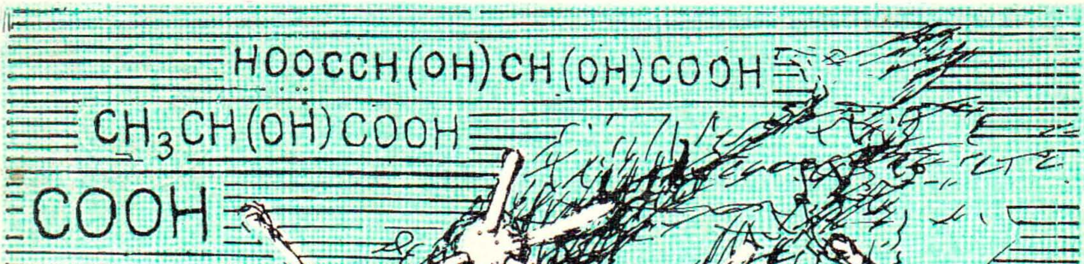
SCIENCE
FOR EVERYONE

G.B. SHUL'PIN

LEARNING ABOUT CHEMISTRY



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About Chemistry

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Химия для всех

Издательство «Знание» Москва

G. B. Shul'pin

Learning About Chemistry

Translated from the Russian by
Natalia Frosina

Mir
Publishers
Moscow

First published 1989
Revised from the 1987 Russian edition

На английском языке

Printed in the Union of Soviet Socialist Republics

ISBN 5-03-000542-0

Contents

Foreword

This book is about chemistry, one of the most important sciences studied by humanity. Chemistry was first formalized during the middle of the 18th century when the law of conservation of mass was established and the flogiston theory was disproved. Further significant steps were made in the 19th century, namely the introduction of the concept of the atom, the discovery of the periodic law of the elements, and the establishment of the structure of organic compounds. Over the last two centuries chemistry has become a well developed science and accumulated a colossal amount of information. A number of young sciences, such as molecular biology, cannot manage without the concepts and methods used in chemistry.

This book consists of a series of essays, each considering one field of chemistry, or a key notion, or an important compound. To paraphrase a well-known proverb, one might say that it is better to perform one experiment than to read about a phenomenon a hundred times in order to understand it. A feature of this book is that each essay is accompanied by descriptions of simple experiments. The reader can easily perform these experiments at home, and the required reagents and equipment can either be found at home or purchased at a pharmacy. The author for instance suggests you an ordinary glass instead of a laboratory beaker. Only a few of the more involved experiments will require a special equipment or relatively rare chemicals. These experiments should be done at school in the chemistry laboratory. The work of a chemist is not simply the manipulation of reagents, flasks, and test tubes. Experimental results are often used as the basis for complex mathematical calculations, after which a final conclusion is made. Finally, modern chemistry has a fundamental theory based on quantum mechanics. Some of the principles by which experimental data are processed are considered and the reader will see how the properties of unstudied substances can be predicted. By carrying out simple calculations, the reader will discover that the *s* orbital is spherical, and the *p* orbital is a dumbbell. Models of molecular orbitals made from plasticine and wire will help the reader understand why certain reactions can occur, while the others are impossible. Thus, the goal of this book is to make the material about chemistry and its problems more understandable.

The book is not intended for reading in a bus or in bed before sleeping. Before you start reading it, you should have certain reagents and utensils. However, you can omit the experiments and simply read their description, but a pencil and a sheet of paper will be necessary, because in order to understand many simulations, a graph should be plotted or a structural formula written out or some mathematical calculations made.

Far from all the branches of chemistry are covered within this small book; but another reason is that many fields of chemistry cannot be considered because the corresponding experiments cannot be described. For example, radiation chemistry requires radioactive sources, which are dangerous, while many organometallic compounds are not domestically available. Nevertheless, the book touches upon many fields of chemistry, such as inorganic, organic, physical, colloid, biological, analytical and stereochemistry branches. Separate sections are devoted to important compounds such as proteins, carbohydrates, dyes, and pharmaceuticals. Certain types of chemical reactions illustrated in the book involve the latest achievements of chemistry.

G.B. Shul'pin is a Candidate of Chemical Sciences and works at the Moscow Institute of Chemical Physics (USSR Academy of Sciences). His main interests are the chemistries of organic, metallocomplex and organometallic compounds, and homogeneous catalysis.

The book will be of interest to anyone who wants a better understanding of the main concepts of chemistry and is mainly intended for senior pupils and chemistry teachers.

A. E. Shilov, Corresponding Member of the USSR Academy of Sciences

Chemistry: the Science of Molecular Transformations

What is the focus of modern chemistry? At first glance, the answer to this question seems quite simple. Indeed, chemistry deals with substances and their transformations. But let us analyze this statement. First, a few words about substances that are encountered. Take, for example, aluminium hydroxide and basic copper carbonate. These substances are of interest to geologists, because they are the main components of the minerals bauxite and malachite, respectively. Bauxite is used to obtain aluminium, while malachite is a good material for masonry work. Substances such as penicillin and haemoglobin are of interest not only to chemists but also to physicians and biologists. Second, what kind of transformations do substances undergo? Ice transforms into water, helium I transforms into superfluid helium II. These transformations have nothing to do with chemistry: they are the focus of physics, because the melting point of a substance is a physical property.

So what is then a chemical property? It is the ability of a substance to react with another substance. A chemical reaction is the transformation of one molecule into another. During chemical transformations, only molecules (which consist of atoms) are destroyed, while the atoms themselves remain unchanged. Transformations of atoms are studied by physics, or, more precisely, atomic and nuclear physics. We have already mentioned that physics also studies transformations in which neither atoms nor molecules are destroyed. So, it looks like physics borders chemistry on two sides, i.e. "below" (atomic level) and "above" (permolecular level).

Two comments should be made. The first concerns the fact that modern chemists are becoming less and less interested in the nonexcited state of a substance, in its composition and structure. Of course, unsolved problems in this field still remain, but their solution is within the physicist's scope of interest. And second, branches intermediate to physics and chemistry exist: when chemical processes are studied by physicists, and, conversely, when chemists investigate physical phenomena. For instance, a chemical process, i.e. interaction of two or several molecules, can be interpreted from the physical viewpoint. A branch of science that studies the physical parameters of chemical transformations is called chemical physics. On the other hand, the physical properties of molecular clusters in a solution called a colloidal solution are investigated in colloid chemistry, a branch of physical chemistry.

Both chemical physics and physical chemistry deal with the properties of all types of substances. These sciences are classified according to the techniques used to initiate chemical reactions (e.g. electrochemistry, photochemistry, and radiation chemistry), or according to the investigation methods employed (e.g. magnetic or optical spectroscopy, and kinetic methods).

There is also another classification of the chemical sciences, which distinguishes between types of substances. All substances are divided into either inorganic or organic ones. Organic compounds are various hydrocarbon derivatives, all of them containing carbon atoms. Molecules of inorganic compounds may include any other elements in different combinations. Carbon atoms possess the peculiar feature of combining into chains, rings, and other configurations, so that one molecule may contain a hundred carbon atoms. It is therefore not surprising that the number of compounds comprising carbon atoms is much greater than the number of inorganic compounds. Organic compounds form the basis of living organisms, and a science that deals with the substances and processes occurring in organisms is called biochemistry. Recent years have seen the appearance of one more new branch of chemistry, i.e. bioorganic chemistry, which deals with the organic reactions proceeding in a cell. Ions of various metals can bind to organic molecules in a living organism to form enzymes (biological catalysts), haemoglobin (the carrier of oxygen), and other important substances. These are the compounds studied in bioinorganic chemistry, a science which appeared a few years ago. There are also other branches of chemistry related to biology, medicine, and agriculture, e.g. pharmaceutical, toxicological, and agricultural chemistries. It is also necessary to mention here a chemistry of high-molecular compounds (polymers). Molecules of these compounds, both organic and inorganic, consist of a large and indefinite number of identical units.

We have briefly informed the reader about the focus of chemistry and the relationship between chemistry and physics. It should be noted, however, that scientists have not yet arrived at a general conclusion on what should be considered the focus of chemistry. Only a few (far from all) branches of modern chemistry were mentioned here; other chemical branches, and the most important chemical concepts, substances and techniques employed in chemistry will be discussed further on.

The Rate of Chemical Transformations

A great number of chemical reactions are known that differ in reacting substances, reaction phase (gaseous phase, liquid, or at the phase interface), and in the heat effect (absorption or evolution of heat during the reaction). In addition, there is another parameter that distinguishes one reaction from another.

...A rifleman pulls the trigger of a rifle, the gunpowder in the cartridge catches fire, and the formed gases push the bullet out of the barrel. The chemical reaction between the components of the gunpowder occurred within fractions of a second. Another type of reaction is the conversion of wood—trunks of dead trees—into coal. This chemical process requires millions of years for its completion. Thus, chemical reactions differ in their rates. But how does one define the rate of a chemical reaction?

First, the velocity of a moving body should probably be defined. It is the path covered by the body divided by the time required by the body to cover this path. Certainly, this division yields the average velocity of the body over this path. In order to determine the instantaneous velocity at a given moment, the time interval over which the velocity is measured should be reduced as much as possible, i.e. it should approach zero. In this case, the velocity will be expressed mathematically as the derivative of the path with respect to time.

Now, imagine that a team of masons are building a brick house. How can one determine the velocity of the building process? One of the ways is to determine the velocity of "disappearance" of the bricks reserved for building. By dividing the total number of bricks by the time spent on building, one can find the average velocity. But the actual velocity varied over time: at first it was high, but then the workers had to carry bricks to higher floors, and the velocity decreased somewhat. The velocity of construction at a given moment can be found by dividing the number of bricks layed just before, and right after, this moment by the time that elapsed between these two moments, and then by making this time interval approach zero.

The same technique is employed in chemistry when determining the rate of a chemical reaction; the only difference is that reacting molecules are counted instead of bricks. But since it is difficult to count molecules at each moment, scientists determine the concentration of substances, i.e. some great number of molecules per unit volume. When determining the rate of a chemical reaction, the concentration of a reacting substance at the initial moment t_1 is determined (let it be c_1), and then the concentration of this reagent is measured at time t_2 (it turns out to be c_2). The difference between the concentrations, $c_2 - c_1 = \Delta c$, is divided by the time interval, $t_2 - t_1 = \Delta t$, and then this interval is made approach zero. The reaction rate W is written as follows:

$$W = -\lim \frac{\Delta c}{\Delta t} = -\frac{dc}{dt} \quad (\text{as } \Delta t \to 0)$$

The expression dc/dt denotes the derivative of concentration with respect to time; a minus sign is placed before the expression to make the rate positive (because the value c_2 is less than c_1).

What does the rate of a chemical reaction depend on? Let's perform an experiment. It is known that sodium thiosulphate reacts with acetic acid to produce colloidal sulphur, which separates in the form of a white opalescent precipitate. The reaction equation is

$$Na_2S_2O_3 + 2CH_3COOH = H_2O + SO_2\uparrow + S\downarrow + 2CH_3COONa$$

Dissolve two teaspoons of sodium thiosulphate (also known as hyposulphite and widely used in photography as a fixing agent) in a glass of water at room temperature. Then, pour this solution into each of four empty glasses: 2 teaspoons of the solution into the first glass; 4 teaspoons into the second; 8 teaspoons into the third; and

16 teaspoons into the fourth glass. Add water to the first three glasses so that the volume of the solution in each of them equals the volume of the solution in the fourth glass. You have prepared four solutions with different concentrations. The concentration of the second solution is twice that of the first solution; the concentration of the third solution is four times greater than that of the first solution and two times greater than the concentration of the second solution. Quickly add a teaspoon of acetic acid to the first solution and record the time that elapses between the moment the solutions are mixed and the moment the turbidity appears. The mixture should be stirred with a spoon during the reaction. Assume that 90 seconds passed until the turbidity appeared. Add a teaspoon of acetic acid to each of the remaining solutions in sequence and record the time when the turbidity forms in these solutions. Assume that it was 40 seconds for the second glass, 22 seconds for the third, and 12 seconds for the fourth. Now take a sheet of graph paper and plot the time history of thiosulphate concentration. Plot the concentration (expressed in teaspoons of the initial solution) along the x-axis, and the time elapsed t_s (in seconds) along the y-axis. A curve drawn through the four points has the form of a hyperbola, and the latter is a graphic representation of an inversely

proportional function. Therefore, if you plot the value that is inverse to time t_s (instead of t_s itself) along the y-axis the experimental points will lie along a straight line passing through the origin. But the inverse of time t_s is proportional to the reaction rate at the initial moment, i.e. $W \sim 1/t_s$. Hence, the greater the concentration of a reacting substance, the greater is the reaction rate. Generally, the reaction rate is described by the following equation:

$$W = kc_A^a c_B^b$$

Here k is the proportionality factor: it does not depend on the concentrations of the reactants and is called the rate constant of a chemical reaction; c_A and c_B are the concentrations of reactants A and B; a and b are, simultaneously, the exponents at c and the coefficients showing the number of A and B molecules involved in the reaction. It is clear that the reaction rate decreases as the reactants are used up. Recall also the previous example with masons, where the velocity of construction decreased with time. However, this analogy is not accurate enough.

The phenomenon under consideration can be illustrated more accurately using a billiard game as an example. First, assume that a chemical reaction occurs between two molecules only when they collide. Then, suppose we have two types of molecules, which are represented by white and black balls. The molecules are in constant thermal motion: we will hit the balls in any sequence or direction along the table. When the white and the black ball collide, they will be removed from the table, i.e. the reaction has occurred, and the molecules of reactants have transformed into the molecules of reaction products. Now, imagine that there are 100 white balls and 100 black balls on the table. It is obvious that they will frequently collide and will immediately be removed from the table. A different situation will happen when only one white ball and one black ball remain on the table: you will have to drive them for a good deal of time before they collide. Now it becomes clear why the reaction proceeds slowly when the concentrations of reactants are low.

The billiard game example gives the answer to the question why the equation for the reaction rate contains the product of concentrations instead of their sum. It was already mentioned that for the reaction to occur, two reacting particles must collide, i.e. they must be at the same place in a reaction mixture at the same time. The probability that a molecule of a given reactant will be at a given place is proportional to the reactant concentration. On the other hand, the probability that two molecules will simultaneously arrive at the same place is equal to the product of probabilities of meeting a molecule of each reactant at this place, i.e. it is proportional to the product of reactant concentrations.

Let us consider other parameters that affect the reaction rate. Dissolve two teaspoons of sodium thiosulphate in a half glass of water. Pour two teaspoons of the solution into each of four empty glasses. Dilute the solutions with water to half a glass. Add a teaspoon of acetic acid (vinegar essence) to the first solution, which is at room temperature (about 20°C, measure the temperature with a thermometer). Record the time it takes for the turbidity to appear (constantly stir the solution). Assume that the time is 75 seconds. Now heat the second solution to 30°C, repeat the above procedure, and record the time of turbidity formation. You will see that the time has been reduced by half (in our case it has been reduced to 35 seconds). At 40°C, the turbidity appears in 20 seconds; and at 50°C, in 10 seconds.

Try to process the results mathematically. If you construct a graph by plotting the temperature and the reaction time along the corresponding axes, you will obtain a curve whose physical meaning is difficult to understand. But if you plot the inverse to the absolute temperature along the x-axis (this quantity is equal to $1/T$, where $T = 273 + t$°C, and t°C is the temperature measured in degrees centigrade) and the natural logarithm of the reaction rate along the y-axis, the experimental points will fall in a straight line. (Natural logarithms can be found in reference tables or calculated on calculators.) The straight line is described by the mathematical equation

$$\ln t_s = b/T + a$$

where a and b are constants. The equation can be transformed into

$$t_s = a_1 e^{b/T}$$

where e is the base of the natural logarithm, and $a_1 = e^a$.

The reaction time t_s is inversely proportional to the reaction rate constant k. Taking this into account, the expression for k can be rewritten as follows:

$$k = Ae^{-b/T}$$

Here A is a new constant for the given reaction.

It is obvious that the molecules interact only when they collide. Experiments demonstrate, however, that not every collision results in a reaction. The reaction proceeds only when the energy of the colliding molecules is not less than a certain quantity E_a, which is specific for each reaction. If E_a and the absolute temperature T of the reaction mixture are known, one can calculate the number of molecules n that enter into a reaction upon colliding. This number is determined via the exponent:

$$n = Ne^{-E_a/RT}$$

where N is the total number of molecules, and R is the universal gas constant. It is not far from here to the famous Arrhenius equation, which relates the reaction rate constant to the temperature:

$$k = Pze^{-E_a/RT}$$

Here z is the number of collisions between reacting molecules per second; P is a factor that shows that the reaction occurs only when specific convenient sites of the molecules collide (P is always less than unity). We can easily arrive at the equation for the rate constant derived from the experimental observation if we assume that $Pz = A$ and $E_a/R = b$. If we determine the reaction rate constant for several temperatures, we can calculate from the Arrhenius equation the value of E_a called the reaction activation energy. The value E_a is found graphically in the following way; we plot $1/T$ along the x-axis and the logarithm of the reaction rate constant along the y-axis. The slope of the straight line obtained is equal to E_a/R. Note that the activation energy is an important characteristic of a reaction; the less the activation energy, the more readily the reaction occurs.

Up to this point, we have been discussing reactions that proceed to the end, i.e. reactions that during a certain period of time completely transform initial substances A and B into substances D and E (although, theoretically, for the reaction to be completely accomplished, a large amount of time is required). Reactions are known, however, where substances D and E can also react to produce substances A and B. These reactions are called reversible and can be expressed by the general equation

$$a\mathrm{A} + b\mathrm{B} \rightleftarrows d\mathrm{D} + e\mathrm{E}$$

Imagine that we have poured together solutions of substances A and B; a reaction has started whose rate is $W_1 = k_1 c_A^a c_B^b$. In the course of the reaction, substances A and B are being used up, and their concentrations decrease; hence, the reaction slows down. On the other hand, substances D and E begin to form, and their concentrations increase. As a result, the reaction between D and E, whose rate is $W_{-1} = k_{-1} c_D^d c_E^e$, accelerates. Finally, the reaction arrives at equilibrium, which is characterized by a constant K (in this case $W_1 = W_{-1}$). The value of K is equal to the ratio of the reaction constants of the forward and reverse reactions:

$$K = \frac{k_1}{k_{-1}} = \frac{c_D^d c_E^e}{c_A^a c_B^b}$$

Mix dilute solutions of iron(III) chloride and ammonium thiocyanate in a glass. Pour the resulting blood-stained solution into each of three empty glasses (keep a certain amount of the solution as a reference). Add a saturated solution of iron(III) chloride to the first glass, a saturated solution of ammonium thiocyanate to the second, and a saturated solution of ammonium chloride to the third. You will notice that the colour of the solutions in the first two glasses becomes more intense (compare it with the colour of the reference solution), while that of the third solution becomes pale. How can the observed changes be explained? The reaction equation is

$$FeCl_3 + 3NH_4SCN \rightleftarrows Fe(SCN)_3 + 3NH_4Cl$$

The equilibrium constant for the reaction is written as

$$K = \frac{[Fe(SCN)_3][NH_4Cl]^3}{[FeCl_3][NH_4SCN]^3}$$

The brackets denote the concentrations of these substances c. The quantity K is constant, therefore when the concentration of $FeCl_3$ (in the first glass) is increased, the equilibrium is shifted to the right, and the concentration of $Fe(SCN)_3$ increases as well. The colour intensity is determined by the concentration of iron thiocyanate $Fe(SCN)_3$. When ammonium chloride is added, the equilibrium shifts to the left, and the concentration of the coloured substance $Fe(SCN)_3$ decreases. We will later return to this reaction which makes it possible to identify iron ions and determine their concentration in a solution. Now, let us make some conclusions. We have briefly considered a field of chemistry that is concerned with the rates of chemical reactions and is called chemical kinetics. You can read about chemical kinetics in books on physical chemistry and popular-science books.

