the overall equation: $4BF_3 + 3H_2O = 3HBF_4 + B(OH)_3$.

Boron does not combine with *hydrogen*, but when Mg_3B_2 is treated with acids together with free H_2, small quantities of a mixture of different *boron hydrides* (or *boranes*) are liberated, among which B_4H_{10} predominates. The latter readily decomposes into B_2H_6 and a number of other boranes, lower in hydrogen.

Boranes are colourless, and very similar in physical properties to the hydrocarbons and silanes of analogous composition, as can be seen from the comparison given below:

C_2H_6	B_2H_6	Si_2H_6	C_4H_{10}	B_4H_{10}	Si_4H_{10}
−183° C	−166° C	−129° C melting point	−138° C	−120° C	−91° C
−88° C	−93° C	−14° C boiling point	0° C	+18° C	+107° C

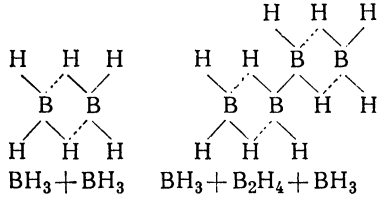
In chemical properties, they resemble silanes. Like the latter (and even more so), boranes are unstable under ordinary conditions. In particular, they are gradually decomposed by water with the liberation of hydrogen, e. g.:

$$B_2H_6 + 6H_2O = 6H_2 + 2H_3BO_3,$$

and the gaseous mixture obtained when Mg_3B_2 is decomposed by acids ignites spontaneously in air. The combustion of boranes is accompanied by the evolution of an enormous amount of heat (484 kcal/mole of B_2H_6), which makes it possible to utilise them as a very efficient rocket fuel.

5) Since boron is trivalent, its hydrogen compounds should have been made up of such molecules as BH_3, B_2H_4, B_3H_5, etc. However, boranes of this composition are unknown.

The molecules of the volatile boron hydrides should apparently be regarded as the result of the combination of the above valence-saturated structures by means of *hydrogen* bonds of a special kind. Thus, from this point of view, the structures of B_2H_6 and B_4B_{10} are represented by the following schemes:



BH_3+BH_3 $BH_3+B_2H_4+BH_3$

Six boron hydrides have been more fully studied than the others; their melting and boiling points are given below:

Substance	B_2H_6	B_4H_{10}	B_5H_{11}	B_5H_9	B_6H_{10}	$B_{10}H_{14}$
Melting point (°C)	—166	—120	—123	—47	—65	+99
Boiling point (°C)	—93	+18	63	48	110	213

All these boranes have an obnoxious odour and are highly toxic.

XI-2. Aluminium. Aluminium ranks fourth in abundance (after O, H and Si) and accounts for about 5.5% of the total number of atoms in the earth's crust. The bulk of aluminium is concentrated in *aluminosilicates* (X-3). A very widespread *product of the decomposition* of aluminosilicate rocks is *clay*, the basic composition of which (corresponding to *kaolin*) is represented by the formula $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. The most important of the other minerals of aluminium are *bauxite*, $Al_2O_3 \cdot xH_2O$, and *cryolite*, $AlF_3 \cdot 3NaF$.

1) Clay is the basic raw material of the ceramic industry. So-called *coarse* ceramics includes the production of bricks, various refractories (fire brick, etc.) and acid-resistant materials (clinker, etc.), clay pots (earthenware production), tiles, etc., and *fine* ceramics covers the production of porcelain and faience.

Elementary aluminium is produced by the electrolysis of a solution of Al_2O_3 in molten cryolite. The process is carried out at temperatures of about 1000° C in electric furnaces, oxygen being liberated at the anode and aluminium at the cathode. The aluminium collects at the bottom of the furnace, from which it is periodically tapped.

The furnace used for aluminium production, is shown schematically in Fig. 150. It consists of an iron box, the internal walls and the bottom of which are lined with a thick layer of carbon *K* which serves as the cathode during electrolysis. A massive carbon electrode *A* is employed as the anode. During the operation of the furnace, Al_2O_3 is added periodically, and the molten metal is removed. Aluminium production is a power-consuming process: each ton of metal requires about 20 thousand kilowatt-hours of electric power.

2) Since it is very difficult to remove impurities from aluminium, the raw materials from which it is obtained must be very pure. Cryolite is usually prepared artificially by jointly dissolving $Al(OH)_3$ and soda in hydrofluoric acid (in accordance with the reaction: $3Na_2CO_3 + 2Al(OH)_3 + 12HF = 2Na_3AlF_6 + 3CO_2 + 9H_2O$). Natural bauxites which contain 40 to 60% Al_2O_3 and a number of impurities (SiO_2, Fe_2O_3, etc.) are subjected to preliminary chemical treatment in order to extract sufficiently pure aluminium oxide (containing no more than 0.2% SiO_2 and 0.04% Fe_2O_3). The methods of treatment greatly depend on the composition of the original bauxite and are rather complicated.

Aluminium is a silvery-white, fairly hard metal of sp. gr. 2.7, which melts at 660° C and boils at 2060° C. It is highly ductile and a good conductor of electricity (0.6 of the electrical conductivity of copper), making it suitable for the manufacture of electric wires.

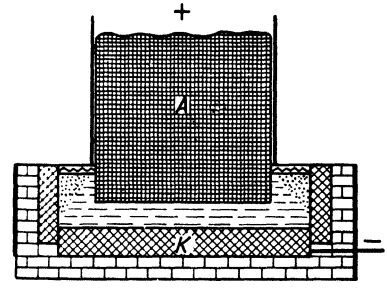


Fig. 150. Diagram of electric furnace for the production of aluminium

Aluminium is much more widely used in the form of various *alloys*, which feature lightness and good mechanical properties. *Duralumin* (approximate composition: 94% Al, 4% Cu, 0.5% each of Mg, Mn, Fe and Si) is particularly important. Its value lies in the fact that while being just as strong as steel, objects manufactured from it are almost three times lighter. Apart from the aircraft industry, where the light weight of the material is particularly important, the lightening of metal structures is of enormous importance in a number of other industries. This becomes especially obvious from the fact that in a loaded goods wagon, for example, about one-third of the total weight is due to the material of the wagon itself, while in passenger coaches, the weight of the wagon is responsible for as much as 95% of the whole load. It is clear that even partial substitution of duralumin for steel would produce an enormous economic effect. In connection with this, and in view of the practically inexhaustible supplies of aluminium in nature, it is rightfully called "the metal of the future". The possibilities of its extensive partial substitution for the principal metal of modern industry—iron—are limited chiefly by the relatively high cost of aluminium.

3) Apart from the fields that have been mentioned, aluminium finds extensive application in the manufacture of domestic utensils, etc. At 100-150° C, aluminium is so plastic that foil less than 0.01 mm thick may be produced from it. Such foil is widely employed in the manufacture of electrical condensers and for wrapping certain foodstuffs. A clean aluminium surface reflects about 90% of the radiation incident upon it (infrared and ultraviolet as well as visible radiation). Therefore, high-quality mirrors which very uniformly reflect rays of different wavelengths, can be produced by applying aluminium to glass

(*vacuum deposition*). Fine aluminium powder is used in the manufacture of weatherproof silver paint. The annual world production of aluminium is at present about 3 million tons (as against 8 thousand tons in 1900).

In air, aluminium immediately becomes coated with a very thin (0.00001 mm) but dense film of oxide which protects the metal from further oxidation. Owing to this, its surface has a slightly dull, instead of shiny appearance. On heating, finely ground aluminium burns vigorously in air. It reacts with sulphur in a similar manner. It combines with chlorine and bromine at ordinary temperatures, but with iodine only on heating. At very high temperatures, aluminium also combines directly with nitrogen and carbon. On the other hand, it does not react with hydrogen.

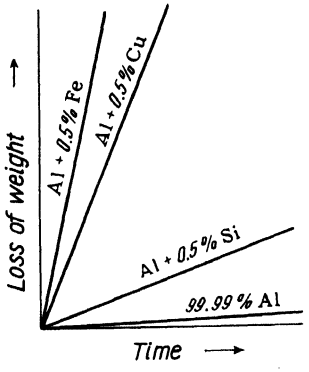


Fig. 151. Effect of admixtures on the rate of solution of Al in HCl

Aluminium is quite resistant to water. Very dilute and concentrated HNO_3 and H_2SO_4 have almost no effect on aluminium, but it is gradually dissolved by these acids at medium concentrations. Pure aluminium is also fairly resistant to hydrochloric acid, but the ordinary commercial metal dissolves in it (Fig. 151). Aluminium dissolves readily in strong alkalis, e. g., in accordance with the reaction:

$$2Al + 2NaOH + 2H_2O = 2NaAlO_2 + 3H_2$$

In the electromotive series, it lies between Mg and Zn. In all its stable compounds, aluminium is *trivalent*.

4) The ease with which aluminium dissolves in strong alkalis is due to removal of the protective oxide film in accordance with the equation: $Al_2O_3 + 2OH' = 2AlO_2' + H_2O$. Since Al is considerably to the left of hydrogen in the electromotive series, exposure of the clean metal surface immediately gives rise to the reactions:

$$2Al + 6H^{\cdot}(\text{from water}) = 2Al^{\cdot\cdot\cdot} + 3H_2 \text{ and } 2Al^{\cdot\cdot\cdot} + 8OH' = 2AlO_2' + 4H_2O$$

The equilibrium of the first of these shifts continuously to the right owing to the second. Other active metals with amphoteric hydroxides, such as Sn, Zn, dissolve in alkalis in a similar manner.

The combination of aluminium with *oxygen* is accompanied by a large evolution of heat (339 kcal/mole of Al_2O_3), much greater than in the case of many other metals. Owing to this, when a mixture of the oxide of such a metal with aluminium powder is heated, a violent reaction ensues, as a result of which the free metal is liberated from its oxide. The method of reduction with the aid of Al (*aluminothermy*) is often employed for obtaining elements (Cr, Mn, V, etc.) in the free state.

Aluminothermy is also sometimes used for welding separate steel parts to each other, particularly, the joints of tramlines. The mixture employed (*thermite*) usually consists of fine aluminium powder and ferroso-ferric oxide, Fe_3O_4. It is ignited by means of a fuse consisting of a mixture of Al and BaO_2. The main reaction proceeds in accordance with the equation:

$$8Al + 3Fe_3O_4 = 4Al_2O_3 + 9Fe + 795 \text{ kcal}$$

During this reaction a temperature of about 3500° C develops.

Aluminium *oxide* is a highly refractory white substance, insoluble in water. Natural Al_2O_3 (*corundum*), as well as that obtained artificially and sudsequently roasted at a high temperature, is very hard and insoluble in acids. Aluminium oxide (*alumina*) can be converted into the soluble state by fusing it with alkalis.

5) *Natural corundum*, which is usually contaminated with ferric oxides, is used for making grinding wheels, whetstones, etc., owing to its extraordinary hardness. In finely divided form, it is used under the name of *emery* for cleaning metal surfaces and for manufacturing emery paper. Aluminium oxide obtained by fusing bauxite (commercial name, *alundum*) is often employed for these purposes.

Transparent corundum crystals, beautifully coloured by slight impurities of other substances, are sold as precious stones: *rubies*, *sapphires*, etc. At present they are made artificially by fusing and subsequently crystallising Al_2O_3 in the presence of suitable admixtures.

Owing to the insolubility of Al_2O_3 in water, the *hydroxide*, $Al(OH)_3$, corresponding to this oxide, can be obtained only indirectly (from salts). It is a bulky, gelatinous, white precipitate, practically insoluble in water, but readily dissolving in acids and strong alkalis.

Aluminium hydroxide is, consequently, *amphoteric* in nature. However, both its basic and especially its acidic properties are rather weak. Aluminium hydroxide is insoluble in excess NH_4OH.

When $Al(OH)_3$ reacts with strong alkalis, the corresponding *aluminates* are formed, for example:

$$Al(OH)_3 + KOH = KAlO_2 + 2H_2O$$

The aluminates of the most active monovalent metals are readily soluble in water, but owing to intense hydrolysis, their solutions are stable only in the presence of a sufficient excess of alkali. Aluminates derived from weaker bases are practically completely hydrolysed in solution, and therefore, can be obtained only by a dry method (by fusing Al_2O_3 with oxides of the corresponding metals). Most of them are insoluble in water.

6) Aqueous solutions of aluminates contain the ions $[Al(OH)_4]'$, $[Al(OH)_5]''$ and $[Al(OH)_6]'''$. Apparently, aluminates obtained from solutions are also of this type, whereas fusing of oxides yields anhydrous salts which are derivatives of $HAlO_2$.

With acids, $Al(OH)_3$ forms salts containing colourless $Al^{\cdots}$ ions in solution. The derivatives of most of the strong acids are readily soluble in water, but are considerably hydrolysed, and therefore, their solutions are acidic. Soluble salts of Al^{3+} and weak acids are still more strongly hydrolysed.

Of the aluminium *halides*, AlF_3 differs greatly in properties from its analogues. Aluminium fluoride obtained by a dry method, e. g., by heating Al_2O_3 in HF vapour, is a colourless crystalline powder melting only at 1040° C. It is practically insoluble in water.

Compounds of aluminium with chlorine, bromine and iodine are colourless and low-melting. They are highly reactive and readily soluble in many organic solvents as well as in water. They are all strongly hydrolysed in aqueous solution, being appreciably volatile even under ordinary conditions, $AlCl_3$, $AlBr_3$ and AlI_3 fume in moist air (owing to hydrolysis).

Aluminium halides form complex compounds, mainly of the type $M_3[AlF_6]$ and $M[AlX_4]$ (where X = Cl, Br or I), with the halogen salts of a number of monovalent metals. The tendency of aluminium halides towards addition reactions is generally strong, especially in the case of $AlCl_3$. It is with this property that the most important industrial applications of the latter are connected, namely, its use as a catalyst in the processing of oils and in organic syntheses.

7) Some of the constants of the aluminium halides are listed below:

Substance	AlF_3	$AlCl_3$	$AlBr_3$	AlI_3
Melting point (°C)	1040	190	98	180
Boiling point (°C)	1260	180 (sublimes)	264	386

The vapour densities of $AlCl_3$, $AlBr_3$ and AlI_3 more or less closely correspond to the double formulas Al_2X_6 at moderate temperatures. The spatial structure of these molecules is that of two tetrahedra with a common edge (Fig. 152). Each aluminium atom is bonded to four halogen atoms, and each of the central halogen atoms is linked with both aluminium atoms. One of the two bonds of each central halogen atom is a coordinate bond (IX-2, suppl. 1), the aluminium atom behaving as the acceptor.

Aluminium *sulphate* is colourless and readily soluble in water. It usually separates out as the crystal hydrate $Al_2(SO_4)_3 \cdot 18H_2O$. With the sulphates of a number of monovalent metals, aluminium sulphate forms colourless complex salts of the type $M[Al(SO_4)]_2 \cdot 12H_2O$. Though quite stable in the solid state, these salts (*alums*) are almost completely dissociated in solution into their separate constituent ions. Besides aluminium, complex sulphates of the alum type are also known for a number of other trivalent metals (E = Cr, Fe, V, etc.). K^+, Na^+, NH_4^+, and a few other ca ions may form part of them as monovalent cations (M).

Of the other derivatives of aluminium, reference should be made to its *acetate*, $Al(CH_3COO)_3$, which is used in the dyeing of cloth (as a mordant) and in medicine (lotions and compresses). This salt is known only in solution (where it is strongly hydrolysed). Aluminium *nitrate* is readily soluble in water. Aluminium *phosphate* is insoluble in water (and acetic acid), but is soluble in strong acids and alkalis.

8) Aluminium *sulphide*, Al_2S_3, may be obtained by the reaction between the elements, and forms white needles (m. p. 1100° C). Powdered aluminium combines with nitrogen above 800° C. Aluminium *nitride*, AlN, is a white powder which remains unchanged on heating up to approximately 2000° C; above

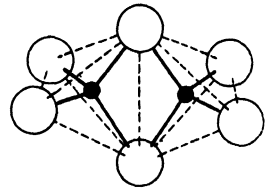


Fig. 152. Structure of an Al_2X_6 molecule

this temperature it begins to decompose into its elements. It is slowly decomposed by water according to the equation: $AlN + 3H_2O = Al(OH)_3 + NH_3$. Yellow aluminium *carbide*, Al_4C_3, is formed when a mixture of aluminium and carbon is heated to approximately 2000° C. Water decomposes it in accordance with the equation: $Al_4C_3 + 12H_2O = 4Al(OH)_3 + 3CH_4$.

9) Although aluminium does not react chemically with hydrogen, aluminium *hydride* can be obtained in the form of a white amorphous mass by an indirect method. It is a highly polymerised product of the composition $(AlH_3)_x$. When heated above 100° C, aluminium hydride decomposes into its elements.

XI-3. Physicochemical Analysis. Though the methods of ordinary chemical analysis enable the composition of the most complex compounds to be determined, they are found to be inadequate in certain cases. This is due to the fact that in order to determine the composition by chemical analysis, it is first necessary *to isolate* the substance under study. If, for some reason or other, such isolation is impossible, the methods of chemical analysis cannot be applied.

Physical methods of investigation may be of great help in such cases. It was pointed out by Lomonosov that it is easier to discern the hidden nature of substances, if physical truths are combined with chemical truths. By carefully studying the variation in the physical properties of any system as its composition or the external conditions change, it is often possible both to detect chemical transformations in the system and to follow them, as well as to obtain definite indications regarding their nature and the composition of the resultants. The object of *physicochemical analysis* is the detection and study of the chemical changes taking place in a system by investigating its physical

properties. A generalised treatment of physicochemical analysis as an independent scientific discipline was first provided by the Russian scientist Kurnakov in 1913.

Let us consider, for example, what indications can sometimes be obtained by studying the rate of cooling. In order to determine the latter, a preheated substance is allowed to cool, its temperature being recorded at fixed intervals. The temperature is then plotted

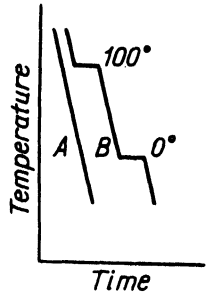


Fig. 153. Diagram of cooling curves

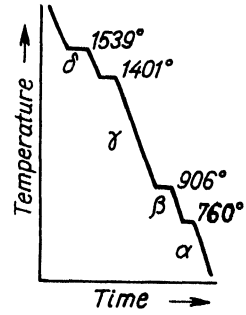


Fig. 154. Cooling curve of iron

against the time which is marked off along the abscissa. The *cooling curves* obtained in this way, serve as the basis for further deductions.

If no internal changes accompanied by evolution of heat take place in the system while it is cooling, its temperature falls continuously (as shown by line *A* in Fig. 153). On the other hand, if such changes do take place, a temporary delay is observed in the cooling of the system. Suppose, for example, that steam preheated to 150° C under atmospheric pressure, is cooled. At first, its temperature falls off smoothly, but at 100 °C, the vapour begins to condense into liquid water, and as this is accompanied by evolution of heat, a *step* appears on the cooling curve (Fig. 153, *B*), the temperature now remains unchanged for a certain period (while the formation of water continues), i. e., the curve runs parallel to the abscissa. After this, from 100° C to zero, the liquid water cools gradually, and the curve again falls continuously. However, at 0° C the water begins to freeze, and this is again accompanied by evolution of heat. In the cooling curve, this is registered as a new step, i.e., by a section running parallel to the abscissas for the period necessary for all the water to freeze. The cooling of the ice is again continuous.

The study of the cooling curve of water does not provide anything basically new, but this is not always the case. For example, the first step in the cooling curve of liquid iron (graph in Fig. 154) corresponds to the conversion of iron into the solid state at 1539° C, while the

presence in the curve of *another three breaks* indicates processes taking place in solid iron which involve evolution of heat. These processes can be only transformations of one allotropic form into another. The cooling curve, consequently, reveals the existence of four allotropic modifications of iron—α, β, γ and δ. At the same time, it accurately defines the regions of their stability. As more detailed investigations

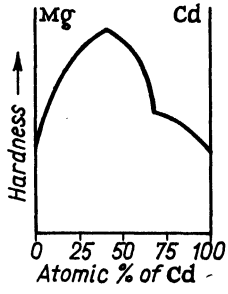


Fig. 155. Hardness of Mg—Cd alloys

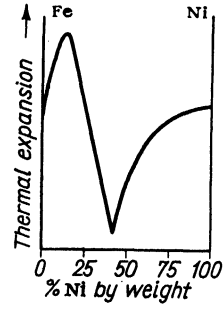


Fig. 156. Thermal expansion of Fe—Ni alloys

show, all four modifications actually exist and differ in some of their properties. Obviously, they could not have been detected by means of ordinary chemical analysis.

Methods of physicochemical analysis are very often employed in the study of systems formed by two substances. The general method employed consists in quantitative determination of some property (or properties) of the system, depending on its composition. The results are recorded as a *composition—property* plot (composition—along the abscissa, property—along the ordinate). The property determined in any particular case depends upon the object of the investigation and the nature of the system. The property may be vapour pressure, melting point, electrical conductivity, viscosity, hardness, etc. Examples of such diagrams are shown in Figs. 155 and 156, from which it can be seen that the character of the change in the property depending on the composition may be fairly complex. The diagrams of most practical importance are composition—vapour pressure and composition—melting point.

Composition—vapour pressure diagrams may provide important indications concerning the formation of complex compounds, their composition and stability. In particular, this applies to crystal hydrates. For example, Fig. 157 shows that copper sulphate forms only three crystal hydrates (1, 3 and $5H_2O$).

A quite definite pressure of water vapour corresponds (at a given temperature) to the dissociation of each of them:

	25°	50°
a) $CuSO_4 \cdot 5H_2O \rightleftarrows CuSO_4 \cdot 3H_2O + 2H_2O$	(vapour) 7.8 mm Hg	45 mm Hg
b) $CuSO_4 \cdot 3H_2O \rightleftarrows CuSO_4 \cdot H_2O + 2H_2O$	(vapour) 4.7 "	31 "
c) $CuSO_4 \cdot H_2O \rightleftarrows CuSO_4 + H_2O$	(vapour) 0.8 "	4.5 "

Therefore, during the dehydration of crystal hydrates, e. g., by keeping in a vacuum over sulphuric acid, the water vapour pressure changes in jumps rather than continuously. Thus, if $CuSO_4 \cdot 5H_2O$ is dehydrated

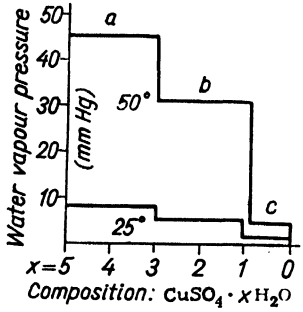


Fig. 157. Crystal hydrates of $CuSO_4$

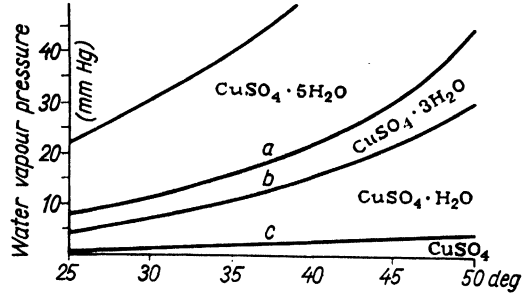


Fig. 158. Stability regions of the hydrated forms of $CuSO_4$

at 50° C, the pressure remains equal to 45 mm as long as there is the slightest amount of undecomposed pentahydrate left, after which it drops instantaneously to 31 mm, etc. (Fig. 157).

For the same reason, only those crystal hydrates over which the pressure of water vapour is greater than its partial pressure in the air, lose water of crystallisation—*effloresce*—on standing in air. For example, if the partial pressure of the water vapour in the air is 12 mm at 25° C, $CuSO_4 \cdot 5H_2O$ will not lose any water of crystallisation in contact with this air, whereas $Na_2SO_4 \cdot 10H_2O$ (water vapour pressure 19 mm) gradually effloresces. The regions of stability of the individual hydrated forms of $CuSO_4$ are shown in Fig. 158. The upper curve shows the pressure of water vapour over a saturated solution of copper sulphate. Under the conditions in the region above this curve, the crystal hydrate $CuSO_4 \cdot 5H_2O$ will *deliquesce*.

Composition—melting point diagrams are employed particularly frequently. The branch of physicochemical analysis devoted to their study is often called *thermal* analysis, and such diagrams are known as *freezing-point diagrams.*

The most typical forms of freezing-point curves for systems of two substances are shown in Fig. 159. Curve *I* represents the rather rare case where the melting point of a mixture of two substances lies *between* their own melting points, no matter what the composition of the mixture. On the other hand, curve *II* corresponds to the most common case where *the melting point of each of the two substances is lowered when the other is added.* The point on the diagram, at which the *lowest* melting point is reached in such a system, is called the *eutectic point.* A diagram of this type is produced, for example, by the system Cd—Bi (Fig. 160).

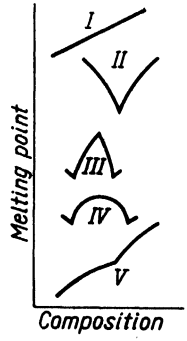


Fig. 159. Curves on freezing-point diagrams

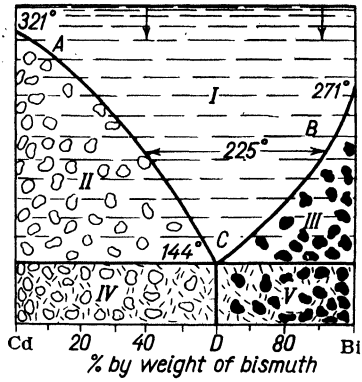


Fig. 160. Freezing-point diagram for the system Cd—Bi

To get a better idea of the meaning of the individual curves and regions of freezing-point diagrams, let us consider Fig. 160 in greater detail. If, for example, a liquid alloy containing 40% Bi is cooled, crystals of cadmium begin to separate out at 225° C, owing to which the composition of the liquid, which has become enriched in bismuth, will change on further cooling in accordance with the lower portion of the curve *AC*. Similarly, when an alloy containing 90% Bi is cooled to 225° C, crystals of bismuth begin to separate out, and the composition of the liquid will then vary in accordance with the lower portion of the curve *BC*. Consequently, *AC* represents the equilibrium between the liquid alloy and cadmium, and *BC*, the equilibrium between the liquid alloy and bismuth. On reaching the eutectic point *C* (144° C), the liquid, which is approximately 40% Cd and 60% Bi, solidifies as a whole and forms a mixture of minute Cd and Bi crystals called a *eutectic mixture*. Below 144° C, no alloy of Bi and Cd can exist in the liquid state, whatever the proportions of these metals.

If a mixture containing 40% Cd and 60% Bi (line *CD*) is cooled below 144° C, the composition of the solid phase formed, is the same as of the liquid alloy, i. e., it is a pure eutectic mixture. When the metals are in other proportions, larger crystals of Cd or Bi will be contained in the eutectic mixture. From this, the significance of the areas denoted by Roman numerals is clear. As is shown schematically in Fig. 160, area *I* represents the conditions for the stability of the liquid alloy, area *II*—the same for a mixture of the latter with crystals

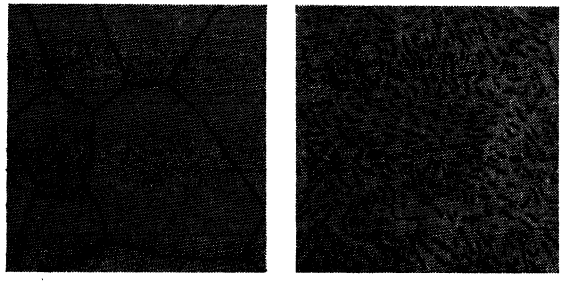


Fig. 161. Microsections of an individual metal and a eutectic

of cadmium, area *III*—for the liquid alloy and crystals of bismuth, area *IV*—for the eutectic mixture and crystals of Cd and, finally, area *V*—for the eutectic mixture and crystals of Bi.

In the study of metals and alloys, use is very often made of the microscope. For such investigations, which constitute the subject of *metallography*, the surface of the specimen is preliminarily subjected to appropriate treatment: grinding, polishing, etching with acids, etc. The patterns observed under the microscope are, generally speaking, extremely varied (Fig. 161). The polished section of individual metals, as a rule, consists of a collection of "crystallites", i. e., relatively large irregularly grown crystals. The existence of boundaries between them, visible on the polished section, is due to the different orientations of these crystallites and separation of part of the impurities in the metal when the latter crystallises. In the case of a eutectic mixture, the surface of the polished section is of an entirely different nature: it consists of a mixture of extremely fine crystals of both components. On solidification of binary alloys of intermediate composition, both the eutectic mixture and the crystallites of one of the components are simultaneously visible on the polished section, and this corresponds, in particular, to areas *IV* and *V* in Fig. 160.

If a reaction between two substances yields a *chemical compound*, a *maximum* corresponding to its composition will be observed on the freezing-point curve. In cases where the compound formed does not

dissociate into its constituents (in accordance with the equation $AB \rightleftarrows A + B$) at its melting point, this maximum is sharp (*III*, Fig.159). When dissociation does take place, the maximum smooths out (*IV*) and the more 50, the more dissociated the compound. Fig. 162 shows that in the system Cu—Mg, two compounds are formed, the

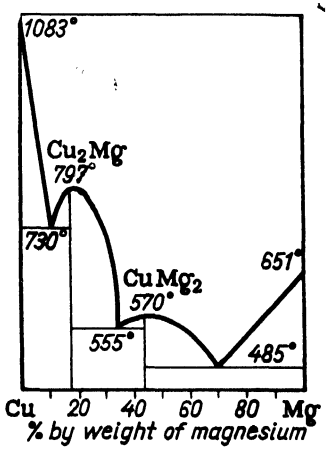


Fig. 162. Freezing-point diagram for the system Cu—Mg

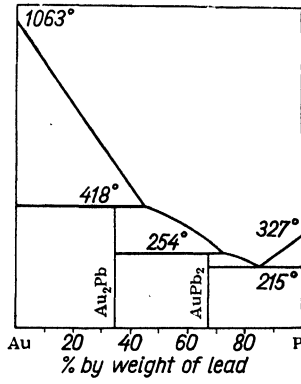


Fig. 163. Freezing-point diagram for the system Au—Pb

second of them being rather unstable. The complete freezing-point diagram of this system represents, as it were, a combination of three separate systems: Cu—Cu_2Mg, then Cu_2Mg—$CuMg_2$ and, finally, $CuMg_2$—Mg.

When an unstable chemical compound is formed, which dissociates completely before even reaching its true melting point, a *break* appears in the freezing-point curve (*V*, Fig. 159). The break corresponds to the dissociation temperature of the compound, and its approximate composition can be found by continuing the lower branch of the curve to its maximum. For example, the character of the curves in the system Au—Pb (Fig. 163) suggests the formation of two unstable compounds corresponding to the simplest formulas, Au_2Pb and $AuPb_2$. As can be seen from the above, freezing-point diagrams make it possible not only to detect the existence of particular compounds between metals (or any other substances), but also to draw definite conclusions concerning their stability.

1) In most cases the composition of *intermetallic* compounds, i. e., compounds made up of metals, has no noticeable connection with the usual valencies of the elements, as can be seen, for example, from the following comparison of some derivatives of the type AB_x : SbSn, $NiBi_2$, $PbPd_3$, $LaAl_4$, $MgZn_5$, $RbHg_6$, KCd_7, $AuZn_8$, KHg_9, $CaZn_{10}$, KCd_{11}, $NaZn_{12}$. Frequently, the same pair of elements forms more than one intermetallic compound.

So far, there is no general theory explaining the composition of intermetallic compounds and indicating the limits of their formation. It has only been observed that members of the same series of analogues, e. g., Zn, Cd and Hg, usually do not form them with one another. Thus, for the formation of intermetallic compounds, the difference in properties of the constituent elements must be greater than that existing within such series. However, the difference need not be considerable. For example, Mg yields compounds both with calcium ($CaMg_2$) and zinc ($MgZn$, $MgZn_2$, $MgZn_5$).

Some intermetallic compounds find direct practical applications. For example, a paste for metal dental fillings is often prepared by mixing Ag_3Sn powder with mercury. The filling hardens subsequently due to the reaction: $Ag_3Sn + 4Hg = Ag_3Hg_4 + Sn$.

2) Somewhat modified relationships are observed in freezing-point diagrams when both components in the system are mixed not only in the liquid state, but

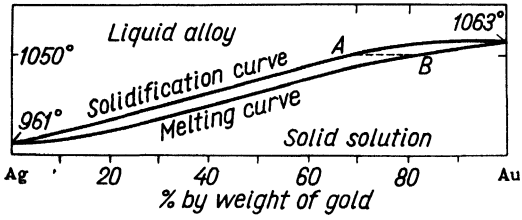


Fig. 164. Freezing-point diagram for the system Ag—Au

in the solid state, to form what are known as *solid solutions*. This occurs if the particles of both components are capable of replacing one another in the crystal lattice (yielding *mixed crystals*). Owing to this replacement, particles of both components are contained in each crystal, and the whole solid phase represents a *homogeneous* system, rather than a heterogeneous one (as in the case of a eutectic).

The main complication introduced by the formation of solid solutions is that in the range of concentrations corresponding to them, solidification of the liquid and melting of the solid phase (of the same composition) take place at different temperatures. Owing to this, two curves appear instead of each single curve on the diagram: a *solidification curve* and a *melting curve*.

The simplest example of a system complicated by the formation of solid solutions, is the system Ag—Au (Fig. 164). The region between the two curves corresponds to simultaneous existence of a liquid alloy and mixed crystals. If the overall composition of the mixtures and the temperatures corresponding to this region, the composition of the liquid alloy always corresponds to the points on the solidification curve, and the composition of the mixed crystals always corresponds to the points on the melting curve.

For example, if an alloy containing 70% Au is cooled, mixed crystals begin to separate out at 1050° C (*A*), the first portion containing 80% Au (*B*). On the other hand, when heated to 1050° C, a solid solution with 80% Au (*B*) begins to melt, and the first portions of liquid contain 70% Au (*A*). Thus, in the process of melting or solidification, the composition of both the liquid and solid phases varies continuously. The electrical and thermal conductivities of a solid solution of two metals are usually lower, and the hardness greater than those of either of the components.

The history of physicochemical analysis provides striking evidence in favour of the general conception that the demands of prac-

tice are the principal stimulus in the development of science. Its most important modern method—thermal analysis—came into being in response to the urgent requirements of metallurgy. Subsequently, this method also began to be applied in the solution of problems in the silicate, chemical and other industries.

While solving technical problems, physicochemical analysis simultaneously provides data of great value to chemistry: concerning the types of intermetallic compounds, the stability of complex compounds, etc. Besides chemistry, physicochemical analysis has numerous applications in adjacent fields.

XI-4. The Gallium Subgroup. The content of each of the members of this subgroup in the earth's crust decreases in the order *gallium* ($4 \times 10^{-4}\%$)—*indium* ($2 \times 10^{-6}\%$)—*thallium* ($8 \times 10^{-7}\%$). All three elements are highly dispersed, and no minerals rich in them are known. On the other hand, small amounts of their compounds are contained as impurities in the ores of many metals, particularly those of Zn. The elements Ga, In and Tl are obtained from the waste products in the processing of these ores.

In the free state, gallium, indium and thallium are low-melting, silvery-white metals. Their most important constants are listed below:

Properties	Ga	In	Tl
Specific gravity	5.9	7.3	11.9
Melting point (°C)	30	156	303
Boiling point (°C)	2240	2000	1460
Electrical conductivity (Hg = 1)	2	11	5

Gallium is similar to lead in hardness, while In and Tl are even softer.

Gallium remains unchanged in air, but indium and thallium slowly oxidise on the surface. When heated all three elements combine vigorously with oxygen and sulphur. They react with chlorine and bromine even at ordinary temperatures, but with iodine only on heating. Being grouped around iron in the electromotive series, Ga, In and Tl are soluble in acids.

The usual valency of gallium and indium is *three*. Thallium yields two series of derivatives, in which it is tri-and monovalent.

Gallium *sesquioxide*, white Ga_2O_3, and its analogues, yellow In_2O_3, and brown Tl_2O_3, are insoluble in water. The *hydroxides*, $E(OH)_3$, corresponding to them (which can be obtained only from salts) are gelat-

tinous precipitates, practically insoluble in water, but readily soluble in acids. The white hydroxides of Ga and In are also soluble in solutions of strong alkalis with which they form *gallates* and *indates*, compounds analogous to aluminates. Consequently, they are *amphoteric*, the acidic properties of $In(OH)_3$ being weaker and those of $Ga(OH)_3$ stronger than those of $Al(OH)_3$. Thus, besides strong alkalis, $Ga(OH)_3$ is soluble in concentrated NH_4OH. On the other hand, the reddish-brown $Tl(OH)_3$ hardly dissolves in alkalis.

Ga^{+++} and In^{+++} ions are colourless, while Tl^{+++} ion has a faintly yellowish colour. The salts of the majority of the acids, derived from them, dissolve readily in water, but are strongly hydrolysed.

While the derivatives of the lower valencies of Ga and In are not typical, the most characteristic thallium compounds are those in which it is monovalent. Therefore, the salts of Tl^{3+} have marked oxidising properties.

Thallous oxide, Tl_2O, is formed as a result of the reaction between the elements at high temperatures, and is a black hygroscopic powder. With water, thallous oxide forms yellow *thallous hydroxide*, TlOH, which easily loses water on heating and changes back into Tl_2O.

Thallous hydroxide is readily soluble in water, and is a *strong base*. Its salts are generally colourless, and crystallise without water. The chloride, bromide and iodide are almost insoluble, but many other salts are readily soluble. The derivatives of TlOH and weak acids are alkaline in solution owing to hydrolysis. Under the action of strong oxidising agents, e. g., chlorine water, monovalent thallium is oxidised to trivalent thallium.

As to the properties of the elements and their compounds, the gallium subgroup is, in many respects, similar to the germanium subgroup. Thus, for Ge and Ga, the higher valency is the more stable, while for Pb and Tl, the lower is the more stable; the chemical nature of the hydroxides changes uniformly in the series, Ge—Sn—Pb and Ga—In—Tl, etc. Sometimes, even finer features of resemblance are observed, such as the low solubility of the halogen (Cl, Br, I) salts of both Pb and Tl. Despite all this, there are substantial differences between the elements of the two subgroups (partially due to their different valencies). For example, the acidic nature of the hydroxides of Ga and its analogues is considerably weaker than in the corresponding elements of the germanium subgroup, and, in contrast to PbF_2, thallous fluoride is readily soluble, etc.

XI-5. The Scandium Subgroup. Besides the principal members of this subgroup—*scandium*, *yttrium*, *lanthanum* and *actinium*—adjoining it are elements 58-71, grouped under the heading of *lanthanides*, as well as the elements numbered from 90 upwards, i. e., *actinides*. These will be considered separately in Secs. 6 and 7.

The content of the members of the scandium subgroup in the earth's crust varies as follows: Sc—2×10^{-4}%, Y—5×10^{-4}%, La—2×10^{-4}%, Ac —5×10^{-15}%. Minerals rich in any one of these occur very rarely. Individual elements of the scandium subgroup and their derivatives have not as yet found any application, and the compounds of actinium have hardly been studied. The few data available indicate that actinium is closely similar to lanthanum.

Only *lanthanum*, whose properties have been studied fairly thoroughly, has been isolated in a more or less pure state (by the electrolysis of fused $LaCl_3$). Lanthanum is a white metal of sp. gr. 6.2, somewhat harder than tin, m. p. 826° C, b. p. 1800° C. The electrical conductivity of lanthanum is approximately twice that of mercury.

The chemical activity of lanthanum is very high. It decomposes water slowly liberating hydrogen, dissolves readily in acids, and reacts vigorously with all the typical nonmetals on heating. The properties of Sc and Y, in so far as they have been studied, are very similar to those of lanthanum. In all their compounds, scandium and its analogues are exclusively *trivalent*.

The *oxides* of Sc, Y and La are highly refractory white powders. They are practically insoluble in water, but combine readily with it to form the white hydroxides $E(OH)_3$.

The *hydroxides* of scandium and its analogues are also almost insoluble. They are all *basic* in nature, fairly weakly so in the case of $Sc(OH)_3$, but increasing rapidly in the order Sc—Y—La so that $La(OH)_3$ is a strong base.

$Sc^{\cdots}$, $Y^{\cdots}$ and $La^{\cdots}$ ions are colourless. Among the *salts* of the common acids corresponding to them, the *chlorides*, *nitrates* and *acetates* are readily soluble, but the *fluorides*, *carbonates* and *phosphates* dissolve sparingly in water. The solubility of the *sulphates* decreases rapidly in the order Sc—La and is lower at increased temperatures than in the cold. In accordance with the rapid increase in the basic character of the hydroxides in the order Sc—La, the hydrolysis of the salts drastically decreases in the same order.

In chemical properties of the elements and their compounds, the scandium subgroup is, in many respects, similar to the titanium subgroup. The middle element, yttrium, is, in general, closer to lanthanum than to scandium in chemical properties.