About Catalysis

We now start with an experiment. Mix ethyl alcohol and vinegar essence in a glass or a test tube, and heat in a pan with boiling water. It is known that alcohol can react with organic acid to form an ester, which has a distinct fruity odour. But you will not smell the odour of the ethyl acetate which is supposed to be the product. Now, add a drop of sulphuric acid to the mixture and heat again. Soon you'll smell the pleasant odour of the ethyl acetate. So, what is the role of sulphuric acid in this reaction?

Sulphuric acid is a catalyst for ethyl acetate formation. The reaction can proceed without the catalyst as well, but it will occur at a very slow rate. Modern science defines catalysts as substances that greatly accelerate chemical reactions; catalysts interact with the reactants and intermediates many times during a reaction cycle, but at the end of the reaction, they are recovered in their initial form. This is an intricate, interesting, and very important phenomenon.

How does a reaction proceed? Consider the following example: substance AB (A and B are components of the molecule) reacts with compound XY to form intermediates BX and AY and products AX and BY. In other words, the molecules exchange their components, as it were. Let us construct a graph, in which the distances between the atoms of interacting molecules expressed in conventional units are plotted along the x-axis (this axis is called the coordinate of a reaction, i.e. its path). The energy of particles is plotted along the y-axis. The left part of the graph describes the state of a system when the distances between A and B in substance AB and between X and Y in XY are small, while the distances between the atoms in substances AX, BX, AY, and BY are large (Fig. 1). This means that only molecules of AB and XY are present in the system. These molecules have a potential energy E_1. The right part of the graph describes the state of the

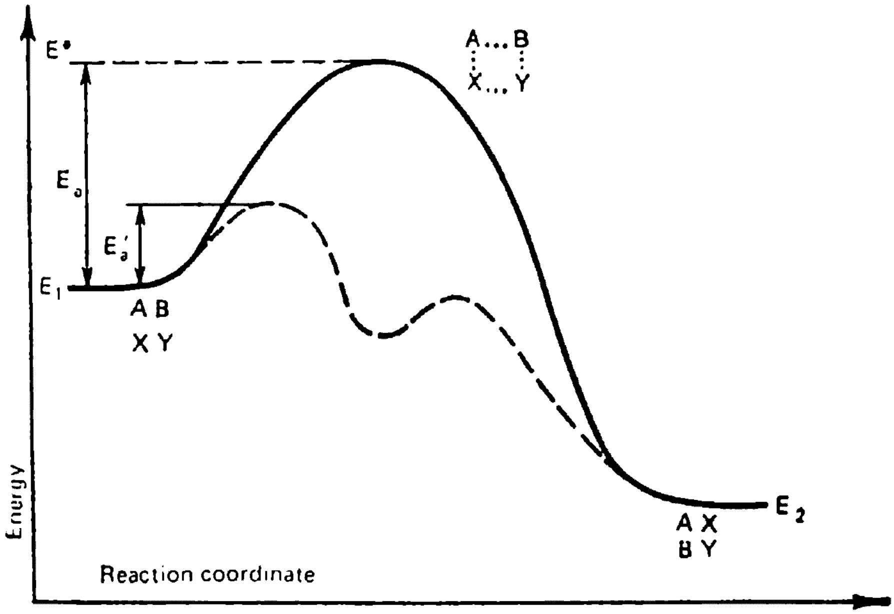


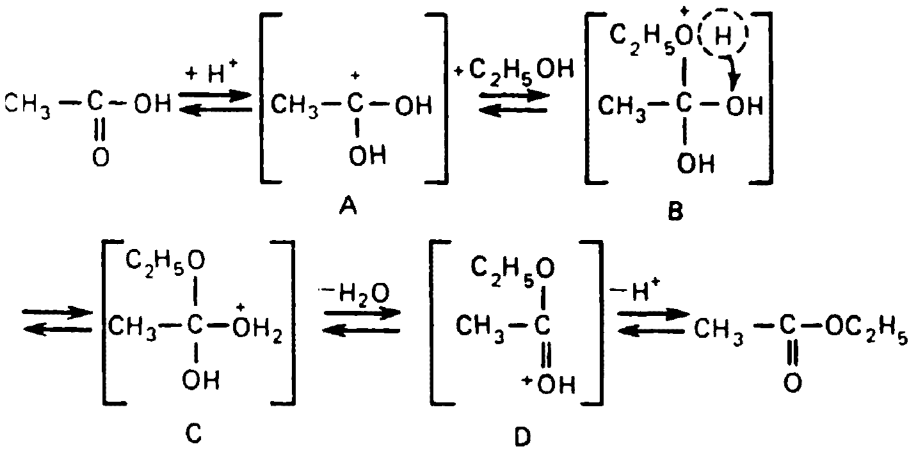
Fig. 1 Energy diagram for a reaction between AB and XY molecules. The change in the energy along the reaction path in the case of a catalytic process is shown by a dash line. E_a' is the activation energy of a reaction being catalyzed

system, which consists of molecules AX and BY. These substances are characterized by energy E_2. Let $E_2 < E_1$, then the state with energy E_2 is more advantageous, and when the substances AB and XY are mixed, they tend to transform into AX and BY.

It can be seen from Fig. 1 that two plateaux (horizontal portions of the graph) corresponding to energies E_1 and E_2 are at opposite sides relative to energy peak E^*. When the distances between atoms of the reacting molecules are intermediate, the so-called transitional state is formed, in which all the four component parts A, B, X, and Y are simultaneously bound. Therefore, the maximal energy E^* corresponds to this transitional state. For the reaction to occur, the system must overcome the energy barrier, and the molecules must acquire additional energy, which is called activation energy $E_a = E^* - E_1$. The rate of the reaction depends on the activation energy: the lower the activation energy, the faster the reaction proceeds. Recall the exponential equation relating E_a with the reaction rate constant k. When the activation energy is very high, the molecules cannot overcome the energy barrier, and the reaction virtually does not proceed.

What does a catalyst do? It interferes with the process and forms an intermediate complex with the initial substances. In this case the energy barrier to be surmounted is not so high. The products are formed when one more low barrier is surmounted. Hence, the reaction proceeds much faster when the catalyst is present.

Let us return to the experiment on the esterification of alcohol with acid. This reaction proceeds in several stages. The first stage is the attachment of a proton H^+ of the sulphuric acid to the carbonyl oxygen in a molecule of acetic acid. As a result, an intermediate compound is formed, which is designated below by letter A (unstable compounds will be enclosed in brackets). The molecule of ethyl alcohol combines with the central carbon atom of the intermediate compound A and transforms into substance B. The driving force for this transformation is the interaction between the positive charge on the carbon atom in the acid and a free electron pair of the oxygen atom in the alcohol. Next, the proton jumps onto another oxygen atom to form complex C. After this, a molecule of water detaches from C, and the process terminates in the separation of a proton from compound D and the formation of an ethyl acetate molecule



It can be seen that the proton that entered into chemical transformations at the first stage was recovered intact at the last stage. Therefore, we can say that this reaction is a catalytic one. It is characteristic of such reactions that the amount of a catalyst participating in them is much less than is required by the reaction equations, or, more precisely, by the equations of any stage. Indeed, the proton that united the acid molecule and the alcohol molecule immediately begins to cross-link another pair of molecules.

There are two types of catalysis. When the catalyst and the reactants involved in a reaction are in different aggregate states (for example, a reaction between gases in the presence of a solid catalyst), heterogeneous catalysis is distinguished. It is heterogeneous catalysis that is used in important chemical transformations of petroleum hydrocarbons. Metals or metal oxides are used as catalysts in such reactions. Owing to heterogeneous catalysis, ammonia is now produced from nitrogen and hydrogen on a large scale.

Liquid catalysts can be used as well. Mix aluminium powder with iodine crystals on a metal plate, and carefully add a drop of water to the mixture. Aluminium vigorously combines with iodine, and the reaction is attended by a flash. This is an example of the catalytic production of a chemical compound from two simple substances. Now perform an experiment demonstrating the catalytic decomposition of a compound. Place a pinch of manganese dioxide (this black powder can easily be obtained by pouring together solutions of potassium permanganate and manganese(II) chloride) in a test tube and carefully add hydrogen peroxide solution. The hydrogen peroxide begins to decompose violently, and oxygen is evolved. The latter can be detected by introducing a smouldering splinter into the test tube; the splinter will ignite.

This time we will decompose hydrogen peroxide in the presence of a catalyst, which, like the reactant, is a solution. This type of catalysis is called homogeneous. Pour a bright yellow aqueous solution of potassium chromate in a glass and add a few drops of hydrogen peroxide. The solution turns violet (the colour of the intermediates), and oxygen bubbles are evolved. Decomposition of hydrogen peroxide can also be accelerated by iron ions. This is a complex process, which occurs in several stages. During the first stage, a reactive hydroxyl radical is formed, which has one unpaired electron:

$$F^{2+} + H_2O_2 \rightarrow F^{3+} + OH^- + OH^\bullet$$

This radical reacts with another molecule of hydrogen peroxide, and a new radical is formed:

$$OH^\bullet + H_2O_2 \rightarrow H_2O + HO_2^\bullet$$

which decomposes into a proton and oxygen anion-radical

$$HO_2^\bullet \rightleftarrows H^+ + O_2^{-\bullet}$$

The latter interacts with iron(III) ion, reduces it, and then itself turns into a molecule of oxygen:

$Fe^{3+} + O_2^{-\bullet} \rightarrow Fe^{2+} + O_2$

Today scientists are interested in unusual catalytic processes, in which the concentration of one form of the catalyst varies in the course of the reaction. Such reactions became known not long ago. Nevertheless, before we begin to discuss these unusual phenomena, let us return to the ABCs of chemical kinetics, and analyze the chemical transformation of substance A into substance B. At the initial moment, a chemist has a 100% amount of pure substance A. When the substance is heated, it begins to transform into product B. If we represent this process graphically by plotting the reaction time along the x-axis and the amount x (in per cent, or concentration) of substance A and product B along the y-axis, two curves will be obtained. The curve that corresponds to the content of A will smoothly fall from 100% at the initial moment to 0% at infinite time. The curve for product B will be a mirror image of curve A, i.e. it will rise from 0% at $t = 0$ to 100% at $t = \infty$. The amount of A at time t can be found by a formula that includes the exponential relationship we have already discussed:

$x_A = 100e^{-kt}$

where k is the reaction rate constant.

However, the reaction may also proceed as follows: when more and more molecules of A are transformed into B, the reverse process can occur, i.e. molecules of B transform into A. Finally, after a long time, the system arrives at equilibrium. For example, when the reaction mixture at equilibrium contains 75% of B and 25% of A, the kinetic curves of the process have the shape shown in Fig. 2*a*. A multitude of reactions are known whose mechanisms are much more involved, e.g. substance A can transform into substance B at a certain rate (determined by constant k_{AB}), while substance B, in turn, transforms into compound C (rate constant k_{BC}):

$$A \xrightarrow{k_{AB}} B \xrightarrow{k_{BC}} C$$

Let us analyze the kinetic curves of accumulation and consumption of all substances in this process. The curve for substance A is similar to that in the previous example, because this substance is "indifferent" to the fact that B will then transform into C. The amount of B will first increase, reach its maximum, and then decrease (Fig. 2*b*). Why is this so? Because when the amount of B is low, the rate of its transformation into C is also low (the greater the amount of a given substance, the higher is the rate). The rate of transformation is determined graphically by the slope of the curve: the higher the reaction rate at a given moment, the steeper the curve is relative to the x-axis. Naturally, when a small amount of B is spent, a small

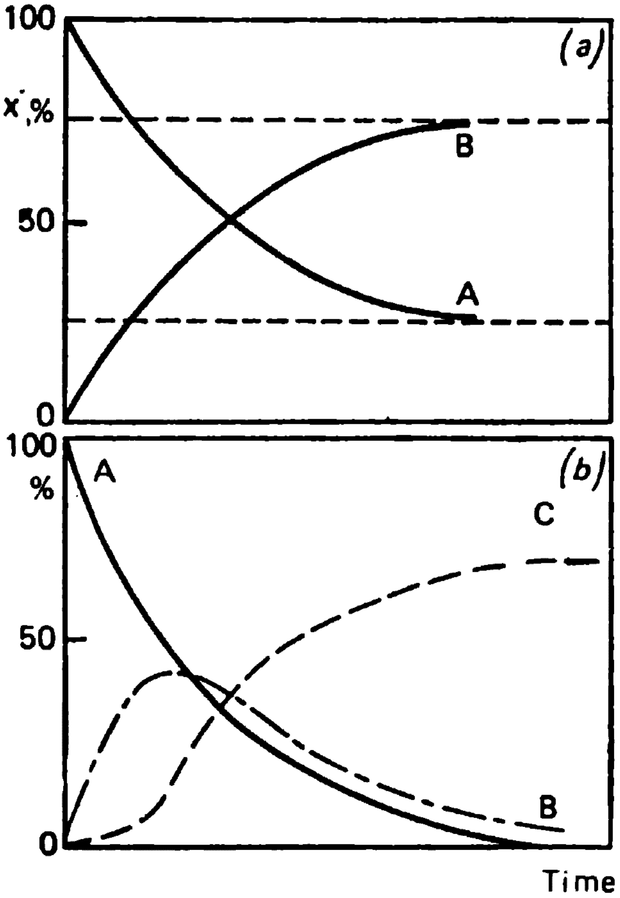


Fig. 2 Kinetic curves for reactions: *a*—transformation of A into B in the case of a reversible process; *b*—consecutive transformation of A into B and of B into C

amount of C is accumulated. Then the situation changes, and the rate formation of C grows. But this growth cannot be infinite, because the reserves of A and B run out. Thus, the rate of formation of C decreases with time and the kinetic curve of accumulation of C has an S-shape. It is easy to guess that the total amount of substances A, B, and C at each moment t equals 100%.

Of course, in various chemical reactions following the A → B → C scheme, different stages have different values of k_{AB} and k_{BC}. As a result, the shapes of the accumulation curves for the intermediate B will be different for various reactions, all of them having a single maximum. But still, is it possible to have a reaction for which there will be several concentration maxima of intermediate substances? For a long time scientists were unaware of such reactions, and many of them believed they could not exist at all. Only at the beginning of the 1950s did the Soviet biochemist B.P. Belousov discover the first reaction in which the concentrations of the intermediates periodically changed many times over the course of the reaction. Some of these intermediates are catalysts of the transformation of the initial substance into a product.

If you dissolve citric acid (2.0 g), cerium(IV) sulphate (0.16 g), potassium bromate (0.2 g), and 2 ml of dilute sulphuric acid (take the concentrated acid and dilute it three times) in water to a volume of 10 ml, the solution will periodically (every 1-2 min) change its colour, alternating between a yellow and a colourless solution. The point is that yellow cerium(IV) sulphate periodically transforms into colourless Ce^{3+} ion. The mechanisms of these oscillating reactions were thoroughly studied by the Soviet physicist A.M. Zhabotinskii, and today these processes are widely known as Belousov-Zhabotinskii reactions. It would not be difficult to perform the first of these reactions at home, but for the lack of potassium bromate and cerium sulphate, which are not accessible chemical reagents. We had better take another reaction of this type, where only cobalt acetate and benzaldehyde are required, which are relatively difficult to obtain, but can be found in a school chemical laboratory.

Prepare two initial solutions. The first solution is made as follows: dissolve 0.3 g of $Co(OCOCH_3)_2 \cdot 4H_2O$ in acetic acid diluted with water (to 40 ml of anhydrous glacial acid add 10 ml of water; 50 ml of vinegar essence can be used instead of the glacial acid). For the second solution: dissolve 0.03 g of NaBr (it can be replaced by KBr, which is used in photography) in 10 ml of 90% acetic acid (or in 10 ml of vinegar essence). Mix the resulting solutions in a glass and heat the latter in a pan with water to 70°C (on an electric stove). The solution should continuously be stirred with a glass rod or teaspoon, but it is even better to use a mechanical stirrer (a motor from a sewing machine or toy will do). Air should be blown through the solution, for which purpose a hair dryer can be used. The stream of air from the dryer is directed via a glass (or rubber) tube into the solution. Now, add 5 ml of benzaldehyde and, while maintaining the temperature 70°C, vigorously stir the solution while blowing air through it. In a few seconds (or minutes), the colour of the solution will change from pink to dark brown, but after a few minutes the solution will again turn light pink. The colour will continue to change in this way for hours.

The explanation is that the concentration of Co^{3+} varies during the reaction: it either increases (when the solution turns dark brown) or decreases, because Co^{3+} transforms into Co^{2+} (the solution becomes pink). In this process, cobalt is a catalyst in the oxidation of benzaldehyde by the oxygen in the air. In the first stage, Co^{2+} is oxidized by oxygen to Co^{3+}. The latter reacts with benzaldehyde, as a result of which Co^{2+} is again produced, in addition to benzoyl radical:

$$Co^{3+} + C_6H_5CHO \rightarrow Co^{2+} + C_6H_5\dot{C}O + H^+$$

This radical reacts with oxygen:

$$C_6H_5\dot{C}O + O_2 \rightarrow C_6H_5CO_3^{\bullet}$$

$$C_6H_5CO_3^{\bullet} + C_6H_5CHO \rightarrow C_6H_5CO_3H + C_6H_5\dot{C}O$$

to produce perbenzoic acid $C_6H_5CO_3H$ and a new benzoyl radical. Next perbenzoic acid oxidizes Co^{2+}:

$$Co^{2+} + C_6H_5CO_3H \rightarrow Co^{3+} + C_6H_5CO_2^{\bullet} + OH^-$$

All these reactions are intricately combined in time and ensure a constant fluctuation of Co^{3+} and Co^{2+} concentrations.

How Much Iron Is There in Tap Water?

The external appearance of a compound frequently does not reveal anything about the elements it contains. But sometimes, one or two chemical reactions are enough to detect certain elements in this compound. Qualitative and quantitative determinations of elements in chemical compounds are the focus of analytical chemistry. Of course, not all the reactions used by analysts to establish the chemical composition of a compound can be performed at home or in a school laboratory. But there are chemical transformations that do not require special equipment or unobtainable reagents. Let us consider what the specific reactions of elements are that are used to identify them. We will look through the "visiting cards" of elements in accordance with their "registration" in the Mendeleev periodic table.

Group I includes alkali metals, and it is rather difficult to detect them in a compound by chemical methods, because alkali metals neither give colour reactions nor produce precipitates. However, they can be accurately identified by spectral methods.

Bend a nichrome wire to form a loop at one end and immerse it into hydrochloric acid. Then heat the loop in the flame of a gas burner until the flame is colourless. Touch the hot loop to some table salt and introduce the attached salt crystals into the flame again. A bright yellow colour of the flame identifies sodium ions in the table salt.

It is known that light of a certain colour has a definite energy. For example, the energy of violet or blue light is greater than the energy of red or yellow light. Sunlight contains rays with different energies, therefore when transmitted through a glass prism, sunlight is resolved into a continuous rainbow, in which one colour is followed by another one. A different picture will result when the light of the flame coloured by the table salt is transmitted through a prism: only one yellow line will be observed, which corresponds to a wavelength of 0.589 μm. The high temperature of the flame causes the outer electron in the sodium atom to go to the higher energy level. This state is not advantageous for the atom, and therefore the electron does not remain in this high-energy level for a long time, but returns to the lower energy level. This process is attended by the emission of energy in the form of light, whose wavelength corresponds to that of yellow light.

The spectra of the rest of the alkali metals are more complex. Lithium, for example, colours the flame red; potassium, rubidium, and cesium impart various shades of lilac. It is interesting to note that the last two elements were discovered by the spectral method and named after the characteristic spectral lines (from the Latin *rubidus*, meaning dark red, and *caesius*, meaning bluish-gray).

In addition to alkali elements, Group I includes copper, silver, and gold, which differ in their properties from alkali elements. It is not difficult to identify these metals in chemical compounds. Salts of divalent copper are usually blue in colour, and when ammonium hydroxide is added to them, blue-violet amines are formed. Another specific reaction for divalent copper is described below.

Add 2 or 3 drops of sulphuric acid and a few crystals of sodium thiosulphate to a test tube containing several drops of blue vitriol. Heat the test tube over a gas burner and observe the precipitation of brown monovalent copper sulphide. Copper is an inactive metal and can easily be replaced by iron or zinc from its salts. If an iron nail is placed into a solution of copper salt, a red deposit from the displaced copper is formed on it. Salts formed by copper and halogens colour the flame green. Silver also has specific reactions: silver salts react with alkali to form a brown precipitate of silver oxide, and when sodium chloride is added to a silver salt, white silver chloride precipitates.

The metals of Group II, i.e. beryllium, magnesium, zinc, and cadmium, are identified with difficulty. They neither give colour reactions nor do they colour the flame. However, other elements of the group, i.e. calcium, strontium, and barium, can easily be differentiated from the rest. When sulphuric acid is added to their salts, white sulphates precipitate, but when the salts are treated with soda or potash, white precipitates of carbonates are formed, which are soluble in dilute acids. Chalk—calcium carbonate—dissolves in acids with the evolution of carbon dioxide bubbles. All the three elements impart different colours to the flame: calcium imparts a brick-red colour; strontium, a carmine-red; and barium, a yellow-green colour. Mercury, which also belongs to this group, can be identified in the following way. Take a copper plate, clean it with emery paper and immerse it in a nitric acid solution for a while. Then, put the plate in a solution of mercury salt: within a few minutes the plate will be covered by metallic mercury. Be careful, since mercury and its salts are very poisonous.

Now, let us consider some representatives of Group III, starting with boron. To prove its presence in boric acid or in borax, mix a few crystals of the substance under investigation with a teaspoon of ethyl ether on a glass slide and add 2 or 3 drops of concentrated sulphuric acid. Set fire to the mixture and observe the green flame of the ethyl borate that was formed. As for aluminium salts, they do not have specific colour reactions, but it is not difficult to distinguish metallic aluminium from other metals. You can perform several experiments with aluminium on your own. Place an aluminium plate or wire in a glass with hydrochloric acid: very soon hydrogen bubbles will evolve. Then, remove the plate from the acid, rinse it with water and place in a glass with concentrated nitric acid for a short time. Again rinse the plate with water and put it back in the glass with hydrochloric acid. You will note that this time hydrogen does not evolve. The fact is that aluminium is passivated with concentrated nitric acid. The second experiment is the following: pour dilute sulphuric acid into a glass, drop a piece of aluminium into it and add concentrated potassium permanganate solution. The violet colour of the solution will fade away. Now comes the last test. Pour alkali solution into a test tube containing a piece of aluminium. The latter will dissolve in the alkali.

The most important and interesting element of Group IV is carbon. Salts of carbonic acid—carbonates—are inorganic derivatives of carbon, and are frequently encountered in nature. They can easily be identified. Apply a drop of acetic acid to a piece of chalk; bubbles of carbon dioxide are formed. Pure carbon is formed when organic compounds are burned or charred. For example, you can heat a piece of sugar until it becomes black and charred. However, there is another way you can obtain pure carbon from organic substances, i.e. by treating them with concentrated sulphuric acid. When sugar or filter paper is wetted with concentrated H_2SO_4, they become black as well. Another important element of Group IV—silicon—must be mentioned. Silicon compounds are widely used in the household in the form of ordinary glass. Among the soluble compounds of silicon, sodium and potassium silicates are the most available. They are called soluble glasses and are used as glues. When dilute acids (e.g. sulphuric acid) are added to a silicate solution, a precipitate of silicic acids is formed. Silicate glue solution reacts with barium chloride to give a white precipitate of barium silicate. Silicic acid is a weak acid; aqueous solutions of its salts are hydrolyzed and react alkaline. That is why silicate glue is slippery to the touch.

Among the elements of Group V there are two highly important elements, i.e. nitrogen and phosphorus. They are frequently found in inorganic acids. The anion of nitric acid, NO_3^-, can be detected by two reactions. Put a few drops of potassium or sodium nitrate in a test tube and add the same amount of concentrated sulphuric acid. Then, drop a small piece of copper into the solution and heat the mixture: yellow gas—nitrogen dioxide—evolves from the test tube. The second identification reaction is carried out on a glass slide, to which a drop of saltpeter (potassium nitrate) should be applied. Next, add several crystals of green vitriol (ferrous sulphate heptahydrate) to the drop and add a drop of concentrated sulphuric acid: the brown ring of a complex salt will be formed around the crystal. Now perform two reactions characteristic of the phosphoric acid anion. Pour a solution of a phosphoric acid salt into each of two test tubes. Add a solution of barium chloride to the first test tube and a solution of silver nitrate to the second one. In the first test tube, a white precipitate of barium phosphate will be formed that is soluble in acids (except for sulphuric acid), and in the second test tube, a yellow silver phosphate, Ag_3PO_4, will precipitate that can be dissolved in nitric acid.

Of the elements of Group VI, only sulphur will be considered. Oxygen, which is the best known element of this group, is contained in almost every substance, but it is not easy to detect it. In inorganic compounds, sulphur is mainly found in the anion of sulphuric acid. When mixed with solutions of barium chloride and silver nitrate, sulphuric acid and its salts give white precipitates of barium sulphate and silver sulphate. Barium sulphate does not dissolve in acids, while silver sulphate is soluble in nitric acid.

Silver nitrate is a universal reagent for the salts of halogen acids formed by elements of Group VII: chlorine, bromine, and iodine. If a drop of a table salt (NaCl) is mixed with a drop of silver nitrate on a glass slide, a white curdy precipitate will be formed that is insoluble in acids, but soluble in ammonium hydroxide. In this case, a complex salt will be obtained, which is decomposed by the action of nitric acid with the formation of a white silver chloride precipitate. Potassium bromide reacts with silver nitrate to give a yellow precipitate that is poorly soluble in ammonium hydroxide.

The salts of metals found in Group VIII, i.e. iron, cobalt, and nickel, can be distinguished by their appearance. Compounds of iron(II) are usually coloured green (for example, iron vitriol) while iron(III) compounds are yellow. Cobalt compounds are usually pink in colour, while nickel salts are green. Iron(III) gives a specific reaction with potassium ferrocyanide to yield the blue precipitate of Prussian blue. Blood haemoglobin contains iron, which is detected by this reaction. For this purpose, a drop of blood is evaporated until dry on a porcelain plate, after which 2 or 3 drops of concentrated nitric acid are added and the solution is evaporated again. The plate with the dry residue is cooled, and the latter is transferred onto a glass slide. Then, a few drops of hydrochloric acid and a drop of potassium ferrocyanide are added to the residue. The reader may recall another reagent for iron—ammonium thiocyanate—which yields blood-red iron thiocyanate with iron salts. This reaction can be used both to detect iron and to determine the amount present in a substance.

Now we have come to the concept of quantitative analysis. Physicians, specialists in the food industry, hydrologists, geologists, and metallurgists all need to know not only the qualitative, but also the quantitative composition of a substance, solution, or alloy. Indeed, the content of carbon, or manganese in steel, that of iron, or calcium in water, as well as carbohydrates, or proteins in bread determine the quality of the steel, tap water, and bread, respectively. The main principles of quantitative analysis can be mastered even in a home laboratory using substances that are always at hand. Two devices, however, will be absolutely necessary: a balance for weighing and a graduated cylinder for measuring volumes of liquids. It is not difficult to make a balance using a wire, cardboard, and thread (coins can be used instead of weights). If you fail to obtain a graduated cylinder, you can use a baby bottle. A burette is often used in quantitative analysis, and you can make it yourself. Take a glass tube 2 cm in diameter and heat it near one end with a gas burner. Draw this end out so that it is 7 mm in diameter. Then, take a rubber tubing that is about 7 mm in diameter and 5-10 cm long and insert a glass bead into it (the bead should fit in the tube very tightly). Attach one end of the rubber tubing to the narrow end of the glass tube, making a burette. The other end should be attached to the wide end of an eye dropper. To test the resulting burette for tightness, pour water into it; the water should not leak out. If you press the bead in the rubber tube with your fingers, you can easily measure out the required amount of a liquid. The burette is graduated by pouring in 5-ml portions of water from a graduated cylinder and marking the level of water on the wall of the burette (you can mark the level on a strip of paper attached to the burette). Divide the interval between the neighbouring marks into five sections and draw even smaller divisions. Now you can measure out the volume of a liquid with an accuracy of up to half a millilitre.

Here is a problem that is most frequently solved by the methods of quantitative analysis. Suppose you are to determine how much alkali there is in a photographic developer, fertilizer, or detergent. An acid is added to the substance under investigation until the alkali contained in it is completely neutralized. This technique is called titration. Once we know the amount of acid spent for neutralization, we can find the amount of the alkali we are interested in, using the reaction equation $H^+ + OH^- = H_2O$. First, the acid solution with the known concentration should be prepared. Carefully add 10 ml of concentrated sulphuric acid (specific gravity 1.8 g/ml) to one litre of cold water. You have obtained a solution that contains 0.018 g of H_2SO_4 in one millilitre, because 10 ml of the acid weighs 18 g. Fill the burette with this solution and prepare the solution from the analyzed substance. If this substance is supposed to contain a considerable amount of alkali, the weight of the sample taken for analysis should be small or the sample should be dissolved in a large amount of water. For example, you have dissolved a sample of 10 g of the analyzed powder in one litre of water and transferred a portion of 100 ml of this solution into a glass. Add 1 or 2 drops of an alcohol solution of phenolphthalein to the glass: the solution turns crimson. Then, add sulphuric acid from the burette dropwise, while constantly stirring the solution with a glass rod. At the moment the solution loses its colour, stop adding the acid and record the volume of the acid spent for neutralization. Suppose it is 7 ml. This means that $7 \times 0.018 = 0.126$ g of H_2SO_4 was spent for neutralization. The reaction equation is $2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O$. The molecular masses of NaOH and H_2SO_4 are 40 and 98, respectively. The following proportion is set up:

for neutralization of 2×40 g of NaOH, 98 g of H_2SO_4 are spent

for neutralization of x g of NaOH, 0.126 g of H_2SO_4 is spent. It follows that $x = (80 \times 0.126)/98 = 0.1$ g. Thus, 100 ml of the solution analyzed contains 0.1 g of NaOH, while one litre contains $10 \times 0.1 = 1$ g of NaOH. The same amount of alkali is in 10 g of the sample powder taken for the analysis, i.e. the sample contains 10% of NaOH.

Titration can be employed not only in neutralization reactions, but in oxidation-reduction reactions as well. When a piece of iron nail is dissolved in dilute sulphuric acid, iron sulphate (green vitriol) is produced. You can determine the concentration of this compound in the solution in the following way: using the burette, add very dilute potassium permanganate solution to the solution under investigation until it acquires a pale pink colour. The equation of the proceeding reaction is $10FeSO_4 + 2KMnO_4 + 8H_2SO_4 =$ $5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O$. The rest of the calculations are similar to those in the previous example.

In general, there are many methods for the quantitative determination of a chemical component. Let us try to determine the quantity of iron(III) in tap water. Here again we shall turn to a reaction with thiocyanate ion, which is sensitive to iron (III). However, in this case the determination of iron by titration will be impossible because there is no sharp change in colour when the concentrations of Fe^{3+} and SCN^- are equal, and because the reaction is reversible, as we have already seen. But what if we add NH_4SCN to the solution under investigation and compare the colour of the obtained solution with that of the standard solution of $Fe(SCN)_3$, in which the concentration of iron(III) is known? To this end, weigh out a definite amount of iron(III) chloride and dissolve it in a measured volume of distilled water. Using this initial solution, prepare several solutions from it with different, low concentrations of iron. Pour 100-ml portions of distilled water into each of several glasses and, using a pipette, add the initial solution of iron chloride to each glass dropwise volumes of 1, 2, 3, and more drops, respectively. To calculate the concentrations of the resulting solutions, you must know the volume of one drop. For this purpose, transfer 20 (or 100) drops of distilled water into a graduated cylinder and note the volume. A drop is equal to a volume that is 20 (or 100) times less than this quantity. Thus, you have a series of solutions with known concentrations of Fe^{3+} and a glass with 100 ml of tap water under investigation. Next, add a definite amount of ammonium thiocyanate solution and a drop of hydrochloric acid to each of the glasses (it is not necessary to know the concentration of ammonium thiocyanate). Now all you have to do is to compare the colour of the tap water under test with the colour of the standard solutions and select which of them has the same intensity as the tap water. In this way you can easily answer how much iron there is in tap water.

Three observations should be made. First, the accurate determination of iron concentration is only possible when there is a sufficient amount of it in the tap water, for example, in tap water from a rusty water pipe. If pure water is taken, the colour of the resulting iron thiocyanate will be very pale. In this case you can only note that the amount of iron in the sample is less than a certain value. Second, standard solutions can also be prepared from an iron(II) salt, e.g. iron(II) sulphate or iron(II) chloride, which is obtained when a previously weighed iron nail is dissolved in hydrochloric acid. Iron(II) can then be easily oxidized into iron(III) by an oxidant, for example, hydrogen peroxide. And finally, when comparing the colour intensity, identical vessels should be used, because the thickness of the layers of solutions that are compared should be the same.

Chemical Reactions and an Electric Current

If you need a small amount of hydrogen, the best way to obtain it is to treat zinc with an acid. Pour a small quantity of dilute sulphuric or hydrochloric acid into a glass and drop a few pieces of zinc into it: the metal will slowly dissolve, and hydrogen bubbles will appear on its surface. Now, drop several pieces of zinc into a solution of copper sulphate (blue vitriol) for a short time and then transfer them to an acid solution. You will notice that this time the metal reacts with the acid more vigorously. How can this be explained? When zinc is dissolved in an acid, the positively charged ions of hydrogen, H^+ from the acid, receive electrons from zinc atoms and are transformed into neutral molecules of H_2. Having lost two electrons, zinc atoms transform into Zn^{2+} ions, which pass into the copper sulphate solution.

But here we have added zinc to a copper salt. As we know, copper is less active than zinc, and therefore electrons migrate from zinc to the copper ions. The positively charged zinc ions that result pass into the solution, while metal copper precipitates on the zinc surface. As a result, zinc with inclusions of copper is formed. But zinc has more free electrons, and they are more easily detached from its atoms. Therefore, zinc willingly gives its electrons to copper, and then electrons from copper migrate to the hydrogen ions, which transform into molecules. The functions of zinc and copper atoms are different: zinc atoms must only pass into the solution in the form of ions, while copper atoms must only reduce H^+ to H_2. In pure zinc, both functions are performed by the atoms of this metal. The surface of zinc is covered by molecules of hydrogen and the dissolution of the metal slows down.

Thus, we have discovered that electrons willingly flow from one metal to another. But if each of these two metals is immersed into a solution of its salt and a metal wire is used to connect them externally, electrons will flow through this wire, i.e. an electric current will be generated. Thus, we have explained the main principle of the chemical source of electricity. Its structure will not be dealt with in greater detail; instead we will use a flashlight battery as a chemical source of electric current for further experiments.

Attach two isolated copper wires, 30 cm long, to the terminals of the battery. Wind the other end of each wire 2 or 3 times around two separate small coins. Connect a bulb from a flashlight in series with the battery. Then, pour water into a glass to one-third of its capacity and immerse the coin electrodes into it such that they do not contact with each other. The bulb will not light up. If you replace the water with a sugar solution, the result will be the same: in other words, no effect will be observed. Now, pour water into the glass again, immerse the coins into it and add several drops of sulphuric acid to the water: the bulb will light up and gas bubbles will rise to the surface from both coins.

In the next experiment, the electrodes are immersed into a table salt solution containing 2 or 3 drops of alcohol phenolphthalein solution. The bulb lights up, and a colourful sight is observed: both coins become immediately covered with gas bubbles, while the coin that is connected to the negative terminal (the cathode) is surrounded by a crimson cloud, which gradually spreads throughout the solution.

How can these phenomena be explained? Electrons from the negative terminal of the battery move to the coin cathode, and thus give it a negative charge. The positive terminal of the battery "absorbs" electrons from the anode, which becomes positively charged. When the two coins are separated by a layer of pure water, electrons can't flow from the cathode to the anode, because water has a very low electric conductivity. For this reason, the bulb will not light up.

Nevertheless, water contains carriers of electric charges; these are H^+ and OH^- ions but their concentration in water is too small. Therefore, the electrolysis of pure water proceeds very slowly. In the idealized form this process is shown in Fig. 3*a*. Having convinced ourselves that the electric conductivity of water is very low, we tried a sugar solution. The result was the same, because sugar molecules do not dissociate into ions in solution.