Of the two subgroups of the third group, the *scandium subgroup* is the one that bears analogy to its typical elements (B, Al) *at the highest positive valency*. This is manifested, for instance, in the regular change in the heats of formation of the higher oxides throughout the series B—La, there being no such regularity in the series B—Tl, as can be seen from the following data (kcal/mole of E_2O_3):

Tl	In	Ga	Al	**B**	Al	Sc	Y	La
120	240	256	399	**345**	399	410	440	457

XI-6. The Lanthanide Family. As has already been noted in the previous section, immediately adjoining lanthanum are 14 elements related to each other, and grouped under the heading of the *lanthanide family*. The members of this family are:

Cerium	Praseodymium	Neodymium	Promethium	Samarium	Europium	Gadolinium
58 2	*59* 2	*60* 2	*61* 2	*62* 2	*63* 2	*64* 2
8	8	8	8	8	8	9
Ce 20	**Pr** 21	**Nd** 22	**Pm** 23	**Sm** 24	**Eu** 25	**Gd** 25
18	18	18	18	18	18	18
8	8	8	8	8	8	8
140.12 2	140.907 2	144.24 2	[145] 2	150.35 2	151.96 2	157.25 2

Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium	Lutetium
65 2	*66* 2	*67* 2	*68* 2	*69* 2	*70* 2	*71* 2
8	8	8	8	8	8	9
Tb 27	**Dy** 28	**Ho** 29	**Er** 30	**Tm** 31	**Yb** 32	**Lu** 32
18	18	18	18	18	18	18
8	8	8	8	8	8	8
158.924 2	162.50 2	164.930 2	167.26 2	168.934 2	173.04 2	174.97 2

As can be seen from the table, the two outermost electronic shells have the same structure for the atoms of almost all the lanthanides, the change taking place in the *third* shell in which the number of electrons increases from 18 in La to 32 in Lu. Since the chemical properties of the elements are connected mainly with the structures of the *outermost* electronic shells, the change in the number of electrons in the third shell has rather a weak effect upon them. In connection with this, *all the lanthanides are similar in properties to one another* and are, as it were, members of a lanthanum "homologous series".

Lanthanides are greatly dispersed in nature, and are always encountered mixed with one another and with lanthanum and yttrium. Their relative content in the earth's crust is shown in Fig. 165 (the content of cerium, 0.0005% being taken as the unit). As can be seen from the diagram, lanthanides with *odd* positive nuclear charges are less abundant than their closest neighbours with *even* positive nuclear charges. In spite of the fact that the content of almost all the lanthanides in the earth's crust is considerably higher than that of such "common" elements as I and Hg, for example, their practical use is still very limited. One of the reasons for this is the difficulty of separating these elements from one another, owing to the extraordinary similarity of their properties.

All the lanthanides are as a rule *trivalent*. Cerium, moreover, yields a series of derivatives in which it is *tetravalent*. Oxides of tetravalent Pr and Tb and some salts of divalent Sm, Eu and Yb are also known.

However, these compounds are considerably less characteristic of the elements than the derivatives in which they are trivalent. The valency of the lanthanides and their closest neighbours in the sixth period, are graphically compared in Fig. 166 (the relative sizes of the dots gives an idea of how typical each particular valency state is for each element).

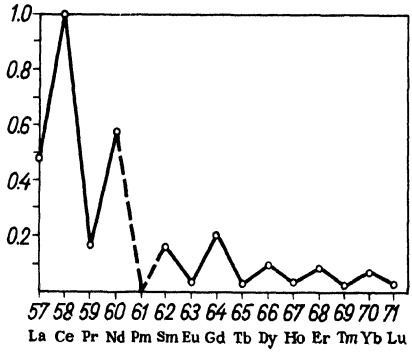


Fig. 165. Relative content of lanthanides in the earth's crust

Only Ce, Pr, Nd, Sm and Eu have been isolated in a more or less pure state. They closely resemble lanthanum in properties (whereas the other lanthanides are more similar to yttrium).

The *oxides* of the lanthanides are refractory powders, which are insoluble in water, but vigorously combine with the latter to form

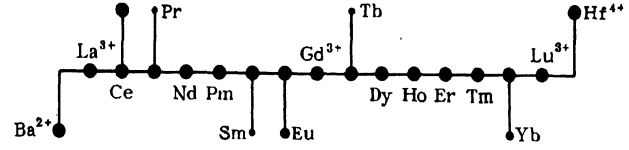


Fig. 166. Valency of the lanthanides and their closest neighbours

hydroxides. The oxides of Ce, Gd, Yb and Lu are colourless, while the rest have the following colours: Eu, Tb and Er—pink, Sm, Dy and Ho—yellow, Pr and Tm—green, Nd—lightblue.

The *hydroxides*, $E(OH)_3$, are almost insoluble in water. They are all *basic* only. As to degree of basicity, the hydroxides of the lanthanides fall into a series coinciding with the order of decreasing ionic radii of the same elements:

Decreasing basic properties of $E(OH)_3$ →

Element	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Sc
Radius of ion (Å)	1.22	1.18	1.16	1.15		1.13	1.13	1.11	1.09	1.07	1.05	1.04	1.04	1.00	0.99	0.83

→ Decreasing radius of E^{3+} ion

The position of $Y(OH)_3$ in this series—between the hydroxides of Dy and Ho—also corresponds to the radius of Y^{3+} (1.06 Å). From the point of view of the concepts considered earlier (V-5), this relationship between the properties of $E(OH)_3$ and the radius of the E^{3+} ions is quite easily understood. In accordance with their basic nature, the hydroxides of the lanthanides are insoluble in alkalis, but react readily with acids.

The *salts* of the lanthanides are very similar in their properties to the corresponding salts of La and Y. The colour of the $E^{\cdot\cdot\cdot}$ ions is usually the same as those of the oxides (with the exception of the pink $Nd^{\cdot\cdot\cdot}$). The colours pink $[Pm(NO_3)_3]$ and yellow ($PmCl_3$) are characteristic of the derivatives of promethium. Chiefly $Ce(NO_3)_3$ finds practical application (in the manufacture of mantles for paraffin lamps).

An important difference between cerium and the other lanthanides is the stability of the highest cerium oxide and certain derivatives of the latter. Pale yellow *ceric oxide*, CeO_2, results when either the metal or its salts are heated in air. Its corresponding *hydrate*, $Ce(OH)_4$, is a yellow gelatinous precipitate. Its basic properties are weaker than those of $Sc(OH)_3$. $Ce(OH)_4$ is almost insoluble in alkalis, but dissolves in acids to form the corresponding salts.

$Ce^{\cdot\cdot}$ ion is orange in colour. Salts of tetravalent cerium are strongly hydrolysed in solution. While trivalent cerium is readily oxidised to tetravalent cerium in alkaline solution (even by atmospheric oxygen), the derivatives of tetravalent cerium are rather unstable in *acid* solution and are strong oxidising agents. Reactions between $Ce(OH)_4$ and oxidisable acids, e. g. HCl, result in salts of trivalent cerium. For this reason, the number of known derivatives of tetravalent cerium is very limited.

Although the tetravalency of cerium in some of its compounds places this element in a somewhat special position among the other lanthanides, the latter, as a whole, exhibit an exceptionally close resemblance to the principal elements of the scandium subgroup, and, with regard to the majority of their properties, very naturally fall between lanthanum and scandium.

XI-7. The Actinide Family. The heaviest elements, following actinium in the periodic table, belong to the actinide family:

Thorium	Protactinium	Uranium	Neptunium	Plutonium	Americium	Curium
2	2	2	2	2	2	2
90 10	*91* 9	*92* 9	*93* 8	*94* 8	*95* 8	*96* 9
18	20	21	23	24	25	25
Th 32	**Pa** 32	**U** 32	**Np** 32	**Pu** 32	**Am** 32	**Cm** 32
18	18	18	18	18	18	18
8	8	8	8	8	8	8
232.038 2	[231] 2	238.03 2	[237] 2	[242] 2	[243] 2	[247] 2

(*Continued from page 348*)

Berkelium	Californium	Einsteinium	Fermium	Mendelevium	Nobelium	
2	2	2	2	2	2	2
97 8	*98* 8	*99* 8	*100* 8	*101* 8	*102* 8	*103* 9
27	28	29	30	31	32	32
Bk 32	**Cf** 32	**Es** 32	**Fm** 32	**Md** 32	**No** 32	**Lr** 32
18	18	18	18	18	18	18
8	8	8	8	8	8	8
[247] 2	[251] 2	[254] 2	[253] 2	[256] 2	[254] 2	[257] 2

Of these elements, only thorium, protactinium and uranium were discovered by ordinary methods. The others were produced artificially. All the actinides undergo radioactive decay (III-2), which is the slowest in the case of thorium and uranium.

Only Th (6×10^{-5}%) and U (2×10^{-5}%) are contained in the earth's crust in any appreciable quantities, but minerals rich in them are encountered very rarely. Among these minerals special mention should be made of *thorite*, $ThSiO_4$, and *uraninite*, U_3O_8, i.e., $UO_2 \cdot 2UO_3$.

1) The protactinium content in the earth's crust is only 8×10^{-12}%. It is contained in uranium ores in the ratio of about 0.3 g of Pa per 1000 kg of U.

The practical importance of Th, U and the other actinides (especially Pu) is connected with the utilisation of nuclear energy. Although the chemistry of these elements is studied intensively, many results of these researches are not published. In particular, almost nothing is known, as yet, about the properties of Bk and the actinides following it.

The elements of the actinide family can be obtained in the free state by the electrolysis of their fused salts. Only the properties of thorium and uranium have been described in more or less detail, and their most important constants are compared below:

Element	Specific gravity	Melting point	Boiling point	Electrical conductivity (Hg = 1)
Th	11.5	1800° C	5200° C	5
U	18.3	1133° C	3500° C	3

Both elements are white, lustrous metals with a greyish (Th) or bluish (U) tint. They are fairly soft and readily machinable. Judging by the fragmental data available, the other actinides possess physical properties closely resembling those of Th and U.

Under ordinary conditions, thorium is resistant to air and water, whereas uranium is oxidised on the surface and slowly decomposes water. Uranium dissolves in acids much more readily than thorium. Alkalis have no effect on either metal.

At elevated temperatures, both elements combine vigorously not only with the halogens, oxygen and sulphur, but also with nitrogen and carbon. They are able to absorb large quantities of hydrogen.

In their compounds, the actinides exhibit a much greater variety of valency states than the lanthanides. Their known valencies are compared below:

Th	Pa	U	Np	Pu	Am
(2,3) **4**	(3,4) **5**	3, 4, 5, **6**	3, 4, 5, **6**	3, **4**, 5, 6	2, **3** (4, 5, 6)

Cm	Bk	Cf
3	(3, 4)	(3)

The most characteristic valencies are printed in bold type, and the least characteristic valencies, or those that have been very little studied, are given in parentheses. As can be seen from the comparison, initially (from Th to U) the most characteristic valency increases, but subsequently (from U to Cm) it decreases.

2) In regard to its characteristic valency states berkelium is similar to cerium. Thus, Bk^{III} is not oxidised by chlorine to Bk^{IV} in hydrochloric acid solution, but this oxidation may be carried out by means of $NaBrO_3$ in nitric acid solution. For californium (and the actinides following it) only the existence of the trivalent state has been established as yet.

The *hexavalent* state, which is the highest valency state attained by the actinides, is the most stable one for *uranium*. On boiling with water, its orange highest oxide, UO_3, is converted into the almost insoluble yellow hydroxide, $UO_2(OH)_2$ or H_2UO_4. The latter is amphoteric, with its basic properties predominating over acidic. It does not pass into solution under the action of alkalis, since all the salts of H_2UO_4 (*uranates*) are sparingly soluble. In contrast, acids dissolve $UO_2(OH)_2$ with the formation of greenish-yellow salts of the UO_2^{2+} (*uranyl*) ion. Of these, uranyl nitrate, $UO_2(NO_3)_2$, is the most common compound of uranium. Oxidising properties are not characteristic of the derivatives of hexavalent uranium. Like the other compounds of U, they are all poisonous.

The highest oxides of Np and Pu, EO_3, have not yet been obtained. The brown hydroxides corresponding to them, $EO_2(OH)_2$ or H_2EO_4, are amphoteric. They are used for obtaining *neptunates* and *plutonates*, on the one hand, and *neptunyl* (NpO_2^{2+}) and *plutonyl* (PuO_2^{2+}) salts, on the other. Solid, but highly volatile fluorides, EF_6, of U, Np and Pu have been obtained, of which PuF_6 is very unstable. An analogous chloride is known only for uranium (UCl_6).

The typicalness of the hexavalent state decreases in the order U—Np—Pu. The highest oxides obtained are: UO_3 for uranium, Np_3O_8, i. e., $NpO_2 \cdot 2NpO_3$ for neptunium, and PuO_2 for plutonium. The formation of the derivatives of Np^{VI} and Pu^{VI} in solution is possible only under the action of the most powerful oxidising agents, neptunium being oxidised more easily than plutonium. The derivatives of Np^{VI} and Pu^{VI} are such powerful oxidising agents in acid solution that they oxidise hydrochloric acid (Np^{VI} slowly, Pu^{VI} fairly rapidly).

Derivatives of the *pentavalent* actinides are characteristic chiefly of *protactinium*, but also partly of U, Np and Pu.

The white, refractory Pa_2O_5 is formed when Pa is heated in oxygen. The hydroxide corresponding to it, $Pa(OH)_5$ is insoluble in water and is very weakly basic. Only a few of the derivatives of Pa are known, in particular, $PaCl_5$. As a rule, compounds of protactinium are colourless.

Of the derivatives of other pentavalent actinides, only a few compounds of uranium—U_2O_5, UF_5 and UCl_5—have been isolated. The possibility of existence of EO_2^+ ions in acid solution has been established for U, Np and Pu, the most stable being NpO_2^+. Oxidising properties in the pentavalent state are characteristic only of plutonium.

A valency of *four* is typical of *thorium*, and plays a more or less significant role in the chemistry of a number of other actinides. For neptunium and plutonium this is one of the most characteristic valencies, whereas compounds of U^{IV} (which may be obtained by the action of Zn on uranyl salts in acid solution) possess distinct reducing properties. The derivatives of thorium are mostly colourless, but compounds of the other tetravalent actinides are coloured (mostly, green).

The EO_2 oxides are solids, practically insoluble in water. The latter also applies to the $E(OH)_4$ hydroxides which are basic. Their salts with various acids are considerably hydrolysed in solution.

The *trivalent* state is most characteristic of curium, americium, and partly of plutonium. The derivatives of Pu^{III} as such are quite stable, but when in solution are readily oxidised by atmospheric oxygen. On passing further to Np^{III} and U^{III}, the reducing activity increases so much that the soluble compounds of trivalent uranium decompose water, displacing hydrogen, i. e., they are oxidised by H^+ ions like the active metals.

The sparingly soluble $E(OH)_3$ hydroxides are basic, and on reacting with strong acids form salts that are only slightly hydrolysed. These salts are similar in solubility to the corresponding compounds of the lanthanides.

By the action of sodium amalgam, i. e., an alloy of sodium and mercury, on solutions of americium compounds, the latter can be reduced to the *divalent* state. This reduction cannot be achieved with any other actinide. Solutions containing Am^{II} possess very powerful reducing properties, and are rapidly oxidised by atmospheric oxygen. However, oxidation can be greatly retarded by precipitating sparingly soluble $AmSO_4$.

In their chemical relationships, americium and curium are very similar to the corresponding lanthanides, europium and gadolinium. Indeed, the ions Eu^{+++} and Am^{+++} are pink, while the ions Gd^{+++} and Cm^{+++} are colourless; Eu and Am can be reduced to the divalent state, while Gd and Cm cannot be reduced. This close resemblance in properties once more confirms the grouping of the heaviest chemical elements into the actinide family.

XII. SECOND GROUP OF THE PERIODIC TABLE

	4			
2	**Be**			
2	9.0122			
	12			
2	**Mg**			
8	24.312			
2				
	20			
2	**Ca**			
8	40.08	*30*		2
8		**Zn**		18
				8
2		65.37		2
2	*38*			
8				
18	**Sr**			
8	87.62	*48*		2
2		**Cd**		18
				18
				8
		112.40		2
2	*56*			
8				
18	**Ba**			
18				
8				
2	137.34			
		80		2
				18
		Hg		32
				18
				8
		200.59		2
2	*88*			
8				
18				
32				
18	**Ra**			
8				
2	[226]			

Group two differs from the groups of the periodic table considered earlier in that the structure of the outermost electronic shell of the atoms of all the elements comprising it is the same. On the other hand, the *second outermost shell*, while being complete, differs in individual members of the second group. This fact affects the properties of the corresponding atoms and ions, and necessitates division of the elements following magnesium into the calcium and zinc subgroups.

The presence of only two electrons in the outermost shell of all these atoms points to the absence of any appreciable tendency towards their further addition. On the other hand, the giving up of electrons, to form, at most, *divalent* positive ions, should take place relatively easily.

As in the case of the pair B—Si, beryllium, in some respects, exhibits a great similarity to the second element of the neighbouring group—aluminium.

XII-1. Beryllium and Magnesium. Beryllium is among the fairly abundant elements: it accounts for about 0.001% of the total number of atoms in the earth's crust. The content of magnesium in the latter is 1.4%, and, consequently, this is one of the most abundant elements. Besides various minerals and rocks, magnesium compounds are invariably contained in the waters of the ocean, and in plant and animal organisms.

In addition to numerous magnesium silicates, this element occurs on the earth's surface chiefly in the form of the carbonate minerals *dolomite*, $CaCO_3 \cdot MgCO_2$, and *magnesite*, $MgCO_3$. The former sometimes forms whole mountain chains, while the latter is also encountered in very large accumulations.

Readily soluble minerals of Mg, the most important being *carnallite*, $KCl \cdot MgCl_2 \cdot 6H_2O$, which serves as the conventional raw material for obtaining metallic magnesium, are also sometimes found under layers of various alluvial rocks together with deposits of rock salt. Huge supplies of carnallite occur in Solikamsk where this mineral is found in seams up to 100 m thick. Beryllium minerals, the most important of which is *beryl*, $Be_3Al_2(SiO_3)_6$ or $3BeO \cdot Al_2O_3 \cdot 6SiO_2$, are much more rarely encountered in nature.

1) Transparent varieties of beryl, coloured by impurities, are used as precious stones. These include green *emeralds*, blue *aquamarines*, etc.

Elementary Be and Mg are usually prepared by electrolysis of their fused chlorides. They are both white metals, which are fairly slowly coated with a thin oxide film in air, this giving them a dull appearance. Their basic constants are compared below:

	Specific gravity	Melting point	Boiling point	Electrical conductivity (Hg = 1)
Be	1.82	1284° C	2470° C	5
Mg	1.74	651° C	1110° C	21

Beryllium, which is greyish-white, is fairly hard and brittle, while magnesium, which is silvery-white, is considerably softer and more plastic. The two elements (especially Mg) find extensive application both individually and in the form of alloys with other metals.

2) The most frequently employed alloys of magnesium are *magnalium* and *elektron*. The first is an alloy of Al with 5-30% Mg, while the name "elektron" covers alloys in which magnesium is the main constituent. The world annual production of elektron is about 150 thousand tons.

3) At present the principal application of beryllium is connected with the utilisation of nuclear energy.

On heating in air, Be and Mg burn to the oxides EO. They combine readily with the halogens and, on heating, with sulphur and nitrogen. The reactions are accompanied by intensive evolution of heat, magnesium usually reacting more vigorously than beryllium.

Water has no effect on beryllium, since the metal is generally coated with a protective oxide film. Magnesium reacts only very slowly with cold water, but the reaction is speeded up appreciably on heating. Both elements dissolve readily in dilute acids. They are *divalent* in all their compounds.

The *oxides* of beryllium and magnesium are highly refractory white powders. They are readily soluble in acids. Beryllium oxide also dissolves in the strong alkalis. The oxides EO combine with water to form hydroxides $E(OH)_2$, the reaction being accompanied by appreciable evolution of heat.

4) Beryllium oxide (like the metal itself) is of great importance for installations utilising nuclear energy. Magnesium oxide obtained by roasting natural magnesite is an important starting product for the manufacture of refractories and of artificial building materials based on *Sorel's cement*. The latter is produced by mixing roasted magnesium oxide with a 30% aqueous solution of $MgCl_2$. Owing to the formation of more or less long chains of the type —Mg—O—Mg—O—Mg— (with hydroxyl radicals or chlorine atoms at the ends), the mixture turns into a white, very hard mass after a few hours.

The white, amorphous *hydroxides* of beryllium and magnesium are very sparingly soluble in water. Dissolved $Mg(OH)_2$ dissociates only as a *base*. $Be(OH)_2$ is *amphoteric* and dissociates in accordance with the overall equation:

$$Be^{\cdot\cdot} + 2OH' \rightleftarrows Be(OH)_2 \equiv H_2BeO_2 \rightleftarrows 2H^{\cdot} + BeO_2''$$

Owing to the weak acidic properties of $Be(OH)_2$, salts containing the anion BeO_2'' (*beryllates*) are strongly hydrolysed in aqueous solution. The basic properties of $Be(OH)_2$ are much more pronounced than its acidic properties, but considerably less than those of magnesium hydroxide, which is a base of medium strength. In accordance with their chemical nature, $Be(OH)_2$ dissolves both in strong alkalis and in acids, while $Mg(OH)_2$ dissolves only in acids.

Most salts of beryllium and magnesium are readily soluble in water. The solutions contain colourless $E^{\cdot\cdot}$ ions. The presence of the $Mg^{\cdot\cdot}$ ion imparts a bitter taste to the liquid, while the $Be^{\cdot\cdot}$ ion imparts to it a sweet, slightly astringent taste. Be salts are appreciably hydrolysed by water even at ordinary temperatures, while Mg salts of strong acids are hydrolysed only when the solutions are heated. All beryllium compounds are very poisonous.

These two elements are generally similar in chemical nature. The chief differences between them are connected with the considerable increase in the ionic radius from Be^{2+} (0.34 Å) to Mg^{2+} (0.78 Å).

XII-2. Crystals. When substances pass from the liquid (or dissolved) state into the solid state, some of them separate out as more or less large particles of a *definite shape*, while others separate out as a *shapeless mass*. Solids of the first type, e. g., common salt, sugar, are called *crystalline*, and those of the second type, e. g., glue, rubber, are called *amorphous*.

Whether a substance will be crystalline or amorphous depends primarily on its own properties, and secondly on the conditions of its conversion into the solid state. By suitably altering these conditions, such typically amorphous substances as rubber and glue have been obtained in the crystalline state. Detailed research has shown that many other amorphous substances actually consist of crystals, but these are so minute as to be imperceptible even under a microscope.

Thus, the basis of the structure of a substance in the solid state is the *crystal*. The size of the latter is greatly influenced by the conditions of crystallisation, which is usually carried out from solution. To obtain small crystals, a solution saturated at a high temperature must be rapidly cooled. If it is desired to form large crystals, the solution should be left to stand at an ordinary temperature so that crystallisation should take place slowly as the solvent evaporates.

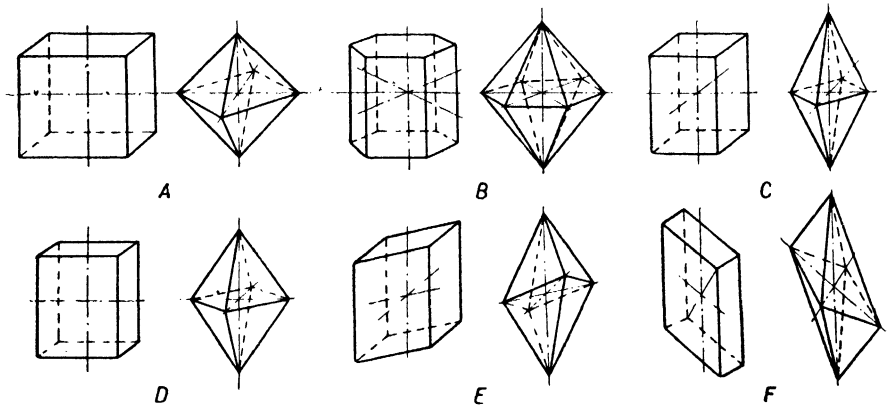


Fig. 167. Prismatic and pyramidal crystals

The most characteristic feature of crystals is their *directional character*, i. e., the non-uniformity of their properties (strength, rate of solution, etc.) in different directions. In particular, this or, more precisely, the different rates of growth of the separate faces, determines the great variety of *crystal shapes*, some of the simplest of which are shown in Fig. 167.

1) All the crystal shapes of different substances can be reduced to 32 classes which are grouped into six crystal systems. The shape of a crystal is characterised by a greater or lesser degree of *symmetry*. The latter depends on the presence or absence of definite *symmetry elements*, these being the *centre*, the *plane* and the *axis* of symmetry.

The *centre of symmetry* is the point which divides in two all the straight lines connecting the outer surfaces of the crystal and passing through the point in *any* direction. As can be seen from Fig. 168, a cube has a centre of symmetry, *C*.

In crystals having a *plane of symmetry* (π or *P*), one part of the crystal is related to the opposite part as an object to its mirror image. If the cube is considered from this point of view (Fig. 168), it is found that 3 planes of symmetry (π) can be drawn through the middle of the edges, and six (*P*), through the corners.

If an *axis of symmetry* (λ or *L*) can be drawn through the crystal, this means that the position of the crystal obtained by rotating about this axis through a certain angle, will coincide completely with its original position. The *order* of the axis depends on the angle of rotation required to achieve this coincidence, and is numerically expressed as the quotient of 360° divided by this angle.

Obviously, upon rotation through 360°, any figure will coincide with itself and, therefore, an axis of the first order does not specify anything whatsoever. Crystals may have axes of 2-, 3-, 4- and 6-fold symmetry. In particular, a cube (Fig. 168) has 3 axes of four-fold symmetry (passing through its face centres), 4 axes of three-fold symmetry (passing through its opposite corners) and 6 axes of two-fold symmetry (passing through the middles of its edges).

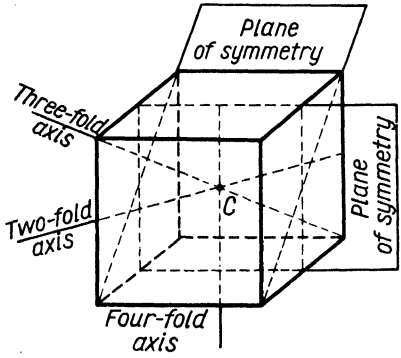


Fig. 168. Elements of symmetry of a cube

The symmetry of the cube is symbolically denoted in *crystallography* (the science of crystals) as follows: $3\lambda^4\ 4\lambda^3\ 6L^2\ C\ 3\pi\ 6P$. As can be seen from this formula, the cube possesses a very large number of symmetry elements. The sphere is an ideal symmetrical figure.

It has already been mentioned (III-7) that research into the internal structure of crystals became possible only after 1912. At present, the internal structure of a great many substances has been established.

The smallest possible volume of the space lattice of a crystal (Fig. 51) which still fully represents all the features of its structure, is called a *unit cell*. The crystal as a whole can be built up by simply adjoining unit cells to one another in three directions in space, as is schematically shown in Fig. 169. Therefore, to establish the internal

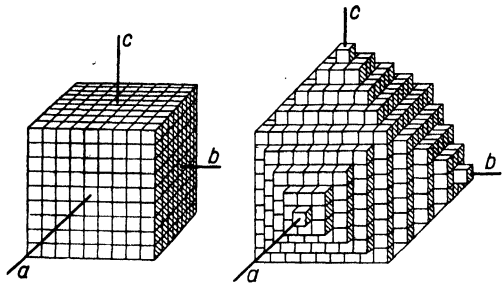


Fig. 169. Building of crystals from unit cells

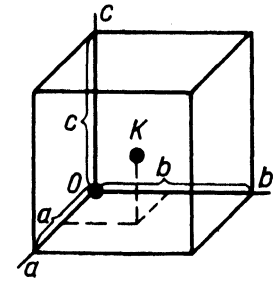


Fig. 170. An example of a unit cell

structure of a particular crystal, it is sufficient to know the *shape* of its unit cell, the *size* of the latter and the *arrangement* in it of the particles of which the crystal is formed (III-7) as well as the nature of these particles.

By way of example let us consider the unit cell shown in Fig. 170. The coordinate axes a, b, c are at right angles to each other: α (i. e., $< aOc$) $= \beta$ (i. e., $< bOc$) $= \gamma$ (i. e., $< aOb$) $= 90°$. The

intercepts on these axes are also equal, i. e., $a=b=c$. The shape of the unit cell is defined by these relationships ($\alpha=\beta=\gamma=90°$ and $a=b=c$): it represents a cube. Its dimensions are fully defined by the length of one side, which is usually denoted in this case by a_w. The arrangement of the particles is given by the three coordinates (a, b, c) of their centres, the corner of the cell occupied by one of the particles being taken as the origin of the coordinates. The numerical values of the coordinates are expressed in fractions of the corresponding edge of the

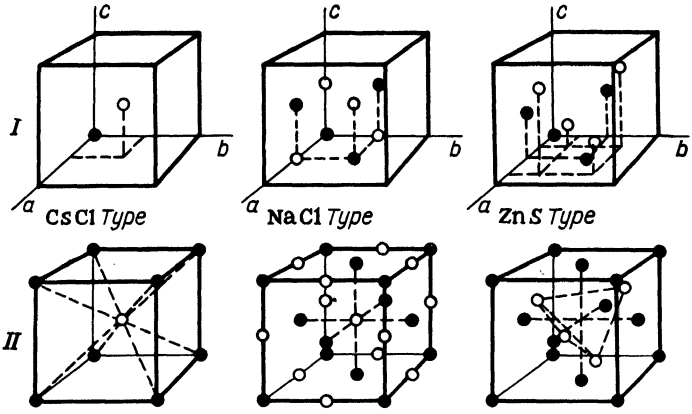


Fig. 171. The most common structures of binary compounds

unit cell. Thus, the coordinates of the particles O and K (Fig. 170) will be respectively (000) and (1/2 1/2 1/2). The shortest distance between the centres of the two particles (d) can be calculated by using a geometrical theorem. In this case it is equal to half the diagonal of the cube, i. e., $d = 0.5\, a_w\sqrt{3} = 0.866\, a_w$.

The arrangement of the individual particles in the crystal depends, above all, on the chemical composition of the crystallising substance. In the case of an ionic compound, the most important factor is its type (AB, AB_2, A_2B_3, etc.). The most frequently encountered structures of the simplest *binary* (i. e., consisting of only two members) ionic compounds are shown in Fig. 171.

The upper part of the figure (*I*) contains a number of cubic unit cells in which the black and white circles represent ions of opposite sign. The structure of the CsCl cell was considered above (Fig. 170). By putting a number of such cells together (along the faces of a cube), the whole crystal of CsCl may be built up. If it is limited to the volume of the unit cell, the latter will be filled with ions as shown in the lower part (*II*) of Fig. 171. These filled cells together with their characteristics (angles, edge lengths and coordinates of structural units) are what is usually quoted in the literature.

A crystal of the CsCl type (otherwise known as the *body-centred* cube) consists, as it were, of two simple cubic lattices (Fig. 172), filled in one case with Cs^+ ions and in the other, with Cl^- ions, and then inserted one into the other as shown in Fig. 173. From the latter it can be seen that each Cs^+ ion is surrounded by eight equidistant Cl^- ions and each Cl^- is surrounded by eight Cs^+ ions. Thus, the *coordination number* of the body-centred cubic lattice is *eight*.

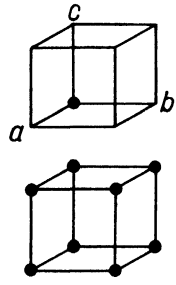


Fig. 172. A simple cubic lattice

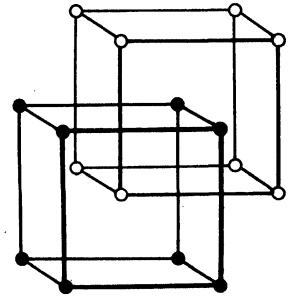


Fig. 173. Diagram of the structure of CsCl

The most frequently encountered lattice of ionic *AB* compounds is that of the NaCl type, the unit cell of which contains eight ions—four positive and four negative (Fig. 171). Each of these ions is surrounded at the closest distance by six oppositely charged ions (this is clearly illustrated by the central ion in the lower part of Fig. 171 at the centre of the cube). The coordination number of a lattice of this type is therefore *six*.

The lattice of zinc blende, ZnS, is an example of the third type of structure, characteristic of a number of *AB* compounds. Its unit cell (Fig. 171) also contains eight ions, but these are differently arranged than in the case of NaCl. The coordination number of a lattice of this type is equal to *four*.

2) Many *chemical elements* (especially metals) have *face-centred cubic* lattices (Fig. 174) or lattices of the *hexagonal close-packed* type, an example of the latter being that of metallic magnesium which is shown in Fig. 175. The coordination number of both structures is twelve. They both permit the maximum possible packing of spheres and, moreover, to equal density. Such packings are shown in Fig. 176.

A knowledge of the nuclear distances, *d*, in crystal lattices permits approximate determination of the absolute dimensions of atoms and ions. Assuming them to be spherical, *d* may be regarded as equal to the sum of the radii of two adjacent particles (more precisely, of their *spheres of action*). Obviously, if they are equal, the radius of each is one

half of d. If the element forms a crystal structure of the type of a huge single particle (III-7), this directly gives the radius of its atom.

The case of ionic structures is more complicated, owing to the fact that here d cannot be simply divided by two. To find the ionic radii

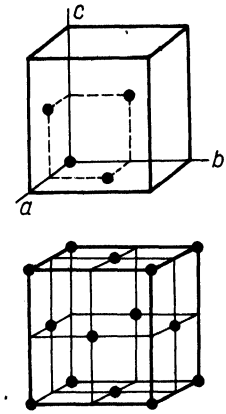


Fig. 174. A face-centred cube

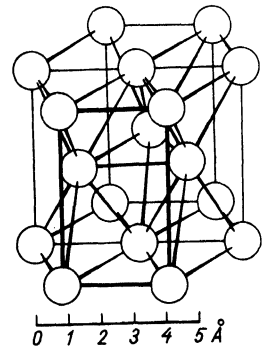


Fig. 175. Lattice of metallic magnesium

knowing the values of d for the lattices of a number of salts, it is necessary first to determine which part of d refers to the cation and which to the anion. This is impossible if none of the ionic radii are known. But knowledge of at least one radius provides a basis for determining all the rest.

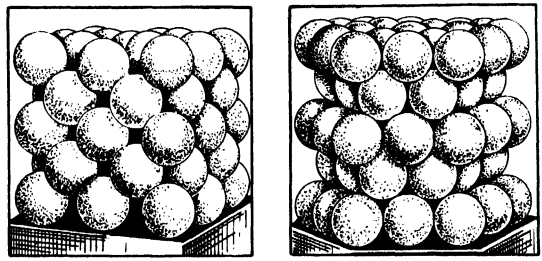


Fig. 176. Closset packings of spheres

The most reliable initial values were obtained for the ions F^- (1.33 Å) and O^{2-} (1.32 Å) by optical methods. After this, determination of the radii of other ions was not difficult. For example, knowing d for the NaF lattice (2.31 Å), we find by simple subtraction that the radius of Na^+ ion is 2.31—1.33 = 0.98 Å. From the known radii of cations, it is easy to find the radii of other anions in exactly the same

way. The relative sizes of elementary ions are shown in Fig. 177, magnified 30 million times.

The *structure* of the crystal of an ionic compound, i. e., the formation by the latter of a particular type of lattice, depends mainly on three factors: 1) the relative number of structural units, 2) the relation between their sizes and 3) their mutual influence on one another. The significance of the first factor is self-evident, because the lattice of a salt of the type MX_2, for instance, cannot have quite the same

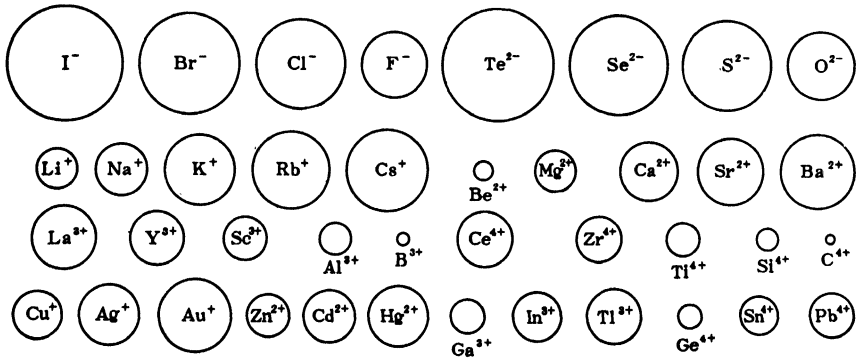


Fig. 177. Relative sizes of ions

build as that of a salt of the type MX, since the former must accommodate twice as many anions as the latter. The third factor depends entirely on the individual nature of the reacting elements.

The influence of the relative sizes of the particles warrants some discussion. Consider a series of analogous compounds, say, of the MX type, in which X is always the same while the chemical nature of M changes successively (or vice versa). At a certain stage the structure of the crystal lattice in the series may change. This phenomenon (known as *morphotropy*) is closely connected with the relative sizes of M and X, and the change in lattice structure occurs when the ratio *radius of M*: *radius of X* reaches a certain value. Examples of this are the following two series of compounds with successively changing $R_{cation} : R_{anion}$ ratios.

Substance . .	BeO	MgO	CaO	SrO	BaO	LiCl	NaCl	KCl	RbCl	CsCl
R_C/R_A	0.26	0.59	0.80	0.96	1.08	0.43	0.54	0.73	0.82	0.91
Type of lattice	ZnS	NaCl				NaCl				CsCl

The change in crystal structure of one and the same substance due to a change in *external conditions* may be regarded as a special case of morphotropy. This phenomenon is known as *polymorphism* and is

observed for very many substances. An example is the change in structure of the ammonium halides, when heated, from the CsCl to the NaCl type:

Salt	NH_4Cl	NH_4Br	NH_4I
R_C/R_A	0.79	0.73	0.65
Transition point	184° C	138° C	—18° C

The data given show that the smaller the R_C to R_A ratio in these salts, the more readily the coordination number of the crystal structure decreases ($8 \rightarrow 6$).

If the radii of any two ions with like charges are sufficiently close, these ions may sometimes participate simultaneously in the formation of the lattice of the same crystal. For example, *mixed crystals*, each of which contains both Cl^- ($r = 1.81$ Å) and Br^- ($r = 1.96$ Å) ions, separate from a mixed solution of KCl and KBr, the quantity of either anion depending only on its relative content in the solution. Owing to the formation of mixed K (Cl, Br) crystals, salts of the composition $Cl_xBr_yK_{(x+y)}$ can be obtained with any values of x and y, i.e., the composition of the substance can change practically continuously from KCl ($y = 0$) to KBr ($x = 0$). In such cases, consequently, the Berthollet principle (I-2) concerning the continuous change in the composition of chemical compounds, is justified.

Substances with the same type of molecular structure (KCl and KBr, $KMnO_4$ and $BaSO_4$, etc.), which form mixed crystals between themselves, are called *isomorphous*. Owing to the close similarity of their lattices, a crystal of one of the isomorphous substances can cause crystallisation in a supersaturated solution of the other, and will continue to grow in its saturated solution as the water evaporates, the crystal being coated with a layer of the second substance. Alums of different composition (XI-2) are a good example of a group of isomorphous salts. Numerous cases of isomorphism are also known for substances of other classes.

XI-13. The Alkaline Earth Metals. The elements of the calcium subgroup are known as the *alkaline earth* metals. The origin of this name is connected with the fact that their oxides (the "earths" of the alchemists) impart an alkaline reaction to water.

Calcium accounts for 1.5% of the total number of atoms in the earth's crust, whereas the content of *radium* in the latter is very small (8×10^{-12}%). The intermediate elements—*strontium* (0.008%) and *barium* (0.005%) are closer to calcium in this respect.

Besides various silicate rocks, Ca, Sr and Ba are encountered chiefly in the form of their sparingly soluble *carbonates* and *sulphates*, such as the following minerals:

$CaCO_3$ — calcite	$CaSO_4$ — anhydrite
$SrCO_3$ — strontianite	$SrSO_4$ — celestite
$BaCO_3$ — witherite	$BaSO_4$ — heavy spar (barite)

Calcium carbonate in the form of *limestone* and *chalk* sometimes forms whole mountain chains. The crystallised form of $CaCO_3$—*marble*—is encountered much less frequently. Calcium sulphate occurs mostly in the form oft he mineral *gypsum*, $CaSO_4 \cdot 2H_2O$, deposits of which are often very large. Another important calcium mineral is *fluorite*, or *fluorspar*, CaF_2.

Strontium and barium sulphate minerals are more abundant than their carbonate minerals. Deposits of radium are associated with uranium ores (1000 kg of uranium ore containing only 0.3 g of radium).

Industrial applications are restricted almost solely to the compounds of these elements, the fields in which each is used depending on its characteristic properties. Radium salts are an exception, their practical importance being due to their common property—radioactivity (III-2). So far, the chemistry of radium and its compounds has been studied very incompletely. In general, it is similar in chemical properties to barium.