When an aqueous solution of sulphuric acid was tested, it proved to be a good conductor, since its molecules dissociate into H^+ and SO_4^{2-} ions. It should be pointed out that dissociation takes place regardless of whether electrodes are immersed into the solution or the electric current passes through it. Positive hydrogen ions, which are present at a high concentration in a

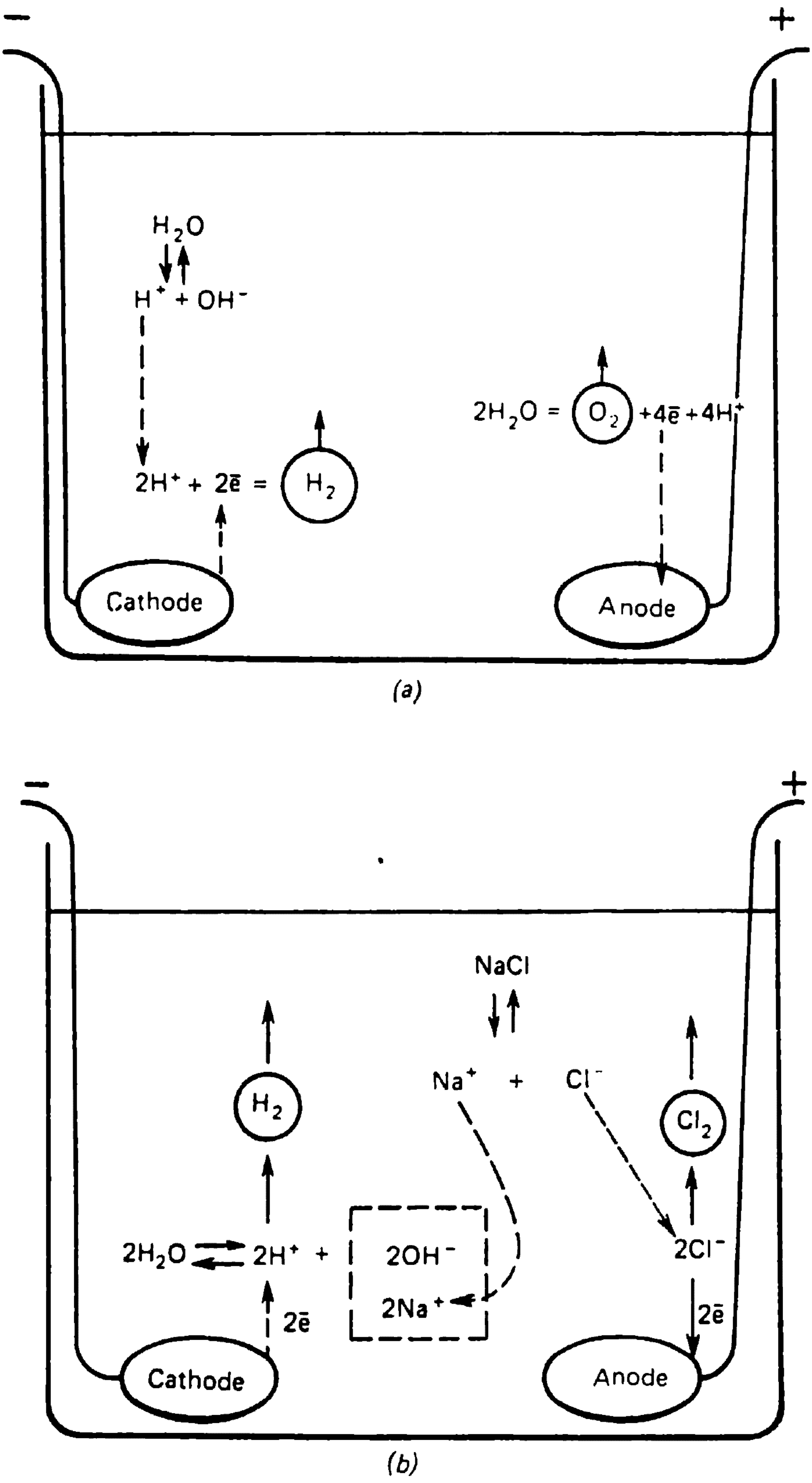


Fig. 3 Electrolysis of (*a*) acidified water and (*b*) sodium chloride

sulphuric acid solution, move towards the negatively charged cathode. At the cathode, H^+ ions receive electrons and transform into hydrogen atoms. Two hydrogen atoms combine to form a molecule of hydrogen gas, which bubbles from the solution. When electrons leave the cathode, the battery has to supply new portions of negative charges to the cathode. This means that an electric current is flowing through the circuit and the bulb lights up.

The electrolysis of a H_2SO_4 solution actually proceeds in a more complex way, and different substances, for example, sulphur derivatives and hydrogen peroxide, can be among the products.

The electroconductivity of water can be increased by adding a solution of any electrolyte (a substance that dissociates in water into ions) to it. In industry, for example, water is decomposed by an electric current into hydrogen and oxygen by adding sodium hydroxide to it.

Now, let us consider the electrolysis of a table salt solution. Sodium chloride in solution dissociates into Na^+ and Cl^- ions. The former move to the cathode; the latter, to the anode. It would seem that sodium ions should receive electrons from the cathode and transform into metallic sodium. But this does not occur, because sodium is a very active metal that cannot exist in water in a free state. Therefore, electrons from the cathode are transferred not to Na^+ ions, but to H^+ ions, which are always present in an aqueous solution. As a result, hydrogen evolves at the cathode (Fig. 3*b*). The other constituent part of water is OH^- ions, which accumulate near the cathode. It is these ions that are responsible for the crimson colour of the solution around the coin cathode when phenolphthalein is added. The latter is known to be a reliable indicator for alkalies.

When chloride ions arrive at the anode, they give their electrons to the anode, and transform into molecules of chlorine gas. Na^+ and OH^- ions, i.e. the components of sodium hydroxide, remain in the solution. Thus, it becomes clear why the electrolysis of an aqueous NaCl solution is used as an industrial method for the production of three important substances: hydrogen, sodium hydroxide, and chlorine.

We have briefly considered the fundamentals of electrochemistry—one of the branches of physical chemistry—that studies chemical reactions induced by an electric current, as well as reactions that produce an electric current. The reader may think that electrochemistry only deals with inorganic substances. But this is not so: many organic substances are of interest to electrochemists. During recent years, the electrosynthesis of many organic compounds has been intensively developed.

Rust as Seen by a Chemist

Chemical transformations usually proceed with evolution or absorption of energy. In the former case, the energy stores of the products are less than the energy stores of the initial substances. In the latter case, the situation is the reverse. How can the changes in the energy stores be determined quantitatively? For this purpose, the concept of free energy, G, is introduced. It is considered that for a reaction that proceeds at constant temperature and pressure, the decrease in the free energy, ΔG, equals the maximal work performed by the given reaction. The change in the free energy, ΔG, is calculated as follows:

$$\Delta G = \sum \Delta G^0 \text{ (products)} - \sum \Delta G^0 \text{ (reactants)}$$

Here ΔG^0 is the change in the free energy for each product or reactant when it is formed from chemical elements at standard conditions, i.e. at 25°C and 1 atm. The symbol $\sum$ represents the sum of these quantities for all reactants and products. The standard free energy of any chemical element is assumed to be zero.

It follows from the above that reactions for which ΔG^0 is negative occur with evolution of energy, and the reaction products have energy stores less than the energy stores of the reactants. Such reactions proceed spontaneously, like a stone rolling down a mountain.

Now, let us look at values of ΔG^0 for reactions between certain metals and oxygen, which yield metal oxides. The changes in the free energy (in kcal per mole of a substance) that correspond to the formation of these oxides are given in parentheses: CuO (—31), NiO (—51), ZnO (—76), SnO_2 (—124), MgO (—136), Fe_2O_3 (—177), Cr_2O_3 (—253), and Al_2O_3 (—378).

What is peculiar about these figures? All these changes in the free energy are negative, which means that the metal oxides listed above are more stable than their metals. It is obvious that aluminium forms oxides most willingly, while copper is not so susceptible. Thus, the above thermodynamic considerations reveal that most metals are unstable in the free state and transform into oxides in an atmosphere containing oxygen. Nevertheless, we know that steel trusses as well as aluminium jars and copper wires do not transform into heaps of oxides, but serve us for a long time. What is the explanation for this? Let us continue our comparison between a metal surrounded by oxygen and a stone on top of a mountain. The stone strives for the mountain's foundation like the metal strives for transformation into its oxide. But far from all the stones that are high in the mountains roll down. There are several reasons for this, and one of them is that the stone is surrounded by mountains. To roll down the mountain, the stone must overcome an energy barrier, which is usually very high; otherwise, the stone can remain in this position for millions of years. Like this immobile stone, a metal can also remain unoxidized for a long time.

Unfortunately, every year, 1-1.5% of all the metal produced is lost as a result of corrosion. Corrosion is the spontaneous destruction of metals under the influence of the environment. Metal corrosion does not always result in metal oxides. Among the products of corrosion are hydroxides, chlorides and salts of other acids. But in any case, the metal transform into an oxidized state.

Corrosion of iron can easily be observed at home. Run the following experiment: wet an iron nail with water and leave it in moist air for several days. Soon, you will notice that the nail is covered with a red deposit of iron oxide. You will not succeed in obtaining iron oxide in a dry atmosphere or in a moist atmosphere containing no oxygen. Hence, rust forms only in the presence of water and oxygen.

During corrosion, iron gives off two electrons: $Fe - 2e = Fe^{2+}$. These electrons reduce oxygen to form hydroxide ions: $O_2 + 2H_2O + 4e = 4OH^-$. Divalent iron combines with hydroxide ion to form iron(II) hydroxide: $Fe^{2+} + 2OH^- = Fe(OH)_2$. The latter gradually loses its water and transforms into iron(II) oxide: $Fe(OH)_2 \rightarrow FeO + H_2O$. The iron(II) hydroxide can be oxidized by the oxygen to iron(III) hydroxide, which also decomposes into water and iron(III) oxide. As a result of all these processes, the iron nail becomes covered by layers of different iron oxides.

There is also another type of corrosion—electrochemical corrosion—which is frequently encountered. The fact is that the metal parts of many types of construction are always in contact with electrolyte solutions such as salts, acids, and bases containing different ions. To get an idea of electrochemical corrosion, let us remember the structure of a chemical source of energy—the voltaic cell. If iron (or zinc) and copper plates are immersed into solutions of their salts and connected to a galvanometer, the latter will measure the potential difference that arises between the plates. The potential difference varies for different pairs of metals. Hydrogen ions that transform into gaseous hydrogen can be considered as one of the electrodes. If the potential of this hydrogen electrode is assumed to be zero (standard electrode), one can determine the standard potential E^0 of the other electrode with respect to the hydrogen electrode. Below are given the standard potentials for certain electrode reactions in volts:

$$\begin{array}{ll}
Na^{+} + e \rightarrow Na & E^{0} = -2.71 \\
Al^{3+} + 3e \rightarrow Al & E^{0} = -1.68 \\
Zn^{2+} + 2e \rightarrow Zn & E^{0} = -0.76 \\
Fe^{2+} + 2e \rightarrow Fe & E^{0} = -0.47 \\
Cu^{2+} + 2e \rightarrow Cu & E^{0} = +0.34 \\
Au^{3+} + 3e \rightarrow Au & E^{0} = +1.50
\end{array}$$

It is clear that the greatest potential differences can be obtained in cells where one of the electrodes is made of sodium or aluminium, while the other one is made of copper or gold. It can easily be seen that iron is oxidized more readily than copper. Therefore, if an iron nail is placed in a solution of a copper salt, the iron will dissolve and the copper metal will precipitate from the solution. The nail will soon be covered with a red layer of metallic copper. The equations of the reactions described above are:

$$\begin{array}{ll}
Fe - 2e = Fe^{2+} & E^{0} = +0.47 \text{ V} \\
Cu^{2+} + 2e = Cu & E^{0} = +0.34 \text{ V} \\
\hline
Fe + Cu^{2+} = Fe^{2+} + Cu & E^{0} = +0.81 \text{ V}
\end{array}$$

The standard electrode potential E^{0} and the free energy change of the oxidation-reduction electrode process are related as follows:

$$\Delta G^{0} = -nFE^{0}$$

where n is the number of moles of electrons transferred in the process, and F is the

Faraday number, which is positive. For the iron-copper system, E^0 is positive, hence, ΔG^0 is negative. It follows then that the process described by the overall reaction is thermodynamically advantageous and proceeds with the evolution of energy.

The question may arise: But what does all this have to do with corrosion? To answer it, run the following experiment. Dissolve a pinch of a table salt in a glass of water. Add some potassium ferricyanide solution and a few drops of alcohol phenolphthalein solution. Then, take iron and copper wires, intertwine them so that they contact at many points, and immerse the wires into the solution. In a few minutes, a crimson colour appears around the copper wire and a blue colour around the iron wire. What has happened? The process is similar to the reaction between metallic iron and a copper salt. The iron passes into the solution in the form of Fe^{2+} ions, which react with potassium ferricyanide to produce Turnbull blue. Simultaneously, on the copper wire, oxygen is reduced to hydroxide ions at the expense of electrons supplied from iron via the wire. The hydroxide ions are identified with phenolphthalein. Now, run the same experiment, but without the copper wire. You will see that this time iron is oxidized very slowly.

Thus, the iron is oxidized, i.e. becomes corroded, under the action of oxygen and when it is in contact with copper in an electrolyte solution. The copper does not change here, because it has a large positive potential.

The two intertwined wires (iron and copper wires) may be compared to a piece of ordinary iron containing billions of microscopic inclusions on its surface. These inclusions work like a copper cathode. Iron corrosion in this case can be represented as shown in Fig. 4. The same mechanism underlies the corrosion of iron objects in a humid atmosphere, which contains various oxides that produce acids with water.

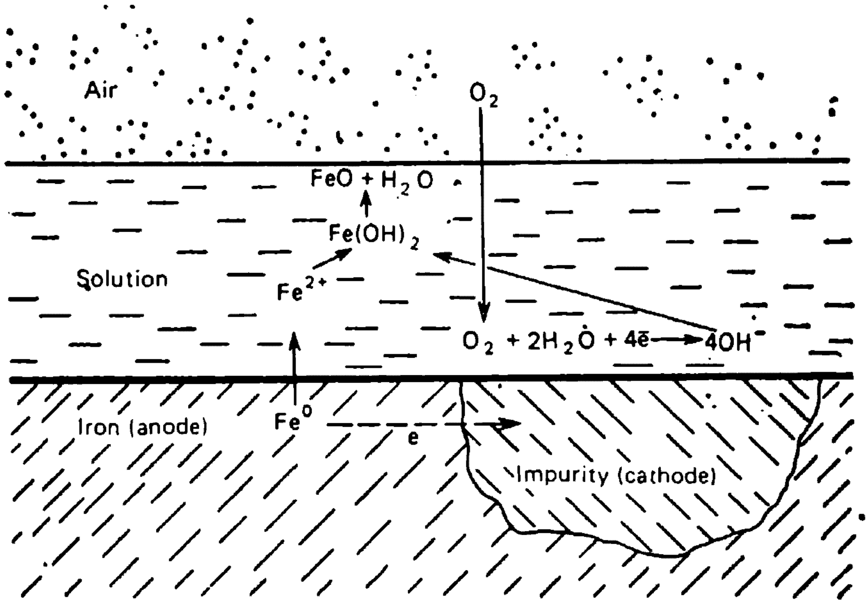


Fig. 4 Corrosion of iron containing an impurity of another metal

Once, a bizzare thing happened to the yacht of a millionaire. The bottom part of his yacht had been made out of copper-nickel alloy and steel. When the yacht was launched, its bottom began to dissolve in the sea water like a sugar in a cup of tea. Any voyages on board the yacht were obviously impossible.

There are many ways of protecting metals from oxidation, and the simplest one was suggested by nature. The surface of the metal can be covered by the oxide film of this metal. This film can be very thin. Aluminium, which is a highly active metal, can be taken as an example. The aluminium becomes covered by a dense film of aluminium oxide, which protects the metal from further oxidation.

Carefully clean an iron nail with sandpaper and lower it into a copper sulphate solution. The nail becomes covered by a red film of copper. Take another nail and hold it in the flame of a burner for a minute until its colour turns yellow. When this nail is immersed in a copper sulphate solution, the red copper film will form on it much later. Take three more nails and calcine them in the flame for 2, 3 and 5 minutes, respectively. As a result, the nails will become red, blue, and gray-green in colour. The time it takes for the copper film to appear on the nails increases with the time of calcination. This is because when the nails are calcined, they become covered with an oxide film, whose thickness and colour depend on the duration of calcination.

A protective film can also form when the metal is treated with concentrated sulphuric acid or nitric acid. Clean two nails with sandpaper and put one of them in a concentrated nitric acid solution for a few minutes. Now rinse both nails with water and place them in dilute sulphuric acid. You will notice that the nail treated with nitric acid will not react with the sulphuric acid, while the other nail reacts vigorously and causes the evolution of hydrogen bubbles from the acid.

A Substance on the Surface or the Chemistry of Laundering

A sheet of paper will not stick to one's finger unless the latter is wetted with water. This "principle" underlies the bad habit of licking one's fingers when turning over the pages of a book. So, why does water change the situation so radically? First, we shall consider the molecular structure of a liquid.

A molecule of water that is in the bulk of the liquid is uniformly surrounded by similar molecules. Therefore, it experiences equal attraction forces in all directions.

Molecules that are on the surface of a liquid are in a different situation. On the one hand, these molecules are attracted from below by similar molecules of the liquid, but on the other hand, they are attracted by the rarely encountered molecules of gases contained in the air above. Obviously, the molecules of the liquid exert a greater attraction, and therefore, they try to pull the surface molecule into the liquid.

Suppose that the area of a surface layer of water in a cylindrical vessel equals S. Incline the vessel somewhat so that the area increases by ΔS. By inclining the vessel, you are forcing some water molecules to emerge from the bulk of the liquid onto the surface. Since you are acting against the forces that try to pull the surface molecules into the liquid, you are performing work. Denote the work required to increase the surface area by ΔW. If you divide this quantity by ΔS, you will obtain an important parameter, $\sigma = \Delta W/\Delta S$, which is called surface tension.

When you increased the surface area, you simultaneously increased the energy of the system. However, the system cannot increase its energy spontaneously; to the contrary, it always tends to decrease it. For this reason, a drop of water acquires the form of a sphere because the latter has the least surface area for a substance of a given volume.

A mercury drop placed on a glass plate acquires the form of a distorted sphere. But when a drop of water is placed on a clean glass plate, it will uniformly spread in a thin layer over the glass surface. What is the reason for the different behaviour of the two liquids? The fact is that mercury atoms are more attracted to one another than to the molecules in the glass, while water molecules are more attracted to the molecules in the glass.

Water and mercury are extreme examples when the complete wetting and non-wetting of glass is observed. When you press your finger against a glass plate, a thin layer of oil is transferred to it. Now, if you pour some water on this spot, the water will form a drop that is slightly spread over the glass surface.