The elements of the calcium subgroup can be obtained in the free state by the electrolysis of their fused salts. They are silvery-white metals. Calcium is fairly hard, but strontium and especially barium are much softer Some of the constants of the alkaline earth metals are compared in the following table.

Properties	Ca	Sr	Ba	Ra
Specific gravity	1.6	2.6	3.6	5.0
Melting point (°C) . . .	851	770	704	600
Boiling point (°C) . . .	1440	1380	1630	1540
Electrical conductivity (Hg = 1)	21	4		

The volatile compounds of the alkaline earth metals impart characteristic colours to a flame: Ca—orange-red, Sr (and Ra)—crimson, Ba—yellowish-green. This is used in chemical analysis for the detection of these elements.

In air, calcium and its analogues immediately become coated with a yellowish film which, along with the normal oxides, EO, also contains small amounts of *peroxides*, EO_2, and *nitrides*, E_3N_2. The alkaline earth metals are to the left of magnesium in the electromotive series, and therefore readily displace hydrogen from water as well as from dilute acids. The vigour of the reaction increases from Ca to Ra. These elements are *divalent* in all their stable compounds.

The alkaline earth metals combine very vigorously with non-metals, liberating a considerable amount of heat, as can be seen from Fig. 178. The *hydrides*, EH_2, which result when calcium and its analogues are heated in a current of dry hydrogen, are particularly interesting. These compounds are typically ionic in nature, the anion being the negatively charged hydrogen ion, H^-. They are vigorously decomposed by water according to the equation:

$$EH_2 + 2HOH = 2H_2 + E(OH)_2$$

The alkaline earth elements combine with such a chemically inert element (in the free state) as nitrogen even when heated comparatively gently. If heated strongly they will also combine with carbon to form *carbides* of the type EC_2.

The *oxides* of calcium and its analogues, EO, are white refractory substances, which combine vigorously with water to form white *hydroxides*, $E(OH)_2$. The latter are strong bases, and dissolve fairly readily in water. The basic properties of the hydroxides increase in the order Ca—Sr—Ba. Their solubility increases very rapidly in the same order.

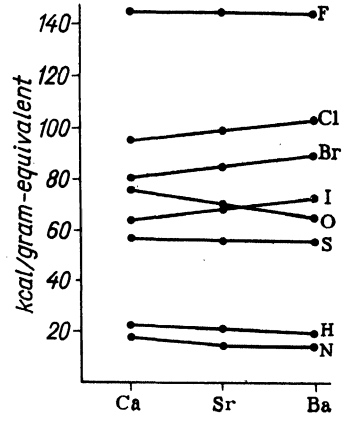


Fig. 178. Heats of formation of Ca, Sr and Ba compounds

1) The properties of the oxides and hydroxides vary fairly regularly not only for the alkaline earth metals, but also throughout the series Be—Ba. This is due to the consecutive increase in radius of the ions E^{2+}, while the type of electronic structure of all of them is the same (that of an inert gas).

Element	Be	Mg	Ca	Sr	Ba
Radius of ion E^{2+} (Å)	0.34	0.78	1.06	1.27	1.43
Melting point of EO (°C)	2520	2800	2585	2430	1923
Heat of hydration of EO (kcal/mole)	3.4	9.7	15.9	19.5	24.5
Solubility of $E(OH)_2$ at 20° C (moles/lit)	8×10^{-6}	5×10^{-4}	2×10^{-2}	7×10^{-2}	2×10^{-1}

For the second dissociation constants of Mg $(OH)_2$, Ca $(OH)_2$ and Ba $(OH)_2$, values were obtained equal to 0.003, 0.03 and 0.23, respectively.

Calcium oxide (*quicklime*) and the product of its reaction with water—$Ca(OH)_2$ (*slaked lime*) are widely employed in building. Chemically, the "slaking" of lime consists in the combination of water with CaO with evolution of heat, in accordance with the equation:

$$CaO + H_2O = Ca(OH)_2 + 16 \text{ kcal}$$

Calcium hydroxide is the most inexpensive strong base, and is therefore most frequently employed in industry. A solution of $Ba(OH)_2$ ("baryta water") is used for detecting CO_2.

Alongside the normal oxides, white *peroxides* of the type EO_2 are known for the elements of the Ca subgroup. Of these peroxides, only *barium peroxide*, BaO_2, is of any practical importance, being used, in particular, as the initial product for the preparation of hydrogen peroxide. The process is based on the reversibility of the reaction:

$$Ba(OH)_2 + H_2O_2 \rightleftarrows BaO_2 + 2H_2O$$

Since H_2O_2 is itself a very weak acid, the equilibrium of the reaction is displaced practically wholly to the left under the action of even such acids as carbonic acid [owing to neutralisation of $Ba(OH)_2$].

Industrially, BaO_2 is prepared by heating BaO to 600° C in a current of air, oxygen adding on according to the reaction:

$$2BaO + O_2 = 2BaO_2$$

Further heating above 800° C leads to dissociation of BaO_2 into barium oxide and oxygen. Therefore, the combustion of metallic barium results only in the formation of its oxide.

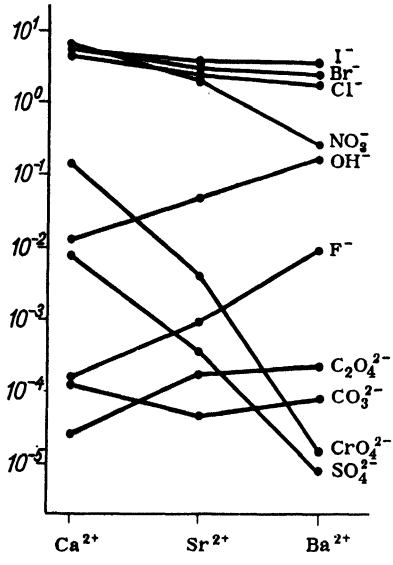


Fig. 179. Solubility of Ca, Sr and Ba salts (moles/litre of H_2O)

On reacting with acids, the oxides and hydroxides of the alkaline earth metals readily form the corresponding salts. The latter are colourless, as a rule. Of the derivatives of the common mineral acids, the salts containing the anions Cl^-, Br^-, I^- and NO_3^- are readily soluble; those containing the anions F^-, SO_4^{2-}, CO_3^{2-} and PO_4^{3-} are sparingly soluble in water. In contrast to $Ca^{\cdot\cdot}$ and $Sr^{\cdot\cdot}$ ions, $Ba^{\cdot\cdot}$ ion is highly poisonous. Many salts of these elements find various practical applications.

2) The solubilities of the most important salts and the hydroxides of Ca, Sr and Ba under ordinary conditions are compared in Fig. 179, from which it can be seen that they vary differently for different anions in the series Ca—Sr—Ba. This fact is important in analytical chemistry. In particular, the sharp difference in solubilities of the *chromates* makes it possible to separate Ba from Sr and Ca. The very low solubility of calcium *oxalate* is utilised for detecting traces of the element (for example, in ordinary drinking water).

The *halides* of the alkaline earth metals fall into two fairly distinct groups with respect to their properties. One of these groups constitutes

the fluorides, while the other embraces the derivatives of the remaining halogens. The fluorides are almost insoluble in dilute acids, as well as in water. They are not known to form crystal hydrates. The chlorides, bromides and iodides are readily soluble in water, and separate out from solutions as crystal hydrates.

Barium *nitrate* crystallises without water under ordinary conditions. The nitrates of Ca and Sr separate out in the form of crystal hydrates. The latter are readily soluble in water, but the solubility of $Ba(NO_3)_2$ [and $Ra(NO_3)_2$] is much lower. Calcium nitrate is widely employed as a nitrate mineral fertiliser. Strontium and barium nitrates are used in pyrotechnics for the preparation of substances that burn with a red (Sr) or green (Ba) flame.

The *sulphates* of Sr and Ba crystallise without water. Above 66° C, calcium sulphate separates out from solution in the anhydrous state, while below this temperature, gypsum, $CaSO_4 \cdot 2H_2O$, is deposited. These sulphates are sparingly soluble in water, the solubility rapidly decreasing in the order Ca—Ra.

Heating to 150° C converts gypsum into a hydrate containing less water—$2CaSO_4 \cdot H_2O$. When a paste of this hydrate is mixed with water (60-80% of its weight), the latter recombines with it, and the whole mass hardens (sets) as a result of crystallisation. Owing to this property gypsum is used to make casts of various objects, and as a binding material in building.

3) The roasting of gypsum to obtain a binder is usually carried out at temperatures not over 180° C. The product is sold under the name of *Plaster of Paris* or *alabaster*. Roasting above 350° C results in a soluble form of anhydrous $CaSO_4$, while above 500° C an insoluble form is produced, which does not add on water any more and therefore cannot be used as a binding material.

The basic salts of the composition $xCaSO_4 \cdot yCaO$, which form when gypsum is roasted at still higher temperatures (900-1200° C), again yield a setting mass when mixed with water. Hardening is due to the addition of water and crystallisation of the material, the crystals formed being closely interlocked and intergrown with one another, which accounts for the high mechanical strength of the set mass. The latter is, at the same time, very resistant to water, changes of temperature, etc. Hydraulic gypsum is used for making steps, window sills, etc., and as a binding material. It was known to the Egyptians in 2000 B.C., who made wide use of it in the erection of various structures.

The *carbonates* of the alkaline earth metals are practically insoluble in water. On heating, they give up CO_2 and change into the corresponding oxides. The thermal stability of the carbonates increases rapidly in the order Ca—Sr—Ba. Calcium carbonate is the most important of them.

The uses of the individual natural varieties of $CaCO_3$ are extremely varied. *Limestone* is used as a raw material for the production of the most important building materials—*lime* and *cement*. *Chalk* is employed as a mineral paint, as the base of polishing compositions, etc.

Marble is an excellent material for sculptural work, electrical switchboards, etc.

The annual world output of *lime* from limestone runs into the tens of millions of tons. The thermal dissociation of $CaCO_3$ takes place with considerable absorption of heat:

$$CaCO_3 + 43 \text{ kcal} \rightleftarrows CaO + CO_2$$

The relation between the equilibrium of this reaction and the temperature is evident from the following data:

Temperature (°C)	550	600	650	700	750	800	850	897
Pressure of CO_2 (mm Hg)	0.4	1.8	6.9	22.2	63	167	372	760

Industrially, the roasting of limestone is most frequently carried out in shaft kilns (Fig. 180). Carbon dioxide is an important by-product of this process.

Lime is widely employed in a number of branches of industry. Considerable amounts are also used in agriculture. However, the most important field of application of lime and one that has been known to mankind since ancient times, is its use as a binding material (mortar) in building for cementing stones, bricks, etc., to one another. Usually, a mixture of lime and sand (1 part to 3 or 4 parts of sand) is prepared, and water is added in sufficient quantity to obtain a paste-like mass. The latter hardens gradually owing to crystallisation of calcium hydroxide and formation of crystalline $CaCO_3$ (at the expense of atmospheric carbon dioxide) in accordance with the reaction:

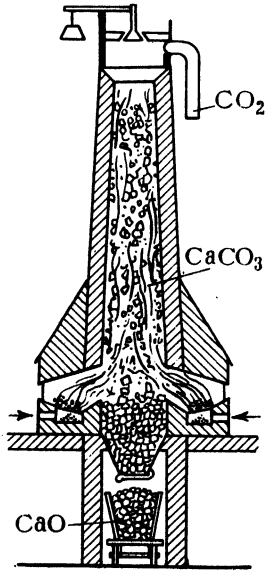


Fig. 180. Limestone roasting shaft kiln

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$

Simultaneously calcium silicates are also formed (owing to the SiO_2 of the sand). Due to liberation of water during the setting of the mortar, buildings in which it has been used remain damp for a long time.

Another binding material used in building—*cement*—has considerable advantages over lime. Apart from the fact that its use eliminates the problem of the prolonged dampness of the buildings, cement can harden under water as well as in air. Moreover, it hardens much more rapidly than mortar. The output of cement in the U. S. S. R. in 1963 was 61 million tons (as against 5.7 million tons in 1940, and 1.5 million tons in 1913).

Cement is a greenish-grey powder, mainly a mixture of different calcium silicates and aluminates, predominantly Ca_3SiO_5, Ca_2SiO_4 and $Ca_3(AlO_3)_2$. When mixed with water, it forms a solidifying mass. The conversion of the latter from a paste-like into a solid state is known as setting, and is usually completed within a few hours. Chemically, the cement-setting process is mainly due to hydration of its constituents.

4) In the production of *cement*, a mixture of finely crushed limestone and clay rich in SiO_2 is roasted in special *rotary furnaces* (Fig. 181) until clinkering beginsat 1400-1600° C. These furnaces are slightly inclined steel tubes, 2-3 m

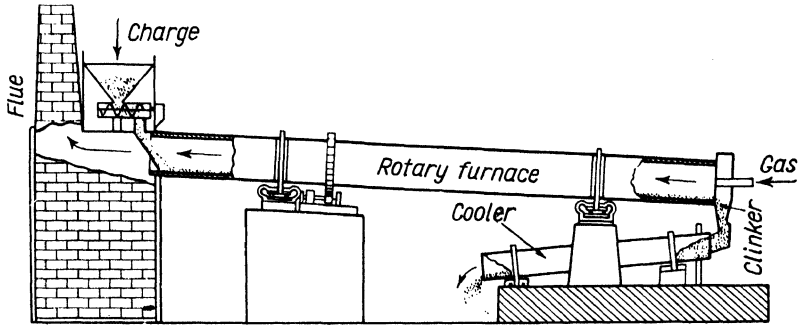


Fig. 181. Cement kiln

in diameter and a few score metres in length lined inside with refractory bricks. The furnace rests on rollers and is slowly rotated by a motor. The initial mixture fed continuously at the top is heated progressively as it gradually moves downwards by the gases or coal dust burning in the furnace. After cooling, the roasted product, cement clinker, is thoroughly crushed.

5) The composition of cements is usually expressed as the percentage by weight of the oxides (mainly CaO, SiO_2, Al_2O_3 and Fe_2O_3) contained in them. The first of these oxides plays the part of a base in the cement, while the others act as acid anhydrides. The ratio by weight $CaO : (SiO_2 + Al_2O_3 + Fe_2O_3)$ is known as the *hydraulic index* of the cement, and is a good indicator of its quality. The numerical value of the *hydraulic index* of ordinary (*silicate*) cement varies around two. Typical approximate results of its analysis are given below (% by weight).

Ignition losses	2	SiO_2	22
Residue insoluble in concentrated HCl	0.5	Al_2O_3	6
		Fe_2O_3	3
CaO	63	$Na_2O + K_2O$	0.5
MgO	1.5	SO_3	1.5

6) The setting of cement is due chiefly to the reactions:

$$Ca_3SiO_5 + 5H_2O = Ca_2SiO_4 \cdot 4H_2O + Ca(OH)_2$$

$$Ca_2SiO_4 + 4H_2O = Ca_2SiO_4 \cdot 4H_2O$$

$$Ca_3(AlO_3)_2 + 6H_2O = Ca_3(AlO_3)_2 \cdot 6H_2O$$

After the initial setting, the hardness of the cement continues to increase over a long period. The principal reason for this, apparently, is extension of the processes of hydration into the depths of the cement grains.

Other very important salts of Ca, Sr and Ba apart from those considered above, are the *acid carbonates* [$E(HCO_3)_2$], which are known only in solution. They form when carbon dioxide dissolved in water reacts with normal carbonates according to the equation:

$$ECO_3 + CO_2 + H_2O = E(HCO_3)_2$$

This reaction is reversible, heat displacing the equilibrium towards dissociation of the bicarbonate. Of the bicarbonates of the alkaline earth metals, only $Ca(HCO_3)_2$ is contained fairly often in natural waters. Its presence lends to the water a pleasant refreshing taste which is absent in distilled water.

The content of salts of divalent metals in natural water is often evaluated in terms of its "hardness", which may be *temporary* or *permanent*. The first is due to the presence in the water of bicarbonates, $Ca(HCO_3)_2$, less often $Mg(HCO_3)_2$, and sometimes also $Fe(HCO_3)_2$. It is called temporary because it can be removed by merely boiling the water, whereupon the bicarbonates are decomposed and their insoluble decomposition products (the carbonates of Ca and Mg, ferric hydroxide) are deposited on the walls of the vessel in the form of *scale*. The content of $Fe(HCO_3)_2$ in the water may be estimated from the colour of the scale: when considerable quantities are present, the scale has a reddish-brown colour.

Permanent hardness of water is due to the presence of salts of divalent metals, which do not form a deposit on boiling, the most common of these being sulphates and chlorides of Ca and Mg. Among these, sparingly soluble $CaSO_4$, which deposits as very dense scale on successive evaporation of large amounts of water, is of particular importance.

If a boiler is operated using hard water, its heated surface becomes covered with scale. Since the latter is a poor conductor of heat, the operation of the boiler becomes uneconomic: a layer of scale 1 mm thick increases the fuel consumption by approximately 5%. On the other hand, the boiler walls, insulated from the water by the layer of scale, may have to be heated to very high temperatures. Consequently, the iron gradually becomes oxidised and the walls lose their strength, which may result in explosion of the boiler. Since steam power is used in many industrial enterprises and in transport, the question of the hardness of water is one of great practical importance.

Hard water is also unsuitable for technological processes in a number of industries. Its use makes the washing of linen and hair, and other operations involving the use of soap, more difficult. This is due to the insolubility of the salts of the organic acids contained in

soap with divalent metals, which soil the articles being washed and cause high non-productive consumption of the soap.

7) In the U.S.S.R., the permanent and temporary *hardness of water* is quantitatively expressed by the number of milligram-equivalents of divalent metals in one litre (mg-equiv/litre). In other countries, conventional "degrees of hardness" are employed, the value of the degree being different in different countries: (1 mg-equiv/litre corresponds to 2.8 German, 3.5 British, 5 French or 50 American degrees). Up to 1952, German degrees were generally used in the U.S.S.R.

The sum of the temporary and permanent hardness is the *total* hardness of the water. The latter is denoted by the following terms: very soft (up to 1.5), soft (1.5 to 3), medium hard (3 to 6), hard (6 to 9), very hard (over 9 mg-equiv/litre). The hardness of natural waters varies widely. In open reservoirs it often depends on the season and even on the weather. Atmospheric water (rain, snow) is the softest, since it contains hardly any dissolved salts.

Since the removal of dissolved salts from water by distillation is too expensive, chemical methods are used for "softening" it in localities where the water is hard. Temporary hardness is usually eliminated by adding $Ca(OH)_2$ to the water in a quantity strictly corresponding to the content of bicarbonates found by analysis. In accordance with the reaction

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3\downarrow + 2H_2O$$

all the bicarbonate is converted into normal carbonate, and is precipitated. Permanent hardness is most frequently eliminated by adding soda to the water, this causing the formation of a precipitate according to the reaction:

$$CaSO_4 + Na_2CO_3 = CaCO_3\downarrow + Na_2SO_4$$

The precipitate is then allowed to settle, and only after this is the water used for feeding boilers or in production. To soften small quantities of hard water (in laundries, etc.), a little soda is usually added to it, and the water is allowed to stand. The divalent metals are completely precipitated in the form of carbonates, while the sodium salts remaining in solution do not hinder the use of soap.

From the above it follows that soda can be used for eliminating both temporary and permanent hardness, while calcium hydroxide can be used only for eliminating temporary hardness. Nevertheless, there is a strong tendency to employ $Ca(OH)_2$ in industry because it is much cheaper than soda.

XII-4. The Zinc Subgroup. Zinc and its analogues are far less abundant in nature than the corresponding elements of the calcium subgroup. The content of *zinc* in the earth's crust is estimated to be 0.001%, that of *cadmium*, 8×10^{-6} % and of *mercury*, 6×10^{-7}%.

All three elements are encountered mainly in the form of sulphides of the type ES. The most important ores of zinc and mercury are the

minerals *zinc blende* or *sphalerite*, ZnS, and *cinnabar*, HgS. The natural cadmium sulphide analogous to them — the mineral *greenockite*, CdS, occurs independently very rarely. But small quantities of CdS are almost always contained in zinc blende. Another important zinc ore is the mineral *smithsonite*, $ZnCO_3$. Zinc minerals are very often encountered together with lead and silver minerals. Cadmium is also contained in the majority of such *potymetallic* ores (so-called because they contain several metals).

The process of extracting elementary zinc from its ores consists of two stages. The sulphide is first converted into the oxide by roasting in air, and then the oxide is reduced with carbon:

$$2ZnS + 3O_2 = 2SO_2 + 2ZnO \text{ and } ZnO + C = CO + Zn$$

The zinc vapour formed in the second reaction is carried away by a current of CO and collects in condensers. However, part of the vapour is carried further away, and then settles in the form of a very fine powder. The latter is partly reprocessed and partly marketed under the name of *zinc dust*.

Electrolysis is also often employed to isolate zinc. In this case, the ZnO obtained by oxidative roasting of the ore is treated with sulphuric acid. The resulting $ZnSO_4$ solution serves as the electrolyte from which zinc is subsequently precipitated.

Owing to the greater volatility of cadmium compared to zinc, it accumulates in the zinc dust. The latter is dissolved in H_2SO_4, and the solution is treated with metallic zinc. Cadmium precipitates in accordance with the equation: $Cd^{\cdot\cdot} + Zn = Zn^{\cdot\cdot} + Cd$.

Owing to the instability of HgO at high temperatures, the preparation of metallic mercury reduces to one reaction:

$$HgS + O_2 = SO_2 + Hg$$

The mercury vapour liberated is collected in special receivers in which it condenses.

The elements of the zinc subgroup are white metals with a bluish (Zn) or silvery (Cd, Hg) tint. In moist air, they become coated with oxide films and lose their lustre. All three metals (especially mercury) are low melting. Their most important constants are listed in the table below.

Properties	Zn	Cd	Hg
Specific gravity	7.1	8.7	13.55
Melting point (°C)	419	321	—39
Boiling point (°C)	907	767	357
Electrical conductivity (Hg = 1) . .	16	13	1

In contrast to ductile and malleable cadmium, zinc is fairly brittle under ordinary conditions. All three metals readily form alloys with one another and with many other metals. The alloys of mercury (*amalgams*), many of which are paste-like or liquid, occupy a special place among them.

1) The annual world production of *zinc* is about 2.5 million tons. Most of the metal produced is used for galvanising iron, i. e., plating it with a thin layer of zinc, in order to prevent it from rusting.

The principal use of *cadmium* is in the manufacture of so-called alkaline cells. Its annual world output is about 7 thousand tons.

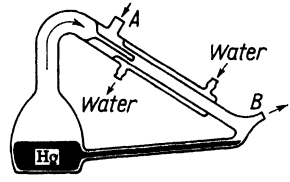


Fig. 182. Mercury vacuum pump

Mercury has a great variety of uses in different fields. Its annual world output is about 6 thousand tons.

2) An important application of mercury is in the production of a high vacuum. This is usually effected with the aid of the *mercury vacuum pump* schematically shown in Fig. 182, which is made of glass or metal. The mercury in the lower part of the vessel is heated to boiling, thus producing a continuous stream of mercury vapour which passes at high speed through a narrow tube into a space cooled externally by water and connected at *A* to the vessel being evacuated. The impacts of the rapidly moving mercury molecules drive the gas molecules being evacuated towards the outlet *B*, where they come under the influence of a coarser pump (fore-pump) which sets up a preliminary vacuum of the order of 0.1 to 0.01 mm Hg in the whole system. The mercury vapour condenses in the cooled space, and the liquid mercury returns to the heated vessel. The apparatus operates continuously and is able to produce a vacuum as low as a hundred millionths of a millimetre of mercury.

When in contact with *dry* air, Zn, Cd and Hg remain unchanged at ordinary temperatures. If sufficiently heated, Zn and Cd burn to the oxides EO, whereas mercury is only slowly oxidised. The reactions of Zn and Cd with sulphur are also very vigorous, but heating is necessary to start the reaction. On the other hand, mercury combines with finely divided sulphur (when both elements are triturated in a mortar) even in the cold. There are analogous differences in attitude towards the halogens, with which mercury reacts under ordinary conditions much more readily than Zn or Cd. This elevated chemical activity of mercury is due to its liquid state which greatly facilitates the course of the reaction. In actual fact, the metallic properties of the elements appreciably decrease in the order Zn—Cd—Hg. This

can be seen, in particular, by comparing the heats of formation of analogous compounds of these elements, given in Fig. 183: they decrease sharply from Zn to Hg in all cases.

In the electromotive series, zinc is situated left of iron, cadmium — just right of it, and mercury—far to the right of hydrogen. Though Zn and Cd are more metallic elements than hydrogen, they do not displace it from water, because the surface of the metals rapidly becomes coated with a protective oxide film. Zinc readily dissolves in dilute HCl and H_2SO_4, but cadmium dissolves slowly, and mercury is insoluble. All three elements dissolve readily in nitric acid. For example, in the case of mercury, the reaction takes place according to the equation:

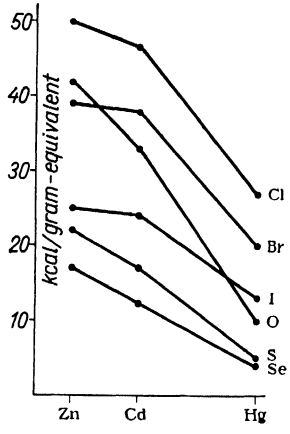


Fig. 183. Heats of formation of Zn, Cd and Hg compounds

$$3Hg + 8HNO_3 = 3Hg(NO_3)_2 + 2NO + 4H_2O$$

Zinc also differs from its analogues in that it is soluble in concentrated solutions of alkalis, for example in accordance with the reaction:

$$Zn + 2NaOH = Na_2ZnO_2 + H_2$$

Zinc and cadmium form only one series of compounds in which the elements are *divalent*. Mercury forms a number of derivatives besides, in which it is electrochemically monovalent. The compounds of this type will be considered separately at the end of the section. In contrast to the not very poisonous derivatives of Zn and Cd, both mercury and its compounds are highly poisonous.

The *oxides* of zinc and its analogues [EO] can be prepared by direct combination of the elements with oxygen on heating. Unlike the white ZnO, the analogous oxides of Cd and Hg are brown (CdO) or bright red (HgO). When very finely ground, mercuric oxide becomes yellow. The oxides of Zn, Cd and Hg are almost insoluble in water, but dissolve readily in acids to form the corresponding salts.

The *hydroxides*, $E(OH)_2$, of zinc and cadmium, corresponding to the EO oxides, separate out in the form of white, gelatinous precipitates when solutions of Zn and Cd salts are treated with strong alkalis. Zinc hydroxide is amphoteric (with basic properties predominating over acidic) and, therefore, dissolves in an excess of a strong alkali to form *zincates*, e. g., Na_2ZnO_2. In the case of cadmium hydroxide, only the basic properties are pronounced. Both hydroxides dissolve readily in acids.

The analogous mercuric hydroxide, $Hg(OH)_2$, loses water at the moment of formation. Therefore, the action of strong alkalis on mercu-

ry salts, for example, by the reaction

$$2NaOH + Hg(NO_3)_2 = 2NaNO_3 + HgO\downarrow + H_2O$$

results in yellow mercuric *oxide* (as a precipitate). It is insoluble in excess alkali, but forms salts readily with acids.

Like the cations Zn^{2+}, Cd^{2+} and Hg^{2+}, the majority of their salts are colourless. The nitrates and sulphates of zinc and its analogues are readily soluble in water. The solubility of the fluorides increases, and that of the other halides (and most other salts) decreases in the order Zn—Cd—Hg. The derivatives of the weak inorganic acids (H_2CO_3, H_2S, etc.) are, as a rule, sparingly soluble in water. A very dilute solution of $HgCl_2$ (mercuric chloride or corrosive sublimate) is a commonly used disinfectant.

Some salts of Cd^{2+} and Hg^{2+} (and partly of Zn^{2+}) are considerably less dissociated in solution than is usual for the MX_2 type. In particular, this is true of the halides of Cd and Hg (with the exception of the fluorides), the degree of dissociation decreasing in the order Cl^-—Br^-—I^-. Mercuric cyanide, $Hg(CN)_2$, is particularly weakly dissociated and hardly conducts electricity in solution. On the other hand, the nitrates and sulphates of Cd^{2+} and Hg^{2+} are normally dissociated.

The normally dissociated salts of Zn and its analogues are considerably hydrolysed, in solution the degree of hydrolysis increasing in the order Zn—Cd—Hg. Some salts of Zn, Cd and Hg readily form complex compounds, among which those of the type $M[EX_3]$ and $M_2[EX_4]$ predominate. An example is colourless potassium tetra-iodomercurate, $K_2[HgI_4]$ which is readily soluble in water.

3) $Zn^{\cdot\cdot}$ and $Cd^{\cdot\cdot}$ ions react with ammonia to form complexes in accordance with the equation: $E^{\cdot\cdot} + 4NH_3 = [E(NH_3)_4]^{\cdot\cdot}$. Substitution of hydrogen in NH_3 is much more typical of Hg^{2+}. Thus, a white precipitate of the *amide* compound NH_2HgCl separates out of $HgCl_2$ solution in accordance with the reaction: $HgCl_2 + 2NH_3 = NH_2HgCl + NH_4Cl$. Various salts of an *imide* base of the formula $HN(HgOH)_2$ are also very characteristic of mercury. The best known of these is the brown iodine salt which precipitates when ammonia (or ammonium salts) reacts with an alkaline solution of $K_2[HgI_4]$:

$$NH_3 + 2K_2[HgI_4] + 3KOH = HOHgNHHgI + 7KI + 2H_2O$$

This reaction is used for the detection of ammonia.

Unlike the other two elements of this subgroup, mercury is known to be electrochemically monovalent in a number of its derivatives. In actual fact, all such derivatives contain the atomic grouping —Hg_2—, in which both atoms of mercury are divalent but one valency of each is used to form a non-polar bond with the other thus:— Hg—Hg—. Since this grouping does not break up on electrical dissociation, solutions of these derivatives contain the complex ion $Hg_2^{\cdot\cdot}$.

Substances containing the —Hg_2— grouping are known as *mercurous* compounds. Hg_2^{2+} ion is colourless. Most of the salts derived from it dissolve poorly in water. The few that are readily soluble are strong-

ly dissociated and appreciably hydrolysed. An example of derivatives of this type is mercurous nitrate, $Hg_2(NO_3)_2$, which is readily soluble in water and forms when HNO_3 reacts with an excess of mercury:

$$6Hg + 8HNO_3 = 3Hg_2(NO_3)_2 + 2NO + 4H_2O$$

The most important in practice is mercurous chloride, Hg_2Cl_2, which is almost insoluble in water and is used in medicine under the name of "calomel".

Under the influence of oxidising agents, mercurous compounds are fairly easily converted into the mercuric derivatives, e. g.,

$$Hg_2Cl_2 + Cl_2 = 2HgCl_2$$

Conversely, reducing agents readily convert mercuric compounds into mercurous derivatives, e. g., in accordance with the reaction:

$$2HgCl_2 + SO_2 + 2H_2O = Hg_2Cl_2 + H_2SO_4 + 2HCl$$

In the presence of an excess of the reducing agent, the process often results in the liberation of metallic mercury.

$$Hg_2Cl_2 + SO_2 + 2H_2O = H_2SO_4 + Hg + 2HCl$$

4) Many Hg_2^{2+} salts dissociate into the corresponding Hg^{2+} salt and metallic mercury: $Hg_2X_2 = HgX_2 + Hg$. In some cases (e. g., Hg_2Cl_2, Hg_2SO_4), this occurs only under the influence of light or heat, and very slowly, in others [e. g., $Hg_2(CN)_2$, Hg_2S] the reaction is so rapid even at the moment of formation of the Hg_2^{2+} salt that the latter cannot be separated at all. For example, $Hg_2(NO_3)_2$ reacts with KCN in accordance with the equation:

$$Hg_2(NO_3)_2 + 4KCN = 2KNO_3 + K_2[Hg(CN)_4] + Hg$$

Comparing Zn, Cd and Hg with the principal elements of group two, beryllium and magnesium, it may be noted that certain properties vary quite regularly in the order Be—Hg. Examples are the melting and boiling points of the elements, which decrease successively from Be to Hg.

However, a similar regularity in the variation of many other properties is still more characteristic of the series Be—Ra. In this series, for instance, the atomic and ionic radii increase very consistently, resulting in a distinct increase in the basic properties of the hydroxides and in their solubility in water, a rise in thermal stability of the salts, etc.

To sum up, both comparisons show that from the standpoint of the regular change in properties of the *elements*, Be and Mg can be included in both subgroups as the first members, but with respect to the properties of their *compounds*, they belong only to the calcium subgroup.

XIII. FIRST GROUP OF THE PERIODIC TABLE

The structure of the outermost electronic shells in the atoms of the elements of group I first of all suggests that they have no tendency to gain electrons. On the other hand, it would seem that the single outer electron should be given up very readily, resulting in stable *monovalent* cations of these elements.

Experiment shows these assumptions to be completely true to fact only when applied to the elements of the left-hand column (Li and its analogues). With respect to copper and its analogues they are only half true, that is, as far as their tendency to gain electrons is concerned. At the same time, the 18-electron shell furthest from the nucleus is not quite fixed in these elements and may lose some of its electrons. As a result, besides the monovalent Cu^+, Ag^+ and Au^+ ions, compounds are known in which these elements have a higher valency.

The discrepancy between the conclusions deduced from the atomic models and the results of experiment shows that a consideration of the properties of the elements only on the basis of their electronic structures, neglecting the other features, is not always sufficient to give even a tentative outline of the chemistry of these elements.

XIII-1. The Alkali Metals. The name *alkali* metals, which is applied to the elements of the series Li—Cs, is due to the fact that their hydroxides are strong alkalis. *Sodium* and *potassium* are among the most abundant elements, accounting respectively for 2.0 and 1.1% of the total number of atoms in the earth's crust. The content in the latter of *lithium* (0.02%), *rubidium* (0.004%) and *cesium* (0.00009%) is much lower, and that of *francium* is negligible.

	3		
1	**Li**		
2	6.939		
	11		
1			
8	**Na**		
2	22.9898		
	19		
1			
8	**K**		
8	39.102		
2			
		29	
			1
		Cu	18
			8
		63.54	2
1	*37*		
8	**Rb**		
18			
8			
2	85.47		
		47	
			1
			18
		Ag	18
			8
		107.870	2
	55		
1			
8	**Cs**		
18			
18	132.905		
8		*79*	1
2			18
		Au	32
			18
			8
		196.967	2
1	*87*		
8			
18			
32	**Fr**		
18			
8			
2	[223]		

In nature, the alkali metals are encountered solely in the form of compounds. Sodium and potassium are permanent constituents of many very abundant silicates. The most important of the individual minerals of sodium is common salt, NaCl, which is contained in sea water and forms huge beds of *rock salt* under layers of alluvial rock in different areas of the earth's surface (in the U. S. S. R., at Solikamsk, Artemovsk, Iletsk, etc.). The upper layers of these beds sometimes contain accumulations of potassium (in the form of the minerals *sylvinite*, $KCl \cdot NaCl$, *carnallite*, $KCl \cdot MgCl_2 \cdot 6H_2O$, etc.), which serve as the principal source for obtaining compounds of this element. Only a few natural potassium salt deposits of industrial value are known. The most important of these is the Solikamsk deposit in the U. S. S. R.

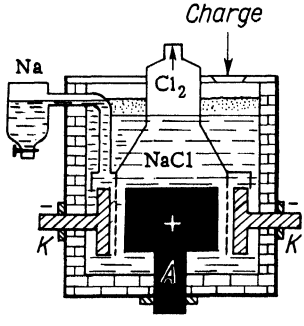


Fig. 184. An electrolytic cell for the preparation of sodium

A number of minerals of lithium are known [e. g., *spodumene*, $LiAl(SiO_3)_2$], but large accumulations are rare. Rubidium and cesium occur almost exclusively as impurities in other alkali metals. Traces of francium are always contained in uranium ores.

Sodium and potassium compounds are of enormous importance to life. Suffice it to recall that a human being requires 5 to 10 kg of NaCl a year. Similarly, potassium salts are essential to plants. In connection with this, about 90% of all the potassium compounds produced are used for the fertilisation of soils. The remaining 10%, and enormous amounts of different sodium compounds, are used in industry. So far, the derivatives of lithium have found applications only in minor amounts, and the applications of Rb and Cs are very limited.

The alkali metals can be isolated as such by electrolysis of their fused chlorides. Sodium is of fundamental practical importance, its annual world output being more than 50 thousand tons.

1) A diagram of an installation for producing metallic sodium by electrolysis of fused NaCl is shown in Fig. 184. The bath is a steel housing lined with fireclay, having a graphite anode *A* and a circular iron cathode K, with a gauze screen between them. The electrolyte is usually not pure NaCl (m. p. 800° C), but the more easily melted mixture of NaCl with 25% NaF and 12% KCl (with which the process can be carried out at 610-650° C). Metallic sodium collects in the upper part of the circular cathode space, from which it passes into a receiver. NaCl is added to the bath periodically.

In the absence of air, lithium and its analogues are silvery-white substances with a strong metallic lustre. All the alkali metals

have low specific gravities, low hardness, low melting and boiling points, and high electrical conductivities. Their most important constants are listed in the table below.

Properties	Li	Na	K	Rb	Cs
Specific gravity	0.53	0.97	0.86	1.5	1.9
Hardness (diamond = 10)	0.6	0.4	0.5	0.3	0.2
Specific heat ($H_2O = 1$) . .	0.84	0.29	0.17	0.08	0.05
Electrical conductivity (Hg = 1)	11	21	14	8	5
Melting point (°C)	186	98	63	39	28
Boiling point (°C)	1336	890	770	680	670

The variation in the relevant constants can be seen from Fig. 185.

Owing to their low specific gravity, Li, Na and K float on water (Li even floats on kerosene). The alkali metals are easily cut with a knife, and the softest of them—cesium—does not exceed wax in hardness. They are all soluble in mercury (lithium less than the others). The alkali metals and their volatile compounds impart characteristic colours to the non-luminous flame of a gas burner: Li—crimson, Na—bright-yellow, K, Rb and Cs—mauve.

Chemically, lithium and its analogues are very reactive metals (their activity usually increasing from Li to Cs). The alkali metals are *monovalent* in all their compounds. Being situated at the extreme left of the electromotive series, they react vigorously with water:

$$2E + 2H_2O = 2EOH + H_2$$

In the reaction with Li and Na, the liberated hydrogen does not ignite spontaneously, but it does in the case of potassium, while with Rb and Cs the reaction takes place eruptively.

In contact with air, freshly cut surfaces of Na and K (and of Li to a lesser extent) immediately become coated with a porous film of oxidation products. For this reason, Na and K are usually stored under kerosene. When heated in air Na and K ignite readily, while rubidium and cesium flare up spontaneously even at ordinary temperatures.

In the presence of traces of moisture the alkali metals ignite in an atmosphere of chlorine. The reactions of Cs, Rb and K with liquid bromine are accompanied by a powerful explosion, whereas Na and Li react only on the surface at ordinary temperatures. With iodine the reactions take place only on heating. In all the reactions with the halogens the resultant is the corresponding salt, EX.

Triturating an alkali metal with powdered sulphur results in the eruptive formation of the *sulphide*, E_2S. On heating in an atmosphere of hydrogen, lithium and its analogues form *hydrides*, EH, having the character of typical salts in which the negative ion is hydrogen (H^-).

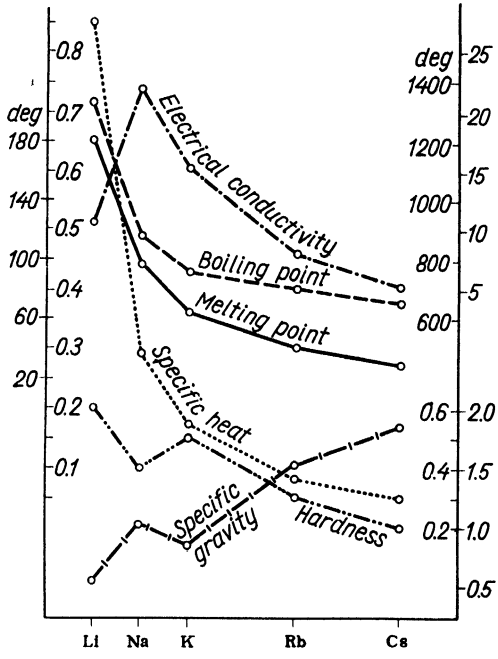


Fig. 185. Properties of the alkali metals

Only lithium combines directly with nitrogen and carbon. The formation of the *nitride*, Li_3N, takes place slowly in an atmosphere of nitrogen even at ordinary temperatures. On the other hand, lithium *carbide*, Li_2C_2, can be obtained from the elements only on heating. The heats of formation of compounds of the alkali metals are compared in Fig. 186.

2) In appearance and in most of their physical properties, the *hydrides* of the alkali metals resemble the corresponding halides. Thus, the best studied of them LiH forms solid, colourless crystals (of the NaCl type) which melt without decomposing at 680° C in the absence of air. The salt-like nature of these hydrides was also proved directly by the liberation of hydrogen at the *anode* during the electrolysis of fused LiH.

The hydrides of the alkali metals are strong reducing agents, and react violently with water: $EH + H_2O = H_2\uparrow + EOH$ or, in ionic form: $H^- + H^+ = H_2\uparrow$.

When alkali metals are burnt in an excess of oxygen, they form compounds of the following composition:

Formula . . .	Li_2O	Na_2O_2	KO_2	RbO_2	CsO_2
Colour of compound	white	white	yellow	yellow	yellow

Of all these substances, only Li_2O is a normal oxide, the others being *peroxides*.

The most important of these is *sodium peroxide*, Na_2O_2, which is prepared by burning metallic sodium in aluminium vessels:

$$2Na + O_2 = Na_2O_2$$

The resulting product is usually a yellow powder or yellow granules.

The reaction between Na_2O_2 and water is accompanied by hydrolysis:

$$Na_2O_2 + 2H_2O \rightleftarrows 2NaOH + H_2O_2$$

The liberation of H_2O_2 in this reaction explains the use of sodium peroxide for bleaching various materials. The reaction between Na_2O_2 and carbon dioxide

$$2Na_2O_2 + 2CO_2 = 2Na_2CO_3 + O_2$$

is the basis for the principal application of sodium peroxide as a source of oxygen in gas masks and in submarines. Sodium peroxide reacts so vigorously with easily oxidisable substances that an explosion may sometimes occur on mere contact.

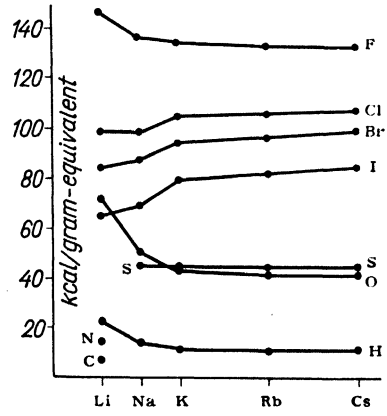


Fig. 186. Heats of formation of the compounds of the alkali metals

3) Sodium peroxide in the pure form or containing various additives (e. g., bleaching powder with an admixture of Ni or Cu salts) is known in commerce as *oxylite*. Mixed oxylite preparations are particularly convenient for obtaining oxygen which they liberate under the action of water.

4) The EO_2-type peroxides of K, Rb and Cs are solids which melt at about 400° C. They are all deliquescent in air, and are very vigorous oxidising agents. They react with dilute acids in the following manner, e. g.,: $2EO_2 + H_2SO_4 = E_2SO_4 + H_2O_2 + O_2$.

The crystal lattice of EO_2 peroxide is similar to the CaC_2 lattice (Fig. 138), i. e., it is built up of E^+ and O_2^- ions. Potassium peroxide, KO_2, is often added to oxylite as one of its components. In this case the oxylite reacts with carbon dioxide according to the overall equation: $Na_2O_2 + 2KO_2 + 2CO_2 = Na_2CO_3 + K_2CO_3 + 2O_2$, i. e., the carbon dioxide is replaced by an equal volume of oxygen.

The normal oxides of the alkali metals (with the exception of Li_2O) can be obtained only indirectly. They are all solids and have the following colours:

Oxide	Li_2O	Na_2O	K_2O	Rb_2O	Cs_2O
Colour	white	white	white	yellow	orange

Lithium oxide hydrates relatively slowly. The oxides of the other alkali metals react with water very vigorously, the reaction being $E_2O + H_2O = 2EOH$ with a great evolution of heat. The oxides of the alkali metals have not yet found any direct applications.

The *hydroxides*, EOH, of the alkali metals are very hygroscopic, colourless substances which attack most materials coming into contact with them. Hence their name—*caustic alkalis*—which is often used in practice.

The hydroxides of the alkali metals are readily soluble in water (and alcohol). Since they are dissociated into ions to a greater degree than the hydroxide of any other metal, the caustic alkalis are the *strongest bases.*

5) The properties of the hydroxides of the alkali metals are listed below:

Substance	LiOH	NaOH	KOH	RbOH	CsOH
Specific gravity . . .	2.5	2.1	2.0	3.2	3.7
Melting point (°C)	450	328	360	300	275
Solubility in water (moles per litre of H_2O):					
at 15° C	5.3	26.4	19.1	17.9	25.8
at 30° C	5.4	29.8	22.6	16.9	20.2

In contrast to the hydroxides of other metals, NaOH and its analogues do not lose water even when heated to their boiling points (NaOH—1388° C, KOH—1324° C). LiOH is an exception; it begins to lose water at about 600° C. Since in the fused state caustic alkalis strongly attack glass, porcelain and platinum (the latter in the presence of air), they are melted in silver, nickel or iron vessels.

6) Under the action of caustic alkalis, the human skin swells and becomes slippery; later, very painful deep burns appear. If an alkali gets onto the hands or clothes it should immediately be washed off with water and the affected spot should then be moistened with a very dilute solution of acid and washed again with water. Cloth made of fibres of animal origin decomposes rapidly when attacked by alkalis, whereas plant fibres are fairly resistant to them (conversely, acids attack fibres of plant origin more rapidly than those of animal origin).

Sodium hydroxide (or caustic soda) is used in the most varied branches of industry. Its annual world production runs into several million tons, most of it being produced by the electrolysis of NaCl solutions. At present, the double decomposition of soda and slaked lime

$$Na_2CO_3 + Ca(OH)_2 = CaCO_3\downarrow + 2NaOH$$

is less often employed.

In the U.S.S.R., the production of NaOH in 1963 was 1049 thousand tons (as against 190 thousand tons in 1940, and 55 thousand tons in 1913). As to the hydroxides of the other alkali metals, only KOH (caustic potash) is of considerable practical importance. It is usually produced by the electrolysis of KCl solutions.

7) The electrolysis of NaCl (and KCl) solutions is one of the principal processes in the chemical industry, because it results in two substances of very great importance in technology—the caustic alkali and free chlorine (VII-2). Hydrogen is also obtained as a by-product.

The most important condition for the correct operation of an electrolytic installation is absence of any reaction between the resultants (alkali and chlorine), this being achieved by preventing ready mixing of the anode and cathode

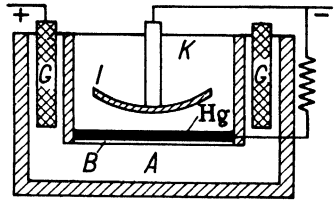


Fig. 187. Installation for electrolysis by the mercury method

liquors. In the *diaphragm* method (cf. Fig. 96), which is particularly frequently employed, the anode and cathode spaces are separated from one another by an asbestos boad diaphragm, which is readily permeable to liquids. The anode is made of graphite and the cathode of iron. In the course of the electrolysis, the alkali chloride solution is fed continuously into the anode space, and a mixture of alkali chloride and alkali flows continuously out of the cathode space. The mixture is evaporated, whereupon the chloride crystallises out. The resulting NaOH solution is evaporated in iron tanks, and the dry residue is remelted.

8) The tank shown in section in Fig. 187 is one of the types of apparatus used for the electrolysis of NaCl solution by the so-called *mercury* method. In this tank, the cathode space *K* is completely separated from the anode space *A* by solid lateral partitions and by a layer of mercury which lies on a thin plate of fine-pore material *B*. Graphite electrodes *G* serve as the anode, while the mercury layer and an auxiliary iron electrode *I* serve as the cathode. During electrolysis of the NaCl solution in the anode space, chlorine is liberated at the anodes *G*, while the cations are discharged by the mercury, resulting in sodium amalgam. As the latter has a lower specific gravity than mercury, it floats to the surface of the layer and reacts with the water in the cathode space, forming caustic alkali and liberating hydrogen (at electrode *I*). The alkali produced by this method is very pure.

The ions of the alkali metals are colourless. Almost all the *salts* they form with the common acids are readily soluble in water. The formation of crystal hydrates is very characteristic of lithium salts in contrast to the salts of K, Rb and Cs, which usually separate out without water of crystallisation. Sodium occupies an intermediate position. Salts of the alkali metals and weak acids give alkaline solutions owing to hydrolysis. Only lithium is known to form complex compounds with the ion of the alkali metal as the complexing agent.

But complex derivatives with ions of the alkali metal in the outer sphere are very common. Many such complexes are distinguished by high stability, increasing in the order Li—Cs.

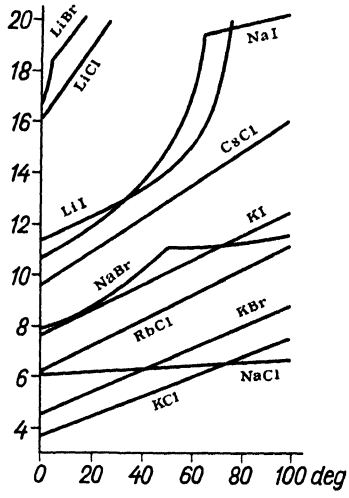


Fig. 188. Solubility of halides (moles/litre of H_2O)

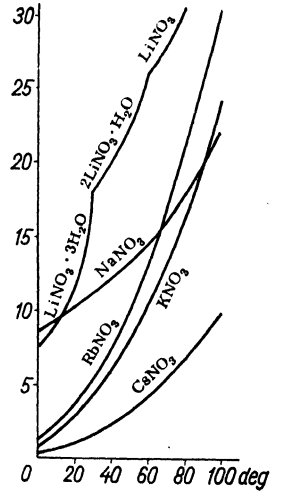


Fig. 189. Solubility of nitrates (moles/litre of H_2O)

The *halides* of these elements are fairly refractory crystalline substances and readily soluble in water except for LiF and partially NaF (Fig. 188). The most important of them is NaCl. Apart from its use with food (as table salt), huge quantities of sodium chloride are used in industry. Its annual world consumption amounts to millions of tons.

The sources for the industrial production of NaCl are natural rock salt deposits, and the sea and salt-water lakes (Baskunchak, etc., in the U.S.S.R.). Rock salt is simply broken out of its beds and crushed. Such salt is often so pure that it does not require further purification. NaCl is extracted from the sea and salt-water lakes by evaporating the brine in the sun or by freezing out the water. Salt obtained in this way is often contaminated with impurities (chiefly $Ca^{\cdot\cdot}$, $Mg^{\cdot\cdot}$ and $SO_4^{\prime\prime}$ ions) and becomes wet in moist air. Perfectly pure common salt is not hygroscopic. Another very important halide of the alkali metals is KCl, the basis of potassium fertilisers.

The *nitrates* of the alkali metals are relatively low-melting and readily soluble in water (Fig. 189). Of these, only $NaNO_3$ and KNO_3 are of practical value, both salts being used mainly as mineral fertilisers. The former is a by-product of nitric acid production (owing to the absorption of nitrogen oxides from waste gases by alkalis),

and the latter is usually obtained by the double decomposition of KCl and $NaNO_3$.

Being dibasic, *carbonic* acid forms salts of two types with the alkali metals: acid salts ($EHCO_3$) and neutral salts (E_2CO_3). Acid carbonates (bicarbonates) are known for all the alkali metals except

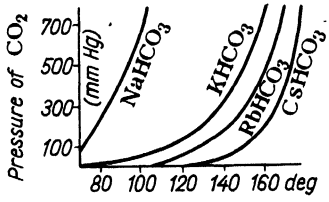


Fig. 190. Dissociation pressure of bicarbonates

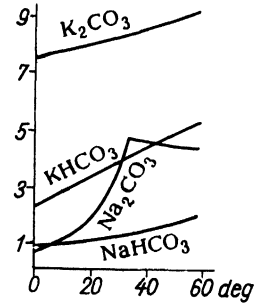


Fig. 191. Solubility of carbonates and bicarbonates (moles/litre of H_2O)

Li. They separate out from solutions without water of crystallisation. On heating, bicarbonates are fairly readily converted into neutral salts of carbonic acid:

$$2EHCO_3 = E_2CO_3 + CO_2 + H_2O$$

Their thermal stability rises in the order Na—Cs (Fig. 190).

With the exception of $NaHCO_3$, these bicarbonates are readily soluble. Owing to hydrolysis their solutions are slightly alkaline. When these solutions are heated, CO_2 is partially liberated (in accordance with the dissociation equation given above), and they become strongly alkaline. In contact with air, solutions of bicarbonates liberate CO_2, though very slowly, even at ordinary temperatures. Practical applications are restricted largely to $NaHCO_3$ ("baking soda"), which is used in medicine, confectionery, etc.

The normal carbonates of the alkali metals, with the exception of Li_2CO_3, are readily soluble in water (Fig. 191), their solutions being strongly alkaline owing to hydrolysis. The most important is *soda*, Na_2CO_3. It is produced either in the anhydrous state ("soda ash") or in the form of the efflorescent crystal hydrate $Na_2CO_3 \cdot 10H_2O$ ("washing soda").

Many industries are consumers of soda. Besides, it is used for washing linen, etc. The production of soda ash in the U.S.S.R. in 1963 was 2.5 million tons (as against 536 thousand tons in 1940 and 160 thousand tons in 1913). Industry (principally glass-making) also consumes considerable quantities of *potash*, K_2CO_3.

The most important method for the production of soda, known as the *ammonia* or *Solvay* process, is based on the reaction

$$NaCl + NH_4HCO_3 \rightleftarrows NaHCO_3 + NH_4Cl$$

the equilibrium being displaced to the right owing to the relatively low solubility of $NaHCO_3$. A concentrated solution of NaCl is first saturated with ammonia and then treated with carbon dioxide (produced by roasting $CaCO_3$). The $NaHCO_3$ which separates out is filtered off and is converted by heating into Na_2CO_3, the carbon dioxide

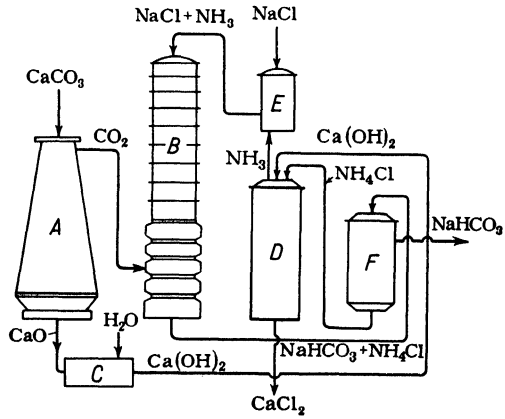


Fig. 192. Production of soda by the Solvay process

given off being returned for re-use. The mother liquor containing NH_4Cl is treated with slaked lime and the ammonia liberated is also returned to the process. The only waste product is $CaCl_2$ which remains in solution.

9) The basic layout of an industrial plant for the production of soda by the Solvay process is shown in Fig. 192. Limestone is roasted in the kiln *A*, the carbon dioxide formed entering the carbonisation tower *B*. The CaO is slaked with water *C*, after which the $Ca(OH)_2$ is pumped into the mixing tank *D* where it comes in contact with NH_4Cl and liberates ammonia from it. The latter is admitted to the absorber *E*, and there it saturates a concentrated solution of NaCl. The solution is then pumped to the carbonisation tower where it reacts with CO_2 to form $NaHCO_3$ and NH_4Cl. The first of these salts is retained on the vacuum filter *F*, while the second is returned to the mixing tank *D*. Thus, NaCl and limestone are continuously used up, and $NaHCO_3$ and $CaCl_2$ are obtained (the latter as a waste product). The sodium bicarbonate is then converted into soda by heating.

10) Where natural sources of Na_2SO_4 are available, the older *sulphate* method for the production of soda may prove profitable. This method consists in fusing a mixture of Na_2SO_4, limestone and coal at 1000° C, to accomplish the reaction

$$Na_2SO_4 + 2C + CaCO_3 = 2CO_2\uparrow + Na_2CO_3 + CaS$$

The soda is separated from the poorly soluble CaS by treating the fused mass with water. The waste product, CaS, may be used as the initial product for obtaining H_2S and then sulphur.

As in the case of the carbonates, the alkali metals are known to form acid and neutral *sulphates* ($EHSO_4$ and E_2SO_4, respectively). Both are readily soluble in water (Fig. 193). The most important in practice are Na_2SO_4 and K_2SO_4, especially the former. Their largest consumer is the glass industry. The crystal hydrate $Na_2SO_4 \cdot 10H_2O$, ("mirabilite" or "Glauber's salt") is used in medicine as a purgative.

The industrial preparation of Na_2SO_4 and K_2SO_4 is based either on their separation from natural minerals or on treatment of the corresponding chlorides with sulphuric acid. In the latter case, the sulphates are by-products of hydrochloric acid production.

A comparison of the properties of the alkali metals and their compounds reveals that, in general, they change in a very regular manner through the series Li—Cs. Like B and Be, the first element in the subgroup, lithium, occupies a somewhat singular position. The low solubility of its salts with the anions CO_3^{2-}, PO_4^{3-} and F^- and of the hydroxide, the comparative ease with which the latter loses water on heating and certain other properties bring lithium closer to magnesium and calcium. However, lithium is basically a typical aklali metal.

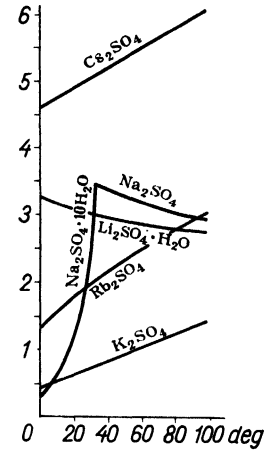


Fig. 193. Solubility of sulphates (moles/litre of H_2O)

XIII-2. The Copper Subgroup. The content of *copper* in the earth's crust is 0.003%, that of *silver*, 2×10^{-6}% and of *gold*, 5×10^{-8}%.

Copper and silver occur chiefly in the form of *sulphide* compounds. The most important copper minerals are *chalcopyrite*, $CuFeS_2$, and *chalcocite*, Cu_2S. The oxygen-containing minerals—*cuprite*, Cu_2O, *malachite*, $(CuOH)_2CO_3$, etc., are of much less industrial value.

Silver sulphide is encountered comparatively rarely as a separate mineral (*argentite*—Ag_2S). But the occurrence of Ag_2S as an impurity in sulphide ores of Pb, Zn and Cu, is very common. The usual form of occurrence of gold in nature is the *native* state: in the form of inclusions in rocks, alluvial gold in sand and separate nuggets. The U. S. S. R. is one of the richest countries in gold deposits.

Like gold, silver and copper also occur sometimes in the native state. This is probably why all three elements were known to mankind even in very ancient times. It appears that copper was the first metal to be used extensively for making tools (Fig. 194).

1) In ancient times and even as late as last century, *gold* was extracted from alluvial deposits formed by the weathering and erosion of gold-bearing rocks by natural waters. At present, gold is extracted directly from such rocks after crushing and grinding.

Since the average content of gold in deposits now worked is only 0.001%, its separation from waste rock by the old method of washing with water, based on the difference in the specific gravities, is no longer economical. Instead, the *cyanide* process is employed, which permits the practically complete separation of gold from even the poorest rock.

To separate Au, the pulverised gold-bearing rock is treated with a very dilute (0.03-0.2%) solution of NaCN in the presence of air. In accordance with the equation $4Au + 8NaCN + 2H_2O + O_2 = 4Na[Au(CN)_2] + 4NaOH$,

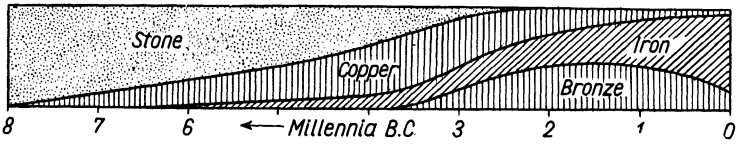


Fig. 194. The chief solid materials of past ages

the gold passes into solution, and is then precipitated by metallic zinc: $2Na[Au(CN)_2] + Zn = Na_2[Zn(CN)_4] + 2Au$. The gold is then refined, most frequently by treating it with hot concentrated H_2SO_4 or by electrolysis.

2) Most of the *silver* extracted at present is obtained not from silver ores, but from Ag-containing sulphide ores of Pb, Zn and Cu. Ag is refined chiefly by electrolysis.

3) *Copper* is produced from its sulphide ores in several stages. First, the ore is roasted in air to burn out the bulk of the sulphur. The roasted ore is then smelted with fluxes. At this stage the waste rock and part of the iron is converted into slug, while Cu_2S, FeS and small quantities of other impurities fuse together into matte (which collects at the bottom of the furnace). The matte is transferred to special converters where the copper is freed from sulphur and iron by blowing air through the molten mass.

The production of copper from oxide ores is much simpler than from sulphide ores, since it consists essentially in reduction with carbon which is accomplished quite easily. This is apparently how copper was extracted in ancient times. Its production in Egypt had reached considerable amounts by 3000 B. C.

4) As the Cu content in run-of-mine ores now rarely exceeds 2%, they can be processed economically only after *concentration*, i. e., upgrading of the ore by separating the copper-bearing minerals from the waste rock. This is done by *flotation* of the ores, a method of concentration based on the difference in adsorptive properties of the surfaces of the metal sulphide and the silicate host rock grains.

If a pulverised mixture of a silicate and a metal sulphide is placed in an aqueous solution of an organic substance of low polarity, the surface of the former will adsorb almost exclusively water molecules, while that of the latter will take up mostly the low-polar organic solute molecules. If air bubbles are passed through such a solution, they will also adsorb almost exclusively the low-polar molecules.

Being coated with identical adsorption layers, the metal sulphide grains and the bubbles passing through the solution adhere readily to each other. On the other hand, the silicates will not adhere to the air bubbles. If finely ground copper ore is agitated in water containing a small amount of a low-polar

organic substance (say, pine oil), and air is blown through the suspension (Fig. 195) the copper sulphide particles will be carried to the surface with the air bubbles and will flow over the lip of the cell as a froth, while the silicate grains remain in the pulp. This is the basis of the flotation method of concentration, by means of which more than 100 million tons of sulphide ores or different metals are processed annually

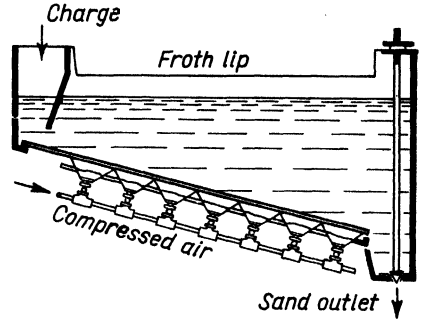


Fig. 195. Schematic representation of the flotation process

In the elemental state, Cu, Ag and Au are red, white and yellow metals, respectively. Their most important constants are listed in the table below, and the variation of their properties within the subgroup can be seen from Fig. 196.

All three metals have considerable specific gravities, fairly high melting and boiling points, and comparatively low hardness. The ductility and malleability of copper

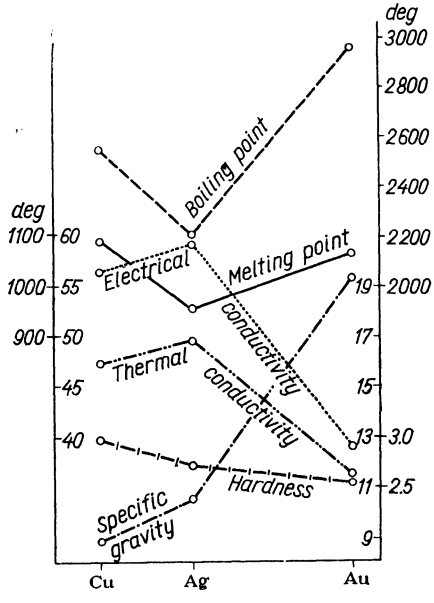


Fig. 196. Properties of Cu, Ag and Au

and its analogues (especially Au) are very high. 1 g of gold can be drawn out into a wire 3 km long, and the metal can be hammered

Properties	Cu	Ag	Au
Specific gravity	9.0	10.5	19.3
Hardness (diamond = 10)	3.0	2.7	2.5
Electrical conductivity (Hg = 1)	57	59	40
Thermal conductivity (Hg = 1)	46	49	35
Melting point (°C)	1083	961	1064
Boiling point (°C)	2880	2160	2850

or rolled into sheets as thin as 0.0001 mm (gold foil). Such sheets are 500 times thinner than a human hair. They are yellow in reflected light, but green in transmitted light. The elements of the copper subgroup have higher electrical and thermal conductivities than any other metal.

Cu, Ag and Au readily form alloys with one another and with many other metals. In particular, they all alloy with mercury (Cu alloys less readily than the others). A method sometimes employed for extracting gold from gold-bearing rocks is based on the fact that Au readily forms amalgams.

5) *Copper* is used mainly in electrical engineering and metallurgy: in the former, chiefly for the manufacture of electric wires, and in the latter, for the production of alloys with other metals such as tin (bronze) and zinc (brass). The annual world output of copper is about 3 million tons.

Silver is chiefly used for making coins, domestic utensils and ornaments. Ag compounds find application principally in the photographic industry. The annual world output of silver is about 6000 tons.

Gold is the basis of the monetary system of most countries. It is also used for making jewelry, for gilding other metals, etc. The annual world output of gold is about 1000 tons.

6) Ornaments and jewelry are usually made of alloys of Ag or Au with copper, the composition ("fineness") of which is now expressed according to the U. S. S. R. standard as the number of parts by weight of the precious metal in 1000 parts of the alloy. In the Soviet Union many objects still bear fineness markings in the former Russian system, indicating the number of zolotniks (4.226 g) of the precious metal per Russian pound (96 zolotniks) of the alloy. In these terms, gold articles usually had a fineness of 56 and silver articles, a fineness of 84. In many other countries (England, U. S. A., etc.) the composition of gold alloys used in jewelry is expressed in carats, meaning the number of parts of pure gold in 25 parts of the alloy. Thus, 24-carat gold is pure gold, 14-carat gold is 14 parts pure gold and 10 parts copper or silver (by weight), etc.

The chemical activity of copper and its analogues is not high, and decreases rapidly in the order Cu—Ag—Au. Gold and silver remain unchanged in air, but copper gradually becomes covered with a dense greenish-grey film of basic carbonates. Only copper combines directly with oxygen (on heating), as to sulphur, both copper and silver combine with it directly. Cu, Ag and Au do not react with hydrogen, nitrogen or carbon even at high temperatures.

Copper and its analogues react much more readily with the free halogens than with any other element. Copper itself readily combines with them at ordinary temperatures, while silver reacts slowly, and gold reacts with the dry halogens only on heating. But gold dissolves readily in an aqueous solution of chlorine (chlorine water). Under these conditions, the reaction is slowest in the case of silver owing to the fact that its surface becomes coated with a layer of poorly soluble silver chloride.

In the electromotive series, all three elements are situated to the right of hydrogen, copper being almost next to the latter, and gold—further away from hydrogen than any other metal. Therefore, in the absence of oxidising agents, even copper does not dissolve in such acids as HCl and H_2SO_4. Copper and silver dissolve readily in acids which are also oxidising agents (HNO_3, etc.), but gold dissolves only when the oxidising properties of the acid are particularly powerful. The best solvent for gold is hydrochloric acid saturated with chlorine, the reaction being:

$$2Au + 3Cl_2 + 2HCl = 2H[AuCl_4]$$

Aqua regia (IX-3) also readily dissolves gold. The elements of the copper subgroup are highly resistant to strong alkalis.

Silver is chiefly *monovalent* in its compounds. Cu and Au each form two series of derivatives which have been fairly well studied, Cu being *mono-* and *divalent*, and Au, *mono-* and *trivalent*. In most cases, the derivatives of *divalent* copper and *trivalent* gold are more stable and more important in practice. All the soluble compounds of Cu, Ag and Au are poisonous.

The most characteristic feature of the majority of compounds of these elements is the ease with which they are reduced to the metals. In accordance with their position in the electromotive series, gold is reduced the most easily, and copper—the most reluctantly. Another pronounced feature is the tendency towards complex formation.

7) The finely divided silver which is obtained by reduction, has an interesting application in sanitary engineering. Experiment has shown Ag^+ ion to posess very powerful bactericidal properties. For example, water which has been kept for some time in silver vessels, may then be kept for a long time without stagnating, since it has been sterilised by the slight concentration of Ag^+ ion produced due to its contact with metallic silver.

The heats of formation of the compounds of monovalent Cu, Ag and Au are shown in Fig. 197. It is evident that they decrease in all cases from copper to gold.

The *oxides* of the type E_2O are the lower or *-ous* oxides (but Ag_2O is often called silver oxide). They all have characteristic colours: Cu_2O is red, Ag_2O is dark brown and Au_2O is grey-violet.

The E_2O oxides are almost insoluble in water, and combine with the latter to form the *hydroxides*, EOH, only to a very small extent. These hydroxides are *bases* of medium strength. Thus, moist Ag_2O imparts a distinct blue colour to litmus paper.

Many *salts* of Cu^+, Ag^+ and Au^+ are coloured even when a colourless anion is present in the molecule. Almost all the derivatives of Cu^+ and Au^+ are practically insoluble in water and are unstable when moist. Owing to this, they are very rarely encountered in practice.

On the other hand, Ag^+ compounds find various applications. Although most Ag^+ salts are poorly soluble in water several readily soluble salts are also known. They are neutral to litmus in solution. The most important in practice is silver *nitrate*, $AgNO_3$, which is obtained by the reaction:

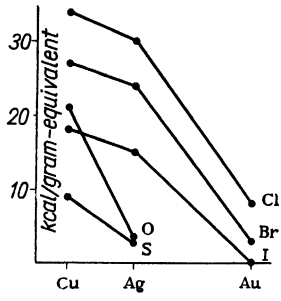


Fig. 197. Heats of formation of Cu, Ag and Au compounds

$$3Ag + 4HNO_3 = 3AgNO_3 + NO + 2H_2O$$

This colourless salt, which is readily soluble in water, serves as the usual parent substance for preparing the other silver compounds. The most important of the latter are the *halides* which are almost insoluble in water—white AgCl, yellowish AgBr and yellow AgI, their dissociation under the action of light with the liberation of metallic silver forming the basis of the photographic process. Like the halides, most other silver compounds are also decomposed gradually by light. For this reason they (and their solutions) are usually stored in brown glass jars.

Salts of monovalent Cu, Ag and Au form complex compounds with a number of molecules and ions (NH_3, CN^-, $S_2O_3^{2-}$, etc.). These complex compounds are for the most part readily soluble and their formation accounts for the solution of many salts that are initially insoluble in water. For example, owing to complex formation,

$$AgCl + 2NH_3 = [Ag(NH_3)_2]Cl$$

insoluble AgCl dissolves in NH_4OH. In the case of Cu^+ and Au^+ derivatives, complex formation often results not only in solution, but in an increase of stability as well.

8) Silver nitrate is widely employed for making mirrors and in medicine (often in the form of a melt containing 1 part of $AgNO_3$ and 2 parts of KNO_3 under the name of "lunar caustic"). A solution of $AgNO_3$ in aqueous ammonia is also sometimes used for making indelible laundry marks. The invisible mark is brought out and fixed by ironing the marked spot slowly with a hot iron. It should be noted that a solution of the ammonium complex of silver must not be stored (because on standing, a highly explosive precipitate falls out).

9) Photographic plates or films are essentially a layer of a fine suspension of an Ag halide (most frequently—AgBr) in gelatin, applied to glass or celluloid. The usual thickness of the layer is about 20 μ.

Exposure of the plate or film results in decomposition of the Ag halide in it, the halogen combining chemically with the gelatin, and the silver forming minute crystal nuclei. The higher the illumination of a given area of the surface, the greater the number of crystal nuclei that emerge on that area. Thus, though a plate or film which has been briefly exposed looks quite uniform it already contains a latent image of the object photographed.

To make it visible, the plate or film is *developed*, this consisting in further reduction of the silver halide to free silver by chemical means. The developer is generally an organic reducing agent. A fact essentially important to the developing process is that the reduction of the silver halide takes place the most rapidly in the neighbourhood of already existing crystal nuclei of Ag. This is evidently due to the adsorption of the developer on the nuclei, on the one hand, and to the role of the nuclei as centres of crystallisation for newly separating metallic silver, on the other hand.

When visible image of sufficient clarity has been obtained by developing, the plate or film is *fixed* in order to make it insensitive to the further action of light. Fixing is accomplished by extracting the remaining undecomposed silver halide from the light-sensitive coating. The fixing agent is generally a solution of sodium thiosulphate ("hypo"), which readily dissolves Ag halides owing to complex formation: $2Na_2S_2O_3 + AgX = Na_3[Ag(S_2O_3)_2] + NaX$.

The light-resistant visible image obtained by developing and fixing, called the *negative*, is a reverse image, the dark places on it corresponding to the light spots on the photographed object, and vice versa. In order to obtain a true image, the negative is placed on another plate, film or paper with a light-sensitive coating, and exposed to light. Since the light passes more easily through the lighter parts of the negative and with greater difficulty through the darker parts, the relation between light and shade is reversed during the "printing" of photographs, and they become true images of the object photographed. The printed photograph, known as the *positive*, is then developed and fixed (or only fixed if the light-sensitive coating was designed for the immediate production of a visible image).

10) Black Ag_2S is the least soluble salt of silver and is therefore deposited by S'' ion from solution of all its compounds. It is formed also on metallic silver under the action of air containing traces of H_2S (this being common in towns).

The reaction $4Ag + 2H_2S + O_2 = 2Ag_2S + 2H_2O$ takes place slowly even under ordinary conditions and causes gradual darkening of silver objects.

Of the compounds in which the elements of the copper subgroup are divalent, only the derivatives of copper have been well studied and are of practical importance. Black *cupric oxide*, CuO, sometimes occurs in nature, and can be readily prepared by heating Cu in air. It is practically insoluble in water, but dissolves in acids to form the corresponding salts.

Cupric hydroxide, $Cu(OH)_2$, separates out as a blue precipitate when solutions of $Cu^{\cdot\cdot}$ salts are treated with an alkali. It is practically insoluble in water, and loses water readily on heating, changing into CuO.

Cupric oxide possesses rather weak *basic* properties. With acids it forms salts, most of which are readily soluble in water. In dilute

solutions the colour of all the salts of divalent copper with colourless anions is a fairly light blue (the colour of $Cu^{\cdot\cdot}$ ion). On the other hand, the colour of the solid Cu^{2+} salts is extremely varied. In particular, the one of greatest practical importance—copper sulphate or *blue vitriol*, $CuSO_4 \cdot 5H_2O$, is blue.

Complex formation is very characteristic of divalent copper. This is already evident from the fact that almost all Cu^{2+} salts separate out of solution as crystal hydrates. With the corresponding salts of the alkali metals, Cu^{2+} salts produce binary compounds containing copper in the complex anions, e. g., $[CuCl_4]^{2-}$. However, most of the latter are unstable, and break up into their constituents in solution. The dark blue complex cation $[Cu(NH_3)_4]^{2+}$ peculiar to divalent copper is considerably more stable, and forms when an excess of ammonia is added to solutions of Cu^{2+} salts, e. g., according to the reaction:

$$CuSO_4 + 4NH_4OH = [Cu(NH_3)_4]SO_4 + 4H_2O$$

The intense colour of this complex makes it possible to use ammonia in testing for copper.

11) Cupric hydroxide is soluble in an excess of concentrated strong alkali owing to the formation of blue *cuprites* ($NaHCuO_2$, Na_2CuO_2, etc.). However, the latter are very unstable, and decompose on dilution into $Cu(OH)_2$. This shows that the acidic properties of cupric hydroxide are very weak.

12) One of the few derivatives of divalent silver is AgF_2, formed by the action of fluorine on finely divided Ag. It is a brownish-black substance which melts at about 690° C. AgF_2 is instantly decomposed by water with the formation of AgF, HF and oxygen (with a considerable content of ozone).

13) When powdered Au is treated with dry chlorine, a dark red compound corresponding to the empirical formula $AuCl_2$ is formed with great evolution of heat. A few more derivatives formally corresponding to divalent gold are known (dark green AuO, etc.). Actually, however, they are all complex compounds which contain mono- and trivalent gold simultaneously: $Au^I[Au^{III}Cl_4]$, $Au^I[Au^{III}O_2]$, etc.

Of the compounds in which the elements of the copper subgroup are *trivalent*, only the derivatives of Au have been well studied. A convenient parent substance for their preparation is brownish-black *auric chloride*, $AuCl_3$, which is formed at about 200° C by the action of excess chlorine on pulverised Au.

Auric oxide, Au_2O_3, can be obtained only by indirect means. It is a dark brown powder, insoluble in water, which readily loses oxygen on heating.

The reddish-brown *hydroxide*, $Au(OH)_3$, is precipitated by the action of strong alkalis on a solution of $AuCl_3$. It is *amphoteric*, its acidic properties being stronger than its basic properties.

Salts of $Au(OH)_3$ with bases—*aurates*—form when the hydroxide is dissolved in strong alkalis, and are derived from the complex acid $H[Au(OH)_4]$. Salts corresponding to the basic properties of

$Au(OH)_3$ can be obtained by dissolving auric hydroxide in strong acids. The majority of derivatives of trivalent gold are coloured mostly in shades of yellow.

A characteristic property of Au^{3+} is its pronounced tendency to form complex anions. For example, when $AuCl_3$ reacts with water in accordance with the equation

$$H_2O + AuCl_3 = H_2[OAuCl_3]$$

the result is a brownish-red solution of an *aqueous acid*, i. e., an acid formed by the complex addition of water to a neutral salt, and with Ag^+ ions this acid gives a yellow precipitate of the sparingly soluble silver salt, $Ag_2[OAuCl_3]$.

The most common compound of trivalent gold is *chlorauric acid* which separates out as the crystal hydrate $H[AuCl_4] \cdot 4H_2O$ on evaporation of a solution of gold in HCl saturated with chlorine. Both the acid and many of its salts (*chloraurates*) are readily soluble in certain organic solvents (alcohol, ether) as well as in water. The very low solubility of cesium chloraurate is sometimes used for detecting this element.

14) The derivatives of *trivalent* silver and copper have been relatively little studied. In particular, the green complex $K_3[CuF_6]$ has been obtained by heating a mixture of KCl and $CuCl_2$ in an atmosphere of fluorine. Derivatives of orthoiodic and orthotelluric acids are also known for both Cu^{3+} and Ag^{3+}.

On comparing the elements of the two subgroups of group I we find but few common features. In particular, all the metals of group I are distinguished by high electrical conductivities and form compounds in which they are monovalent. However, Li and its analogues are only monovalent, whereas the elements of the copper subgroup may also exhibit (and in the case of Cu and Au, even preferably exhibit) a higher valency. In this respect, silver is somewhat closer to the alkali metals than the other elements of the copper subgroup.

XIII-3. Complex Compounds. Having mastered the material of the preceding sections of the course, we can examine complex compounds in greater detail than before (IX-2). Although the basis for the modern treatment of this extensive and important section of general chemistry was laid fairly long ago (Werner, 1893) and the classification of complex compounds was worked out in great detail, our knowledge of their properties is still far from complete. Therefore, the relationship between the structure of complex compounds and their properties can, for the present, only be given in general outline.

Confining ourselves, to begin with, to complexes with ionic *addenda* (complex-added particles), the first thing we notice is the analogy between the methods of formation of such complexes and

certain oxygen compounds, for example:

$$H_2O+SO_3=H_2[SO_4] \qquad K_2O+SO_3=K_2[SO_4]$$
$$2HCl+PtCl_2=H_2[PtCl_4] \qquad 2KCl+PtCl_2=K_2[PtCl_4]$$

Oxyacids and their salts may, consequently, be regarded as a particular case of complexes of this type (so-called *acid complexes*). Besides oxygen, chlorine and other elemental negative ions, such acid radicals as CN^-, NO_2^-, NO_3^-, CO_3^{2-}, SO_3^{2-}, SO_4^{2-}, etc., may also behave as addenda in the formation of acid-complexes, i. e., compounds with complex anions. On the other hand, very many elements can be complexing agents and, moreover, often in different valency states. Therefore, the number of known acid complexes is very large, and their

Coordination number	Examples of simple compounds	Examples of complex compounds
1	ClF	—
2	OF_2	$M[HF_2]$
3	BF_3	$M[MgF_3]$
4	SiF_4	$M_2[FeF_4]$; $M[BF_4]$
5	PF_5	$M[ThF_5]$
6	SF_6	$M_3[AlF_6]$; $M_2[SiF_6]$; $M[SbF_6]$
7	IF_7	$M_2[NbF_7]$
8	OsF_8	$M_4[SnF_8]$; $M_3[TaF_8]$

composition is greatly varied, as can be seen, for example, from the comparison given for the fluorides (M being a monovalent metal).

The *structural type* affects the properties of a complex compound often to an even larger extent than the chemical nature of the constituents. The type is characterised, primarily, by the *coordination number* of the complexing agent. The coordination number is, generally speaking, *variable* and, apart from the nature of the complexing agent and the addenda, depends also on the conditions of formation of the complex (chiefly, the concentrations of the constituents and the temperature).

Experiment shows, however, that for many complexing agents, definite types of structures are preferably formed in the presence of various addenda and at different concentrations of the latter. This provides a basis for indicating the coordination numbers characteristic of these complexing agents (under ordinary conditions). For example, the coordination number 6 is characteristic of Co^{3+} and Pt^{4+}, and the coordination number 4 is characteristic of Pt^{2+}.