The shape of a drop, or more strictly, the angle between the surface of a solid and a tangent to the surface of the drop drawn through the contact point can be determined as

$$\cos\theta = \frac{\sigma_{s,\,g} - \sigma_{l,\,s}}{\sigma_{l,\,g}}$$

where $\sigma_{s,g}$ is the surface tension at the solid-gas (air) interface, $\sigma_{l,s}$ is the surface tension at the liquid-solid interface, and $\sigma_{l,g}$ is that for the liquid-gas interface.

The surface tension for various liquids can even be determined at home. Construct a beam balance using a glass or metallic rod as a lever and a thread to suspend two pans. One pan can be made of foil, and the other of a thin copper wire bent into a square frame. Balance the beam in a horizontal position by putting some weights (for example, made of modelling clay) on the foil pan. Now, place a glass of water under the balance in such a way that the square frame "sticks" to the water surface. By adding weights, we can fix the moment when the frame separates from the water surface: this will allow us to determine the surface tension in conventional units. In practice, σ is determined in erg per cm^2. The surface tension for water at 20°C is equal to 73 erg/cm^2. Ethyl alcohol has a significantly lower surface tension, e.g. 22 erg/cm^2, and for glycerine it is 62 erg/cm^2, which is close to that of water.

Dissolve a small piece of soap in a glass of water, and using the balance, determine whether the surface tension of the soap solution has been sharply reduced. A molecule of soap consists of two parts with different properties. One part is a sodium substituted carboxyl group, i.e. $—COONa$. It "dissolves" perfectly in the water, and readily attracts water molecules. The other part is a long "tail" consisting of a hydrocarbon chain, e.g. $—(CH_2)_{16}CH_3$. The CH_2 groups in the tail repel water molecules. When the soap molecule gets into water, its carboxyl part becomes surrounded by water molecules, while the tail tries to get out of the water layer. As a result, the molecule becomes located at the surface with its tail lying on the water-air interface, and its carboxyl part is submerged in the bulk of the water. The whole water surface becomes occupied by the molecules of the soap, which as a surface-active agent diminishes the surface tension of water.

When you dissolved the soap in a glass of water, you obtained a turbid solution, which indicates that the solution is a colloidal one. The molecules of the soap combine into microscopic aggregates. When acetic acid is added, the solution becomes still more turbid, and within a few minutes a white oily layer forms at the surface, while the solution becomes more transparent. This process can be accelerated if sulphuric acid is used instead of acetic acid. The sulphuric acid replaces free stearic acid, $C_{17}H_{35}COOH$, from sodium stearate, which is the main part of the soap. First, the stearic acid forms a white colloidal solution, which then coagulates into large particles and forms the oily layer.

In addition to stearic acid salt, soap also contains a salt of oleic acid $[CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH]$ whose chain has a double bond. This bond can be identified when the acids separated from the soap are treated with bromine water.

The latter will become colourless, because bromine is added at the site of the double bond. Stearic and oleic acids are very weak acids, therefore their sodium salts are partly hydrolyzed in aqueous solution to form free acids and sodium hydroxide. Therefore, the soap solution reacts alkaline.

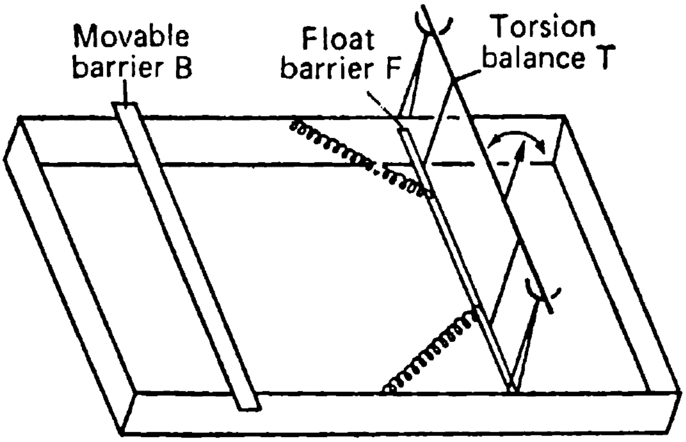


Fig. 5 Modification of Langmuir's balance

This can be verified experimentally. Dissolve a piece of soap in a small amount of an alcohol or eau de Cologne and then add a grain of phenolphthalein. If water is gradually added to the resulting solution, the latter turns more and more crimson, since the hydrolysis increases.

Now, let us investigate the physico-chemical properties of surface-active substances. Construct a device called the Langmuir film balance (Fig. 5). It has the following design. The rectangular trough is filled to the edge with water and a surfactant is added to it, which spreads over the water surface. The trough has a movable barrier B, which can change the area of the trough, surfactant, and a float barrier F, which is connected to a thin spring and a torsion balance T. The pointer of the torsion balance indicates the pressure on the float barrier.

Take a small amount of a surfactant (a mixture of fatty acids extracted from soap and dissolved in ether, or from a grain of camphor) and add it to the water surface in the trough. The surfactant immediately spreads over the water. Since the amount of the surfactant is very small, a layer of the surfactant that is one molecule thick will form on the water surface. The surfactant molecules tend to spread over the water surface, but the float barrier will not permit this. The pressure of the surfactant on the float barrier can be measured by the torsion balance.

Now to see how the pressure on the float barrier changes, decrease the surfactant area by moving barrier B. Next, construct a graph of the pressure P versus the area S occupied by the surfactant. In segment AB, the pressure increases in proportion to the decrease in the area (Fig. 6). The product of the pressure and the area turns out to be proportional to the product of the universal gas constant and the absolute temperature, i.e. $PS \sim RT$. But the latter is similar to the ideal gas equation $PV =$

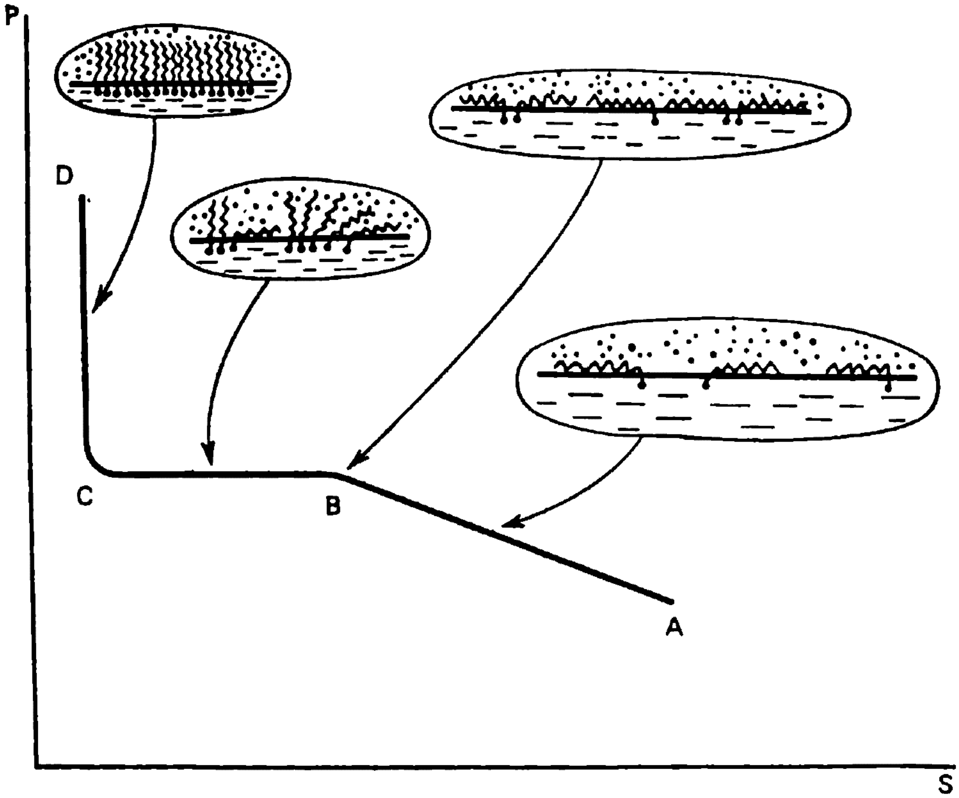


Fig. 6 The pressure P on a movable barrier versus the surface area S. Black dots represent the COOH groups, while zigzag tails are hydrocarbon radicals

RT. Here *V* substitutes *S*. Hence, it looks as if a two-dimensional gas is in segment AB, where the molecules are located far from one another. Continue to decrease the area, and at point B the whole surface becomes occupied by surfactant molecules. With further compression (section BC), the molecules become so tightly packed that some of the tails of the surfactant molecules are pushed out from the surface, and the islands of molecules with their tails sticking up look like drops of a liquid in a sea of dispersed molecules. By decreasing *S* in this section, you will increase the number of molecules with raised tails, while the number of dispersed molecules per unit area remains unchanged. Therefore, the pressure on barrier F doesn't change in this section. Finally, at point B, all the tails of the closely packed molecules protrude from the surface. One could say that a two-dimensional type of liquid has been obtained. It is known that liquids are incompressible, and a slight decrease in the area causes a sharp increase in the pressure. Once we know the amount of the surfactant taken and the area of water surface, we can determine the length of a stretched-out molecule and the diameter of its tail.

So, why does soap have such surprising properties? There are several reasons. We have already established that surfactants reduce the surface tension of water more than twice. This means that the liquid can penetrate and wet the smallest pores in a piece of fabric where a stain has formed. But this is far from all. Suppose that a drop of grease has stained a cotton fabric. If this fabric is immersed in pure water, the stain will spread. We know that the shape of a drop is determined by the relationship between the surface tensions at the phase interface. The stain will then be covered by a layer of water and that will be that. If you now add a surfactant to the water, its molecules will disperse over the water and the soil surfaces. The greasy stain that has spread in the fabric will form a drop again. The tails of the surfactant molecules will be directed towards the interior of the drop, while the heads will be outside the drop with water molecules surrounding them. After this, the drops will tend to detach from the fabric and enter the water. The surfactant does not permit the drops to combine into large drops, therefore, a stable emulsion is formed. The latter can easily be removed with water and the fabric becomes clean.

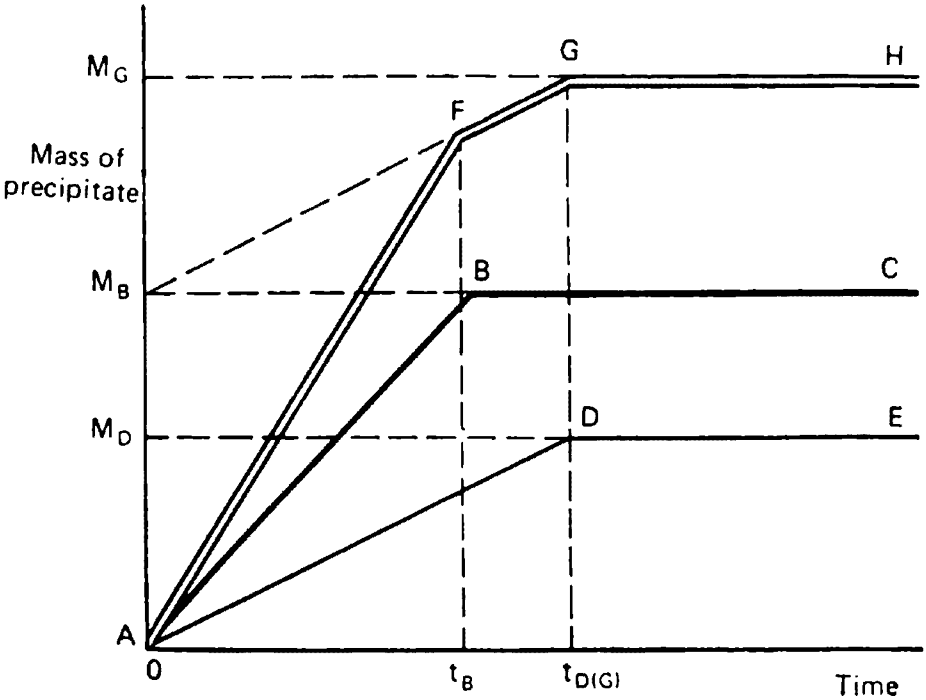
Why Is the Sky Blue?

The beauty of science consists in that when faced with a problem, rather than solving it directly, straight off, it usually finds an indirect and wholly elegant method. Imagine that you are asked to find the diameter of a football or an apple. There's nothing simpler than to place it between two planks and measure the distance between them with a ruler. But when the diameter of a particle of dust or tooth powder is to be found, the ruler will be of no use. The diameter can be found, however, by stirring the powder with water and measuring the rate of sedimentation. Of course, to obtain precise measurements, accurate instruments are required. Still, one can approximately determine the particle size at home with the aid of a simple device, whose design is given below. We leave it to the reader to make any improvements on its actual construction.

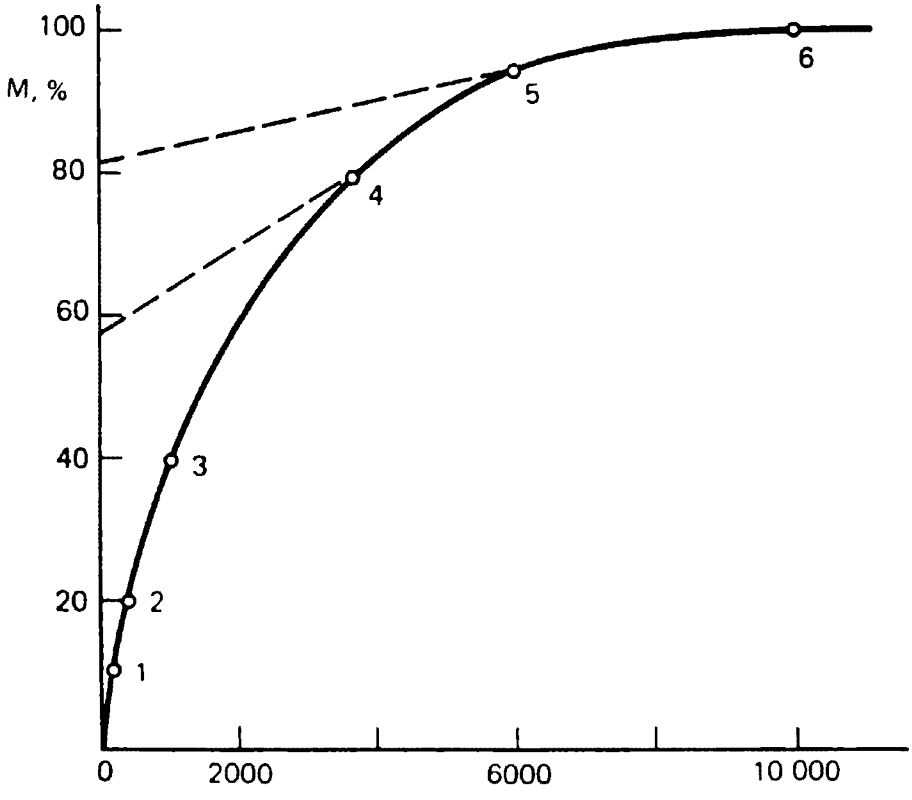
The main objective of the experiment is to determine the mass of the precipitate; therefore, a balance will be needed. Any laboratory or drug-store balance will do. You will not have to determine the absolute mass of the precipitate in grams, but only the relative weight; for this reason, squares made from tin or foil with the same dimensions can be used as weights. The principle of the experiment is simple: one of the balance's pans is submerged in the suspension of tooth powder in a glass of water close to the bottom. The powder then gradually precipitates onto the pan, as a result of which the latter sinks still lower. The tin (or foil) weights are added to the opposite pan at certain intervals of time to counterbalance the submerged pan. The time and mass are recorded in a table.

The formula that relates the rate of precipitation of a suspension particle to its radius (derived from Stokes' law) is as follows:

$$r=\sqrt{\frac{9\eta h}{2\Delta dg}}\sqrt{\frac{1}{t}}=k\sqrt{\frac{1}{t}}$$


M_G
G
H
F
Mass of precipitate
M_B
B
C
M_D
D
E
A
0
t_B
t_D(G)
Time

(a)


100
M, %
80
60
40
20
0
2000
6000
10 000
Time, s
1
2
3
4
5
6

(b)

where r is the particle radius; η is the viscosity of a liquid; Δd is the difference between the densities of the particle and liquid; h is the height from which the particle falls during time t; g is the acceleration due to gravity; and k is a factor that is constant for a given device and system. Assume that all the particles in the suspension have the same mass and hence the same radius. In the coordinate system mark off the time along the x-axis and the mass of the powder precipitated on the pan at each time point along the y-axis. The above relationship appears to be a straight line *OB* that passes through the origin (Fig. 7*a*). Indeed, at time $t = 0$, all the powder particles are suspended. Assume that after 10 seconds 1000 particles, whose mass is 1000 relative units, have settled on the pan. Since precipitation is a uniform process, in 20 seconds, 2000 particles will have settled on the pan, and in 60 seconds, 6000 particles, weighing 6000 relative units, will have reached the pan. At time t_B all the particles will be precipitated on the pan, and the mass of the precipitate will remain unchanged. The straight line *OB* transforms then

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Fig. 7 Curves for the settlement of a precipitate containing particles of one or two size fractions (*a*), and of a pricipitate that is a mixture of particles with different size (*b*) into the straight line BC, which is parallel to the abscissa. Note that t_B is the time when the last particles have precipitated. Obviously, at $t = 0$, these particles were at a maximum height from the submerged pan, i.e. they were near the surface. Once we know this maximum height (it can easily be measured by a ruler), and the time it takes for the particle to precipitate from this height, we can calculate the particle radius from Stokes' formula.

Now let us consider another case when the suspension is made up of particles with two different radii and, hence, masses. Here the precipitation curves can be constructed separately for the lighter and heavier particles. Suppose that the precipitation of the heavier particles corresponds to OB mentioned above. The lighter particles precipitate slower, therefore the straight line OD, which corresponds to their precipitation, is longer and flatter. So, how does the mass of the precipitate change when particles of two different sizes are used to prepare a water suspension? In order to obtain a graph illustrating this change, the ordinates of the two curves OBC and ODE should be summed up. The result will be the curve $OFGH$. Point F on this curve corresponds to the time when the last heavy particle has precipitated, while at point G all the light particles are on the pan. Segment M_BM_G is equal to segment OM_D.

But OM_G is the mass of the whole precipitate, while OM_D is the mass of the light fraction. Hence, OM_B is the mass of the heavy fraction, and M_BM_G is the mass of the light fraction.

What can be determined from the graph? By substituting the times that correspond to the salient points on the curve into Stoke's formula, one can find the radii of the particles in the light and heavy fractions. The corresponding intercepts on the coordinate axes will indicate the masses of these fractions.

Plan your experiment with tooth powder so that 5-6 weighings are performed during the precipitation of the powder, after which the mass of the precipitate on the pan remains constant. Take into account that at the beginning of the experiment, the mass of the precipitate changes more quickly than at the end. It is clear that the tooth powder consists of particles that are not only nonuniform in size, but even belong to a multitude of different size fractions. The number of particles with different radii that form the suspension changes continuously within certain limits. Therefore, the time intervals that were chosen will bound certain conditional fractions.

Fill in the table with the results of the experiment: time (in seconds), precipitate mass (number of weights), precipitate mass (in per cent), mass of a given fraction

M (in per cent of the total precipitate mass), radius of particles r (in metres), and the quantity $M/\Delta r$. When calculating the radius, it is convenient to first calculate k. Take $g = 9.8$ m/s^2, $\eta = 0.001$ n·s/m^2, $\Delta d = d$ (chalk) — d (water) $= 2700 - 1000 = 1700$ kg/m^3, and $h = 0.1$ m. Then $k = 0.0002$. Plot the results from the table onto the graph. In this case the precipitation curve will be similar to the curve in Fig. *7b*, because the powder contains a multitude of different size fractions. It becomes clear that the precipitation curve in Fig. *7b* is the limiting case of the broken line with an infinite number of fractions. To the first approximation, however, six sections can be distinguished in the curve.

The first section *O-1* is considered to be linear and describes the precipitation of the largest particles, which terminates at point *1*. The given fraction makes up about 5% of the total. The section corresponds to OM_B in Fig. *7a* and it turns out that it is obtained when line *1-2* is continued to intersect the *y*-axis. The content of fraction *1-2* is determined when line *2-3* is continued to intersect the *y*-axis and the per cent content of the previous fraction is subtracted. In this way the relative contents of the chosen fractions can be calculated.

To construct the differential precipitation curve (Fig. 8), plot the boundary radii of the particles in a given fraction along the x-axis and the value $M/\Delta r$ (where M is the relative content of the fraction and Δr is the difference between the boundary radii in the fraction) along the y-axis. The

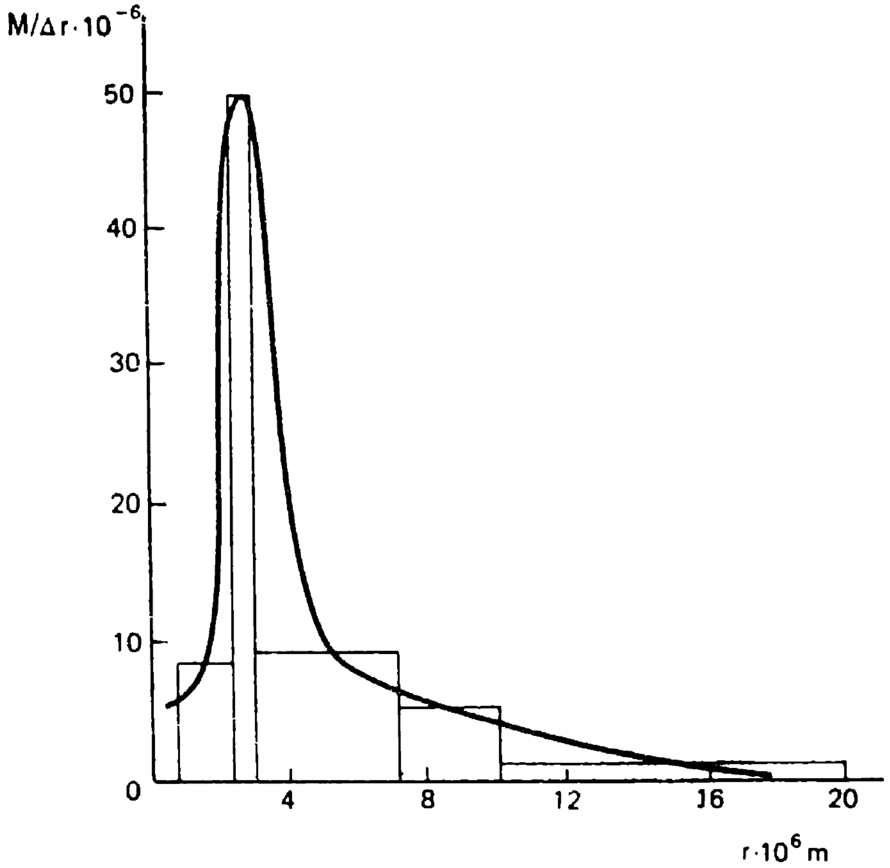


Fig. 8 Differential curve for the distribution of tooth powder particles in size fractions

area of each rectangle is equal to the weight content of the fraction. By connecting the middle points of the rectangle bases by a smooth curve, we can obtain the pattern of the differential distribution of particles in the fractions. Now you can see which particle size predominates in the suspension.

We have discussed one of the tasks of sedimentation analysis, which is a branch of colloid chemistry. It studies the precipitation process and sedimentation of particles suspended in liquids. These processes are important in technology and in everyday life, because one frequently deals with mixtures. The mixtures include suspensions (systems in which solid particles are dispersed in liquids), emulsions (liquid droplets dispersed in another liquid, in which they don't dissolve) and aerosols, i.e. mists or fogs (a suspension of liquid droplets or solid particles in a gas). Actually, dyes and milk are emulsions, as well as many drugs that are used in the form of ointments.

If a suspension of finely divided powder in water is examined under a microscope, a curious phenomenon can be observed: the small particles of the powder are continuously moving. This phenomenon was first discovered by the English botanist Robert Brown and named after him. How can this Brownian movement be explained? Suppose a large particle is floating in water. At every moment it is attacked by water molecules, which are numerous and bump into each other and into the particle. Since the particle is large, billions of molecules collide with it from different sides. In this situation, the particle will not move. But when the size of the particle is about that of water molecules, the situation may occur when, for example, 20 water molecules attack the particle from one side and only 15 water molecules from the other. As a result, the particle will move, but this motion will be random and continuous. This nonuniform distribution of water molecules in different volumes of space is called fluctuation. Fluctuation is inherent in systems that consist of a huge number of particles. It is known that even a droplet of water consists of billions of molecules. There can be situations when the concentrations of water molecules surrounding the particle from different sides are the same or when the velocities of water molecules on the left-hand side are greater than those on the right-hand side. Finally, an intermediate situation can occur when both the concentrations and the velocities of the neighbouring water molecules are different.

One negligent student was asked at an exam: "Why is the sky blue?" After thinking for a while, he answered: "Because the sea is reflected in it." Of course this answer must have amused the teacher greatly. How can the blue colour, however, be explained? It is common knowledge that when light is incident on a particle, it is absorbed by it, and warms it up. But some part of the light is scattered by the particle. The English scientist Rayleigh derived an equation that describes light scattering by minute particles. It follows from the equation that the intensity of the scattered light is inversely proportional to the wavelength of the incident light to the fourth power. Violet and blue rays have the smallest wavelengths in the spectrum of visible light, and therefore, they are scattered to a greater extent than yellow or red light. For this reason the sky is said to be blue. Here a question arises: Which particles scatter the sunlight? It turns out that the role of these particles is played by fluctuations of air density. In the huge mass of gas molecules in the atmosphere there appear, from time to time, small regions with increased or decreased density. It is in these regions where the incident light is scattered more than in any other regions of the atmosphere.

At first, we discussed large particles, such as particles of tooth powder. Then we proceeded to molecules. Now let us treat something intermediate, such as particles whose size is only several times greater than that of molecules. These particles form colloidal solutions. It is not difficult to prepare a colloidal solution at home; this can be done using several methods. Dissolve a small amount of rosin in ethyl ether and then dissolve a teaspoon of this solution in a glass of water. The second method entails dissolving iron(III) chloride in boiling water and then boiling the resulting solution for several minutes more. Finally, the third method requires that a dilute iron (III) chloride solution be gradually added to a strongly diluted solution of potassium ferrocyanide with constant stirring. Each method results in a differently coloured colloidal solution. One can easily prove that these solutions are colloidal, rather than true, solutions. To this end, illuminate the glasses containing these solutions with a narrow beam of light from the side and observe the slightly turbid cones (opalescence) in the solutions. The opalescence appears as a result of the scattering of light by colloidal particles in the solutions.

In concluding, it should be mentioned that colloidal systems are extremely widespread and knowledge of their properties is necessary when, for example, purifying natural water or extracting oil.

Chemistry and Light

Quite often, to initiate the interaction of two substances, they must be heated. Heat is the most widespread stimulant of chemical transformations. However, other types of energy are also known, e.g. light energy. Can light induce chemical reactions? Remember how pleasant it is to go sunbathing on a breezy sunny day, when the skin doesn't sense the heat of the sun and only light induces the formation of brown pigment in the skin. The reverse process is also well known, i.e. the fading of textile dye in bright light. Decomposition of organic dyes under the action of light is also a chemical process. Thus, light is an excellent stimulant of chemical reactions. How does light interact with a substance? First, we shall remind the reader that visible light occupies a quite narrow interval in the scale of electromagnetic waves: it ranges from 4000 to 8000 Å. Different sections of this interval are perceived by the human eye as light of a different colour. For example, light with a wavelength of 4000 Å (or 400 nm) is violet; that of 530 nm, is green; while red light has a wavelength of 660 nm. White light is a mixture of all light rays.

Light can be treated not only as waves, but also as a flux of particles called quanta or photons. The energy of light quanta E is related to the frequency or wavelength of the light as follows:

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

where h is the Planck constant equal to 6.62×10^{-27} erg·s; ν is the light frequency, s^{-1}; λ is the wavelength, and c is the speed of light. It thus follows that the smaller the wavelength of the light, the greater is the energy it carries. Therefore, violet, and particularly ultraviolet, light has more energy than red or yellow light. Remember the sunbathing example: one can quickly tan under the action of invisible ultraviolet light, but nobody has yet become tan near a hot stove, which mainly radiates red and infrared light.

At the beginning of the nineteenth century, the first law of photochemistry was discovered. Photochemistry is a science that studies chemical transformations induced by light. This law, however, is quite obvious: chemical reactions are only induced by the light that is absorbed by a substance. But the reverse statement is wrong, i.e. not all of the absorbed light causes the chemical reaction. Indeed, the energy of light can be spent to simply heat the substance. Another law of photochemistry can also be easily grasped: the chemical effect of light, as a rule, is proportional to the light intensity and exposure time. The most important law was formulated by Einstein, who established that every absorbed light quantum induces the transformation of only one molecule of a substance. The number of quanta can be measured like that of molecules. A special unit equal to one mole of quanta (6.02×10^{23}) was introduced and called an einstein. Using the above formula, one can see that the energy of an absorbed einstein of light with a wavelength of

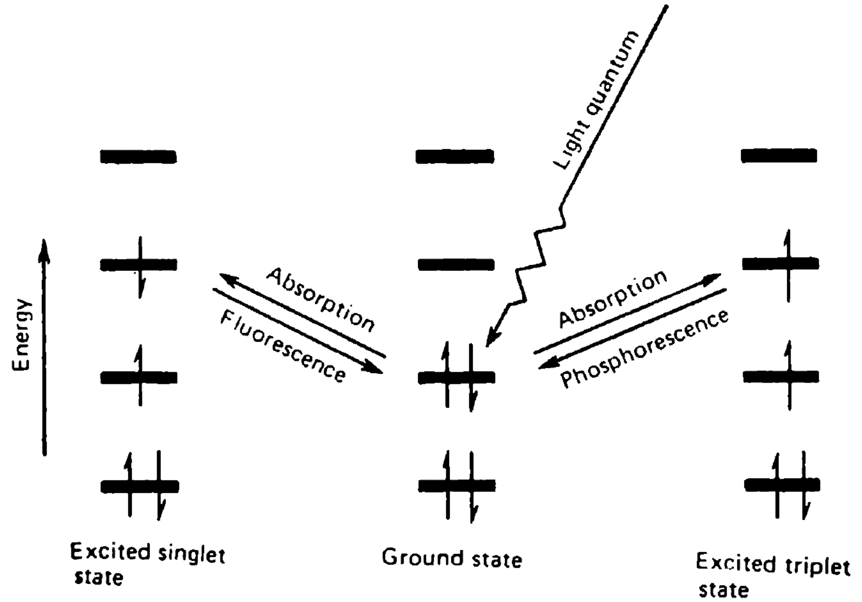


Fig. 9 Interaction of light with a molecule of a substance

400 nm is equivalent to 71 kcal/mol. The energy of one einstein of red light with $\lambda \approx 800$ nm is equivalent to 36 kcal/mol.

What happens when a light quantum has reached a molecule? In any molecule, the atoms are bound together by electrons. These electrons are located in different electron shells (Fig. 9). To illustrate this, consider a molecule with 4 electrons located in 4 shells. In the stable (ground) state of a molecule, these electrons are arranged in the two lower shells, with two electrons in each shell. Note that electrons are designated by arrows that are pointing in opposite directions. This means that electron spins have opposite signs. Schematically, this representation signifies that electrons rotate in opposite directions about their axis. The light quantum that reaches a molecule interacts with one electron giving its energy to the latter. As a result, the electron "jumps" to a higher energy shell. During this jump, the direction of rotation around the axis can remain unchanged, and then the system transforms into the excited state called the singlet state. Though the electrons are in different shells in this state, their spins are paired. The molecule cannot remain in this state for a long time, and very soon, within 10^{-8} second, the electron slides down to the lower shell. This electron fall is accompanied by the emission of light quantum making the substance glow as it were. This emission is called fluorescence, and it can easily be observed. Put a green leaf in an ethyl ether solution, and when the solution turns green, filter it through cotton wool or filter paper. Put a glass or test tube with the chlorophyll solution obtained in the light. You will notice that in the reflected light (if you look at the solution from the side), the solution fluoresces red.

Another excitation variant is possible when the electron not only jumps to a higher shell, but also changes the spin orientation to form an unstable particle in the triplet state. The lifespan of this particle can extend to several seconds. But after this time, the electron also returns to the lower shell, as a result of which light emission called phosphorescence can be observed. Fluorescence occurs only when the substance is illuminated by light, while phosphorescence is an afterglow and can be seen for a few seconds after the light source has been removed. A recipe is given here for a mixture producing green phosphorescence. Thoroughly mix the following triturated components: 10 g of chalk, 0.5 g of sodium sulphate, 0.4 g of borax, 3 g of sulphur, 0.3 g of sugar; add 0.5 ml of a 5% bismuth nitrate. Calcine the resulting mixture at 800-900°C for 15 minutes.

The energy of fluorescence and phosphorescence is, as a rule, lower than the energy of the incident light. For example, benzene illuminated at —200°C by light at $\lambda =$ 254 nm fluoresces in the ultraviolet region at $\lambda = 290$ nm, while it phosphoresces at $\lambda = 340$ nm.

Until now we have discussed processes when the illuminated system returned to its initial state with time. But excitation caused by light quantum may be enough to break old chemical bonds between the atoms and create new bonds; in other words, it may be enough to induce a chemical reaction. In this case, the transition of an electron to a higher level is only the first stage of reconstruction of the whole electron system.

Pour a small amount of concentrated hydrogen peroxide into a test tube and put it in bright light (be careful not to spill the hydrogen peroxide on your skin). You will see bubbles of evolving oxygen: $2H_2O_2 + h\nu \rightarrow 2H_2O + O_2$. (Here $h\nu$ denotes light quantum.) This reaction begins with the formation of hydroxyl radicals: $H_2O_2 + h\nu \rightarrow 2HO\cdot$.

Light can split not only the hydrogen peroxide molecule. Light quantum that is incident on a silver bromide crystal (which consists of alternating positive silver ions and negative bromide ions) knocks out an electron from bromide ion to deliver it to the silver ion. As a result, metallic silver and free halogen are formed: $2AgBr + h\nu \rightarrow 2Ag + Br_2$. It is not difficult to model this process, which underlies modern photography. In a dark room, add a solution of table salt or potassium bromide to a silver nitrate solution in a glass. Carefully apply the silver halide precipitate obtained to a piece of filter paper in a thin layer and dry it in a dark room. The effect will be more pronounced if the resulting silver halide precipitate is preliminarily mixed with gelatin that has been soaked in water. Now put a stencil made of dark paper on the prepared "photographic plate" (a figure cut out of dark paper can be used instead of the stencil) and put the plate in bright light. In a few seconds remove the stencil and exemine the plate in a dark room. You will see that the places that were illuminated by light became dark.

Unlike the human eye, silver bromide (and the more so, silver chloride) is more sensitive to ultraviolet light. Therefore, sensitizers, which mainly consist of silver halide, are introduced into black-and-white emulsions. Usually, organic dyes are used as sensitizers, which pick up the energy of the incident light and transfer it to silver halide particles. This makes the spectral sensitivity of modern photographic film similar to that of the human eye (Fig. 10). Sensitizers are not applied to photographic paper, because the emulsion is only sensitive to blue and violet light. Therefore, one can handle photographic paper in red light.

An enormous number of different chemical reactions induced by light are known. They include decomposition of organic compounds, addition of various substances, for example, oxygen, and isomerization. And finally, an important reaction is known that occurs in green plants. It is photosynthesis. It is precisely photosynthesis that makes life on Earth possible: it converts tons of carbon dioxide in the atmosphere into oxygen, which is so needed by living organisms. The general scheme of photosynthesis can be written as $CO_2 + H_2O^* + h\nu \rightarrow (CH_2O)_n + O_2^*$, where $(CH_2O)_n$ is a carbohydrate, e.g. glucose, starch, or cellulose. The asterisk indicates that the oxygen evolved by a plant does not come from carbon dioxide, but from water, which takes place in the reaction. The above equation is a simplified one. In reality photosynthesis is an involved process that has not yet been completely unravelled.