A comparison of the experimental data on complex compounds reveals that the most common structures are those corresponding to the coordination numbers 6 and 4. All other coordination number values are encountered much more rarely.

The *spatial structure* of the inner sphere of a complex depends mainly on the coordination number and the tendency to achieve the

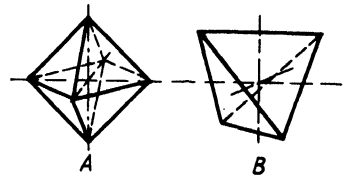


Fig. 198. Octahedron (*A*) and tetrahedron (*B*)

maximum compactness (closeness) of packing the particles. If a complexing agent is visualised as being at the centre of a particular figure, then for a coordination number of 6, the addenda are typically arranged at the corners of an octahedron (Fig. 198, *A*), while for a coordination number of 4, they are arranged at the corners of a tetrahedron (Fig. 198, *B*). An octahedral addenda arrangement was

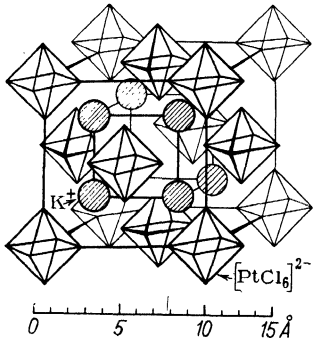


Fig. 199. Crystal structure of $K_2[PtCl_6]$

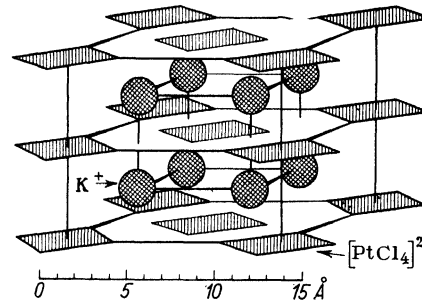


Fig. 200. Crystal structure of $K_2[PtCl_4]$

established, in particular, for the ion $[PtCl_6]^{2-}$ (Fig. 199). When the coordination number is 4 or less, the individual peculiarities of the complexing agent and the addenda play an important part in determining the relative stability of a particular spatial arrangement. Therefore, for example, when the coordination number is 4, an arrangement of the addenda at the corners of a square (with the complexing agent in the centre) becomes possible in addition to the tetrahedral arrangement, this being characteristic, in particular, of the derivatives of divalent platinum (Fig. 200).

Besides oppositely charged ions, such molecules as NH_3 and H_2O may also be attracted to the complexing agent. Owing to the absence of any charge on the addenda in this case, the complex ions retain the original charge of the complexing agent. As the latter is usually a cation, complex compounds with neutral addenda mostly have complex *cations*.

1) From the material considered earlier (IX-2), it follows that typical complexing agents should be multi-charged ions of relatively small volume. Since elementary anions have small charges and fairly large volumes, they do not often serve as complexing agents. However, individual examples of such complexes are known. For example, if AgI is dissolved in a concentrated solution of $AgNO_3$, the binary compound $AgI \cdot 2AgNO_3$ results, and a study of this compound indicates the structure $[IAg_3](NO_3)_2$, where I^- ion is the complexing agent.

The complex compounds considered above may be called *homogeneous* because all the addenda are *identical*. *Heterogeneous* complexes, containing two or more *different* addenda simultaneously in the inner sphere, are much more numerous.

It is clear that substitution of a neutral addendum for an ionic one or vice versa should affect the charge of the complex ion as a whole. For example, by successively substituting Cl^- ions for the ammonia molecules in the compound $[Pt(NH_3)_6]^{4+}$, the following series of complex cations can be obtained:

$$[Pt(NH_3)_6]^{4+} \quad [Pt(NH_3)_5Cl]^{3+} \quad [Pt(NH_3)_4Cl_2]^{2+} \quad [Pt(NH_3)_3Cl_3]^{+}$$

Substitution of one more Cl^- for ammonia results in the *neutral* complex $[Pt(NH_3)_2Cl_4]$. Finally, replacing the last two ammonia molecules gives the complex anions $[Pt(NH_3)Cl_5]^-$ and $[PtCl_6]^{2-}$.

Substitution of one addenda for another in the inner sphere is often accompanied by a sharp change in the colour of the complex, as for instance, in the following series of chlorides containing the cation $[CrA_6)^{3+}$ (where $A = NH_3$ or H_2O):

$[Cr(NH_3)_6]^{3+}$	$[Cr(NH_3)_5OH_2]^{3+}$	$[Cr(NH_3)_4(OH_2)_2]^{3+}$
yellow	orange-yellow	orange-red
$[Cr(NH_3)_3[OH_2)_3]^{3+}$	$[Cr(NH_3)_2(OH_2)_4]^{3+}$	$[Cr(OH_2)_6]^{3+}$
pale red	violet-red	violet

No compound of the composition $[Cr(NH_3)(OH_2)_5]Cl_3$ has been obtained so far. Judging by the change in colour, it should be reddish-violet.

Besides the violet compound corresponding to the empirical formula $CrCl_3 \cdot 6H_2O$, two more crystal hydrates of the same composition (light green and dark green) are known. This is, therefore, our first encounter with *isomerism* in complex compounds, i. e., the existence among them of formations identical in composition but of different structure (X-2).

The nature of the isomerism of the hydrates of $CrCl_3$ can be made evident by referring to the different behaviour of their freshly prepared solutions towards $AgNO_3$. When treated with this reagent, the violet compound precipitates at once all three of its chlorine ions, while in the case of the light green compound, two ions are precipitated, and in the case of the dark green compound, only one. On the basis of these experimental results, and bearing in mind that the characteristic coordination number of Cr^{3+} is six, the following structures should be ascribed to these isomeric crystal hydrates:

$[Cr(OH_2)_6]Cl_3$	$[Cr(OH_2)_5Cl]Cl_2 \cdot H_2O$	$[Cr(OH_2)_4Cl_2]Cl \cdot 2H_2O$
violet	light green	dark green

The fact that on standing in a desiccator over sulphuric acid, the violet crystal hydrate does not become anhydrous at all, while the dark green crystal hydrate loses only two molecules of water, is also in good agreement with these formulas.

This isomerism depending on different arrangements of water molecules (*hydrate* isomerism), is known for a number of compounds. *Ionisation* isomerism is closely similar, being connected with the different ease of dissociation of the ions in the inner and outer spheres. For example, two isomers are known for the compound having the composition $Co(Br)SO_4 \cdot 5NH_3$, one reddish-violet and the other red. A freshly prepared solution of the former does not yield a precipitate with $Ag^{\cdot}$ ions, but yields a precipitate with $Ba^{\cdot\cdot}$ ions, while the opposite is true of the latter isomer. Hence, these isomers correspond to the following structures:

$[Co(NH_3)_5Br]SO_4$	$[Co(NH_3)_5SO_4]\,Br$
reddish-violet	red

Compounds with two complex ions in their molecule may exhibit *coordination* isomerism which involves different distribution of the addenda between the two complexing agents. Examples of this are the compounds:

$$[Co(NH_3)_6]\quad [Cr(CN)_6]\quad \text{and}\quad [Cr(NH_3)_6]\,[Co(CN)_6]$$

Cases in which isomerism is due to different *spatial* arrangement of the addenda of a heterogeneous complex in *the same* sphere, stand somewhat apart from those just considered. Most typical of those are *cis-* and *trans*-isomerism.

For example, the compound $[Pt(NH_3)_2Cl_2]$ may exist in two forms, of which one is orange-yellow and the other pale yellow. Besides colour, the two forms differ both in method of formation and in a number of properties. A close study of the latter indicates that the relative arrangement of the addenda in the square inner sphere (characteristic of complex derivatives of divalent platinum) differs as shown

in the schemes given below:

Cl NH$_3$	Cl NH$_3$
Pt	Pt
Cl NH$_3$	NH$_3$ Cl
cis-isomer	trans-isomer
(orange-yellow)	(pale yellow)

Each of these two compounds is able to gain two atoms of chlorine (with an increase in the valency of platinum to four and in its coordination number to six), whereupon the resulting compounds are again found to have different properties. In particular, the cis-isomer is orange, while the trans-isomer is yellow. The structures of both of them are shown in Fig. 201. Similar isomerism is known for a number

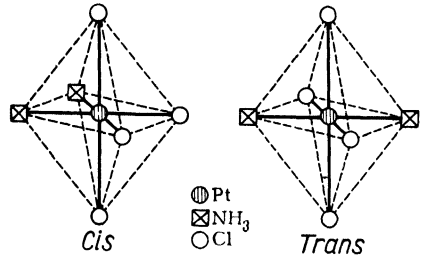


Fig. 201. Diagram of *cis-trans* isomerism

of other complexes with six addenda, of which two differ from the other four. When there are three or more different types of addenda in the inner sphere, the number of possible space isomers is still higher.

As complex compounds are dealt with mainly in aqueous solution, the most frequent substitution reaction in the inner sphere is *hydration*. The latter takes place gradually and the position of equilibrium and the speed of the process may, to a certain extent, serve as a measure of the relative stability of the bond between the central atom and the addendum. Knowing, for instance, that in the complex $[Co(NH_3)_3X_3]$, where $X = NO_2^-$, Cl^- or NO_3^-, the first of these acid radicals (as well as ammonia) is not displaced by water, the second is partially displaced and the third is completely displaced, it may be said that NH_3 and NO_2^- are linked with Co^{3+} more firmly than Cl^-, and the latter is linked more firmly than NO_3^-.

In practice, we mostly have to deal with the mutual substitution of NH_3 and H_2O in accordance with the overall equation:

$$[E(NH_3)_x] + xH_2O \rightleftarrows [E(OH_2)_x] + xNH_3$$

The position of equilibrium in this system is a measure of the stability of amines in aqueous solution. The fact that the stability varies greatly for different complexing agents is widely taken advantage of in analytical chemistry.

XIV. EIGHTH GROUP OF THE PERIODIC TABLE

26		*27*		*28*	
Fe	2	**Co**	2	**Ni**	2
	14		15		16
	8		8		8
55.847	2	58.9332	2	58.71	2
44		*45*		*46*	
	1		1		0
Ru	15	**Rh**	16	**Pd**	18
	18		18		18
	8		8		8
101.07	2	102.905	2	106.4	2
76		*77*		*78*	
	2		2		1
	14		15		17
Os	32	**Ir**	32	**Pt**	32
	18		18		18
	8		8		8
190.2	2	192.2	2	195.09	2

The eighth group of the periodic table differs essentially from all the others in that it contains no elements of the *short* periods. Nor does it contain subgroups of elements differing sharply in electronic structure and atomic properties. In fact it would be more correct to treat it as *triads* of elements occupying central positions in the long periods, rather than as a single group equivalent to the others.

As the outermost shells of all these atoms contain not more than two atoms, one would hardly expect to find in them a characteristic tendency to gain more electrons. The elements of the eighth group should, therefore, have only metallic properties.

Experiment shows that Fe, Co and Ni are fairly close to one another in their overall properties, and differ substantially from the other elements of the group. Hence, it is reasonable to consider Fe, Co and Ni jointly as members of the *iron family*. On the other hand, most of the properties of the elements in the Ru—Rh—Pd and Os—Ir—Pt series are similar, so that they can be grouped into what is known as the *platinum metals family*.

XIV-1. The Iron Family. *Iron* accounts for about 1.5% of the total number of atoms in the earth's crust. The content in the latter of *cobalt* (0.001%) and *nickel* (0.003%) is much smaller.

Most of the iron in the upper layers of the earth's crust is in the form of oxygen compounds, the most important industrial ores of this metal being *magnetite*, $FeO \cdot Fe_2O_3$, *hematite*, Fe_2O_3, and *limonite*, $Fe_2O_3 \cdot 2Fe(OH)_3$. Besides, considerable amounts of iron occur as the mineral *siderite*, $FeCO_3$, as well as in combination with sulphur and arsenic. Cobalt and nickel occur mostly as sulphides and arsenosulphides. Examples of their minerals are *pentlandite*, $FeS \cdot NiS$, and

cobaltite or cobalt glance, CoAsS. The U. S. S. R. possesses very rich iron ore deposits in a number of districts (the Ural, Krivoi Rog, Kerch, Kursk, etc.). Of the elements of the Fe family, iron is of quite exceptional importance, being the basis of all modern engineering. Its special role is evident from the fact that more than 200 million tons of iron is used annually throughout the world.

The consumption of nickel is much lower, and that of cobalt is still lower. These two elements are used mainly in various alloys with other metals.

1) The most difficult stage in the extraction of nickel and cobalt from their ores is separation of these elements from one another and from other metals contained in the ore. This greatly complicates the whole process and makes it necessary to adapt it, in each case, to the nature of the ore. The annual world output of nickel is about 250 thousand tons, and that of cobalt is about 15 thousand tons.

Iron is smelted from its ores in special vertical furnaces, 25 or more metres high, with an outer steel casing and an inner lining of refractory bricks, known as *blast furnaces*. The capacity of a blast furnace may be as high as 2 thousand tons of metal per day.

A blast furnace (Fig. 202) is a continuous-operation unit. Once put into operation ("blown in"), it is run for several years without stopping. In order to maintain the process, which consists essentially in the reduction of iron oxides, a charge, consisting of alternate layers of iron ore, coke and fluxes (special admixtures—mostly $CaCO_3$—intended to lower the melting point of the slag formed) is introduced at the top. A blast of air, preheated to 600-800° C, is continuously blown in at the bottom of the furnace through special ducts, called tuyeres. The burning coke maintains the temperature in the lower part of the furnace at approximately 1800° C. The temperature gradually decreases towards the top of the furnace, and is about 400° C at the top. The molten iron and liquid slag which accumulate at the bottom of the furnace are tapped periodically through special openings known as notches. The successive stages of the blast-furnace process are represented in Fig. 202.

2) About 2 thousand tons of iron ore, 1 thousand tons of coke, 400 tons of limestone and 3 thousand tons of air are used up for every thousand tons of metal smelted in the blast-furnace process. Besides 1 thousand tons of metal, about 500 tons of slag and 5 thousand tons of blast-furnace gas are produced.

3) The gases leaving the furnace contain approximately 30% carbon monoxide and have a calorific value of about 1000 kcal/m^3. They are utilised mainly by burning in stoves for heating the air entering the tuyeres. Before this, they are usually freed from dust (in special chambers) and organic impurities (by washing with water in scrubbers).

4) Blast-furnace slags consist mainly of CaO, SiO_2 and Al_2O_3. These slags are often used for manufacturing cement (slag cement), concrete and artificial building stones. Sometimes they are chemically combined with valuable impurities, contained in the original iron ore. For example, the slags left after smelt-

ing Kerch ores serve as a very good raw material for obtaining vanadium and its compounds.

5) A diagram of a blast-furnace plant in a steel works is shown in Fig. 203. The mechanical loader *A* supplies the blast furnace *B* periodically with fresh batches of the charge. The gases formed during the process pass through the dust catcher *C* and the scrubber *D*, and are burnt in the hot blast stove *F* to heat its brick checkerwork. Parallel with this, the blower *G* drives air through the other hot blast stove *E*, which has been previously heated in a similar manner, into

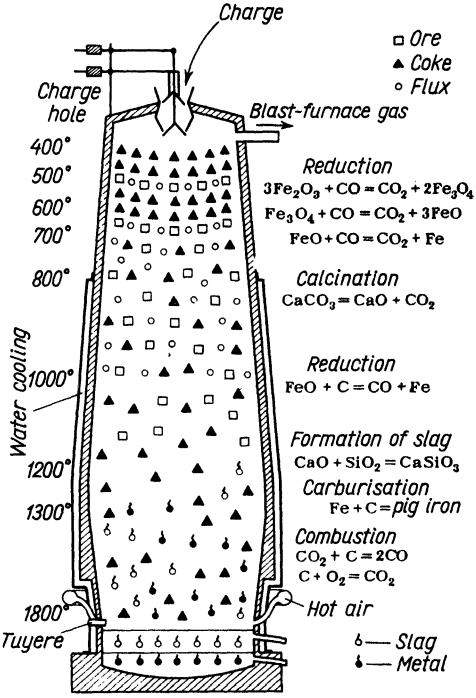


Fig. 202. Diagram of the blast-furnace process

the blast furnace tuyeres. After a certain period, the roles of the hot blast stoves *F* and *E* are reversed: the first is cooled, while the second is heated. Each blast furnace usually operates in conjunction with several stoves.

6) When the air used for the blast contains an increased (as against the usual) percentage of oxygen, preheating becomes unnecessary, and the hot blast stoves can be eliminated. At the same time, an oxygen blast considerably raises the productivity of the blast furnace, and improves the quality of the by-products, i. e., gas and slag. In particular, the gases obtained under these conditions, apart from the increase in their calorific value (owing to the gasification of the coke), become suitable for use in various catalytic syntheses. Thus, the blast furnace becomes an integrated unit, producing semifinished products simultaneously for the metallurgical (pig iron), chemical (gas) and building (slag) industries.

The metal obtained in the blast-furnace process is an alloy of iron and carbon, containing other impurities, mostly Si, P, Mn and S. The presence of all these elements greatly affects the mechanical properties of the metal. Carbon plays a particularly important part. When the content of the latter is more than 1.7%, the resulting metal is called *pig iron*, the end product of the blast-furnace process. The output of pig iron in 1963 in the U. S. S. R. was 58.7 million tons (as against 14.9 million tons in 1940, and 4.2 million tons in 1913).

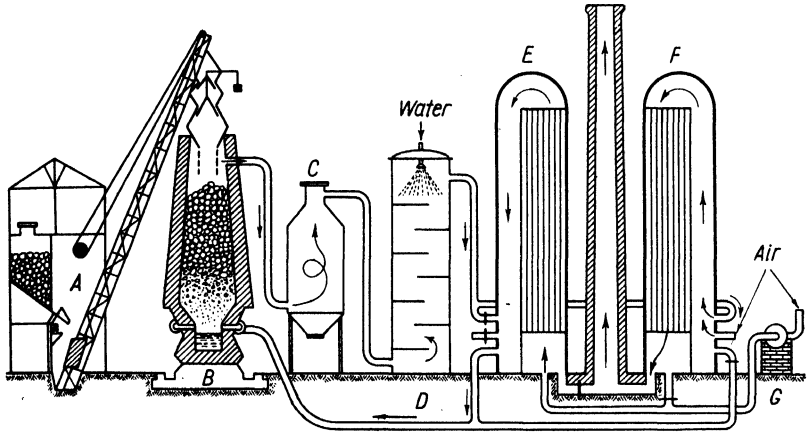


Fig. 203. Blast-furnace plant of a steel works

The range 1.7-0.2% C corresponds to various grades of *steel*, and metal with a still lower carbon content is known as *wrought iron*. Pig iron is hard, but brittle and, as a rule, can be neither forged nor rolled. It is chiefly used for casting various heavy machine parts (frames, etc.). Steel is very hard and, at the same time, elastic. Consequently, it is employed in the manufacture of all structures and components for which particular strength is required. Wrought iron is distinguished by its softness and is used to make roofing, wire, nails, etc.

In order to reduce the content of carbon in pig iron obtained by the blast-furnace process, iron oxides are added, and it is kept at a high temperature in a current of air. During this process, the carbon (as well as most of the other impurities) is burnt out, and steel or wrought iron results. By introducing admixtures of other elements into ordinary carbon steel, various grades of *special steels* are produced to meet the most varied requirements of mechanical engineering.

Usually the output of steel exceeds that of pig iron because a large quantity of scrap iron is remelted into steel. The output of steel in the U. S. S. R. in 1963 was 80.2 million tons (as against 18.3 million tons in 1940, and 4.2 million tons in 1913).

7) The solidification point of blast-furnace pig iron is usually about 1200° C (the transition from the liquid to the solid state being accompanied by an increase in volume). In order to reprocess it into steel (or wrought iron), the principal method employed is the *open-hearth* process, which is based on the use of a regenerative furnace. The method consists essentially in burning the impurities out of the pig iron, by passing atmospheric oxygen over the molten metal and adding iron oxides to it (in the form of rusty scrap iron or pure iron ore). The high temperature necessary to keep the metal liquid is produced by burning a mixture of inflammable gas and excess air which has been strongly heated by waste gases. This is accomplished in the open-hearth furnace by periodically reversing the flow of gases. Suppose (as shown by the arrows in Fig. 204) the combustible gas *A* and air *B* enter originally from the left. After mixing

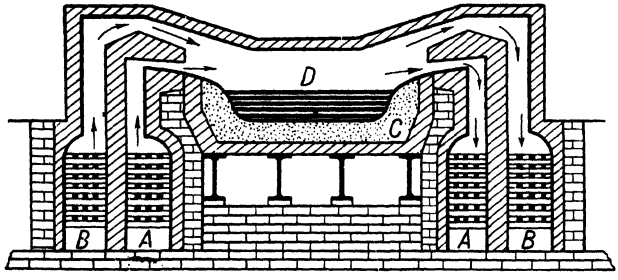


Fig. 204. Open-hearth furnace

at the entrance to the space *D* over the molten metal, the gases burn, and the waste gases heat the chambers *A* and *B* on the right-hand side of the furnace. After these chambers have been sufficiently heated, the flow of gas and air is reversed. The right-hand chambers now give up their heat to them, and the left-hand chambers are heated by the waste gases, etc. When oil (sprayed directly into the space over the metal) is used to heat the furnace, chambers *A* become unnecessary.

Owing to the rather long duration of the open-hearth process (several hours) it can easily be controlled so as to obtain metal of the desired composition. Depending on the nature of the original pig iron, the lining of the furnace hearth (*C*, Fig. 204) is made "acidic" (of silicate materials) or "basic" (of roasted dolomite). The use of air previously enriched with oxygen offers great possibilities for intensification of this process.

8) The addition of various admixtures to ordinary carbon steel affects its properties substantially. Thus, silicon mainly increases its elasticity, manganese enhances its ductility, tungsten raises its hardness, etc. By combining these additions in suitable proportions, special steels with most varied properties are obtained.

9) Certain grades of steel contain a large quantity of *nickel*. For example, ordinary stainless steel is about 18% Cr and 9% Ni.

10) *Cobalt* is mostly employed in the form of alloys used for manufacturing tips for cutting tools, drills, etc. These *superhard* alloys ("VK", "pobedit", etc.) are usually tungsten carbides cemented by cobalt (78 to 88% W, 6 to 15% Co and 5 to 6% C). Their valuable property is their ability to withstand very high cutting speeds, as their hardness does not decrease even at 1000° C.

Iron, cobalt and nickel can be obtained in the chemically pure state by reduction of their oxides with hydrogen or by electrolysis

of solutions of their salts. All three elements are lustrous white metals with a greyish (Fe, Co) or silvery (Ni) tinge. Their most important constants are listed below.

Properties	Fe	Co	Ni
Specific gravity	7.9	8.9	8.9
Melting point (°C)	1539	1495	1455
Boiling point (°C)	2740	2250	2140
Electrical conductivity (Hg = 1) . .	10	10	14
Thermal conductivity (Hg = 1) . . .	10	8	7

Iron and nickel are easily forged and rolled. Cobalt is harder and more brittle. Unlike other metals, Fe, Co and Ni are attracted by a magnet.

In chemical properties, iron, cobalt and nickel are metals of medium activity. In the absence of moisture, they do not appreciably react under ordinary conditions even with such typical non-metals as O, S, Cl and Br. However, when heated, they react with all of them fairly vigorously, especially if pulverised.

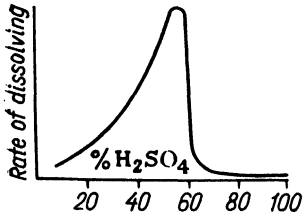


Fig. 205. Reaction between Fe and sulphuric acid

11) Besides the non-metals enumerated above, Fe, Co and Ni can combine with C, Si, P, As and Sb on heating. In particular, their carbides have the composition E_2C. All three elements of the iron family (especially when finely divided and at increased temperatures) absorb fairly considerable quantities of hydrogen. However, no definite chemical compounds are formed.

12) When finely divided Fe, Co and Ni are heated in an atmosphere of CO, they form *carbonyl* compounds (X-1). The composition of the latter corresponds to the formulas $Fe(CO)_5$, $[Co(CO)_4]_2$ and $Ni(CO)_4$. Nickel carbonyl, a colourless liquid (m. p. —25° C, b. p. 42° C), forms more readily than the others (even at ordinary pressure). Its formation and subsequent thermal decomposition are sometimes used for extracting nickel from its ores.

Co and Ni, which lie between iron and tin in the electromotive series, are closer to the latter. Therefore, both metals dissolve in dilute acids much more slowly than iron. The dependence of the rate of the reaction between Fe and sulphuric acid on the concentration of the latter is shown in Fig. 205. The resistance to concentrated HNO_3 decreases rapidly in the order Fe—Co—Ni. Strong alkalis have no effect on any of the three elements.

Cobalt, nickel and chemically pure iron (in the compact form) are resistant to air and water, but impure iron is subject to *corrosion* (i. e., rusts) under the joint action of moisture, carbon dioxide and

atmospheric oxygen. The layer of rust which forms on iron objects consists mainly of a hydrated ferric oxide, the composition of which approximately corresponds to the formula $Fe_2O_3 \cdot H_2O$. This layer is friable and porous and does not protect the metal from further rusting. The amount of Fe lost annually all over the world due to corrosion corresponds to a *quarter* of the world output for the same period.

The principal reaction involved in the corrosion of metals on contact with water or moist air is *displacement of hydrogen*, which takes place, in the case of iron, according to the equation:

$$Fe + 2H^{\bullet} = Fe^{\bullet\bullet} + 2H$$

In addition to the nature of the metal and the hydrogen ion concentration, the rate of the process depends greatly on the speed at which the equilibrium of this principal reaction is displaced to the right owing to secondary reactions which bind the products formed.

The reaction is usually due mainly to the oxygen (atmospheric) dissolved in the water. It oxidises $Fe^{\bullet\bullet}$ to $Fe^{\bullet\bullet\bullet}$, and atomic hydrogen to H_2O. To sum up, the rusting of iron may be represented thus:

$$4Fe + 2H_2O + 3O_2 = 2(Fe_2O_3 \cdot H_2O)$$

To reduce corrosion losses, iron objects are usually insulated from water and air by means of a coat of oil paint or a metal which is stable under ordinary conditions. For this purpose, zinc or tin is mostly used ("galvanised iron" and "tinplate"). Frequently, nickel plating is also employed. However, all these methods of protection are effective only while the coating remains intact. Hence, their use does not completely prevent rusting, but only more or less retards it.

13) When a chemically pure metal reacts with moist air or water, the hydrogen initially liberated is retained to a greater or lesser degree on the surface of the metal and protects the latter from further corrosion. When two different metals are in contact, a galvanic pair results (V-8, suppl. 1), and hydrogen deposits on the less active of them, thus protecting it from corrosion. Conversely, the more active metal is, in this case, rapidly attacked. Thus, for example, galvanised iron and tin plate rust in entirely different ways when the protective layer is damaged. In the first case (*A*, Fig. 206), the local damage to the surface leads to further destruction of the protective zinc layer, but the rusting of the iron is retarded. In the second case (*B*, Fig. 206), the iron rusts rapidly, beginning from the damaged spot and continuing under the rest of the tin layer which remains unaffected. The feathered arrows in both diagrams of Fig. 206 indicate the direction of electron transfer in the contacting metals.

The formation of such local galvanic pairs is the principal reason for the relatively rapid corrosion of impure metals (cf. Fig. 151). Not only different metals, but other dissimilar parts of the system may act as the individual elements of the pair (cathode and anode). On the other hand, the high homogeneity of very pure metals sharply increases their resistance to corrosion. Metals with the structure of solid solutions for example, stainless steels (XI-3, suppl. 2) are also highly resistant to corrosion.

14) The further left a metal stands in the electromotive series, the more susceptible it should be to corrosion. However, there are departures from this rule. The latter are observed when the surface of the metal readily becomes covered with a dense, elastic film of an insoluble compound. Though this film is sometimes so thin and transparent as to be imperceptible, it keeps the metal from contact with the surrounding medium, thus protecting it from corrosion. An

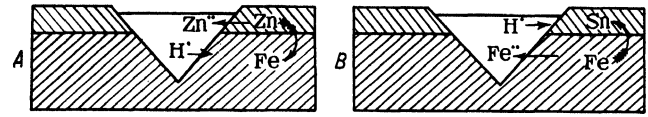


Fig. 206. Corrosion of galvanised and tinned iron

example of this is the Al_2O_3 film on aluminium (XI-2) which imparts a slightly dull appearance to objects made of this metal but protects them reliably against corrosion under ordinary conditions.

A thin protective film such as that on aluminium may also be formed on iron under special conditions, namely, by bringing the metal in contact with concentrated nitric acid. The resulting oxide film is so thin that it is imperceptible, and in contrast to ordinary rust is extremely dense. However, it is very friable and therefore, the passive state of Fe is easily disturbed. Much more durable protective films are obtained by coating the surfaces of iron objects with a layer of Mn and Fe phosphates (*parkerising*), and this is sometimes used in industry.

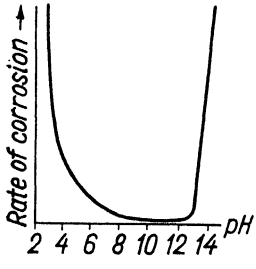


Fig. 207. Relation between the corrosion of zinc and the pH value

15) Any conditions promoting the formation of protective films or an increase in their durability will, obviously, raise the resistance of the metal to corrosion. In particular, the OH' ion is an agent which acts in this way (corrosion *inhibitor*) with respect to iron. On the other hand, an increase in the H^+-ion concentration (owing, for example, to dissolving of CO_2 in water contacting the metal) considerably speeds up corrosion. In the case of metals that form amphoteric hydroxides, maximum resistance to corrosion is observed at certain medium pH values (Fig. 207).

Any influence which promotes the removal or loosening of the protective film on a metal, intensifies its corrosion. One of the most vigorous *stimulators* of corrosion is Cl'; in particular, the action of this ion accounts for the especially rapid destruction of most metals by sea water. A tremendous part is played by the presence in the water of dissolved oxygen which speeds up corrosion by binding the primary products of the latter.

In their stable compounds, Fe, Co and Ni are almost exclusively di- and trivalent. Both valencies are approximately equally characteristic of iron, whereas on passing over to cobalt and especially to nickel, the trivalent state becomes progressively less important. The derivatives of the other valencies of these elements, being rather unstable, are of no practical importance.

The oxygen compounds of the divalent elements of the iron family form a series of *lower oxides* having the general formula EO. These oxides—black FeO, greyish-green CoO and green NiO—are practically insoluble in water and alkalis, but dissolve readily in acids. They can be reduced to the metal by hydrogen on heating, the ease of this reduction increasing slightly in the order Fe—Co—Ni.

The hydroxides of Fe, Co and Ni of the general formula $E(OH)_2$, corresponding to the EO oxides, can be obtained only by indirect methods. They are all practically insoluble in water and solutions of the usual strong alkalis but dissolve readily in acids. Therefore, chemically, these hydroxides are characteristically *basic*.

The common method for obtaining the $E(OH)_2$ hydroxides is by the action of strong alkalis on solutions of the corresponding salts of Fe and its analogues. The resulting bulky precipitates—white $Fe(OH)_2$, pink $Co(OH)_2$ and apple-green $Ni(OH)_2$—differ greatly from one another in their behaviour towards atmospheric oxygen. While $Ni(OH)_2$ does not react with the latter, and $Co(OH)_2$ is oxidised relatively slowly [to brownish-red $Co(OH)_3$], ferrous hydroxide changes rapidly to brownish-red *ferric hydroxide*:

$$4Fe(OH)_2 + O_2 + 2H_2O = 4Fe(OH)_3$$

The intermediate oxidation products are different hydroxyl derivatives simultaneously containing di- and trivalent iron and coloured in shades of dirty green (from pale to almost black). Therefore, pure $Fe(OH)_2$ can be obtained only in the complete absence of oxygen (including that dissolved in the reacting liquids).

The *salts* of strong acids and the E^{2+} cations are almost all readily soluble in water, their solutions being slightly acid owing to hydrolysis. The sparingly soluble salts include many of those of relatively weak acids, in particular, derivatives of the anions CO_3^{2-} and PO_4^{3-}.

The hydrated $E^{\cdot\cdot}$ ions have various colours: $Fe^{\cdot\cdot}$ is pale green, $Co^{\cdot\cdot}$ is pink and $Ni^{\cdot\cdot}$ is bright green. The same colours are peculiar to the crystal hydrates of their salts. On the other hand, in the anhydrous state the individual salts have different colours which do not always coincide with the natural colour of the ions Fe^{2+} (colourless), Co^{2+} (reddish) and Ni^{2+} (yellow), but also depend on the kind of anion.

The most important of these salts practically is $FeSO_4 \cdot 7H_2O$, which is called *green vitriol* or *copperas*. Its large pale green crystals partially effloresce if kept in air, the divalent iron being gradually oxidised to trivalent:

$$4FeSO_4 + O_2 + 2H_2O = 4Fe(OH)SO_4$$

Most other ferrous salts behave likewise towards atmospheric oxygen, whereas the salts of divalent cobalt and nickel remain unchanged in air.

Certain salts of complex *ferrocyanic* acid, $H_4[Fe(CN)_6]$, are important derivatives of divalent iron, principally, yellow $K_4[Fe(CN)_6]$ (potassium *ferrocyanide* or yellow prussiate of potash), which is readily soluble in water, and the practically insoluble blue ferric ferrocyanide, $Fe_4[Fe(CN)_6]_3$ (Prussian blue).

The *trivalent* state becomes less and less characteristic in the order Fe—Co—Ni. In the case of iron, the derivatives of Fe^{2+} and Fe^{3+} are approximately equally numerous among both simple and complex compounds. A very large number of stable complexes, but only a few fairly unstable simple salts are known for Co^{3+}. As to Ni^{3+}, very few derivatives are known at all, and none of them are simple salts.

The trivalent oxygen compounds form the higher *oxide series*. Dark brown cobaltic oxide, Co_2O_3, and greyish-black nickel sesquioxide, Ni_2O_3, can be obtained by carefully heating the nitrates, $E(NO_3)_2$, which decompose according to the equation:

$$4E(NO_3)_2 = 2E_2O_3 + 8NO_2 + O_2$$

Both oxides react with acids as very powerful oxidising agents. Thus, hydrochloric acid is oxidised by them to free chlorine:

$$E_2O_3 + 6HCl = 2ECl_2 + Cl_2 + 3H_2O$$

Owing to the insolubility of the E_2O_3 oxides in water, the corresponding *hydroxides* $E(OH)_3$ can be obtained only by indirect methods. Black $Ni(OH)_3$ results when $Ni(OH)_2$ is treated in alkaline solution with a powerful oxidising agent, such as free chlorine:

$$2Ni(OH)_2 + 2NaOH + Cl_2 = 2Ni(OH)_3 + 2NaCl$$

In the case of cobalt, the divalent hydroxide is oxidised slowly to brownish-black $Co(OH)_3$ even by atmospheric oxygen:

$$4Co(OH)_2 + O_2 + 2H_2O = 4CO(OH)_3$$

Both hydroxides react with acids with the reduction of Co or Ni to the divalent state, and (in the absence of oxidisable substances) with the liberation of free oxygen, e. g., in accordance with the equation:

$$4E(OH)_3 + 4H_2SO_4 = 4ESO_4 + O_2 + 10H_2O$$

16) Besides oxidation of $Ni(OH)_2$ by purely chemical means, it can be converted to the trihydroxide by electrical oxidation in alkaline solution. This reaction and the reverse process of obtaining an electric current by utilising the powerful oxidising properties of $Ni(OH)_3$ are the operating basis of the alkaline storage cell, known also as the *Edison cell*. One electrode of this cell is moulded of powdered metallic Fe, and the other, of hydrated nickel sesquioxide. The electrodes are immersed in a solution of KOH. The processes taking place on discharging and charging may be represented by the scheme:

$$Fe + 2Ni(OH)_3 \underset{\text{charging}}{\overset{\text{discharging}}{\rightleftharpoons}} Fe(OH)_2 + 2Ni(OH)_2$$

The difference of potentials between the terminals of the alkaline cell is approximately 1.3 volts on discharging, and 1.8 volts on charging. At present, cadmium is often employed instead of iron in the manufacture of alkaline cells.

Unlike the lead storage cell (X-5, suppl. 4), the alkaline cell is well able to withstand overloading or being left in a discharged state for a long time. Owing to this, as well as to its relatively small weight and robustness, it is often used for various portable devices. The basic disadvantage of the alkaline cell is its considerably lower efficiency. For this reason, lead storage batteries are preferred for large station ry plants.

Brownish-red ferric oxide, Fe_2O_3, is readily obtained by the dehydration of $Fe(OH)_3$. Unlike the hydroxides of Co^{3+} and Ni^{3+}, ferric hydroxide often occurs in the form of various minerals, most of them approximating in composition the formula FeO(OH) (or $Fe_2O_3 \cdot H_2O$) and thus containing less water than the normal hydroxide [$Fe(OH)_3$, i. e., $Fe_2O_3 \cdot 3H_2O$]. The latter can be obtained as a reddish-brown precipitate by adding an alkali to a solution of a trivalent iron salt:

$$FeCl_3 + 3NaOH = 3NaCl + Fe(OH)_3$$

Ferric hydroxide is practically insoluble in water (but readily forms colloidal solutions). Dilute acids rapidly dissolve freshly precipitated $Fe(OH)_3$, forming the corresponding salts of trivalent iron. Thus, ferric hydroxide is basic in nature. But it also exhibits slight acidic properties, dissolving appreciably in hot concentrated solutions of strong alkalis (but not of ammonia).

17) The salts corresponding to the acid function of ferric hydroxide—*ferrites*—are analogous in composition to aluminates, and are derived from monobasic *ferrous* acid, $HFeO_2$. They can be obtained both from solutions of $Fe(OH)_3$ in concentrated alkalis and by the dry method (for example, at 1100° C, in accordance with the equation: $Na_2CO_3 + Fe_2O_3 = CO_2\uparrow + 2NaFeO_2$).

18) The mineral *magnetite* (or magnetic iron ore), $Fe(FeO_2)_2$, may be regarded as a derivative of ferrous acid with $Fe(OH)_2$ as the base. Black ferroso-ferric oxide which corresponds to it in composition, forms as scale during the heat treatment of steel ingots.

Salts of ferric oxide can be obtained readily by oxidising the corresponding salts of ferrous oxide. Most of them are readily soluble in water. Since the basic properties of $Fe(OH)_3$ are very weak, salts of trivalent iron are greatly hydrolysed in solutions. The resulting basic salts impart the characteristic yellowish-brown colour to solutions of Fe^{3+} derivatives. Hence, this colour does not coincide with the natural colour of $Fe^{\cdot\cdot\cdot}$ ion, which (like the anhydrous Fe^{3+} ion) is itself colourless. When an excess acid is added, hydrolysis diminishes and the solutions lose their colour.

The most important Fe^{3+} salt is *ferric chloride*, which is usually sold as the yellow crystal hydrate $FeCl_3 \cdot 6H_2O$. It is prepared by treating a solution of Fe in HCl with chlorine, and is chiefly used in the

manufacture of organic dyes. Since $FeCl_3$ brings about the rapid coagulation of proteins, it is sometimes used in solution to stop bleeding from cuts.

Salts of trivalent iron often form binary compounds with the corresponding salts of the alkali metals and ammonium, an example being the *iron alums* having the general formula $M[Fe(SO_4)_2]\cdot 12H_2O$. Complex formation is particularly characteristic of the salts of many weak acids, e. g., complex *ferricyanic* acid, $H_3[Fe(CN)_6]$, a derivative of HCN, the most common salt of which is potassium *ferricyanide*, $K_3[Fe(CN)_6]$ ("red prussiate of potash"). Trivalent iron forms readily soluble complex compounds with many organic substances as well. In particular, the use of citric acid for removing rust stains from fabrics is based on this property.

In the anhydrous state, Fe^{3+} salts are capable of adding ammonia, but these complexes are completely hydrolysed by water. On the other hand, the ammines of trivalent cobalt are very stable, and yellow complex cation $[Co(NH_3)_6]^{3+}$ forms salts which crystallise readily with a number of anions, the simple salts of which are not known for Co^{3+}. Replacement of the ammonia in it by other molecules or acid radicals, results in a great variety of complex compounds of trivalent cobalt, the majority of which are quite stable both in the solid state and in solution. An example of the product of the complete substitution of ammonia in $[Co(NH_3)_6]^{3+}$ by acid radicals is the complex anion $[Co(NO_2)_6]^{3-}$, which yields sparingly soluble crystalline precipitates of the composition $M_3[Co(NO_2)_6]$ with monovalent cations (except Li^+ and Na^+). The formation of the corresponding yellow salt of potassium is used for the detection of the latter.

19) The most interesting of the other derivatives of these elements are the compounds of *hexavalent* iron. The action of Cl_2 (or Br_2) on a suspension of $Fe(OH)_3$ in hot concentrated KOH results in the formation of the potassium salt of *ferric acid*, H_2FeO_4, according to the reaction: $2Fe(OH)_3 + 10KOH + 3Cl_2 = 2K_2FeO_4 + 6KCl + 8H_2O$. The dark red solution of this salt gradually decomposes with the liberation of oxygen: $[4K_2FeO_4 + 10H_2O = 8KOH + 4Fe(OH)_3 + 3O_2]$. When the solution is treated with $BaCl_2$ a mauve precipitate of sparingly soluble barium ferrate ($BaFeO_4\cdot H_2O$) is thrown down. The readily soluble ferrates of the alkali metals are much more difficult to precipitate.

Free ferric acid and its corresponding anhydride—iron trioxide, FeO_3, have not been obtained. When solutions of ferrates are acidified, the oxygen is liberated and the iron is reduced to the trivalent state. All ferrates are extraordinarily strong oxidising agents. For example, they oxidise ammonia: $2K_2FeO_4 + 2NH_4OH = 2Fe(OH)_3 + N_2 + 4KOH$.

From the above discussion it follows that almost all the simple compounds of Co and Ni are derivatives of divalent elements. On the other hand, with iron the di- and trivalent states are approximately equally common. Therefore, the conditions under which the one changes into the other should be briefly considered. Since oxidation or

reduction of compounds in the solid state can proceed only from the surface, i. e., very slowly, it is assumed that they are in solution.

Oxidation of the derivatives of divalent iron occurs even under the action of atmospheric oxygen. The acidity or alkalinity of the solution is of great importance as regards the rate of the process: the higher the hydrogen ion concentration, the slower the oxidation. Therefore, $FeSO_4$ solution, for example, which has been strongly acidified with sulphuric acid, keeps for a long time without changing, whereas a $Fe(OH)_2$ precipitate formed in the presence of excess alkali, is oxidised so rapidly that it cannot be obtained in the pure state in the presence of air. Thus, compounds of divalent iron are reducing agents which are more active in alkaline than in acid solution. However, they can also be readily oxidised in the latter to the corresponding Fe^{3+} derivatives by the action of such powerful oxidising agents as Cl_2 and $KMnO_4$. In particular, the reaction

$$5Fe^{\cdot\cdot} + MnO_4^{\prime} + 8H^{\cdot} = 5Fe^{\cdot\cdot\cdot} + Mn^{\cdot\cdot} + 4H_2O$$

is used for the quantitative detection of $Fe^{\cdot\cdot}$ ions.

In contrast to the compounds of divalent iron, Fe^{3+} derivatives are quite stable against atmospheric oxygen. They behave as oxidising agents towards readily oxidisable substances and, are the more active, the higher the hydrogen ion concentration. Therefore, the salts of trivalent iron are readily reduced in acid solution to the corresponding salts of the lower oxide by powerful reducing agents, such as H_2S, SO_2 and HI. In particular, the reaction $2Fe^{\cdot\cdot\cdot} + 2I^{\prime} = 2Fe^{\cdot\cdot} + I_2$ lies at the basis of one of the methods for the quantitative determination of $Fe^{\cdot\cdot\cdot}$ ions.

XIV-2. The Platinum Metals. All the platinum metals are unabundant elements. The percentage of each of them in the earth's crust is estimated to be as follows:

Ru	Rh	Pd	Os	Ir	Pt
9×10^{-7}	2×10^{-8}	2×10^{-7}	5×10^{-7}	9×10^{-9}	5×10^{-8}

Accumulations of the platinum metals occur very rarely and contain them almost exclusively in the native state as slight impurities in other products of rock erosion. The amount of platinum in these alluvial deposits (analogous to gold) is usually much larger than that of the other metals of the platinum group. The separation of the latter from platinum and from each other presents considerable technological difficulties, which partly accounts for the high cost of these elements.

1) The annual world output of the platinum metals is about 25 tons. Considerable quantities of palladium (and platinum) are obtained as by-products during the processing of nickel ores, rather than from platinum deposits. The output of platinum and palladium is much larger than that of the other platinum metals.

In the free state, the elements of the platinum group are refractory, non-volatile metals and are sometimes divided according to specific gravity into the light (Ru, Rh, Pd) and heavy (Os, Ir, Pt) platinum metals. Their most important constants are listed below:

Properites	Ru	Rh	Pd	Os	Ir	Pt
Colour	silvery-grey	silvery-white	silvery-white	bluish-grey	silvery-white	greyish-white
Specific gravity	12.2	12.4	12.0	22.6	22.5	21.5
Melting point (°C)	2500	1966	1555	2700	2450	1774
Boiling point (°C)	4230	3670	3100	4600	4150	3700
Electrical conductivity (Hg = 1)	10	19	10	11	16	10

Palladium and platinum are easily machinable, whereas Ru, Rh, Os and Ir are harder and more brittle. A characteristic property of most of the elements of the platinum group is the ability to take up certain gases, in particular hydrogen.

2) Osmium is the least active with regard to hydrogen, and hardly absorbs this gas in the compact state. The most active is palladium, one volume of which is able to occlude more than 700 volumes of hydrogen at ordinary temperatures. The metal swells and becomes brittle and covered with minute cracks. The solubility of hydrogen in platinum is much lower than in palladium (becoming appreciable only at elevated temperatures). On the other hand, platinum dissolves oxygen better than palladium does: at 450° C, one volume of platinum can take up about 70 volumes of oxygen, while one volume of palladium can occlude only 0.07 volumes.

The elements of the platinum group are extraordinarily resistant to chemical influences. In the compact form most of them (except Pd and Pt) are insoluble in aqua regia as well as in the common acids. Aqua regia readily dissolves platinum, while palladium is soluble in HNO_3 as well.

Even the most active non-metals have no effect on the compact platinum metals at ordinary temperatures. More or less vigorous reactions can be brought about by heating, interesting individual peculiarities of the different elements being observed: platinum is more resistant to oxygen than the other metals, while ruthenium is more resistant to sulphur, iridium is more resistant to chlorine and rhodium is more resistant to fluorine. The most vigorous reactions take place in the case of osmium, which in finely divided form is slowly oxidised in the air (to OsO_4) even under ordinary conditions. The other plati-

num metals are also less stable chemically in the finely divided * than in the compact state.

The element of greatest practical importance in the platinum group is platinum itself. It is used for manufacturing various equipment for chemical plants, electric-furnace heating coils, instruments for measuring high temperatures, etc. It also finds extremely important applications as a catalyst for various production processes in the chemical industry. However, about half of the total world output of platinum is used non-productively for jewellery and in dentistry.

The compounds of the platinum group elements have not found any significant practical applications so far. They are very numerous and varied in type, since derivatives corresponding to different valencies from I to VIII are known for some of the metals. However, some of these valencies are not very characteristic and are encountered only as exceptions. All the elements of the platinum group display a very strong tendency towards complex formation.

Derivatives of the *divalent* elements are particularly characteristic of *palladium* and partly of *platinum*. The latter forms a very large number of complex compounds, but only a few simple ones. On the other hand, the divalent state is the most stable for palladium in either case.

Of the simple compounds of Pd^{2+}, the most important are its salts, most of which are readily soluble. In solution, $PdCl_2$ is readily reduced to the metal under the influence of carbon monoxide, even at ordinary temperatures:

$$PdCl_2 + H_2O + CO = CO_2 + 2HCl + Pd$$

Its use for the detection of CO is based on this property.

The complex derivatives of divalent palladium and platinum are very numerous and varied in composition. One of the most stable of these compounds is *platinocyanic* or *cyanoplatinic acid*, $H_2[Pt(CN)_4]$. The *chloroplatinites* or *platinochlorides*, which are salts of the complex acid $H_2[PtCl_4]$, are also very typical of platinum.

Rhodium and *iridium* are most apt to form compounds in which they are *trivalent*. Their hydroxides—yellow $Rh(OH)_3$ and green $Ir(OH)_3$—are practically insoluble in water. Both are very weak bases and readily lose water on heating to form the black oxides E_2O_3. Besides ordinary salts, very many diverse complex compounds are known for both elements.

Dioxides EO_2 corresponding to the *tetravalent* state of the elements are known for all the platinum metals (partly only in the hydrated form). Other derivatives of this valency state are particularly common

* In the finely divided state the platinum metals are often called "blacks": platinum black, palladium black, etc.

with *platinum*. Reddish-brown $Pt(OH)_4$ is soluble both in acids and in strong alkalis, the reaction products being, as a rule, complex compounds rather than simple salts. For example, the reactions with NaOH and HCl take place as follows:

$$2NaOH + Pt(OH)_4 = Na_2[Pt(OH)_6]$$

$$Pt(OH)_4 + 6HCl = H_2[PtCl_6] + 4H_2O$$

The formation of complex ammines is peculiar to platinum only, most of them being of the types $[Pt(NH_3)_6]X_4$ and $[Pt(NH_3)_4X_2]X_2$. In contrast, anionic complexes of the general formula $M_2[EX_6]$ (where X is mostly a halogen) are known for all the metals of the platinum group. The most stable of them are the derivatives of platinum.

Free *chloroplatinic* acid, $H_2[PtCl_6]$, the usual commercial preparation of this element, can be obtained by dissolving platinum in hydrochloric acid saturated with chlorine:

$$Pt + 2Cl_2 + 2HCl = H_2[PtCl_6]$$

The formation of yellow precipitates of the poorly soluble *chloroplatinates* of NH_4^+, K^+, Rb^+ and Cs^+ is sometimes used for the detection of these cations.

The *hexavalent* state is the most characteristic of *osmium* and *ruthenium*. When fused with alkalis in the presence of oxidising agents, both metals form salts of *osmic* or *ruthenic* acid, respectively, with the general formula M_2EO_4, e. g., in accordance with the equation:

$$E + 3KNO_3 + 2KOH = K_2EO_4 + 3KNO_2 + H_2O$$

Both *osmates* and *ruthenates* are rather unstable under ordinary conditions, but the predominant nature of the changes involved is essentially different. Ruthenates are easily reduced to RuO_2, the most stable oxygen compound of ruthenium. Osmates are easily oxidised to OsO_4.

Compounds where the elements are *octavalent* are known only for *osmium* and *ruthenium*. The reaction between powdered metallic osmium and fluorine at about 250° C results in the formation of colourless OsF_8 vapour, which condenses on cooling to lemon-yellow crystals (m. p. 34° C, b. p. 48° C). Chemically, osmium octafluoride is characterised by pronounced oxidising properties. It is gradually decomposed by water:

$$OsF_8 + 4H_2O = 8HF + OsO_4$$

Osmium tetroxide is the most stable oxide of this element under ordinary conditions, and forms slowly from the finely ground metal and all its compounds when just stored in air. Ruthenium tetroxide, which is analogous in composition, can be obtained by treating a solution of K_2RuO_4 with an excess of chlorine ($K_2RuO_4 + Cl_2 = 2KCl + RuO_4$). Both tetroxides are highly volatile, pale yellow (OsO_4) or

golden-yellow (RuO_4) crystalline substances. They are fairly soluble in water, the solutions exhibiting no acid reaction to litmus.

Although both tetroxides are powerful oxidising agents, the difference in their stabilities is rather sharp. Whereas OsO_4 boils at 131° C without decomposing, ruthenium tetroxide decomposes explosively into RuO_2 and oxygen if heated to 108° C. Under ordinary conditions and when not in contact with reducing agents, OsO_4 does not undergo any change, whereas RuO_4 can be stored only in the absence of light and moisture. Osmium tetroxide is readily soluble in alcohol, being reduced by the latter to OsO_2 only slowly, but RuO_4 explodes when in contact with alcohol. In general, consequently, RuO_4 is much less stable than OsO_4, and its oxidising properties are much more pronounced. The vapours of both tetroxides are highly toxic.

Despite the great variety of compounds formed by the platinum group elements, their primary practical use in chemistry is connected with the catalytic properties of the free metals. In speeding up chemical processes, they sometimes especially promote reactions that take place in the presence of gaseous hydrogen. The most interesting in this respect is palladium, in the presence of which, hydrogen, even in the cold and in the dark, reduces chlorine, bromine, iodine and oxygen, converts SO_2 into H_2S, ClO_3' into Cl', $FeCl_3$ into $FeCl_2$, etc. In the simultaneous presence of oxygen and water, palladium saturated with hydrogen is able to convert N_2 into NH_4NO_2, i. e., effect the combination of free nitrogen under ordinary conditions of temperature and pressure.

3) Since the catalytic activity of a metal grows with its surface area, the catalysts are prepared preferably with as highly developed a surface as possible. For this purpose, the metal is often deposited on an inert porous material such as asbestos. In particular, *platinised asbestos* may be obtained by impregnating asbestos with a dilute (1 or 2%) solution of $H_2[PtCl_6]$ and then roasting it, causing decomposition according to the equation: $H_2[PtCl_6] = 2HCl + 2Cl_2 + Pt$.

However, metallic catalysts are often prepared without an inert base. The degree of division of the metal most suitable for each specific case is achieved by separating it out using different methods. For example, *sponge platinum* may be obtained by gently roasting $(NH_4)_2[PtCl_6]$; *platinum black*, in which the metal is more finely divided, is made by reducing a solution of $H_2[PtCl_6]$ with metallic zinc ($H_2[PtCl_6] + 3Zn = 3ZnCl_2 + H_2 + Pt$); and still more finely divided *colloidal platinum* is prepared by reducing the same solution with stannous chloride ($H_2[PtCl_6] + 2SnCl_2 = 2SnCl_4 + 2HCl + Pt$).

In spite of many individual differences, the platinum metals are, in general, similar to the elements of the iron family. Both groups consist of silvery-white or grey low-volatile metals, their melting points varying fairly regularly within the group, decreasing upwards and from left to right (osmium being the highest-melting and nickel the lowest-melting). All the metals of group VIII feature high cata-

lytic activity. Their ions have a strong tendency towards complex formation. Their compounds are mostly coloured.

Almost all the elements of group VIII form compounds corresponding to several different valencies, the latter changing from one to another fairly easily. The most typical valency for any element decreases, in general, upwards and from left to right within the group, as can be seen from the comparison given below.

Fe	Co	Ni
III, II	II, III	II
Ru	Rh	Pd
IV	III	II, IV
Os	Ir	Pt
VIII	III, IV	IV, II

Individual features of closer resemblance can be discerned between the elements of the vertical columns. For example, all the elements of the series Co, Rh, Ir form ammines of the type $[E(NH_3)_6]X_3$ (in contrast to the other elements of the group). The members of the series Fe, Ru, Os are particularly active as catalysts in the synthesis of ammonia from its elements, while Ni, Pd and Pt behave similarly with respect to reactions of hydrogen addition to organic compounds. Oxygen compounds are more common to Fe, Ru and Os than sulphur compounds, whereas in the series Ni, Pd, Pt, the opposite is the case. In this and in some other respects, Fe, Ru and Os resemble Mn, Tc and Re, while Ni, Pd and Pt are similar to Cu, Ag and Au. In chemical properties, therefore, the members of group VIII are *transitional* between the adjoining elements of the manganese subgroup, on the one hand, and the copper subgroup, on the other.

XIV-3. A Concluding Survey of the Elements. Comparing the properties of the different chemical elements, we find that most of these properties are *periodic* functions of the positive charge on the nucleus, and that only a few of them depend on it *linearly*. In particular, as can be seen from Fig. 208, the characteristic X-ray frequencies of the elements vary linearly (they correspond to the lines *K*, *L* and *M*, depending on their hardness). A good example of a clearcut periodic regularity is that of the *atomic volumes*, i. e., the volumes occupied by one gram-atom of each element in the solid state.

The linearity of variation of the vibration frequencies is due to the fact that they depend directly on the magnitude of the positive charge on the nucleus. On the other hand, the properties that vary periodically are related to the outer parts of the atom, viz., the spatial arrangement of the electrons surrounding the nucleus. But the periodic

law states essentially that with increasing positive charge on the nucleus (and, consequently, with increasing number of outer electrons), *the atomic structures build up consecutively with a periodic recurrence of similar electronic systems.* Therefore, all the properties due to the electron arrangement in the atoms must also vary periodically, this being the case, in particular, with the atomic volumes.

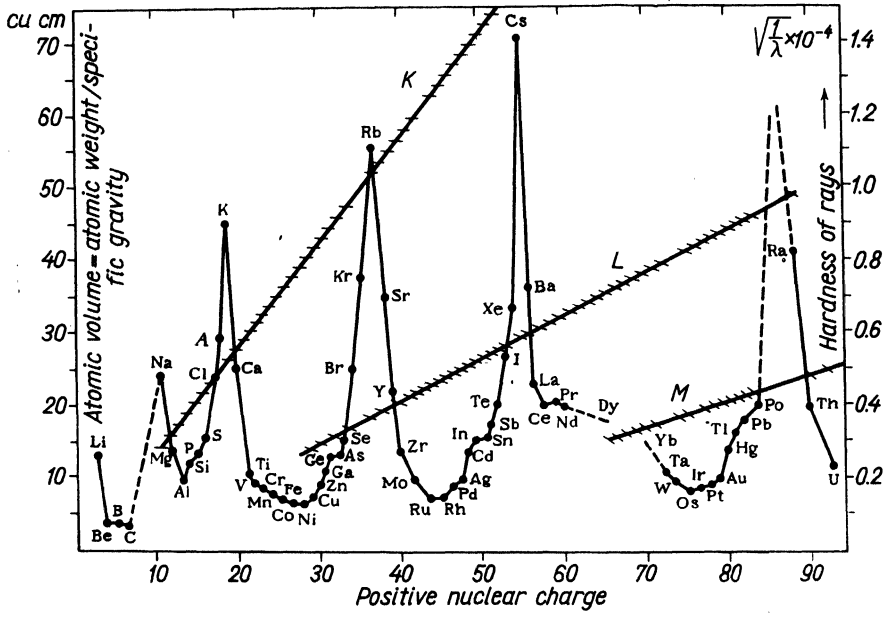


Fig. 208. Periodic and non-periodic properties of the elements

One of the most important practical characteristics of the elements is their *abundance in nature.* The figures listed below are the atomic percentages for the most abundant elements in the earth's crust:

1. **O** 52.32	4. **Al** 5.53	7. **Ca** 1.48	10. **Ti** 0.22	13. **Mn** 0.03
2. **H** 16.95	5. **Na** 1.95	8. **Mg** 1.39	11. **C** 0.14	14. **N** 0.03
3. **Si** 16.67	6. **Fe** 1.50	9. **K** 1.08	12. **P** 0.04	15. **S** 0.03

It is evident from these data, that of the total number of atoms composing the earth's crust (all three layers—the atmospheric, the aqueous and the upper part of the solid layer), 99.4% comprise only 15 elements, the content of all the rest taken together being only 0.6%. Fig. 209 shows that the relative abundance of the elements is definitely a *periodic* function of the positive nuclear charge, although this function is very complicated.

Only H, N, O, F, Cl and the inert gases, i. e., only the elements in the upper and right-hand parts of the periodic table, are gaseous under ordinary conditions. Br and Hg are liquid under ordinary conditions. Cs (m. p. +28° C) and Ga (m. p. +30° C) are also frequently encountered in the liquid state, owing to supercooling which sets in readily in these elements. The other elements are solid under ordinary conditions.

In the free state, most of the elements have a metallic appearance with colours that vary from silvery-white to dark grey, this being

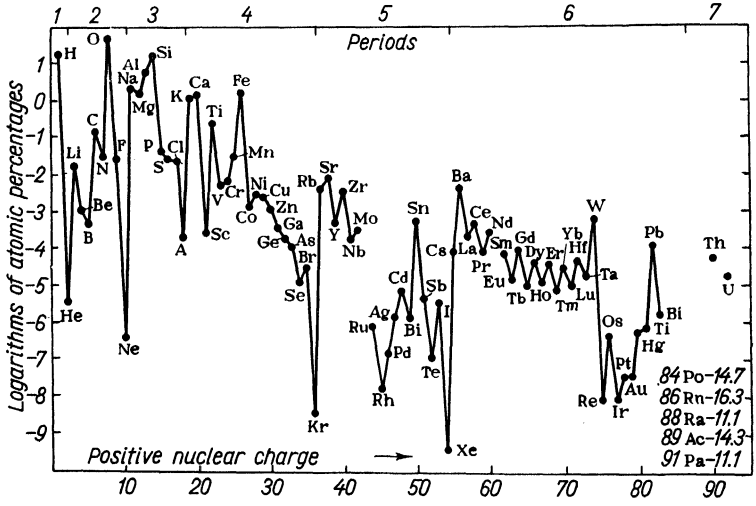


Fig. 209. Relative abundance of the elements in the earth's crust

true not only of typical metals, but also of a number of non-metals such as C (graphite), Si, As, Se, Te. Only a few elements have other colours while preserving their general metallic appearance. Thus, Cu is red, Au is yellow, Bi is reddish, Pb is bluish and I is dark violet. Of the elements that are not metallic in appearance, S is yellow, F, a very pale greenish-yellow, Cl, yellowish-green and Br, reddish-brown. Only white phosphorus and carbon (diamond) of the solid elements, as well as H, N, O and the inert gases, are colourless. It is evident from the above list, that all the elements of periods 4 to 7 have a metallic appearance, except bromine and the inert gases. The elements that do not have a metallic appearance are concentrated in the upper right-hand part of the elaborated form of the Periodic Table (p. 171).

Such physical properties as atomic radius, melting point, specific gravity and hardness, depend on the type of crystal lattice and, strictly

speaking, are comparable only for elements with identical lattice types. In general, all these properties exhibit a more or less clearcut *periodic* dependence on the positive nuclear charge.

In general chemical nature, most of the elements are metals. They are all situated in the left-hand and lower parts of the table; Be, Al, Ge, Sb and Po may be regarded as borderline elements. The upper right-hand part of the table is occupied by elements of non-metallic nature, the borderline elements being B, Si, As, Te and At. Thus, the approximate boundary between metals and non-metals can be found by drawing a line between these two series of elements.

From left to right and upwards in the short periods (except the first), the metallic nature of the elements distinctly decreases and their non-metallic nature increases. A more complicated regularity is observed in the long periods, where the same general rule holds for analogue series, 1-3 and 14-17, while series 4-13 display no clearly consistent change in properties from left to right, and usually an increase rather than a decrease in metallic nature of the elements on passing upwards through the Table. Comparison of analogue series within the same group (1 and 11, 2 and 12, etc.) reveals that the metallic properties of the elements in the left-hand series are always more clearly defined than those of the right-hand series. Hydrogen stands somewhat apart in the series of its analogues, its non-metallic properties being less prominent than those of iodine (owing to its small nuclear charge). In general, therefore, the most active metals are the elements in the lower left-hand corner (Fr, Cs, Ra), and the most active non-metals are the elements in the upper right-hand corner (F, O, Cl) of the periodic table.

As a rule, the more elements differ from one another in their chemical nature, the more vigorously they react with one another. Therefore, for example, the heats of formation of compounds between members of the same period are usually the greater, the further away they are from one another. As an example illustrating this rule, the heats of formation of several compounds between elements of periods 3 and 2 are given below. Since the formulas of these compounds differ, the data for them cannot be compared directly, and must first be reduced to a comparable form. For this purpose, the heat of formation of one gram-molecule is divided by the number of valency bonds in the compound to refer its value to one gram-equivalent (heat of formation per bond). The resulting figures can be compared with one another. The method of calculation is clear from the data in the table on page 420.

The *valencies* of the chemical elements are compared in Fig. 210, the more characteristic valencies being denoted by larger dots. Although, generally speaking, the valency depends on the nature of both of the interacting atoms (and also on the external conditions), it is

Compound	NaCl	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_5	Li_2O	BeO	B_2O_3	CO_2	N_2O_5
Molecular heat of formation (kcal)	98.3	153.3	166.8	150.1	106.5	142.3	147.0	345.0	94.4	13.1
Number of valency bonds	1	2	3	4	5	2	2	6	4	10
Heat of formation per bond (kcal)	98.3	76.7	55.6	37.5	21.3	71.2	73.5	57.5	23.6	1.3

practically constant for many elements. Others (e. g., Mn, Ru), however, exhibit a very large range of valencies.

Among the elements of the short periods (1-3), variable valency is characteristic only of N, P, S and Cl. It is much more common among the members of the long periods (4-7), the tendency to form compounds

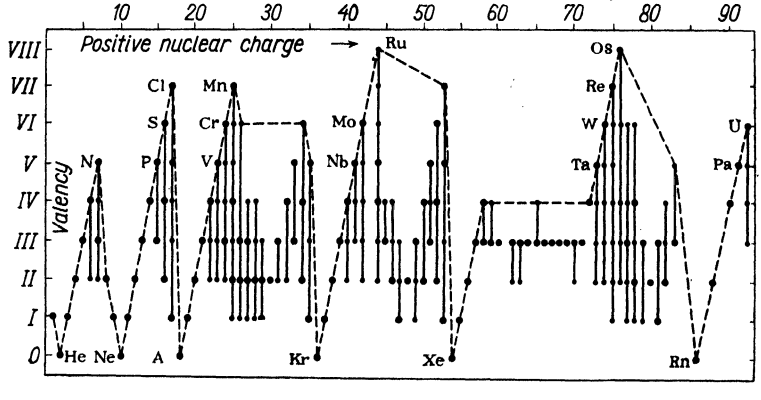


Fig. 210. Valencies of the chemical elements

of *lower* valencies increasing *upwards* at the beginning of the periods (series 4 through 10) and *downwards* at their ends (series 13 through 16). Elements of variable valency usually display their highest valencies in oxygen and fluorine compounds, and their lowest, in compounds with the other halogens (and especially in complex cyanides).

XV. THE ATOMIC NUCLEUS

As has already been noted (III-2), the discovery of radioactivity was the main impulse to the development of the theory of atomic structure. However, in contrast to ordinary chemical processes, the phenomenon of radioactivity could not be explained from atomic models.

The fact that atomic models cannot be applied with equal success in both cases is due to the radical difference between radioactive decay and ordinary chemical reactions. While the latter are connected with changes in the outer shells of the atoms, radioactive decay is a process which takes place *inside the atomic nucleus.*

It is obvious that the elaboration of a general theory of the structure of atomic nuclei and their characteristic reactions would mean a major further deepening of the science of substances and their transformations. No such theory has been worked out so far but this new field of chemistry—*the chemistry of atomic nuclei* is now in a stage of rapid development.

XV-1. Natural Radioactivity. A few years after the discovery of radioactivity (1896), it was found to be peculiar not only to uranium, but to a number of other heavy elements as well (Th, Ra, Po, etc.). Subsequent study of the problem during the first quarter of this century showed that radioactive decay is a very complex process which occurs in a number of successive stages.

The methods employed in the study of radioactive phenomena are based chiefly on certain effects caused by alpha (α), beta (β), and gamma (γ) rays (III-2). First and foremost among these effects is that of the phosphorescence of many solids, in particular, crystalline ZnS. If, for example, a piece of cardboard is coated with ZnS, and a radioactive compound is placed close to it, luminescence of this screen can be clearly observed in a darkened room. With the aid of a lens or microscope of small magnification, it can easily be seen that the luminescence is composed essentially of separate flashes (*scintillations*) which are due to collisions between α-particles and the substance of the screen. These scintillations are particularly conveniently observed in a spinthariscope, the design of which is shown in Fig. 211 (*A*—radioactive substance, *B*—screen, *C*—lens). Scintillations are in themselves the most vivid proof of the reality of atoms (III-1).

1) Luminescence induced by radioactive substances is used in the preparation of permanently luminous compositions. These compositions are usually based on powdered crystalline ZnS and a very small quantity (about 0.01 g

per kilogram of the composition) of a radioactive element. Other admixtures (Bi, Cu, etc.), are almost always added to increase the intensity of luminescence or change its colour. Such compositions then serve to prepare paints used for coating the objects to be made visible in the dark (parts of measuring instruments, various signalling devices, etc.). It should be noted that the luminous

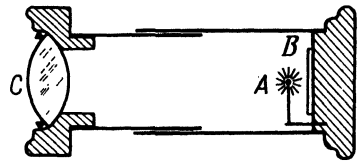


Fig. 211. A spinthariscope

composition gradually decays under the action of the radioactive radiation, and its luminescence becomes less intense. The complete useful service life of such a composition usually does not exceed 10 years.

The action of radioactive radiation on a photographic plate forms the basis of another method. This method depends to a great extent on the use of relatively thick light-sensitive coatings, enabling the whole track of the charged particles to be photographed.

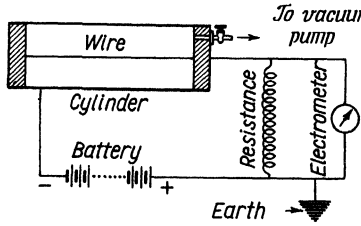


Fig. 212. Diagram of an ionisation counter

The cloud chamber method (III-2) is very widely employed in the study of radioactive phenomena. Its refinement by applying a magnetic field to the chamber made it possible not only to register the tracks of charged particles, but also to ascertain their nature.

Finally, the most commonly used method is based on the direct recording of the ionisation of the air under the action of radioactive radiation. This latter method is extremely sensitive, since the presence of even very weak ionisation can be detected with the aid of electrical instruments.

2) The most widely used electrical instrument, which has been employed since 1908 for the study of radioactive processes, is the *ionisation counter*. A diagram of the latter is shown in Fig. 212. The counter consists of a metal cylinder containing rarefied air (or some other gas), with a fine metal wire stretched along its axis. A high voltage, almost high enough to cause an electrical discharge, is applied between the wire and the cylinder walls. When radioactive radiation enters the cylinder (through ports in the walls closed with pieces of thin metal foil), it ionises the air and causes a discharge which is immediately registered by suitable electrical instruments. The ionisation counter is so sensitive that it responds to each separate α- or β-particle. By somewhat complicating the design of the apparatus, automatic recording may be incorporated.

The ionising action of α-rays is much stronger than that of β-rays, and the action of the latter is much stronger than that of γ-rays (in the approximate ratio of 100,000 : 1000 : 1). On the other hand, γ-rays have the strongest ability to penetrate different substances. Thus, α-rays can be stopped completely by a sheet of metallic aluminium only 0.1 mm thick, while for the complete absorption of β-rays, a sheet of Al 5 mm thick is necessary, but γ-rays are hardly arrested at all by such an aluminium sheet. By making use of this, and also of the different behaviour of α-, β- and γ-rays in an electric or magnetic field (III-2), each kind of radioactive radiation can be isolated and studied separately.

3) The effect of radioactive radiation on surrounding matter is very sharp. For example, it decomposes water according to the equation $H_2O \rightleftarrows H + OH$, subsequently partially forming H_2, H_2O_2 and O_2. In all chemical reactions, α-rays have the greatest effect, β-rays have a smaller effect and γ-rays have the smallest effect. Radioactive substances should be handled with care, strictly observing the necessary precautionary measures.

Alpha rays are streams of α-particles, i.e., helium nuclei (He^{2+}) with an atomic weight of 4 and a charge of 2+. Simultaneously with the ejection of the particle, the original atom also loses two electrons from its outer shells. It has been calculated on the basis of the observation of scintillations that one gram of pure radium ejects 37 thousand million α-particles every second. Although this number is tremendous, it corresponds to the disintegration of only one atom in every 72 thousand million per second.

An activity of 37 thousand million disintegrations per second is usually accepted as the unit of radioactivity and is called the *curie* (c). Recently, a more convenient unit called the *rutherford* (rd), equal to 1 million disintegrations per second, was suggested.

By studying the deflection of α-particles in electric and magnetic fields, it was established that these particles are ejected by the nuclei of radioactive atoms with an initial velocity of up to 20 thousand kilometres per second. It is interesting to note for comparison that the initial velocity of a shell fired from a modern gun is usually no higher than 2 km/sec.

The kinetic energy of an α-particle is tens of millions of times greater than the energy of a gas molecule under ordinary conditions. If an α-particle encountered no obstacle, it could fly around the earth in 2 seconds. Actually, however, it collides in its path with a great number of molecules of the component gases of the air. As a result of these collisions, tens of thousands of molecules are ionised, and the α-particle rapidly loses velocity. As can be seen from Fig. 213, it produces the greatest ionisation of the air at the end of its path.

Experiment shows that the normal (at 15° C and 760 mm Hg) *range* of α-particles in air is several centimetres. Other conditions

being equal, this range is approximately proportional to the third power of their initial velocity.

It is a very important fact that the range of most of the α-particles emitted by a given radioactive substance is constant. This enables its use as a characteristic of radioactive elements. For example, radium can be characterised by the range of the α-particles it emits,

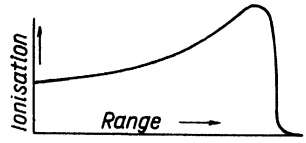


Fig. 213. Ionisation of air by an α-particle

which is equal to 3.31 cm, the same can be said of thorium, which emits α-particles with a range of 2.59 cm, etc. In dense media, the range of α-particles usually does not exceed 0.1 mm.

At the end of its flight, the helium nucleus emitted as an α-particle takes on two electrons and changes into a neutral atom. Each gram of radium (together with its decay products) yields about 0.16 cm^3 of helium annually. For this reason, radioactive minerals usually contain helium, sometimes in considerable quantities (up to several litres per kilogram).

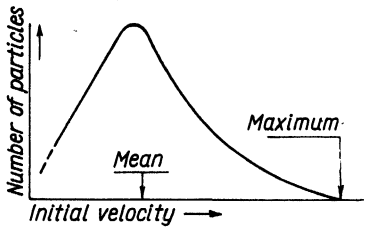


Fig. 214. Distribution of velocities of β-particles

Beta rays are streams of electrons ejected by the nuclei of radioactive atoms. In contrast to α-rays, even β-rays originating from the same element have *different* initial velocities (Fig. 214), varying from relatively low ones to a certain maximum which may be very high (almost 300,000 km/sec). The range of β-particles is up to 100 cm.

Like β-rays, the γ-radiation of a radioactive atom is also non-uniform. Gamma-rays are similar in all respects to X-rays (III-3), but usually have even shorter wavelengths, which are often measured in X-units. An X-unit equals 10^{-11} cm, i. e., one thousandth of an angstrom.

The principal unit for measuring the *energy* of radioactive radiation is the *electron-volt* (eV), i. e., the energy acquired by an electron on passing through an accelerating field with a potential difference of 1 volt. The electron-volt corresponds to 1.6×10^{-12} erg for one particle or photon and 23.06 kcal for the number of them in one gram-molecule (6.02×10^{23}). Much more frequently one has to employ a unit one million times larger—the mega-electron-volt (MeV).

4) The relation between the wavelength of γ-rays (λ in X-units) and the radiation energy (E in MeV) is given by the equation $\lambda E = 12.4$. This relation is valid not only for γ-rays but for the entire electromagnetic spectrum (Fig. 30).

Shortly after the discovery of radium, it was noticed that the substances around it become radioactive too. The origin of this "induced" radioactivity became clear only when it was established that radium decays in accordance with the equation Ra = He + Rn, and that one of these inert gases—radon—undergoes further decay. The products of the latter settle on substances exposed to the radon, and cause the induced radioactivity.

As has been noted earlier (III-2), almost simultaneously with radium, another radioactive element—polonium—was discovered, whose α-particles have a range of 3.84 cm, and which, chemically, is an analogue of tellurium. A detailed study of induced radioactivity showed that Po is contained in the decay products of radon. On the other hand, it was known that radium is always contained in uranium ores, and that the latter always contain at least one non-radioactive element—lead. This naturally suggested that these elements — U, Ra, Rn, Po, Pb—are somehow related to one another, in spite of the difference in their atomic weights and chemical properties. Further work on the problem confirmed this assumption: it was found that they are all, in fact, members of the same *radioactive series*, which begins with uranium and ends with lead. Similar series are known for actinium and thorium. All three series are shown in the table on pp. 428-429.

As an example, let us consider the uranium series in somewhat greater detail. Uranium ejects an α-particle and is thereby transformed into UX_1. Since an α-particle has a charge of 2+ and a mass of 4, the atomic weight of UX_1 is lower than uranium by four units, and its positive nuclear charge is equal to 90. This explains why UX_1 is similar in chemical properties to thorium rather than uranium.

During the further decay of UX_1 a β-particle separates from the nucleus. Since the mass of a β-particle is very small (1/1820 in atomic mass units) and its charge is negative and equal to one, the atomic weight remains practically the same, while the nuclear charge becomes more positive by one unit. Therefore, the resulting UX_2 is similar in chemical properties to protactinium rather than thorium. Similar decay of UX_2 results in UII, which is similar in chemical properties to ordinary uranium (sometimes called UI), but differs from the latter in atomic weight.

Examination of this small part of the uranium series already shows that radioactive transformation is attended by the splitting off of either an α- or a β-particle from the nucleus of the decaying atom (sometimes with simultaneous emission of a γ-ray). The ejection of an α-particle involves the loss of two electrons from the outermost

shell, while the ejection of a β-particle is attended by the addition of one electron to the outermost shell. In the first case, the decay product shifts *two places to the left* in the periodic table, while in the second, it moves *one place to the right* (the *Displacement Law*). The loss of an α-particle (α-transformation) decreases the atomic weight by 4 units, whereas β-transformation does not affect the atomic weight appreciably.

The further decay of UII takes place with the successive ejection of five α-particles from the nucleus; ionium, radium, radon, RaA and RaB are formed as intermediate products. The last-named product loses a β-particle and is transformed into RaC for which two different ways of further decay are possible. The major part of it loses first a β- and then an α-particle (transformation through RaC'), and a minor portion first loses an α- and then a β-particle (transformation through RaC''). The result in both cases is RaD, which successively loses two β-particles, being transformed into polonium (through RaE). Finally, with the splitting off of an α-particle, Po is transformed into lead, which completes the uranium series. The process of decay in the actinium and thorium series takes place in an analogous manner, both of these series being very similar to the uranium series in their general nature.

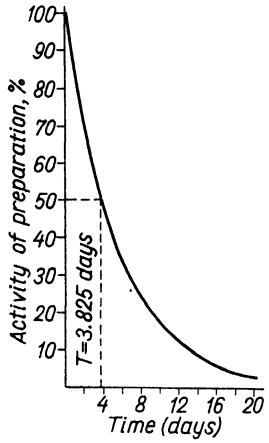


Fig. 215. Decrease in activity of radon

Owing to the difference in chemical properties of the members of one and the same radioactive series, they can be separated from each other. For example, only RaE is deposited on a strip of metallic copper immersed in a solution containing a mixture of RaD and RaE, whereas RaD remains in solution. Similarly, a current of air passed over a radium preparation will carry away gaseous radon, thus separating it from the radium.

A study of the radioactivity of air containing radon has shown that as the total amount of radon decreases (owing to decay), its further decay becomes progressively slower, as can be seen from Fig. 215. Subsequently, it was found that other radioactive substances decay in accordance with very similar curves (only with a different scale on the abscissa). Consequently, the same law lies at the basis of all these processes. This *law of radioactive decay* states, essentially, that *the number of atoms of a radioactive element decaying in unit time is proportional to the total number of atoms present.*

The curve in Fig. 215 shows that the decay of radon and other radioactive substances can end completely only after an infinitely

long period. Therefore, the *half-life* (T), i. e., the time required for *half* the original number of atoms to decay, is generally used to characterise the stability of a radioactive element. The half-life of radon is about 4 days (more exactly 3.825 days). As can be seen from the data given in the table below, the value of T for the other radioactive elements varies over an extremely wide range—from thousands of millions of years to fractions of a second.

An important conclusion concerning the quantitative relation between the different members of a radioactive series follows from the law of radioactive decay. Suppose we have a certain amount (for example, 1 g) of perfectly pure radium. When it decays, radon is formed, which in turn undergoes further decay. Since the rate of decay of both radium and radon depends on the quantities present, at first, while there is little radon, much more of it will form (from radium) than decay. However, as radon accumulates, its decay will speed up and, finally, a state of equilibrium will set in, when just as many atoms of radon will be decaying as are being formed in the same time. But the number of radon atoms being formed is equal to the number of radium atoms decaying. Hence, at equilibrium, an *equal* number of atoms of Ra and Rn decay in unit time.

Obviously, similar reasoning can be applied to any other pair of consecutive members of this radioactive series, e. g., RaA and Rn, Ra and Io, etc. Therefore, there must finally be established a *radioactive equilibrium* between all of them, characterised by the fact that *the number of atoms decaying per unit time is the same for all the members of the series* (except the last).

But the average life time of radioactive elements may vary widely. The longer the half-life of an element, the more of its atoms must be present to ensure decay of a given number of them per unit time. Therefore, the quantities of the individual members of the series in equilibrium with one another will be different, and will be the greater, the longer their respective half-lives. Denoting the number of atoms in equilibrium respectively by A_1, A_2, etc., we have

$$\frac{A_1}{T_1} = \frac{A_2}{T_2} = \frac{A_3}{T_3} = \dots$$

throughout the given radioactive series.