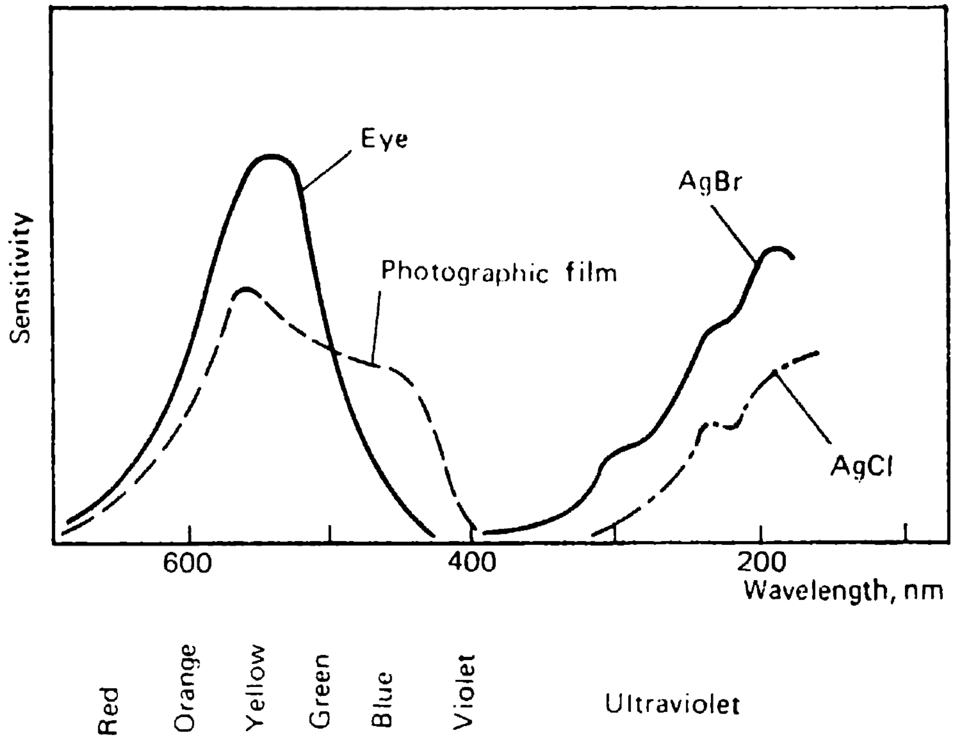


Fig. 10 Spectral sensitivity of a human eye, photographic film, and of silver halides

Photosynthesis occurs in two stages: the light-dependent stage and the light-independent stage. Chemical reactions in the first stage proceed in the light (light reactions). The light reactions of photosynthesis begin with chlorophyll. The "head" of a chlorophyll molecule is a porphyrin ring with a central atom of magnesium, while the long phytol "tail" is really a hydrocarbon. When a chlorophyll molecule is exposed to light, it becomes excited by a light quantum, and an electron jumps to a higher energy level. After this, the molecule can return to its ground state and a light quantum can be emitted. Chlorophyll fluorescence was discussed above. Carbon dioxide does not participate in the first light stage of photosynthesis, while water is decomposed by light in the presence of chlorophyll. Water donates electrons to nicotinamide adenine dinucleotide phosphate ($NADP^+$ for short). This compound converts to its reduced form designated as $NADP \cdot H$ according to the reaction: $2H_2O + 2NADP^+ + h\nu \rightarrow 2NADP \cdot H + 2H^+ + O_2$. Simultaneously another process takes place, i.e. addition of the phosphate group to adenosine diphosphate (ADP) to yield adenosine triphosphate (ATP). With this, the light stage is over. What are the results? First, a good biological reducer, $NADP \cdot H$, is produced; second, a biochemical accumulator is charged with energy: ATP is obtained from ADP.

Now, the second stage—the dark stage—begins, where the substances obtained are consumed in the reduction of carbon dioxide to carbohydrate. The reaction of the dark stage is: $6CO_2 + 18ATP + 12NADP \cdot H + 12H^+ \rightarrow C_6H_{12}O_6 + 18$ Phosphate groups $+ 18ADP + 12NADP^+ + 6H_2O$.

Thus, photosynthesis products are oxygen and carbohydrates, e.g. starch. This can easily be verified. Take a shoot of water thyme, a plant which is commonly found in home aquariums, and immerse it in a glass of carbonated water. Cover the plant with a funnel turned upside down. Fill a test tube with the same kind of water, cover the mouth with your finger and quickly turn it over onto the stem of the funnel. The plant should be "fed" with carbon dioxide, provided by the carbonated water, or water that has had a pinch of sodium carbonate added to it. Place the glass in bright light and observe how the test tube becomes filled with a gas. Introduce a burning splinter into the test tube: it will flare up, which proves that the evolving gas is oxygen.

In the second experiment, place a house plant in a dark room for a few days, and then expose it to bright light, while covering one of the leaves with dark dense paper, in which a figure has been cut out. In a day, put the leaf that was covered first into boiling water and then into boiling alcohol. When the leaf becomes colourless, rinse it with cold water and immerse it in a glass with a solution of iodine and potassium iodide in water. Iodine reacts with starch to produce a blue colouration that is observed only in places illuminated by light.

Yellow Dye from Black Carbon

Formerly, students who entered Moscow University were often asked the following question at the entrance examination in chemistry: How can one prepare picric acid (trinitrophenol) from carbon and an inorganic substance? To answer this question, the student must know the main chemical reactions and properties of substances, and, like a chess-player, be able to foresee the further possible stages. This question is of interest to us, because by tracing the reaction path from carbon to picric acid, we can get acquainted with an important branch of chemistry—organic synthesis. It is exactly due to the achievements of organic synthesis that thousands of new substances, such as drugs, dyes, pesticides, and perfumes, are industrially prepared today from coal, oil, and natural gas.

Picric acid is bright yellow in colour and was formerly used as a dye for silk and wool. Different methods for the synthesis of this compound will be discussed here. You can carry out certain stages in your home laboratory, but the whole synthesis requires special equipment.

During the first stage, carbon must be

converted into any kind of derivative, from which an organic substance can then be obtained. The relevant reaction is the one between carbon and calcium oxide at a high temperature, which yields calcium carbide. The next "move" in our chemical "match" is probably obvious to the reader: calcium carbide must be treated with water to evolve acetylene.

To prepare acetylene and study its properties, a simple setup is used. Horizontally fix a test tube in the clamp of a ring stand and plug it with a stopper provided with a gas-discharge tube bent at a right angle. Lower the end of the gas-discharge tube into a second test tube close to the bottom. Now, put a small piece of calcium carbide in the first test tube and drip a few drops of water on it. Quickly stopper the test tube and lower the end of the gas-discharge tube into the second test tube filled with dilute potassium permanganate solution. The evolving acetylene will soon decolorize the pink permanganate solution. Acetylene is oxidized by potassium permanganate to oxalic acid HOOC—COOH, which also reacts with permanganate to form carbon dioxide and water. Potassium permanganate transforms here into a colourless manganese(II) salt. Now repeat the experiment, but this time pour $AgNO_3$ solution (to which ammonium hydroxide solution was added until the initially formed precipitate had dissolved) into the second test tube. When acetylene is passed through this solution, a yellow silver acetylide, $AgC{\equiv}CAg$, precipitates. The precipitate should not be dried, because in the dry state it easily explodes when heated or knocked.

In 1922 the Soviet chemists Zelinsky and Kazansky discovered that when acetylene is passed over activated carbon at 500°C, it forms a trimer called benzene. Later, it was established that this transformation is possible under milder conditions using various metal compounds as catalysts. Thus, we have "obtained" benzene. In industry, however, benzene is produced in another way. Because it is contained in oil, it is produced by dehydrogenation of saturated hydrocarbons, e.g. cyclohexane.

There are several reaction paths by which benzene is obtained from picric acid (Fig. 11). First, let us trace the one that results in the synthesis of benzenesulfonic acid. Mix a few drops of benzene with a two-fold amount of concentrated sulphuric acid in a test tube. Heat the test tube in a boiling water bath while carefully shaking the contents. When the solution becomes homogeneous, pour the contents into a glass with water. Benzenesulfonic acid readily dissolves in water and the liquid becomes transparent. If solid benzenesulfonic acid is fused with an alkali, hydroxybenzene, or

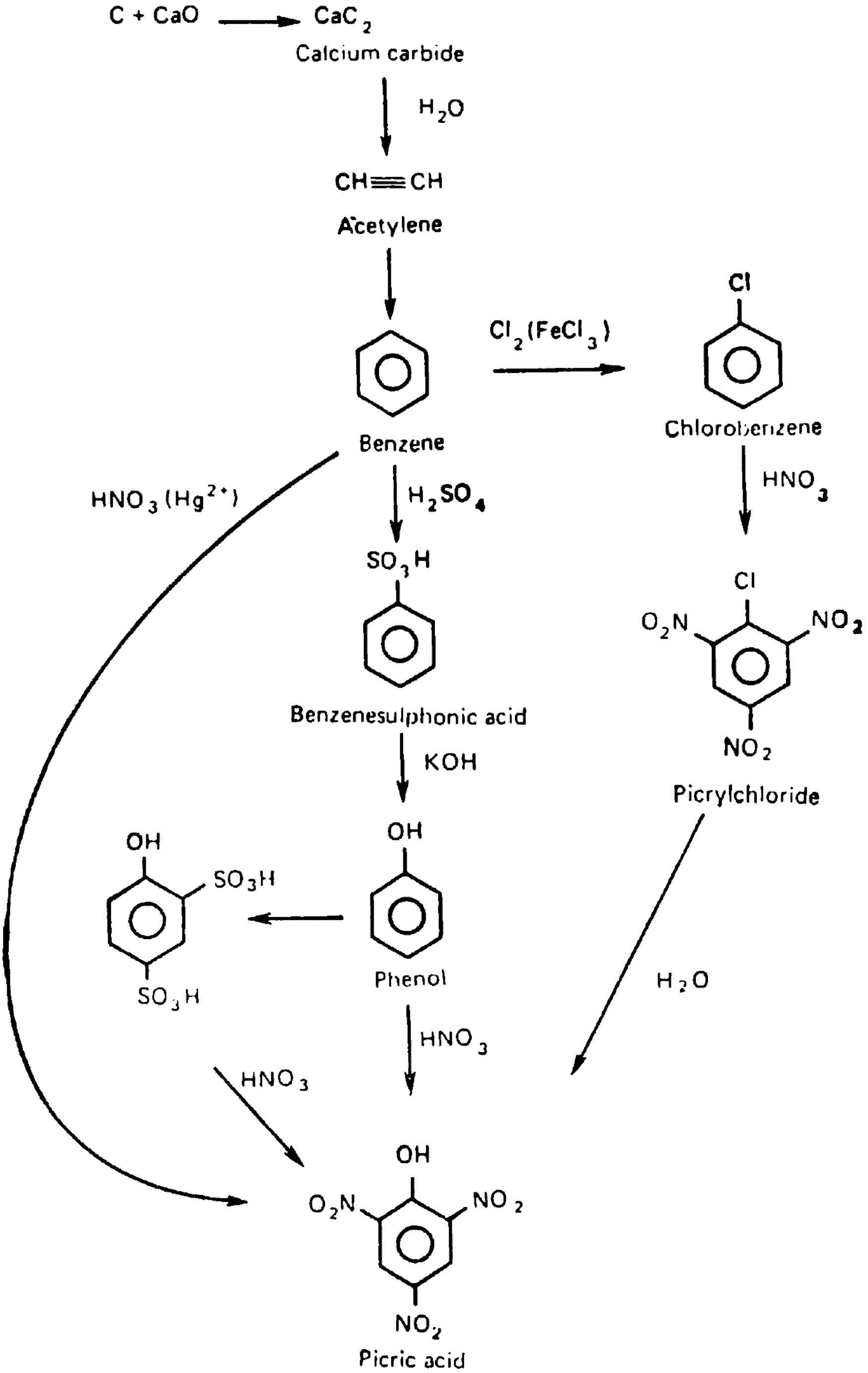


Fig. 11 Ways of the synthesis of picric acid

phenol, is formed. We have almost reached our goal now, and all we have to do is to nitrate the phenol. However, if dilute nitric acid is used, only mononitrophenol is produced. Dissolve a few crystals of phenol in a small amount of water in a test tube. In another test tube dilute concentrated nitric acid twice with water and add this acid to the phenol solution dropwise; cool the solution obtained with cold water. After the reaction is over, pour the contents of the test tube into a glass with water. Two nitrophenol isomers, i.e. ortho- and para-nitrophenol, are produced in the form of an insoluble oil that has the odour of bitter almond. When a more concentrated solution of nitric acid is used, the products will contain the dinitrophenol and picric acid that we are interested in. This reaction, however, is not convenient, because it proceeds vigorously and produces a lot of resin.

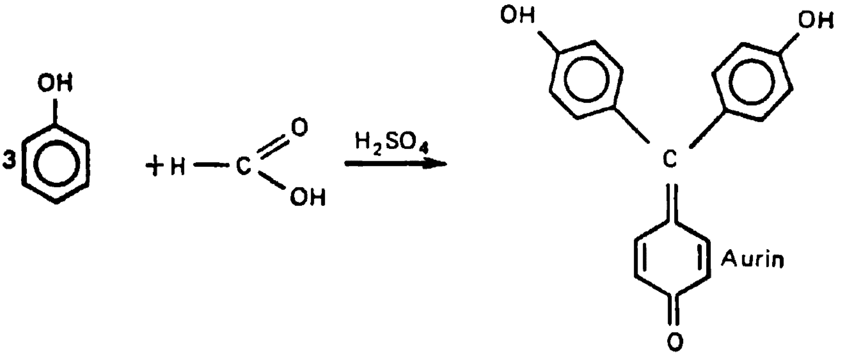
Picric acid can also be obtained by the chlorination of benzene in the presence of iron(III) chloride as a catalyst. Then the obtained chlorobenzene is nitrated with nitric acid to yield trinitrochlorobenzene, also called picrylchloride. A remarkable feature of picrylchloride is the high activity of its chlorine atom, which can be replaced by hydroxyl group when treated with water.

One more way of producing picric acid is to first synthesize phenoldisulfonic acid.

You can perform this model reaction under milder conditions and obtain phenolmonosulfonic acid. For this purpose put a few crystals of phenol in a test tube and add two drops of sulphuric acid. Heat the test tube in a boiling water bath for several minutes. Then pour the reaction mixture into a glass with water. A transparent solution of phenolmonosulfonic acid is formed. Phenoldisulfonic acid is prepared under more rigorous conditions, and then it is nitrated with nitric acid. As a result, both sulpho groups are replaced by nitro groups. In addition, the nucleus also contains a third nitro group, and the desired picric acid is formed.

Finally, picric acid can be directly synthesized from benzene when the latter is treated with nitric acid in the presence of a mercury salt catalyst. The reader may say that this is the shortest method and therefore the best, while the remaining multistage methods are of no use. The fact is that the shortest way is not always convenient for laboratory or industrial production. The efficiency of the method is determined by the output of the target product. But the amount of resin formed must be small so that it can be separated from the product.

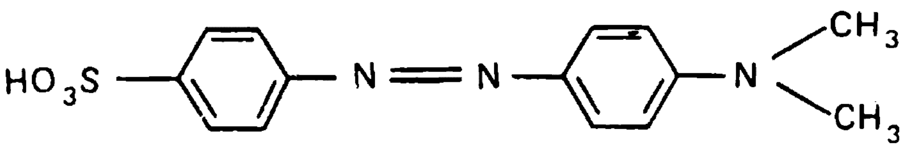
We have discussed one of the yellow dyes, whose preparation is rather involved. However, it is possible to obtain another yellow dye—aurin—from phenol by a simpler method. Put several crystals of oxalic acid and a somewhat greater quantity of phenol in a test tube. Add 1 or 2 drops of sulphuric acid and carefully heat the test tube. You will see how the mixture in the test tube gradually becomes yellow. The reaction is actually a condensation of phenol with formic acid that is formed from oxalic acid:



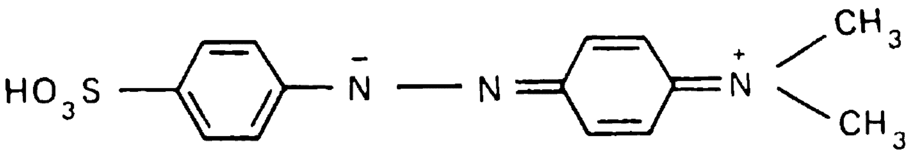
Cool the reaction mixture and dilute it with water. When an alkali is added to the solution obtained, the latter turns orange.

Thus we have produced two dyes—trinitrophenol and aurin. What other dyes are known? And, in general, what properties should an organic substance have to be a dye? It was noticed long ago that the colour of a substance depends on how many conjugate double bonds are contained in a dye molecule. For example, vitamin A and carotene contain several such bonds and are coloured yellow. The same is the case with condensed benzene rings. Naphthalene and anthracene, which contain two and three condensed rings, respectively, are colourless, while compounds with five and six benzene rings are green or blue in colour.

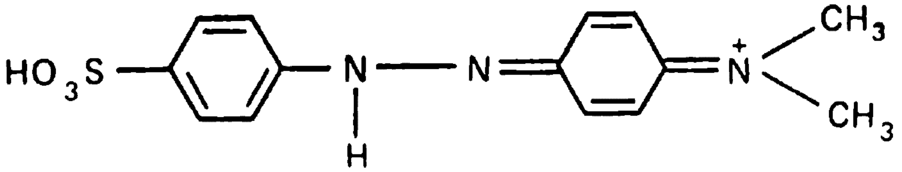
According to one theory, the colour of a substance is explained by the presence of chromophore groups, for example, $-C=C-$, $-N=N-$, $-NO$, and $-NO_2$. Auxochrome groups, such as $-COOH$, $-SO_3H$, $-OH$, $-NH_2$, and $-N(CH_3)_2$, make the colour of the substance intense. The quinoid group (the bottom part of the aurin molecule) also imparts colour to the substance. To illustrate this, take, for example, methyl orange, which is widely used as an acid indicator. The molecule of this dye contains chromophore groups with a double bond between nitrogen atoms, an auxochrome dimethylamino group, and a long chain of conjugate double bonds



The molecule does not contain a quinoid group, but the structure can also be represented as follows:



Actually, methyl orange is an intermediate between these two forms. Add an acid to methyl orange. This means that a hydrogen ion (proton) is added to one of the nitrogen atoms. A quinoid group with a positive charge is present in the resulting compound

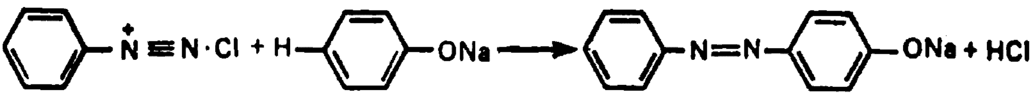


Therefore, the colour of the substance must be more intense. Indeed, the protonated form of the dye has a red colour. This property makes it possible to use methyl orange as an indicator for acids.

In general, organic dyes are substances that relate to different classes of organic compounds. Azo compounds contain an azo group, —N=N—, and are widely used as dyes. They 'are prepared from diazo compounds and phenols or aromatic amines. Diazo compounds, in turn, can be synthesized from aniline derivatives by diazotization or an azo coupling reaction. To perform this reaction, aniline and sodium nitrite will be required. In a glass, dilute concentrated hydrochloric acid three-fold with water. Mix 3 or 4 teaspoons of the diluted acid with a half teaspoon of aniline and let the obtained solution cool in a pan with crushed ice. During this time, prepare a solution of potassium iodide and starch in water, or use the following solution instead: dilute iodine tincture with water and then react it with ascorbic acid until the yellow iodine becomes colourless; add some starch. Now add sodium nitrite dropwise to several teaspoons of the prepared and cooled solution, while stirring and cooling the reaction mixture. After adding several drops of sodium nitrite, perform a test reaction: mix a drop of the reaction mixture with a drop of the iodine-starch solution on a glass slide. As soon as a blue colouration appears on the slide, stop adding sodium nitrite to the aniline solution. You have obtained benzene diazonium chloride. Here is the chemism of these reactions. Aniline reacts with hydrochloric acid to form aniline salt: $C_6H_5NH_2 + HCl \rightarrow C_6H_5-\overset{+}{N}H_3\cdot Cl^-$. Free nitrous acid forms in the following reaction: $NaNO_2 + HCl \rightarrow HNO_2 + NaCl$. Aniline salt and the nitrous acid produce benzene diazonium chloride: $C_6H_5-\overset{+}{N}H_3\cdot Cl^- + HNO_2 \rightarrow C_6H_5-\overset{+}{N}\equiv N\cdot Cl^- + 2H_2O$. An excess of nitrous acid can easily be established, because this acid oxidizes potassium iodide to free iodine, which when mixed with starch results in a bluish colour.