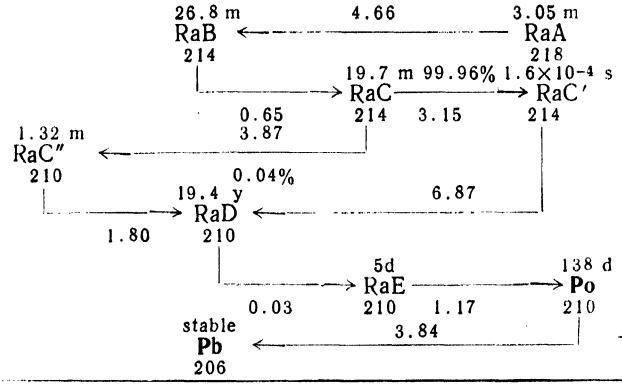
This relation permits certain important calculations to be made. Suppose, for example, it is required to determine the half-life of uranium. Taking radium as the second member of the series, we obtain:

$$\frac{A_U}{T_U} = \frac{A_{Ra}}{T_{Ra}}, \quad \text{whence} \quad T_U = \frac{A_U}{A_{Ra}} \cdot T_{Ra}$$

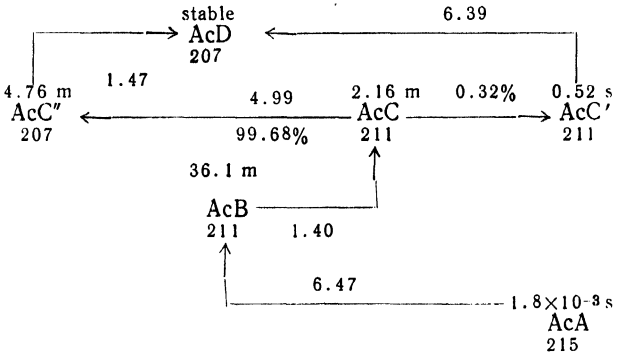
Chemical analyses of uranium ores show that the number of atoms of uranium in them is always (in accordance with radioactive equilib-

Groups of periodic table	III	IV	V	VI
Positive charge of nucleus	81	82	83	84

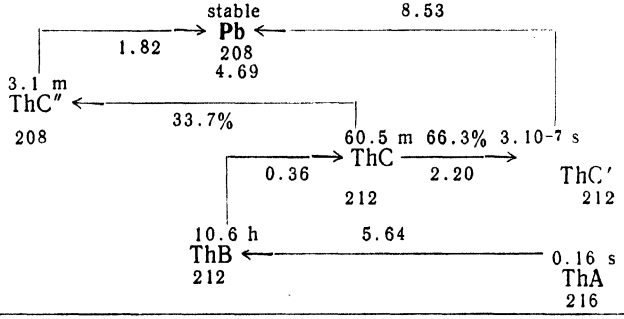
Uranium series



Actinium series



Thorium series

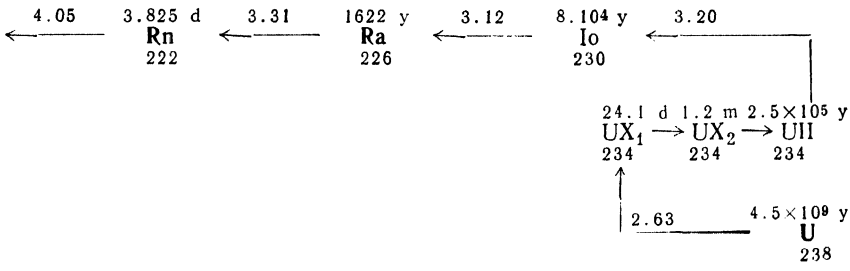


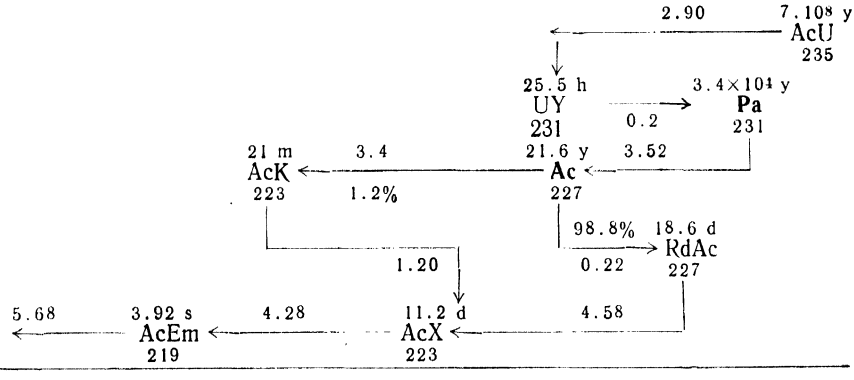
Path in cm ← α-transformation

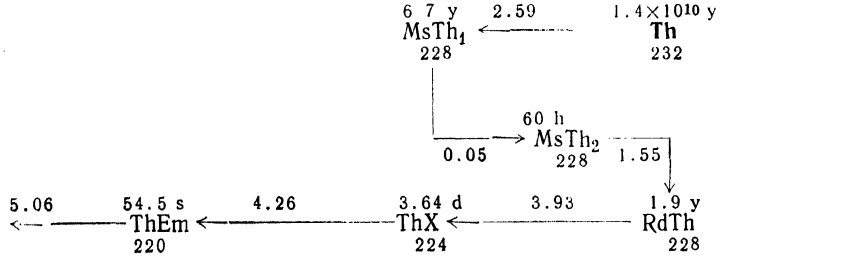
β-transformation → Maximum energy

ACTIVE SERIES

VII	0	I	II	III	Actinides		
85	86	87	88	89	90	91	92







HALF-LIFE:
y—years
d—days
h—hours
m—minutes
s—seconds

rium) 2.8×10^6 greater than of radium. Hence, $T_U = 2.8 \times 10^6 \times \times T_{Ra} = 2.8 \times 10^6 \times 1622 = 4.5 \times 10^9$ years. Thus, this number, which it is clearly impossible to establish by directly observing the decay in time, is easily determined by chemical analysis and simple calculation.

As can be seen from the above, radioactivity is typical of relatively few elements, viz., those having the greatest positive nuclear charges. One would naturally wonder whether any of the other, lighter elements possess the same property. Experiment supplies a positive answer to this question: radioactivity (though very weak) has been detected in samarium, rhenium, lutecium, rubidium and potassium. The first of these elements emits α-rays (and is transformed into Nd), the others emit β-rays (and are transformed into Os, Hf, Sr and Ca, respectively). There are also indications that lanthanum and cesium are radioactive.

The causes directly responsible for radioactive decay have not been ascertained so far. But the nature of the decay and the resulting products have been studied in great detail. It was found that of all the members of the natural radioactive series considered above, only 8 occupy definite places in the periodic table and that there are no vacancies in the table for the rest. The difficulties that arose in this connection were overcome only after the conception of *isotopes* had been established.

XV-2. Isotopes. Although many products of radioactive decay became known shortly after the discovery of radioactivity, the problem of which groups of the periodic table they belonged to remained at first completely unsolved. This was chiefly due to the fact that the chemical properties of the intermediate members of the radioactive series were not understood at the time.

Only about 1910 did it become clear that the chemical properties of, say, thorium (Th), ionium (Io) and radiothorium (RdTh), or radium (Ra) and mesothorium ($MsTh_1$), etc., were identical. At the same time it was established that the end products of the decay of all three series were practically identical in chemical properties with each other and with ordinary lead. After the elaboration of the displacement law in 1911-13, it was experimentally tested and confirmed by determining the atomic weights of lead samples of different origins. It was found that Pb from the purest (not containing Th) samples of pitchblende has an atomic weight of 206.05, while Pb from the purest thorite (almost free of U impurities) has an atomic weight of 207.9 as would be expected from the displacement law ($U^{238} - 8He^4 = = Pb^{206}$ and $Th^{232} - 6He^4 = Pb^{208}$). Ordinary lead with an atomic weight of 207.19 thus proved to be a mixture of leads with different atomic weights, but with the same chemical properties.

Owing to the fact that in 1912 the periodic law had acquired a new foundation—the positive nuclear charge, the difference in mass between the end products of U and Th decay could no longer serve as an obstacle to accommodating them in the *same* square of the periodic table. Uranium and thorium leads, *which have identical nuclear charges but different atomic weights*, were thus found to be *isotopes* ("occupying the same place").

The difficulties of accommodating the products of radioactive decay in the periodic table also fell away with the establishment of the

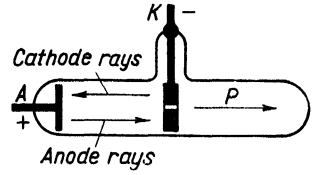


Fig. 216. Diagram of a discharge tube

conception of isotopes. Indeed, all the members of the series with a positive nuclear charge of, say, 90 (Io, UX_1, UY, RdAc, RdTh) should be put into the same square as Th, irrespective of their atomic weights, while all the members of the series with positive nuclear charge of 88 (AcX, $MsTh_1$, ThX) should be isotopes of Ra, etc. This arrangement became universally adopted by about 1915, but isotopy was then regarded as mysterious exception peculiar to only the radioactive elements, rather than a general rule.

This approach to the problem was due to the deep-routed idea that all the atoms of one and the same element were *absolutely* identical.

Although the possibility of a partial non-equivalence of atoms had been suggested by individual scientists (in particular, Butlerov), it seemed to their contemporaries to be based on nothing but imagination, and contradictory to all chemical experience.

The discovery of the isotopy of the non-radioactive elements followed a detailed study of the processes taking place during an electrical discharge. As far back as 1886, it was discovered that besides cathode rays (III-2), another type of emission arises in a discharge tube, travelling from the anode to the cathode. By using a pierced cathode (*K*, Fig. 216), a pencil of these rays (*P*, Fig. 216) was admitted into the space beyond the cathode, making it possible to investigate their nature. They were found to be streams of positively charged ions formed from the atoms or molecules of the gas in the tube by the action of the cathode rays. For this reason the anode rays have been called *positive* rays. Like cathode rays, they affect a photographic plate, and this property is taken advantage of for studying them.

Positive rays obtained under different conditions differ from one another in the velocity of the particles, their charge and mass. The *velocity* depends mainly on the distance from the cathode at which ionisation takes place, and can vary over a wide range for individual particles. The *charge* is determined by the number of electrons detached during ionisation. Since the first electron is detached from the neutral atom much more easily than the second, etc., there are always many more singly charged positive ions than doubly charged, etc. Finally, the *mass* of a positive ion is practically equal to the mass of the atom or molecule of the gas (or vapour) in the tube.

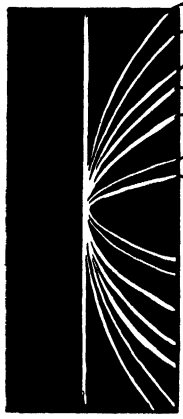


Fig. 217. Ion parabolas

Under the influence of electric and magnetic fields, the ions forming the positive rays are deflected from their rectilinear path. In constant fields, this deflection is the greater, the lower the velocity of the ion and the higher *its charge-to-mass ratio*. If the two fields are arranged in a definite way (perpendicular to the beam), all the ions, having different velocities but the same charge-to-mass ratio (e/m), jointly form a branch of a parabola on the photographic plate. By reversing the direction of both fields, the second branch of the same parabola can be photographed. The photographs obtained by the parabola method (Thomson, 1913) have the appearance shown in Fig. 217.

From the nature of the photographed parabolas and the known field intensities, the charge-to-mass ratio can be calculated for each type of ion formed in the discharge tube. In conjunction with previous knowledge of the nature of the gas under study, this enables determination of the mass of *each individual* ion, which cannot be done by ordinary chemical methods of investigation, as they give only *average* values.

Since gases and vapours of diverse compositions can be studied in a discharge tube, the field of application for the analysis of positive rays is very wide.

With the aid of this method, it was discovered that ordinary neon (at wt. 20.183) forms parabolas corresponding to masses of 20 and 22. This work was the first to give experimental indications of the isotopy of non-radioactive elements. However, in the years that followed, it remained the only study in this line and attracted no particular attention.

Further developments became possible only as a result of considerable improvement of the parabola method. By suitably altering the relative disposition of the electric and magnetic fields, an arrange-

ment was achieved whereby all the ions with the same charge-to-mass ratio and *regardless of their velocity* landed on the same spot on the photographic plate (Aston, 1919). Substitution of one small spot for the branch of a parabola sharply increased the sensitivity of the method. At the same time, the accuracy of determination of the masses of individual particles with the aid of the new instrument (the *mass-spectrograph*) was increased to 0.1%. The achievement of fundamental importance resulting from mass-spectrographic investigations was the establishment of the fact that by taking oxygen (O = 16) as the basis, the relative weights of individual atoms could be expressed as *whole* numbers, within the accuracy of the measurements. The fractional values of the chemical atomic weights which were usual for many elements were thus obtained only because of the presence of isotope *mixtures*. The single exception to this general rule was hydrogen, the atomic weight of which was found to be equal to 1.008, in agreement with ordinary methods.

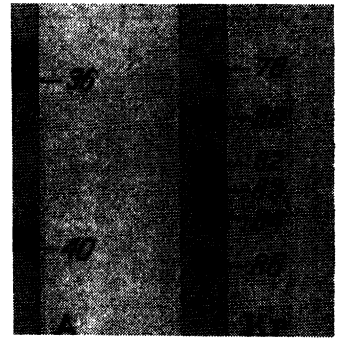


Fig. 218. Mass spectra of argon and krypton

In Fig. 218, the "mass spectra" of argon and krypton are shown as an example. As is evident from the illustration, ordinary argon proved to be a mixture of two isotopes with masses of 40 and 36. Knowing its practical atomic weight (39.947), it was possible to calculate approximately that it contained 98.5% of A^{40} and 1.5% of A^{36} atoms. The fact that the first of these isotopes makes a much darker spot on the photograph is due to the considerable preponderance of A^{40}.

The case of krypton is considerably more complicated, since this gas consists of 6 isotopes. The relative amounts of each of these in the mixture can be estimated by comparing the relative density of the corresponding spots. Thus, it can be seen in Fig. 218 that as regards their content in the mixture, the isotopes of Kr should be arranged in the following sequence of masses: 84, 86, 82, 83, 80, 78. By carefully studying these photographs, it was found possible to calculate accurately the isotopic composition of the elements. Part of the data obtained in this way are given in Fig. 219.

Investigations with the aid of the mass-spectrograph showed that in most cases, elements are "mixed", i. e., consist of mixtures of several isotopes. The greatest number of the latter so far (ten) has been discovered for tin (practical atomic weight 118.69), the lightest and the heaviest of them having masses of 112 and 124, respec-

tively. Thus, ordinary tin contains atoms differing in atomic weight by 12 units, i. e., by 10%. Among the other "mixed" elements, of special interest is neon, for which not only the existence of atoms with masses of 20 and 22 was confirmed, but another isotope, Ne^{21} (0.3% of the mixture), was found.

With the improvement of research technique, more and more new isotopes are being discovered for a number of the mixed elements. For example, a third isotope of argon, A^{38} (0.06%), has been found,

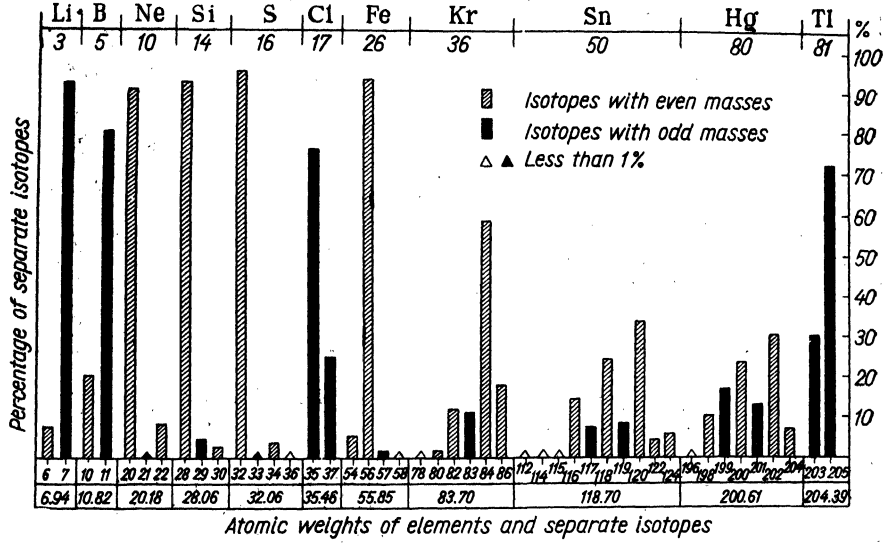


Fig. 219. Isotopic composition of some of the elements

and in the case of uranium, an isotope U^{234} (0.006%) has been detected in addition to the earlier known U^{238} (99.3%) and U^{235} (0.7%). At the same time, the number of "pure" elements (those consisting of atoms of equal masses) has diminished. Thus, in the case of helium, an isotope He^3 has been discovered, its relative abundance being only one ten-thousandth of one per cent.

Isotopes were also found for oxygen, nitrogen, carbon and hydrogen. The abundance ratios of the individual isotopes are set out below:

$O^{16} : O^{18} : O^{17}$	$N^{14} : N^{15}$	$C^{12} : C^{13}$	$H^1 : H^2$
2700 : 6 : 1	270 : 1	90 : 1	7000 : 1

The heavy isotope of hydrogen (H^2) has been given a separate name—*deuterium* (D). The name *protium* was proposed for the light isotope (H^1), but is used comparatively rarely.

When comparing the data on isotopy, a striking difference between the elements with odd and even positive nuclear charges becomes evident. The cause of this difference is not clear as yet, but its very existence compels us to consider the "odd" and "even" elements separately.

Many of the "odd" elements are "pure" (F, Na, Al, P, etc.), while most of the others consist of *only two* isotopes. As a rule, the latter have *odd* atomic weights (the exceptions being H^2, Li^6, B^{10} and N^{14}). All the "even" elements are "mixed" (with the exception of Be and Th). As a rule, each of them has *more than two* (five on the average) isotopes. Among the latter, isotopes with *even* atomic weights predominate. A good illustration to all this is Fig. 219.

Owing to the fact that their nuclear charges and the structure of their electronic shells are the same, the *chemical* properties of isotopes are so similar that in most cases they can be regarded as practically identical. Therefore, the separation of isotopes is usually based on the difference between those *physical* properties that depend directly on the *mass* of the atoms (rate of diffusion, etc.). The most complete separation of this kind is achieved in the mass-spectrograph, but it separates only a negligible amount of the substance (of the order of one ten-millionth of a gram per hour).

The isotopes H^1 and H^2 possess important specific features, the difference between the masses of their nuclei being relatively so large that it clearly affects their chemical properties as well.

Experiment shows that electric current decomposes mainly molecules of ^1H_2O ($M = 18$) rather than those of ^2H_2O ($M = 20$) into oxygen and hydrogen. By sufficiently prolonged electrolysis of ordinary water and subsequent distillation of the residue, "heavy water" can be obtained in a practically pure state.

Heavy water, D_2O, differs appreciably from ordinary water in properties. It has a freezing point of $+3.8°$ C, a boiling point of 101.4° C and a specific gravity of 1.1059 at 20° C. Salts are less soluble in it than in ordinary H_2O. Heavy water does not sustain the life of animal and plant organisms. Other derivatives of deuterium may be obtained from it.

1) The simplest reaction of heavy water is ion exchange: $H_2O + D_2O \rightleftarrows 2HDO$. The equilibrium of this reaction is displaced to the right ($K = 3.3$).

In the molecule of HDO, the D^+ ion is bound with the oxygen more firmly than the H^+ ion, and this causes deuterium to accumulate in ordinary water when it is electrolysed. The process consumes a great deal of power: the production of 1 kg of D_2O requires more than 60,000 kWh, i. e., three times more than is needed to produce a ton of aluminium.

2) Reactions between heavy water and acids or bases are accompanied by partial replacement of hydrogen by deuterium, equilibrium being established more or less rapidly. The same is true of ammonium salts and ammonia (including complex-combined ammonia). When organic compounds come in contact with heavy water, only the hydrogen atoms bonded directly to the oxygen or

nitrogen atoms contained in the structure of the molecule are, as a rule, substituted by deuterium (before equilibrium). On the other hand, H atoms bonded to carbon atoms do not usually take part in the exchange reaction.

3) Alongside heavy hydrogen, isotopes of other elements can also be used as "tagged atoms" for solving various chemical problems. In particular, a number of interesting investigations have been carried out with the aid of O^{18}. For example, the reaction for preparing esters (X-2) can, generally speaking, take place with the formation of water according to two schemes: a) combination of the hydrogen atom of the acid with the hydroxyl radical of the alcohol, b) combination of the hydroxyl radical of the acid with the hydrogen atom of the alcohol. If the first is correct, then on saponification of the ester, the oxygen of the water should report in the alcohol formed, while if the second is correct, the oxygen should report in the acid. By carrying out a saponification reaction with water enriched with molecules of H_2O^{18}, it was established that the second equation is the correct one.

The fact that most elements actually consist of *mixtures* of isotopes compels us to regard the ordinary atomic weights of most elements as certain mean values which in themselves do not correspond to any definite species of atoms. Experiment shows, however, that the ratio of individual isotopes contained in any given element is practically always the same (disregarding isolated exceptions due to radioactive decay). That is why ordinary atomic weights are also constant, and fully retain their value for practical calculations in chemistry.

With the discovery of isotopy, a more precise definition of the concept "chemical element" (I-3) was required. For example, the six isotopes of krypton could be regarded either as six separate elements or as varieties of the same element. Since it is not the weight but the *charge on the nucleus* that determines the chemical properties of atoms, the second interpretation is the more reasonable. If elementary ions are included in the concept "atom", a *chemical element* may be defined as a *species of atoms with a definite positive nuclear charge.*

Since isotopy is widespread among the chemical elements, it is natural to expect the existence of atoms of *different nuclear charge, but identical mass.* Such *isobars* ("having the same weight") are actually known. Examples are A^{40}, K^{40}, and Ca^{40}, Cr^{54} and Fe^{54}, Zn^{70} and Ge^{70}. In some cases, two elements have two, three and even four pairs of isobars. For example, atoms with masses of 124, 126, 128 and 130 are known for both Te and Xe. The existence of isobars is a vivid proof that the mass of the atom does not in itself determine its chemical properties.

XV-3. The Composition of Atomic Nuclei. Each atomic nucleus has two fundamental characteristics—charge and mass. Since the structural units of the simplest atom—the atom of hydrogen—are a proton and an electron, the most natural assumption was that the atomic nuclei of the heavier elements were also made up of similar particles. From this standpoint, the mass of any given nucleus can be

due only to the protons it contains, the mass of each proton being approximately one atomic mass unit (while the mass of an electron is only 0.00055 of this unit). It followed that the number of protons contained in the atomic nucleus of a given element must be equal to its atomic weight (A).

Such accumulation of protons should impart to the nucleus a positive charge (Z), numerically equal to its atomic weight. Actually, however, the positive charges of atomic nuclei are much smaller. Therefore, part of the protons must be neutralised by electrons contained in the nucleus. The number of nuclear electrons (E) was determined from the difference between the atomic weight and the positive nuclear charge, i. e., $E = A - Z$. This *proton-electron* interpretation of the composition of atomic nuclei persisted in science until 1932, when an essentially different approach to this problem became possible, owing to the discovery of new elementary particles.

In 1930 it was discovered that when beryllium was bombarded with α-particles, a kind of radiation appeared which easily traversed a layer of lead several centimetres thick. At first it was thought to consist of very hard γ-rays. However, it was subsequently proved (Chadwick, 1932) that, actually this "beryllium radiation" consisted of a stream of *particles with a mass approximately equal to unity and a charge equal to zero*. These particles were called *neutrons*.

Having no electric charge, a neutron is not deflected from its rectilinear path by the nuclei of any atoms it encounters (provided it does not collide with them directly), and passes freely through their electronic shells. This explains the insignificant retardation of neutrons by different substances.

As to the nature of the neutron, it was originally thought to be the product of intimate union of a proton and an electron, i. e., a complex particle made up of two simpler particles. However, it soon became clear that another interpretation was possible.

During the operation of cloud chambers, it was noticed that occasionally, tracks appeared even when no radiation was deliberately admitted from without. These spontaneous tracks are engendered, as a rule, in the material of the chamber and are directed downward. By automatic photographing, more than 500 such tracks were recorded (Blackett and Occhialini, 1933).

These tracks arise as a result of *cosmic rays* which are constantly reaching the earth from interstellar space. Studies of these rays indicated that with increasing altitude above sea level, their intensity varies in accordance with the curve shown in Fig. 220.

Nothing definite is as yet known concerning the origin of cosmic rays. They are non-homogeneous in composition and possess enormous stores of energy, owing to which different substances have very little retarding effect on them. Thus, it was proved by direct experiment

that a layer of water one kilometre thick still does not stop them completely.

The spontaneous tracks sometimes observed in cloud chambers are produced by cosmic rays. Blackett and Occhialini found that when such a chamber was subjected to the action of a magnetic field, "forks" appeared in some of the photographs consisting of two tracks of the same nature and length, but deflected in opposite directions (Fig. 221). Since one of them belonged to an electron, the other must have corresponded to a *particle possessing the same mass as an electron, but an opposite charge.* This conclusively confirmed the assumption made somewhat earlier (Anderson, 1932) of the existence of *positrons.*

The life of a positron (in air) is of the order of millionths of a

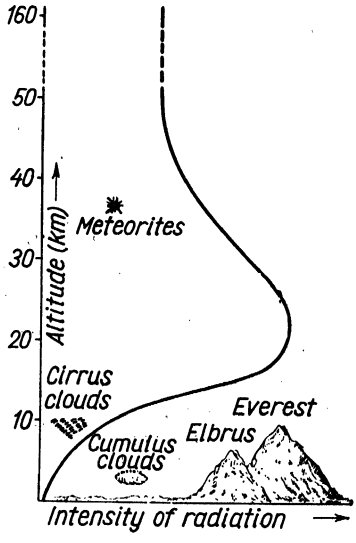


Fig. 220. Intensity of cosmic rays vs. altitude

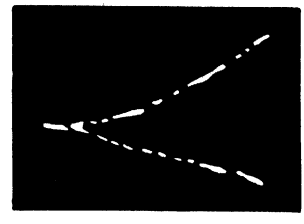


Fig. 221. Tracks of an electron-positron pair

second. It is long enough to form a track in a cloud chamber, but short enough to explain why the positron had not been discovered by other methods. Since combination of a positron with a neutron should produce a proton, the latter could be regarded as a complex particle consisting of two simpler particles.

1) *Primary* cosmic rays are composed mainly of protons (and partly of nuclei of helium and heavier atoms). On reaching the earth's atmosphere, they begin to interact at a height of about 50 km with the atomic nuclei they encounter, and this leads to the formation mainly of *mesons* (mesotrons). The latter are "medium-weight" particles with masses of 0.55 (k), 0.53 (τ), 0.15 (π) or 0.11 (μ) in atomic mass units, and a negative or positive charge. These particles are very unstable and decay rapidly, eventually forming electrons or positrons.

In the atmospheric layer between 20 and 50 km, almost all the primary cosmic rays use up their energy completely, transferring it to the *secondary* cosmic radiation they induce. The latter consists mainly of mesons, electrons, positrons and γ-rays. As can be seen from Fig. 220, the total ionising power of cosmic radia-

tion is maximal at an altitude of 22 km, and falls off rapidly with decreasing altitude. Each square centimetre of the earth's surface at sea level receives 1 or 2 particles of cosmic radiation every minute.

2) The pair shown in Fig. 221, appeared due to the simultaneous "birth" of an electron and a positron in accordance with the equation: γ-electron + positron. Such a process may occur when a photon with an energy above 1.02 MeV passes close to the nucleus of an atom. The excess energy of the photon (above 1.02 MeV) is converted into the kinetic energy of the nucleus and of the "newborn" particles. On the other hand, the interaction between a positron and an electron results in two photons travelling in opposite directions, the energy of each of them being equal to 0.51 MeV (plus half the total kinetic energy of both particles). This ends the brief terrestrial existence of the positron.

As a result of the discoveries just considered, the number of "simple" structural units of atomic nuclei became equal to *four*: the electron, the proton, the neutron and the positron. The more complex formations that are particularly important in nuclear chemistry are helium nuclei—*helions* (α-particles) and deuterium nuclei—*deuterons*. These particles are characterised by the following data:

Name	electron	proton	neutron	positron	helion	deuteron
Symbol	β	p	n	e^+	α	d
Charge	1—	1+	0	1+	2+	1+
Mass	0.00055	1.00757	1.00893	0.00055	4.00280	2.01416

The masses are expressed in atomic mass units, each of which is 1/12 of the mass of a C^{12} atom (and equal to 1.66×10^{-24} g).

In addition to the particles enumerated above, one more particle should be mentioned. This particle—the *neutrino* (ν)—has a zero charge and a negligibly small mass.

3) The existence of the neutrino follows primarily from theoretical considerations. For example, the energy of β-decay of any given radioactive element ought to be constant, but in actual fact, the electrons are ejected with very different velocities, i. e., energies (Fig. 214). This contradiction can be removed by assuming that a neutrino is simultaneously ejected, its energy being defined as the difference between the maximum possible energy and that of the electron.

In its zero charge and negligible mass, the neutrino resembles the photon, but these particles differ greatly in penetrating power: while photons are more or less readily absorbed by many substances, i. e., impart their energy to them, all substances are practically transparent to the neutrino. That is why neutrinos cannot be observed directly. However, their existence is confirmed by certain nuclear effects.

Since any nucleus is specified by its positive charge (Z) and atomic weight (A), its composition can be expressed in terms of only *two* of the four "simple" particles considered above. The problem may be regarded, generally speaking, from three different points of view which are set out below:

I	II	III
protons (A) and *electrons* ($A-Z$)	*protons* (Z) and *neutrons* ($A-Z$)	*neutrons* (A) and *positrons* (Z)

The *second* point of view, according to which *the atomic nucleus is made up of Z protons and (A — Z) neutrons* (Ivanenko, 1932), is universally adopted. The other two schemes contradict a number of theoretical considerations which preclude the presence of charged particles of small mass in the nucleus.

In the proton-neutron theory of nuclear structure, *both* are regarded as elementary particles. At the same time, they are assumed to be capable of changing into one another:

$$\text{neutron} \rightleftarrows \text{proton} + \text{electron}$$

$$\text{proton} \rightleftarrows \text{neutron} + \text{positron}$$

These transformations involve the participation of a neutrino.

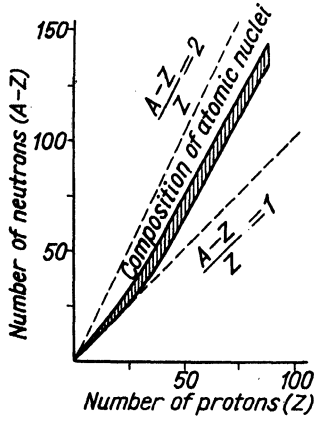


Fig. 222. Compositions of atomic nuclei

From this point of view, the electron or positron does not exist beforehand in the heavy particle, but is "born" during the transformation of the latter (like a photon during the transition of an excited atom to the normal state). An electron is thus "born", in particular, during radioactive β-decay.

The particles of which atomic nuclei are composed (neutrons and protons) are combined under the heading of *nucleons*. A diagrammatic representation of the composition of atomic nuclei of different elements is shown by the shaded strip in Fig. 222. As can be seen from the latter, the ratio between the number of neutrons $(A - Z)$ and the number of protons (Z) increases with increasing atomic number (Z). In other words, the nuclei of the heavy atoms are relatively richer in neutrons. The fact that the composition of the nuclei is represented by a strip rather than a line, is due to isotopy.

Nothing very definite is as yet known concerning the mutual position of the separate components of the nucleus. The construction of any theory in this direction meets, in the first place, with difficulties connected with the extraordinary density of nuclear structure. Thus, the radius of the uranium nucleus is not more than 1×10^{-12} cm, i. e., one five-thousandth of the radius of the hydrogen atom. At the same time, 92 protons and 146 neutrons must be accommodated in some way within the tiny volume of this nucleus.

In spite of the accumulation of particles with like charges (protons) in the atomic nucleus, the latter, as a rule, not only does not disintegrate, but is very stable. Obviously, this stability can be secured only by the emergence of powerful attractive forces between the components of atomic nuclei. The nature of these forces is as yet not clear.

4) The radii (r) of individual atomic nuclei can be approximately represented by the formula $r = 1.5\ A^{1/3} \times 10^{-13}$ cm. From this it follows that the volume of the nucleus is directly proportional to its mass (A), and the density of all nuclei is approximately the same. It is expressed by an enormous figure of the order of 10^{14} g/cm^3, i. e., one cubic centimetre of nuclear matter should weigh about 100 million tons.

A nucleus is in its normal state when its nucleons occupy the lowest possible energy levels; successive filling of the latter probably leads to a shell structure of heavy nuclei, which is to some extent analogous to the structure of the electronic shells in atoms.

5) The basic features of *nuclear forces* are their very considerable magnitude and very small radius of action. The latter amounts to only about 2×10^{-13} cm, i. e., a nucleon is thus able to interact only with its closest neighbours.

The nature of the forces of attraction between a neutron and a proton is interpreted as owing its origin to the exchange of a π-meson in accordance with the equations:

$$n + p \rightleftarrows p + \pi^- + p \rightleftarrows p + n$$
$$p + n \rightleftarrows n + \pi^+ + n \rightleftarrows n + p$$

This theory (Yukawa, 1935) was developed before the discovery of the π-meson, and correctly forecast its properties. It does not account for the forces of attraction between like nucleons, but they can be explained with the aid of neutral π-mesons—*neutrettos* (the existence of which was recently proved).

In contrast to forces of attraction, a mutual electrostatic repulsion operates between all the separate positive charges in the nucleus. Therefore, the repulsion increases rapidly with increasing total nuclear charge. "Dilution" of the highly charged nuclei with neutrons increases their stability, since it weakens the electrostatic repulsion. This determines the general nature of the change in nuclear composition with increasing positive charge (Fig. 222).

In itself, the presence of powerful attractive forces in the nucleus is confirmed directly by the considerations set forth below, which are based on the exact values of the atomic weights. Improved methods of mass-spectrography have made it possible to establish that the masses of the individual isotopes exhibit departures from whole numbers. Although these departures amount to less than 0.1% of the *mass number*, i. e., the whole number nearest the atomic weight, still they undoubtedly exist, as can be seen from the following examples:

Type of atom	He^4	Cl^{35}	Cl^{37}	Sn^{120}	Hg^{200}	O^{16}
Exact atomic weight . . .	4.00390	24.9787	36.9775	119.912	200.016	**16**

To find the masses of the atomic nuclei, the masses of the outer electrons should be subtracted from these figures. For example, the mass of the helium nucleus (α-particle) is $4.00390 - 2 \times 0.00055 = 4.00280$.

Proceeding from the idea of the synthesis of nuclei from elementary particles, the formation of the helium nucleus may be regarded as taking place in accordance with the equation: $2p + 2n = \alpha$. However, this involves a discrepancy in mass values. Judging by the equation for its formation, the mass of the α-particle would be expected to be $2 \times 1.00757 + 2 \times 1.00893 = 4.03300$, whereas actually

it equals 4.00280. The difference is only 0.03020, but, even so, the existence of this difference must somehow be accounted for.

The way to the explanation was first outlined by Mendeleyev (1872): "There is no reason to think that n parts by weight of an element or n of its atoms, on forming one atom of another substance, would also give n parts by weight, i. e., that an atom of the second element would weigh exactly n times as much as an atom of the first. Regard the law of constant weight as only a special case of the law of constant forces or momentum. Of course, it all depends on the particular kind of motion of matter, and there is no reason to deny the possibility of this motion being transformed into chemical energy or any other form of motion."

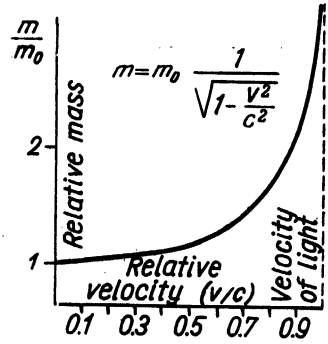


Fig. 223. Mass vs. velocity

The quantitative relation between mass and energy was revealed much later (Einstein, 1905). If the mass (m) is expressed in grams and the energy (E) in ergs, the equation for the relation, known as Einstein's equation, has the form $E = mc^2$, where c is the velocity of light (3×10^{10} cm/sec).

According to this equation, there is a corresponding change in mass for each change in energy, and vice versa. Therefore, for example, the mass of a moving body is greater than that of a stationary body, the mass of a hot body is greater than that of a cold body, etc. However, owing to the enormous numerical value of the factor c^2, such changes in mass are infinitesimal in all ordinary processes, and therefore remain unperceived.

6) The relation between the mass of a particle (m) and its velocity (v) is shown in Fig. 223, from which it is evident that an appreciable increase in mass occurs only at very high velocities. Thus, even at 100.000 km/sec, the increment is only 12%, the mass is doubled only at 260 thousand km/sec. On the other hand, at still higher velocities, it increases very rapidly, asymptotically approaching infinity for a velocity equal to the velocity of light in a vacuum (3×10^{10} cm/sec). From this it follows that the latter cannot be attained by any particle which possesses a rest mass (m_0) other than zero.

The state of rest of a particle should, of course, be understood only as the absence of its mechanical motion. Any rest and any equilibrium is merely relative, and only has meaning in relation to some definite form of motion.

7) From the discussion in the basic text it follows that the *law of conservation of mass* in chemical reactions (I-2) is not strictly accurate. Since nearly all such reactions are accompanied by evolution or absorption of energy, the mass of the reacting substance must alter. But an energy effect of 1 kcal corresponds to a change in mass of only 5×10^{-11} g. According to calculation, the most energy-consuming of all ordinary chemical reactions is (per gram of reactant) the thermal dissociation of the hydrogen molecule. The energy of this

reaction is about 50 kcal per gram, which corresponds to a change in mass of only 2.5×10^{-9} g. As this value is far beyond the limits of usual accuracy of weighing, the law retains its value in conventional chemical practice.

It is different with nuclear transformations. As is shown above, the formation of a helium nucleus from elementary particles involves an appreciable decrease in mass (known as the *mass defect*). This means that *the process must be accompanied by an enormous energy effect*. Since one atomic mass unit corresponds to an energy of 931 MeV, the complete equation for the formation of four grams of helium nuclei takes the form:

$$2p+2n=\alpha+931\times 0.03020=\alpha+28 \text{ MeV}$$

According to calculation, this amounts to 646 million kcal per 4 grams of helium nuclei. To produce such a quantity of energy by burning coal, about 80 tons would be required. This comparison shows graphically that the energy effects of nuclear processes are incomparable with those observed in conventional chemical reactions.

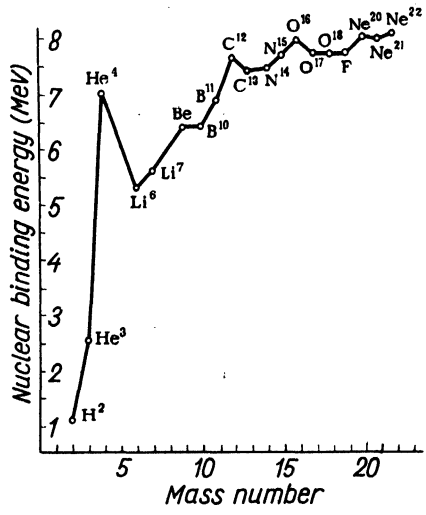


Fig. 224. Binding energies of the lighter atoms

If the total energy of formation of any nucleus from elementary particles (called the *packing effect*) is divided by the mass of the nucleus (in atomic mass units), the quotient is known as the "*binding energy per nucleon*" and it supplies a comparative characteristic of the *stability* of the nucleus in question. This energy varies irregularly for the light atoms (Fig. 224), but then rises fairly smoothly to a flat maximum (at about 8.6 MeV), which embraces the elements of the 4th and 5th periods. After this, the binding energy begins to fall off gradually to 7 MeV in the 7th period. This decrease in stability of the nuclei is in good agreement with the pronounced radioactivity of the heaviest elements.

XV-4. Transmutation of Elements. The first *artificial* transmutation of elements was accomplished in 1919 by Rutherford with the aid of radioactive α-radiation. It had been known earlier that on colliding with hydrogen molecules, α-particles sometimes knock protons out of them, having a much greater velocity and range than the original α-particles. This phenomenon can be studied by means of the apparatus shown in Fig. 225.

The apparatus consists of an air-tight brass box, with a radioactive preparation inside, applied to a plate *A*. The box has a small hole *B* in its side wall, covered with very thin metal foil. A zinc sulphide screen *C* is placed close to the hole, and the scintillations on the screen are observed with the aid of a microscope *M*. The cocks *D* are used for filling the apparatus with the gas under study and for lowering the pressure (to increase the path length of the particles).

By varying the distance from *A* to *B* or by inserting thin sheets of mica in the space between *B* and *C*, the velocity required for a particle to reach the screen can be controlled and thus the faster particles

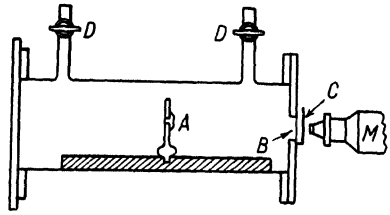


Fig. 225. Diagram of Rutherford's apparatus

can be separated from the slower. This is how it was established when working with hydrogen, that even when the α-particles were completely stopped, weak flashes appeared occasionally on the screen, due to incident protons. The path length of the latter (calculated on the basis of their motion in air) was up to 28 cm.

Obviously, knocking protons out of hydrogen molecules is not transmutation of elements. But when nitrogen was placed in the apparatus instead of hydrogen, Rutherford again detected scintillations, which were due to the impacts of rapidly moving protons on the screen. The maximum range of these protons was 40 cm, i. e., different from that in the case of hydrogen. Further study showed, moreover, that the protons are ejected in all directions in approximately equal quantities. All this indicated definitely that they had emerged from *the nuclei of nitrogen* under the action of the α-particles incident on these nuclei. The comparative rarity of appearance of proton scintillations on the screen was in good agreement with this concept. A count of the scintillations showed that approximately 50,000 α-particles were required to knock out one proton.

The use of the cloud chamber for photographing the tracks of the collisions of α-particles with nuclei made it possible to get a better insight into the process. It was found that after collision, the track of the moving α-particle branches into two (Fig. 226). This shows that the α-particle splitting the nucleus is *captured* by it and does not recoil, because if it did, *three* branches would have been observed (corresponding to the knocked-out proton, the residue of the nucleus and the

α-particle itself). The ratio between the path lengths of the proton and the nuclear residue, which should be the greater, the heavier the residue, leads to the same result. Accurate measurement of both branches in photographs, such as that shown in Fig. 226, definitely indicates that the mass of the nuclear residue of nitrogen must be 17 and not 13. The whole process is therefore a *nuclear substitution reaction.*

Since in the transformation from the original to the final atoms, the sum of the atomic numbers, i. e., of the nuclear charges, must be conserved, as well as the sum of the mass numbers, this reaction must be that of the formation of an oxygen isotope, in accordance with the equation:

$$_2He^4 + {}_7N^{14} = {}_1H^1 + {}_8O^{17}$$

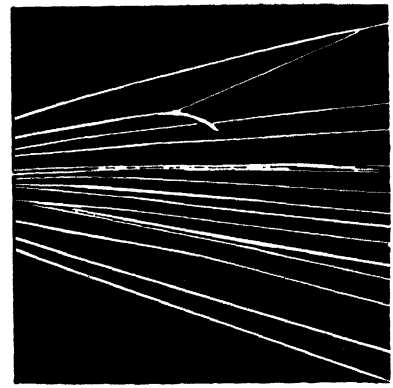


Fig. 226. Collision between an α-particle and a nitrogen nucleus

Calculation on the basis of the path lengths shows that the total kinetic energy of the products formed from the nitrogen nucleus is *less* than that of the incident α-particle.

According to Einstein's equation, the energy effect of a nuclear reaction is determined by the difference between the masses of the initial and final products. In this case, we have: 14.00751 + 4.00390 = 18.01141 and 17.00450 + 1.00812 = 18.01262, i. e., the final products are heavier than the initial ones. This signifies that in this particular transmutation energy (1.1 MeV) is *absorbed.* On the other hand, in an analogous process proceeding according to the equation

$$He^4 + Al^{27} = H^1 + Si^{30}$$

energy (2.3 MeV) is *liberated.* At the same time, the transmutation of Al occurs even less frequently than that of nitrogen, being caused by only one α-particle in every 125 thousand.

The quantities of the elements transmuted are negligible in both cases. This is due largely to the fact that bombardment by α-particles of radioactive origin can hardly be controlled. Neither the number of "missiles" nor the energy of each of them can be changed appreciably, and the direction of their flight is entirely out of control. The number of successful impacts is therefore negligibly small compared to the number of shots, and nuclear transmutation is caused by only one α-particle in several tens or hundreds of thousands.

The method of bombarding atomic nuclei with an *artificially* produced stream of charged particles—protons, deuterons or heli-

ons—offers much wider possibilities. These particles are readily formed by the action of electrical discharges on a suitable rarefied gas (hydrogen, deuterium or helium) and, broadly speaking, more "missiles" can be obtained from a litre of the latter than would be emmitted by a ton of pure radium in a week. By subjecting the particles produced to the combined effect of electric and magnetic fields, they can be focussed into a narrow beam, to which a definite velocity and direction can be imparted. Such a beam is therefore highly controllable, and that is what radically distinguishes this method from the bombardment of nuclei with α-particles of radioactive origin.

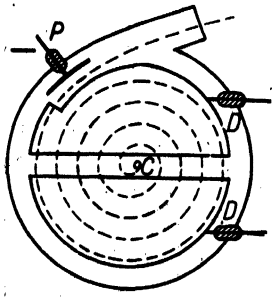


Fig. 227. Diagram of a cyclotron

The most practical device for obtaining powerful beams of rapidly moving charged particles is the *cyclotron* (Lawrence, 1932). The principal working part of the apparatus consists of closely-spaced hollow metal half-discs (*D*, Fig. 227) situated in a vacuum chamber. They are both connected to a high-frequency alternating current generator and subjected to the effect of a strong magnetic field in a direction normal to their plane.

Under the action of the magnetic field, the beam of charged particles entering the gap between the two half-discs ("dees") of the cyclotron from the central part of the device (*C*), is set in circular motion. The frequency of the alternating electric field is chosen so that each time the particles come *between* the two half-discs, they are *accelerated*. Owing to the successively increasing accelerations, the general path of the particle acquires the form of a spiral. At the end of its path, the beam of particles is deflected by a negatively charged electrode *P*, and emerges from the device at a predetermined velocity.

1) In order to ensure correct operation of the cyclotron, the accelerating field must be in resonance with the revolutions of the particles, which depend on their charges and masses. The applicability of the original version of the cyclotron was limited by the rapid increase in mass of the particles at very high velocities (Fig. 223), which upsets the conditions necessary for resonance. It was found possible to maintain these conditions by employing the *synchrotron* principle (Weksler, 1945), which allowed for the change in mass of the particles. This was done by suitably varying the frequency of the alternating electric field and/or the strength of the magnetic field. The different versions of synchrotrons are known as synchrocyclotrons, frequency-modulated cyclotrons, proton synchrotrons, etc. An apparatus called the *betatron* has been constructed for accelerating electrons to predetermined velocities.

Even before the development of the cyclotron, a large number of nuclear transmutations were studied by using α-particles of radioactive origin as missiles. However, the presence of two positive charges

in the α-particle limited the applicability of this method to relatively light elements: atoms with large positive nuclear charges repel α-particles so strongly that the likelihood of the latter penetrating the nucleus becomes insignificantly small. That is why transmutations by α-particles of radioactive origin have been observed only in the case of elements with atomic numbers no higher than about twenty.

While the maximum energy of α-particles of radioactive origin is 8.8 MeV (ThC'), modern cyclotrons produce directed beams of charged

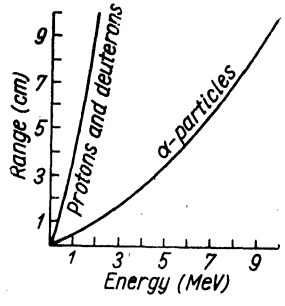


Fig. 228. Range in air vs. energy of particles

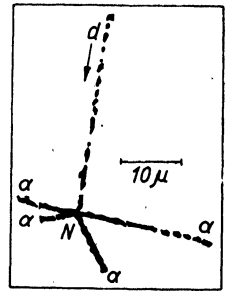


Fig. 229. Transformation of nitrogen into helium

particles with energies up to *thousands* of MeV, which contain more α-particles than would be emitted within the same time by a kilogram of pure radium. This greatly extends the field of application of α-particle bombardment.

However, the use of protons and deuterons has still greater potentialities. As can be seen from Fig. 228, their penetrating power at equal kinetic energy is much greater than that of α-particles. This is due to the fact that the latter are doubly charged and therefore ionise the molecules they encounter to a much greater extent than the other particles, this being connected with higher energy losses. Also, the lower charge of protons and deuterons greatly facilitates their approach to atomic nuclei.

Transmutations of very many chemical elements have been accomplished by means of protons and deuterons. For example, the reaction

$$H^1 + Al^{27} = He^4 + Mg^{24}$$

can be brought about by proton bombardment of aluminium. This process is the reverse of those usually observed during bombardment with α-particles in that a simpler rather than more complex nucleus results.

The tracks produced in a thick-emulsion film by the deuterons bombardment of nitrogen in accordance with the equation

$$D^2 + N^{14} = 4He^4$$

are shown in Fig. 229.

This reaction is accompanied by the evolution of a considerable amount of energy (6.2 MeV), owing to which the α-particles formed have high kinetic energies. As can be seen from the figure, their path lengths in the film are only a few microns or tens of microns, i. e., are incommensurable with their path lengths in air.

The most effective "missile" for bringing about nuclear transmutations is the *neutron*. The absence of an electric charge on them makes it very easy for neutrons to penetrate atomic nuclei in head-on collisions. Therefore, the probability of bringing about nuclear transmutations by the action of neutrons is much higher than when α-particles, deuterons or protons are used.

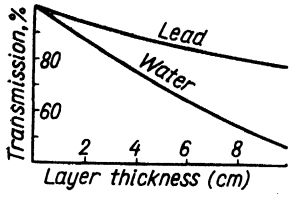


Fig. 230. Transparency to fast neutrons

The simplest source of neutrons is a glass ampoule containing powdered beryllium mixed with a radium salt. By the reaction

$$He^4 + Be^9 = C^{12} + n$$

0. 1 g of this mixture produces some hundreds of thousands of neutrons per second.

Much more powerful beams of neutrons can be produced with the aid of a cyclotron by bombarding a sheet of metallic beryllium with deuterons:

$$D^2 + Be^9 = B^{10} + n$$

Neutrons obtained by any method usually possess a high kinetic energy and an enormous initial velocity. As has already been noted, such fast neutrons pass readily through fairly thick layers of different substances. A fact of fundamental importance is that the "transparency" of substances to neutrons is entirely different than to other radiations. For example, all types of radioactive radiation are retarded much more effectively by lead than by water, whereas for neutrons, the opposite is the case (Fig. 230).

This is due to the fact that the neutrons are retarded owing to loss of velocity on colliding with the nuclei of atoms they encounter. Since the transfer of the kinetic energy of the neutron to a light nucleus is more effective than to a heavier one, media made up of the lightest atoms are the best moderators of fast neutrons.

As a result of the loss of velocity on colliding, the kinetic energy of the neutrons eventually becomes commensurable with the kinetic energy of the molecules of an ordinary gas. Such neutrons are known as "thermal" neutrons. From this it follows that in order to moderate neutrons, it is sufficient to pass a stream of them through a more or less thick layer of a substance rich in light atoms; graphite, paraffin or water are usually employed for this purpose.

The course of a neutron reaction greatly depends on the velocity of the neutron. After capturing a *fast* neutron, the nucleus usually

ejects either an α-particle or a proton. On the other hand, the capture of a *slow* neutron is usually accompanied by the emission of a γ-ray only, and the formation of a heavier isotope of the original element. Cadmium, for example, behaves in this way, thermal neutrons being almost completely arrested by a cadmium sheet 1 mm thick.

The simplest example of a nuclear reaction with the participation of neutrons is the transformation of protium, H^1, into deuterium by slow neutron capture:

$$H^1 + n \rightarrow D^2 + \gamma$$

This reaction takes place partly when paraffin or water is bombarded with neutrons. Unlike ordinary water, heavy water, D_2O, captures hardly any neutrons.

The use of the methods of acting on atomic nuclei considered in this section enables artificial transmutation of all the elements. However, in contrast to natural radioactive transmutations, the nuclear reactions described above continue only as long as the external influence is acting. The discovery of artificial radioactivity bridged the gap between the first and second type of process.

XV-5. Artificial Radioactivity. During a detailed study of the reactions between aluminium and α-particles from polonium, the following reaction was found to take place (Irène and Frédéric Joliot-Curie, 1934):

$$Al^{27} + \alpha \rightarrow Si^{30} + n + e^+$$

When the source of α-rays was removed, the emission of neutrons instantly stopped. But the emission of positrons continued, its intensity decreasing *in accordance with the law of radioactive decay* (XV-1). From this it followed that the reaction actually takes place in two stages: during the first, *a radioactive isotope of phosphorus* ("radiophosphorus") is formed:

$$Al^{27} + \alpha = P^{30} + n$$

which then decays spontaneously in accordance with the equation:

$$P^{30} = Si^{30} + e^+$$

The half-life of P^{30} was found to be equal to 2.5 mins.

The discovery of *artificial radioactivity* showed that besides α-decay and β-decay, *positron* decay is also possible. Since the emission of a positron results in a decrease in the positive nuclear charge by one unit, in this case, the displacement law requires the decay product to shift one place to the left in the Periodic Table (without changing its mass number). Positrons are completely analogous to β-rays with respect to distribution of velocities (Fig. 214).

After the work of the Joliot-Curies, other cases of artificial radioactivity were discovered. More than 1000 radioactive isotopes are now known, and they have been obtained for all the chemical elements.

Radioactive isotopes are generally obtained by bombarding atomic nuclei with positively charged particles (p, d, α) or neutrons. Occasionally, very hard γ-rays are also used. A particular radioelement can often be produced in several different ways. For example, another reaction suitable for obtaining P^{30} is:

$$S^{32} + d = P^{30} + \alpha$$

The half-lives of most artificial "radioelements" are relatively short, being of the order of seconds, minutes, hours or days. Only occasionally do they exceed a year, and isotopes with a half-life longer than a thousand years are exceptions. That is why natural mixtures of isotopes do not contain the radioelements.

As a rule, artificial radioelements decay, splitting off an electron or a positron. Usually, the following general law is observed: radioactive isotopes that are relatively heavy (relative to the average atomic weight of the element) emit electrons, while the relatively light ones emit positrons. Fairly often, γ-rays are emitted simultaneously. Alpha decay, which is very typical of the members of the natural radioactive series, occurs in artificial radioelements only as a relatively rare exception. Another feature of most artificial radioelements is that they undergo a direct transformation from a radioactive initial substance to a non-radioactive end product.

1) Apart from the ways of radioelement transmutation considered above, the nuclei of some of them are converted into the stable state by capturing an electron from one of their *own* electronic shells. Since electrons are usually captured from the K-shell, which is the nearest to the nucleus, this transmutation is known as K-capture. As a result of this, the atomic number of the element is reduced by one. An example is "radiomercury", Hg^{197}, which forms according to the reaction $Hg^{196} + n = Hg^{197} + \gamma$. In the course of three days, half of the initial amount of Hg^{197} is transmuted into Au^{197} by K-capture. This reaction is interesting because in principle it fulfils the alchemists' dream of producing gold from mercury.

When radioelements are produced artificially, they are usually formed in very small quantities and, moreover, they are dispersed throughout the original material. In this connection, *chemical* methods of investigation play a very important part in the study of artificial radioactivity. Only with their aid is it possible to solve the two main problems involved, viz., determining the nature of the activity carriers and separating the corresponding radioelement in an enriched state.

Since the chemical properties of isotopes are practically identical (XV-2), each radioelement behaves chemically in the same way as the corresponding ordinary element. The solution of the two problems

mentioned above is based on this fact. If, for example, an iron plate which has been bombarded with neutrons is dissolved in nitric acid, addition to the solution of a small quantity of a manganese salt and subsequent treatment with $KClO_3$ causes MnO_2 to precipitate out, while the iron remains in solution. A separate investigation of the solution and the precipitate shows that the radioactivity is concentrated in the latter, i. e., that the carrier of radioactivity is radiomanganese. Hence (in conjunction with the recording of protons), there follows the equation for the nuclear transmutation:

$$Fe^{56} + n \rightarrow Mn^{56} + p$$

At the same time, the radiomanganese obtained (β, γ-decay, $T =$ $= 2.6$ hours) is found to be concentrated in the MnO_2 precipitate.

On the other hand, the fact that the chemical properties of isotopes are identical enables direct and conclusive solution of many important chemical and biological problems with the aid of "radioelements". The partial substitution of a radioactive isotope for corresponding ordinary element in a compound does not change the chemical properties of the compound, but the latter becomes radioactive. All the subsequent transformations of the compound (more exactly, of the radioactive atom contained in it) in different processes may therefore be traced with the aid of very sensitive methods for detecting radioactivity. As has already been noted, artificial radioactive isotopes have been produced for all the stable elements. Thus, *radioactive indication* is becoming, in principle, a universally applicable method for carrying out research into most varied scientific and technical problems. A great deal of such research has been carried out by means of "tagged atoms".

In order to record the ways in which radioelements are formed or other nuclear reactions take place, an abbreviated notation is often employed. The essentials of this notation will become clear from the following examples in which it is compared with the usual equations:

$$Co^{59} + n = Co^{60} + \gamma \qquad Co^{59}(n, \gamma)\, Co^{60}$$

$$Li^{6} + n = H^{3} + \alpha \qquad Li^{6}(n, \alpha)\, H^{3}$$

Radiocobalt Co^{60} (β, γ-decay, $T = 5$ years) which is obtained from ordinary Co^{59} by the first reaction, is a good substitute for radium in the treatment of cancer, etc. An isotope of hydrogen with mass 3, called *tritium* (T), is formed in accordance with the second equation. This isotope undergoes a transmutation according to the equation $H^3 =$ $= He^3 + \beta$, the half-life being about 12.5 years.

2) Besides that given above, there are about ten more nuclear reactions resulting in tritium. Some of them are occasionally caused by cosmic rays, and this provides a permanent minute quantity of tritium in nature (one atom of tritium for every 10^8 atoms of protium).

The filling of the gaps in the Mendeleyev periodic table by synthesis of the elements which are unavailable in the earth's crust—*technetium*, Tc, *promethium*, Pm, and *astatine*, At,—was an achievement of importance to general chemistry. Several radioactive isotopes of each of them have been obtained. In all such cases of elements that are unknown in the stable state, the mass number of their longest-lived isotope is conventionally accepted as the atomic weight (it is enclosed in square brackets to distinguish it from ordinary atomic weights).

3) The radioactive properties of the longest-lived isotopes of Tc, Pm and At, as well as those of Fr^{223} which is identical to AcK of the actinium series, are set out below:

$Tc^{99} \rightarrow Ru^{99} + \beta$ ($T = 2 \times 10^5$ years) Pm^{145} (K-capture) $\rightarrow Nd^{145}$ ($T = 30$ years)

At^{210} (K-capture) $\rightarrow Po^{210}$ ($T = 8.3$ hr) $Fr^{223} \rightarrow AcX^{223} + \beta$ ($T = 21$ min)

$Po^{209} \rightarrow Pb^{205} \rightarrow \alpha$ ($T = 100$ years) $\rightarrow$ (K-capture; $T = 1.5$ hours) Tl^{205}

Technetium can be obtained by the reaction $Mo^{98}(n, \beta)Tc^{99}$, polonium and astatine—by the reaction $Bi^{209}(d, 2n)Po^{209}$ and $Bi^{209}(\alpha, 3n)At^{210}$, promethium—by the reaction $Sm^{144}(n, \gamma)Sm^{145}$ (K-capture) Pm^{145}.

It should be noted that Tc^{98} has also been found to exist (it disintegrates into $Ru^{98} + \beta$ with $T = 2 \times 10^6$ years). It can be obtained by bombardment of Mo by deuterons, but only in the form of an impurity in other radioactive atoms.

The synthesis of the *transuranic* elements, i. e., the elements with atomic numbers of 93 and higher, is of enormous importance. When U^{238} reacts with slow neutrons, U^{239} results, and its further decay leads to the formation of the first two members of the transuranic series—*neptunium*, Np, and *plutonium*, Pu:

$$_{92}U^{238} \xrightarrow{+n} {}_{92}U^{239} \xrightarrow[T=23\text{ min}]{\beta} {}_{93}Np^{239} \xrightarrow[T=2.3\text{ days}]{\beta} {}_{94}Pu^{239}$$

The resulting Pu^{239} undergoes α-ray transformation (passing into U^{235}) and has a half-life of 24,400 years.

The following transuranic elements have been obtained only in very small quantities: *americium*, $_{95}Am$, *curium*, $_{96}Cm$, *berkelium*, $_{97}Bk$, *californium*, $_{98}Cf$, *einsteinium*, $_{99}Es$, *fermium*, $_{100}Fm$, *mendelevium*, $_{101}Md$, element No. 102 and *lawrencium*, $_{103}Lr$. They are all highly radioactive.

4) The chief radioactive properties of the longest-lived or best known isotopes of the transuranic elements are set out below.

Isotope	Np^{237}	Pu^{244}	Am^{243}	Cm^{247}	Bk^{247}	Cf^{249}	Es^{254}	Fm^{253}	Md^{256}	No. 102^{256}	Lr^{257}
Type of decay	α	α	α	α	α	α	α	α	k	α	α
Half-life	2×10^6 years	4×10^5 years	8×10^3 years	4×10^7 years	7×10^3 years	360 years	480 years	3 days	90 min	8 sec	8 sec

5) The production of the series of transuranic elements naturally gives rise to the question as to how far the series can be extended. Calculations made as far back as 1939 showed that the stability of heavy atomic nuclei diminishes as the ratio Z^2/A increases, Z being the nuclear charge and A its mass. The critical value of this quantity at which the nucleus becomes quite unstable is about 40, which approximately corresponds to the element having the atomic number 100. Thus, theoretically, there is little probability of stable existence of elements with still higher atomic numbers.

As can be seen from the above, the study of the nuclear transmutations of uranium and the elements following it, is of fundamental importance not only as such, but from the point of veiw of the periodic law as a whole. An even more important point is that this research has offered the first solution of the problem of utilising nuclear energy.

XV-6. Nuclear Fission. The study of natural radioactivity showed that nuclear reactions involve huge amounts of energy. Thus, the total energy liberated when 1 g of radium is transformed into lead is equivalent to that obtained from burning half a ton of coal. However, leaving aside the cost of radium, this energy cannot be utilised owing to the slowness of the decay.

In the course of research into the artificial transmutation of elements, a number of nuclear reactions were discovered, which are accompanied by the liberation of very considerable amounts of energy. For example, the proton bombardment of lithium is represented by the following equation:

$$Li^7 + H^1 = 2He^4 + 400 \text{ million kcal}$$

The transmutation of 7 g of lithium is thus equivalent to burning 50 tons of coal. However, this transmutation is brought about so infrequently (by approximately one bombarding particle in every million) that it is found to be extremely uneconomical.

Generalisation of experience in the transmutation of elements leads to the conclusion that the only kind of nuclear reaction whose energy can be utilised is one which, having once begun, will continue spontaneously (in the same way as fuel which, once ignited, continues to burn). Real prospects in this direction appeared only with the discovery of a new type of nuclear disintegration.

In the theory of atomic nuclei, a model is often used, which likens the nucleus to *a charged drop of liquid*. A calculation of such a system shows that when the charge on the drop becomes sufficiently high, there is a probability of *the drop dividing into two parts of more or less the same size* (Fig. 231).

A similar fission of atomic nuclei was established experimentally in 1939 while studying the interaction between uranium and neutrons. Almost at the same time it was found that uranium nuclei

may also undergo spontaneous fission but such fission occurs comparatively rarely. Fig. 232 shows a cloud chamber photograph of two tracks running in opposite directions, which emerge from a collodion film coated with UO_3. These tracks are due to the "nuclear fragments" resulting from the fission of a uranium nucleus.

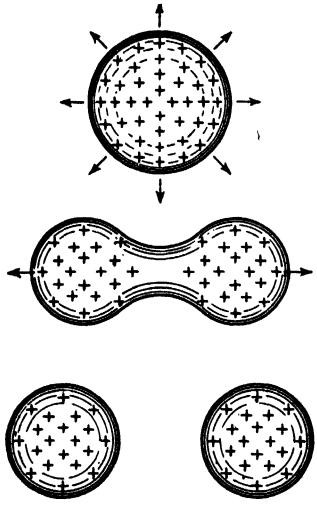


Fig. 231. Division of a charged drop

1) The chemical nature of the nuclear fragments may vary, but the sum of their atomic numbers is equal to the atomic number of uranium. Usually, one of them is considerably heavier than the other. Characteristic combinations are Ba + Kr, Cs + Rb, La + Br, Xe + Sr, etc.

The nuclear fragments contain more neutrons than the stable isotopes of the elements they represent (for instance, the heaviest isotopes of barium and krypton

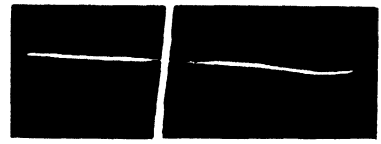


Fig. 232. Fission of a uranium nucleus

have masses of 138 and 86, respectively, the sum being only 224). In connection with this, each of them undergoes β-ray transformations ultimately forming a stable isotope of an element with a higher atomic number. The following series is an example of this:

$$Xe^{140}(16\ sec) \rightarrow Cs^{140}(66\ sec) \rightarrow Ba^{140}(12.8\ days) \rightarrow La^{140}(40\ hr) \rightarrow Ce^{140}$$

Thus, the fission of the uranium nucleus involves artificial radioactivity, most of the radioelements formed having half-lives of the order of seconds, minutes or hours.

The two principal isotopes of uranium — U^{238} and U^{235} — differ substantially in their attitude to neutrons. Although the nucleus of the first is fissionable by fast neutrons, simple *capture* of the neutron with transformation into U^{239} occurs much more frequently. On the other hand, when U^{235} interacts with a neutron, it undergoes *fission* (slow neutrons being the most effective in this case).

It is of main importance that the fission of U^{235} nuclei is accompanied by the *emission of neutrons* (2 or 3 per fission), which can in turn bring about the fission of neighbouring U^{235} nuclei. This makes possible, in principle, not merely spontaneous continuation of a process once started, but its *avalanche-like self-acceleration* (Fig. 233).

The fission of U^{235} nuclei releases an enormous amount of energy—about 18 mill. kcal per gram of fissioning nuclei. This energy is approximately equal to that produced by the explosion of 18 tons (i. e., 18 million times the amount) of a conventional explosive. From this comparison, together with the possibility, in principle, of avalanche-like self-acceleration of the fission process, directly followed the idea of the "atomic bomb". The problem of making the latter was solved during the years 1942-45 by the joint efforts of a large group of scientists of different countries.

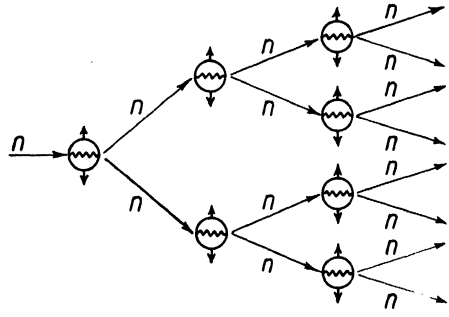


Fig. 233. Diagram of avalanche fission

To produce an explosion, the process of disintegration must be propagated through the whole mass of the explosive material at an adequate velocity.

Applied to the atomic bomb, this means that for avalanche-like development of disintegration, each neutron must be utilised as far as possible. In other words, wasteful (from the point of view of explosion) losses of neutrons by simple capture or escape from the reacting system without interaction with nuclei, must be reduced to a minimum.

The first source of loss can be adequately reduced by thoroughly removing from the "explosive material" those atoms whose nuclei are capable of simple neutron capture. As to the escape of neutrons from the reacting system without interacting with nuclei, this is the less probable, the larger the compact mass of the "explosive". If it is less than a certain critical mass, too many neutrons are wasted and the avalanche does not build up at all. If the mass is near critical, the avalanche builds up relatively slowly, and the bomb simply breaks up without exploding. Finally, if the mass is above critical, the avalanche builds up instantaneously (in a matter of millionths of a second) and an explosion takes place.

From the above it follows that no explosion can occur in two separate pieces of an "explosive", if the mass of each of them is below critical. But if these pieces are joined very rapidly, an explosion will

take place immediately (since the stray neutrons necessary to initiate an avalanche are always present owing to spontaneous fission). This was the principle actually employed for initiating the explosion of the atomic bomb: it was detonated by using one part of it as a target and the other as a missile.

A schematic diagram of the simplest atomic bomb is shown in Fig. 234. The reflector is designed to scatter neutrons ejected from the uranium, and therefore a considerable part of them are returned instead of being lost. This substantially reduces the critical mass of uranium.

2) The diagram shown in Fig. 234 presupposes a spherical shape for the U^{235} charge at the moment of explosion. Under these conditions, the critical mass of U^{235} is no more than a few kilograms, and the radius of the sphere is no larger than a few centimetres.

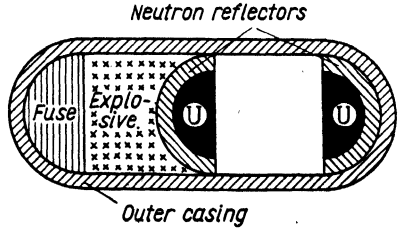


Fig. 234. Diagram of the simplest atomic bomb

A good reflector should greatly scatter the neutrons and capture few of them. Besides graphite, this requirement is fulfilled for example, by metallic beryllium and its oxide. Other conditions being equal, the longer the period allowed for the development of the avalanche (in this case, millionths of a second are important), the more completely is the U^{235} charge utilised for the explosion. For this reason the casing of the atomic bomb is made of the strongest material possible. The power of such a bomb is restricted by lower and upper limits, since the total mass of U^{235} can lie only in the range between one and a few critical masses.

In the first version of the atomic bomb, U^{235} was used as the "explosive". The content of this isotope in natural uranium is only 0.7%; U^{238}, which is quantitatively predominant, has a very great tendency to capture neutrons. The exceedingly difficult problem of separating U^{235} was solved mainly with the aid of a specially constructed electromagnetic isotope separator operating on the mass-spectrograph principle.

The possibility of producing another version of the atomic bomb was established when it was found that Pu^{239} *behaves like* U^{235} *in regard to fission*. Since Pu^{239} itself forms as a result of the capture of a neutron by the U^{238} isotope, the latter is transformed from nonproductive waste (in the first version) into a valuable fertile material. This fact is in itself of enormous importance, since it permits much

fuller utilisation of natural uranium (inasmuch as it contains 140 times more U^{238} than U^{235}).

Practical realisation of the second version demanded the artificial production of considerable quantities of plutonium. For this purpose, special large-scale nuclear reactors (piles) were built, which were filled with graphite interspersed with metallic uranium

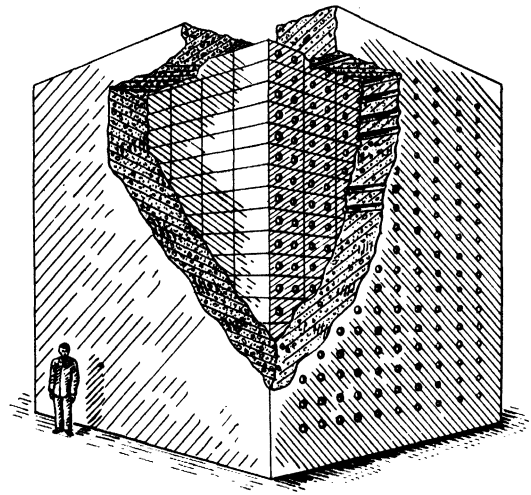


Fig. 235. A nuclear reactor

rods (Fig. 235). The graphite is used for moderating the neutrons passing from one rod to another in order to make maximum use of them for nuclear fission.

3) Nuclear reactors using heavy water as a neutron moderator have some substantial advantages over graphite reactors (D_2O slows down neutrons better than graphite and absorbs less of them). They can contain uranium not only in the form of metallic rods, but also as a solution of its salts. If the uranium is sufficiently enriched in U^{235}, the reactor is able to operate using ordinary water.

The principal processes taking place in the nuclear reactor may be represented by the following equations:

$$n + U^{235} \rightarrow \text{nuclear fragments} + 2n$$

$$n + U^{238} \rightarrow Pu^{239} + 2\beta$$

$$n + Pu^{239} \rightarrow \text{nuclear fragments} + 2n$$

The reactor is designed so as to ensure the first reaction, which is the chief source of neutrons. Owing to the quantitative predominance of U^{238}, the second reaction takes place readily. Finally, the third reac-

tion becomes appreciable only upon sufficient accumulation of plutonium, and it makes up for the decrease in U^{235} nuclei.

A schematic diagram of a nuclear reactor is shown in Fig. 236. The reaction space *A* filled with graphite and uranium, is surrounded by a neutron reflector *B* and a thick shield *C* for protection against radiation from the reactor. Its operation is controlled by an ionisation chamber *D* which transmits signals to an amplifying system *E*. The latter automatically controls the operation of the reactor by withdrawing or inserting a rod *F* that is a strong neutron absorber.

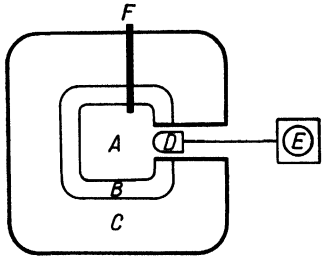


Fig. 236. Diagram of nuclear reactor

The processes taking place in the reactor are accompanied by the liberation of huge amounts of energy, and this rapidly increases the temperature. Since this is disadvantageous from the point of view of plutonium production, provisions must be made for intensive internal cooling of the reacting space.

The uranium rods are periodically removed from the reactor (new ones being inserted instead) and subjected to complex chemical processing to recover the plutonium. Since the plutonium yield is small, it is very expensive in the long run. However, the cost of producing plutonium is smaller than that of separating an equivalent amount of U^{235} from a mixture of isotopes. Moreover, plutonium production can be conducted on a much larger scale.

The latter is also true of another type of nuclear "fuel"—the isotope U^{233} (α-decay, $T = 1.6 \times 10^5$ years)—formed as a result of the capture of a slow neutron by thorium:

$$Th^{232} \xrightarrow{+n} Th^{233} \xrightarrow[T=23.5\ \text{min}]{\beta} Pa^{233} \xrightarrow[T=27.4\ \text{days}]{\beta} U^{233}$$

U^{233} is similar to U^{235} and Pu^{239} with respect to fission. Since there is three times as much thorium as uranium in the earth's crust, the use of U^{233} considerably increases the possibilities of nuclear energy production.

4) Thorium can be converted into U^{233} by the neutrons of an ordinary uranium reactor. After a sufficient amount of U^{233} has accumulated thorium, like natural uranium, becomes a fertile material for independent reactors, during the operation of which the concentration of U^{233} rises (since more U^{233} is formed than is expended in fission).

5) Nuclear reactors are employed as powerful sources of neutrons for producing radioelements. Some of these form part of the "radioactive ashes" of the reactor, i. e., are nuclear fragments. For example, fission of each gram of U^{235} results in 0.025 g of Tc^{99}, this element not being generally encountered in nature. The fragments can be partially separated by processing the uranium rods.

Radioelements are much more extensively synthesised by temporarily placing specially selected fertile materials in the reactor (or between it and the protective shield). For example, the long-lived isotope of carbon, C^{14} (β-decay, $T = 6000$ years), which is of great importance in chemical and biological research, is produced from NH_4NO_3 by the reaction $N^{14}(n, p)C^{14}$.

6) Owing to the great harmfulness of the very powerful radioactive radiation accompanying the production of plutonium (and U^{233}), all its stages are controlled either by automatons or under the protection of shields. The possibility of employing the explosion products of an atomic bomb as a radiation weapon is based on this same harmfulness.

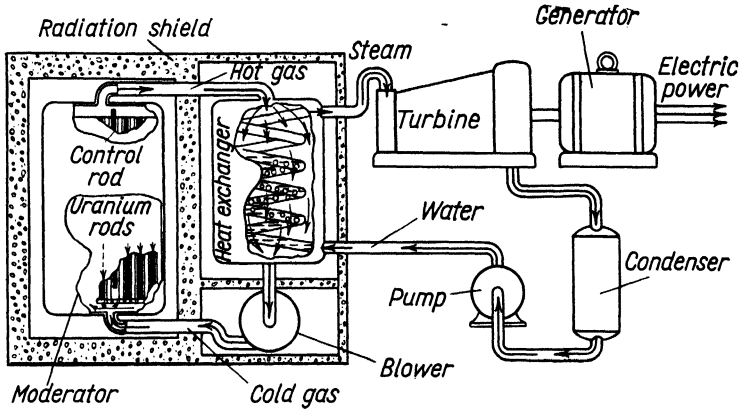


Fig. 237. Key diagram of installation for utilising nuclear energy

If the operating conditions of a nuclear reactor are regulated for the generation of energy, such a reactor can be used as the basis for a high-capacity power station which does not require continual fuel replenishing. A key diagram of such an installation is shown in Fig. 237. The world's first experimental industrial atomic power station with a capacity of 5000 kW began to operate in summer 1954 in the U.S.S.R. At the present time, installations of a similar type are successfully installed in certain means of transportation such as sea-going ships.

Though the direct utilisation of nuclear energy in various types of engines is not yet practicable, it is not impossible. The crux of the problem is to find methods for "dosing out" this energy, but there is no reason to doubt that this problem will be successfully solved.

At the same time, it has been established in recent years that tremendous quantities of energy can be produced through nuclear reactions of a completely different type, which may be figuratively described as "bringing the sun down to the earth".

XV-7. Thermonuclear Processes. The source of the energy of the sun (and of other stars) is not the disintegration, but the *synthesis*

of atomic nuclei, the most important reaction being the formation of helium from hydrogen:

$$4p = \alpha + 2e^+ + 565 \text{ mill /kcal}$$

Actually, this reaction does not take place in such a simple way, but goes through a number of intermediate stages.

1) The direct synthesis of helium nuclei from protons requires the simultaneous collision of *four* particles, which is practically inconceivable even under the conditions most favourable for the reaction. It is much more realistic for this process to take place through successive reactions, each of which requires the collision of only two particles. Thus, it would seem that the following sequence of processes is evidently characteristic of relatively cold stars:

$$p + p = d + e^+ + 9 \text{ mill. kcal} \qquad p + d = He^3 + \gamma + 125 \text{ mill. kcal}$$

$$p + He^3 = \alpha + e^+ + 431 \text{ mill. kcal}$$

Another way, which is called the *carbon-nitrogen cycle*, is characteristic of hotter stars (energies evolved in MeV):

$$C^{12}(p, \gamma)N^{13} \quad N^{13}(e^+)C^{13} \quad C^{13}(p, \gamma)N^{14} \quad N^{14}(p, \gamma)O^{15} \quad O^{15}(e^+)N^{15} \quad N^{15}(p, \alpha)C^{12}$$
$$1.9 \qquad 1.2 \qquad 7.5 \qquad 7.3 \qquad 1.7 \qquad 4.9$$

The overall result is represented by the equation given above, viz., $4p = \alpha + 2e^+ + 24.5$ MeV, and the average time taken to complete the whole cycle is estimated to be 5 million years. It is highly probable that this carbon-nitrogen cycle is one of the main sources of solar energy.

A necessary condition for spontaneous fusion of atomic nuclei is a temperature of the order of millions or tens of millions of degrees. Since the temperature in the central regions of the sun amounts to some 20 million degrees, at tremendous pressure this condition is fulfilled there.

Realisation of these thermonuclear processes under terrestrial conditions was found to be feasible only with the aid of the high temperature (of the order of hundreds of millions of degrees) resulting from the explosion of an atomic bomb. Only the latter could serve as the "match" capable of initiating the artificial reactions of the fusion of atomic nuclei.

The heavier they are, the more readily do the nuclei of hydrogen atoms enter into the various conceivable processes of this type. The nucleus of tritium—the *triton* (*t*)—is the most reactive. It was found that only with its participation are systems created which can be "triggered off" by an ordinary atomic bomb.

Since the production of tritium is extremely complex and expensive, it is desirable to reduce its content in the original "fuel" to a minimum. It was established that a mixture of tritium and deuterium is suitable in practice, this mixture reacting according to the following principal equation:

$$d + t = \alpha + n + 400 \text{ mill. kcal}$$

This reaction yields over four times more energy per gram of spent "fuel" than the fission of uranium or plutonium nuclei.

Artificial thermonuclear processes have so far been realised only in the form of the *hydrogen bomb*, schematic diagram of which is shown in Fig. 238 (AB is an ordinary atomic bomb, $D + T$ is a mixture of

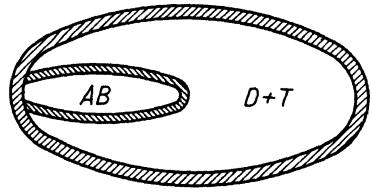


Fig. 238. Diagram of a hydrogen bomb

deuterium and tritium). Since the reaction $d + t$ is accompanied by a sharp rise in temperature, certain other nuclear reactions may become involved in the further course of the process.

2) The liberation of a great number of neutrons by the explosion of a hydrogen bomb causes the formation of large quantities of different radioelements, which may serve as radiation weapons. This danger is particularly high if radioelements are formed from the bomb casing. Unlike the ordinary atomic bomb, the hydrogen bomb has no upper power limit and its size is restricted only by technical considerations.

Since thermonuclear processes must be extremely difficult to control, there appear to be no clear prospects for their peaceful utilisation. This does not mean, however, that such prospects do not exist. Considering the tremendous progress made in recent years, it can hardly be doubted that we are on the threshold of even greater achievements. "Human reason has discovered many amazing things in nature and will discover still more, and will thereby increase its power over nature" (Lenin).

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