Diazonium salts are highly reactive substances and can react with water at elevated temperatures. Heat a test tube with a small amount of the benzene diazonium chloride in a boiling water bath. Bubbles of the evolving nitrogen can be observed and a phenol-like odour can be detected: $C_6H_5-\overset{+}{N} \equiv N\cdot Cl^- + H_2O \rightarrow C_6H_5OH +$ $+ N_2 + HCl$. In another test tube, mix benzene diazonium chloride with potassium iodide solution and heat the test tube in boiling water. When the nitrogen bubbles stop evolving, iodobenzene, a heavy liquid, forms at the bottom of the test tube.

Diazo compounds can replace the hydrogen atom in the molecules of phenols and aniline. In this way azo compounds are obtained.



To run this reaction, add some sodium hydroxide solution and benzene diazonium chloride to a phenol solution in a test tube. The yellow precipitate of an azo compound forms. In this azo compound, hydroxyl is an auxochrome group. This group is also required for another reason: it causes the dye molecule to strongly adhere to wool or silk fiber. The simplest dye can be prepared directly on a piece of cotton fabric by first impregnating the cloth with an alkali solution of phenol and then immersing it in a diazonium salt solution.

You have noticed that aniline is an indispensable component of azo dyes. However, aniline can also be used to prepare another type of dye. When aniline is oxidized, a stable black dye, called black aniline, is produced. Oxidation can be carried out in several ways. Put a few drops of aniline and dilute hydrochloric acid in a test tube and add potassium bichromate solution or calcium hypochlorite. The solution turns dark blue. Stir the mixture of aniline with water in a test tube and add a solution of potassium bichromate in dilute hydrochloric acid to this emulsion. When the resulting solution is heated in boiling water, a black precipitate separates. A piece of cloth can be soaked in aniline emulsion and then immersed in the acid solution of potassium bichromate; the cloth will be dyed black.

One more dye can be prepared from some known drugs. Put a tablet of Sulfathalidine (phthalylsulfathiazole) and a pinch of resorcinol (which is used as an antiseptic) in a test tube and add several drops of concentrated sulphuric acid. Carefully heat the test tube over a burner and then cool the mixture. Next, add sodium hydroxide to the melt and pour the contents of the test tube into a glass filled with water. You can observe a beautiful yellow-green fluorescence. This emission is already visible when only one part of the dye obtained (called fluorescein) is dissolved in 40 000 000 parts of water. Fluorescein is used to trace the course of underground springs. A small amount of the dye is poured into the spring and then water samples are tested for fluorescence at the sites where underground springs rise to the surface.

We have synthesized several dyes, but none of them was separated as a pure product. There are, however, many methods by which a substance can be separated from the reaction mixture and purified. The best way to purify crystalline substances is to recrystallize them. The principle is as follows. A substance usually contains a very small amount of admixtures. This is why saturated solutions of these admixtures are not formed, even by cooling. Thus, if a hot saturated solution of a substance is cooled, crystals of the substance precipitate, while admixtures remain in solution.

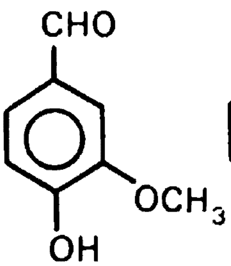
Let us synthesize nitronaphthalene. Add a teaspoon of naphthalene to 1 or 2 teaspoons of concentrated nitric acid in a glass, and then heat the glass in a boiling water bath for 2 or 3 minutes. Now, pour the contents of the glass into another glass half-filled with cold water. Yellow α-nitronaphthalene is precipitated. This substance can be purified by recrystallization. Carefully pour off the liquid from the precipitate into a glass and add some ethyl alcohol to it. Heat the glass in a boiling water bath, while adding alcohol in portions until the yellow precipitate dissolves almost completely. Then, pour the hot solution into another glass and observe how pure nitronaphthalene precipitates in the form of yellow acicular crystals.

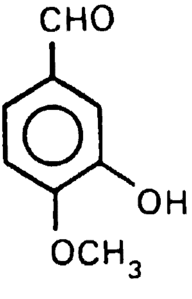
There are certain solids that can sublimate, i.e. transform directly into vapour, completely bypassing the liquid state. When the vapour is condensed again into crystals, the substance is purified from nonvolatile admixtures. Put a pinch of naphthalene in a glass jar and cover the latter with a metallic plate. Heat the jar bottom over a gas burner. You will see that naphthalene crystals deposit on the cold metallic plate.

Perfume from Naphthalene

Vision and hearing are much more important for a human being than the sense of smell. But how much we would miss, and how much duller the world would become, if we could not perceive smells. What does the odour of a substance depend on? Why do certain substances have a pleasant odour, while others have an unpleasant odour or none at all?

The reader probably remembers the smell of bitter almond. It turns out that several different substances have this odour. When you treated benzene with nitric acid, you discovered that the nitrobenzene that has formed smelled like almond. Perhaps a benzene ring and a nitro group are a necessary and sufficient condition for the appearance of an almond odour? No, this is not so, because benzaldehyde, in which an aldehyde group is connected to a benzene ring, also has the same odour. Thus, it looks as if a benzene ring together with other functional groups is responsible for an almond odour. But this statement is not true either, since phenol, which contains a benzene ring and hydroxyl group, by no means smells like almond. On the other hand, propionitrile (ethyl cyanide) and hydrocyanic acid, which do not contain a benzene ring, do smell like almond. The following two substances are very much alike, but they differ in the position of the OH and OCH_3 groups:





This slight change in the molecular structure radically changes the odour of the substances. The first substance is called vanillin and has the odour of ordinary vanilla, while the second substance is almost odourless. Vanillin is a phenol derivative, which can be established by the reaction between an alcohol extract of vanillin and iron(III) chloride resulting in a violet coloration.

So, is there any relationship between the molecular structure and the odour of a substance? At present, there is no strict and commonly accepted theory about odour, because this problem is rather complex. Nevertheless, the opinion exists that any odour can be separated into constituent elements. Molecules of different substances that have the same type of odour must have similar spatial structures. It does not matter which atoms, i.e. carbon, oxygen, or nitrogen, are in a given molecule. The main thing is that the skeleton of molecules that have the same odour should be similar. The point is that what happens when you smell a substance is that a molecule of the substance arrives at a special receptor where it fits into a particular slot. The slot has a specific form that corresponds to the form of a given molecule. In other words this principle is similar to that of a lock and key.

This theory was used to classify odours. All the known odours were divided into the following seven types: putrid, pungent, aromatic, minty, flowery, musky and camphoraceous. Most of substances with the above-listed odours can be synthesized in well-equipped laboratories or in industry. These syntheses are usually very complex, but some of them can be carried out in your home laboratory.

All of you know that hydrogen sulphide smells like rotten eggs. It forms from certain amino acids in the proteins of rotten eggs. Hydrogen sulphide can be produced by treating metal sulphides with acids. Note that this gas is poisonous. Formaldehyde is an example of a substance with a pungent odour. An aqueous solution of formaldehyde is readily available. Other aldehydes have more pleasant odours, for example, acetaldehyde CH_3CHO smells like musty apples. This substance forms when ethyl alcohol is oxidized. Dilute a teaspoon of sulphuric acid with a teaspoon of water in a glass and add an aqueous solution of potassium bichromate. Carefully add a few drops of ethyl alcohol to the solution obtained, and observe how the colour changes from yellow to green due to the formation of a chromium(III) derivative. Ethyl alcohol is oxidized here to acetaldehyde, which can be detected by the odour of musty apples. If the methyl radical in formaldehyde molecule is replaced by ethylene radical, acrolein is formed. This substance with a pungent unpleasant odour can be produced from glycerol or oil. Put a pinch of potassium bisulphate on a pan and add two drops of sunflower oil.

Heat the pan with a gas burner. The evolving acrolein has a pungent odour that irritates the mucosa of the nose.

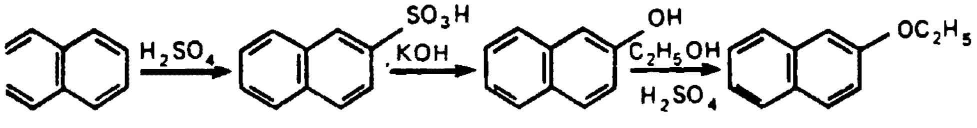
The odour of diethyl ether is probably familiar to everyone, because it is widely used in medicine. Another substance that will remind you of the doctor's office is iodoform. You can prepare it from ethyl alcohol. Put 2 or 3 teaspoons of ethyl alcohol in a glass and add a few iodine crystals (iodine tincture diluted with water can be used instead). Then, add a sodium hydroxide solution until the colour of iodine disappears. Heat the contents of the glass in a warm water bath. After the solution has cooled, yellow crystals of iodoform, CHI_3, precipitate. This substance is used in medicine as an antiseptic.

All esters, which are substances that are formed by organic acids and alcohols, have pleasant fruity odours. They can easily be prepared by heating a mixture of an organic acid and alcohol in the presence of a few drops of concentrated sulphuric acid in a water bath. The ester of isoamyl alcohol and formic acid (isoamyl formate) has an odour of plum; that of isobutyl alcohol and acetic acid (isobutyl acetate) smells like pineapple; isoamyl acetate smells like pears; benzoyl formate smells like jasmine; while phenylethyl formate has an odour of chrysanthemum.

A specific odour of natural products is

due to the presence of a particular substance in a given product. For example, the main component of turpentine, which is responsible for its odour, is a pinene, a cyclic compound with a double bond. The double bond can easily be identified when a potassium permanganate solution is added to a few drops of turpentine in a glass while stirring. As a result, the pink colour of potassium permanganate disappears and brown manganese dioxide precipitates. In contrast to turpentine, bread has an odour defined by a complex mixture of different substances, i.e. ketones, aldehydes, and organic acids. But the odour of bread is mainly due to the presence of the heterocyclic aldehyde furfural. This substance can be produced from sugars containing five carbon atoms. The latter, in turn, are obtained by treating wood with an acid. Put a small amount of sawdust in a test tube, wet it with dilute hydrochloric acid, and heat the mixture to boiling. After cooling, neutralize the acid with soda (sodium carbonate), add some water and heat again. As a result, furfural evaporates with the steam and can be identified by its specific odour.

Those who have gained experience in conducting chemical experiments can carry out the more involved synthesis of perfume, thus modelling a chemical production process. From naphthalene, try to obtain a substance that smells like a mixture of acacia and oranges. Put two teaspoons of naphthalene in a beaker and add concentrated sulphuric acid to 1/4 of the beaker's volume. Heat the mixture over the low flame of a gas burner while stirring until the mixture becomes homogeneous. Cool the beaker and add some water. Soon crystals of β-naphthalenesulphonic acid precipitate. If there is no precipitate, cover the beaker and put it in a refrigerator. Next, pour off the liquid and add 1 or 2 teaspoons of granulated potassium hydroxide and water to the crystals. Heat the reaction mixture over a burner for a few minutes. The resulting gray mass of β-naphthol should be poured into a glass half filled with water. Separate the solution from the precipitate by filtration and add concentrated sulphuric acid dropwise to the filtrate. Filter off the precipitated β-naphthol and dry it on filter paper in the air. Then transfer the dried precipitate to a test tube and add ethyl alcohol and a drop of concentrated sulphuric acid to it. Heat the test tube in a water bath until the alcohol evaporates. The residue in the test tube is β-naphthol ethyl ether (Nerolin II, or bromelia), a compound with the mild pleasant odour of flowers and fruits. The reactions that occurred are the following:



If methyl alcohol (be careful, it is very poisonous) is used instead of ethyl alcohol during the last stage, β-naphthol methyl ether (Nerolin I) is produced. This substance smells like bird cherry flowers and is widely used in the perfume industry.

The "Black Box" of Chemical Transformations

Run two experiments. The first one is simple: add one drop of a table salt solution to an aqueous solution of silver nitrate. A white precipitate of silver chloride immediately forms. The second experiment is more involved. Put several drops of concentrated sulphuric acid in a test tube and carefully add the same amount of concentrated nitric acid dropwise. Cool the test tube in cold water and add several drops of benzene. Then, plug the test tube with a stopper fitted with a long glass tube and heat it in a hot water bath (the temperature of the water should not exceed 50°C). After several minutes, pour off the upper layer into another test tube and add 1-2 teaspoons of water to it. The nitrobenzene that is obtained has an almond scent; it is heavier than water and therefore sinks to the bottom.

As can be seen, the two experiments differ substantially. The first reaction proceeds at normal temperature within fractions of a second; the second one requires heating for several minutes. This is explained by the fact that in the first reaction when the silver and chloride ions meet, they immediately form a compound that is insoluble in water. Almost all inorganic reactions proceed sufficiently quickly. In the second reaction, benzene is nitrated with nitric acid in the presence of sulphuric acid. When the acids are mixed, nitronium cation NO_2^+ is produced: $HNO_3 + 2H_2SO_4 = H_3O^+ + 2HSO_4^- + NO_2^+$.

The reaction mixture also contains benzene. The benzene molecule accommodates six π electrons, which interact with nitronium cation to form a π-complex. The NO_2^+ cation in the π-complex is simultaneously "attached" to each of the six carbon atoms of the benzene ring (Fig. 12).

Let us represent the course of a reaction by an energy diagram. The energy of a reaction system should be plotted along the vertical axis. Obviously, if a system passes from one point in the diagram to another point that corresponds to a higher energy level, then the system must obtain energy from somewhere: it may be derived from

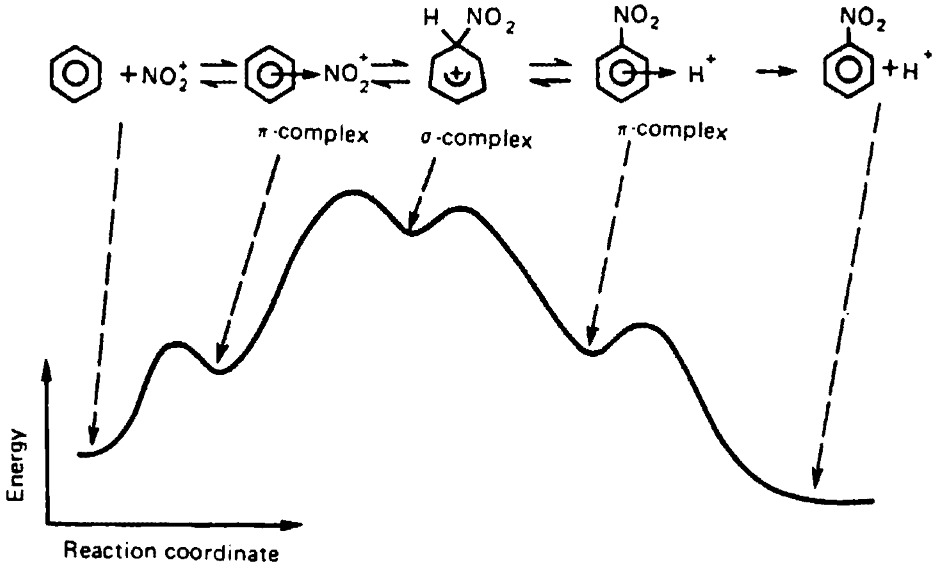


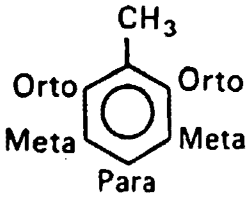
Fig. 12 Energy diagram for the nitration of benzene with nitronium cation

the energy stores of the random motion of particles. Transition from a higher point in the diagram to a lower one can be spontaneous. Therefore, the higher the point in the diagram, the more unstable is the corresponding state of the system, and the easier the system returns to a stable state.

In the diagram shown in Fig. 12, transition from one local energy minimum to a neighbouring one corresponds to a reaction stage, and the reaction path along the course of the stage can be considered as the mutual rearrangement of the reacting molecules, particles, or their parts. At the beginning of a reaction, the reacting particles are far from each other, and when they approach, they first repel each other. Therefore, the curve in the diagram ascends. As a result of interaction, a relatively stable intermediate is produced, and the curve drops to the minimum. The described portion of the curve corresponds to the formation of the π-complex of benzene and nitronium cation. Since the stability of this complex is not high, the latter can decompose into its initial components, and the curve will follow the reverse course. However, the π-complex that was obtained can undergo reconstruction and transform into a σ-complex, in which nitronium cation forms a covalent bond with one of the carbon atoms of benzene ring. The hydrogen atom attached to this carbon atom protrudes from the plane of benzene ring, and the positive charge from the nitronium cation "slides down" and becomes "dispersed" over the remaining five carbon atoms. The formation of the σ-complex is depicted in the diagram by a small valley "high in the mountains".

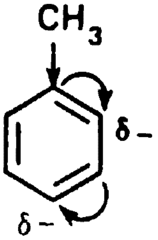
The next stage is the detachment of a proton from the carbon atom and the formation of a π-complex with the proton. The proton does not remain for long in the π-complex: it is soon detached from the π-complex, as a result of which nitrobenzene is produced. In this way the replacement of a hydrogen of benzene by a nitro group, which seems to be a simple reaction at first glance, occurs. This reaction is widely known in chemistry and is called an electrophilic replacement. The electrophilic (having an affinity for electrons) group here is the nitronium cation, and benzene is the substance that supplies electrons. Electrophilic replacement reactions also include chlorination, bromination, and sulphonation of benzene or other aromatic compounds. In these reactions the electrophilic species can also be ions of mercury, thallium, or lead.

All the six hydrogen atoms in a molecule of benzene are equivalent. Toluene presents a different case, because an electrophilic particle has a choice: it can replace the hydrogen in the *ortho* or the *para* position. In addition, there is one more position—that of *meta*:

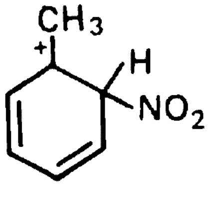


There are two *ortho*- and *meta*-protons, and only one *para*-proton.

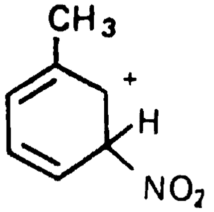
The electron density is shifted from the methyl group in toluene towards the benzene ring, where it is distributed nonuniformly. To determine the sites where the electron density is higher, it is convenient to represent the structure of benzene in the traditional form, though it does not reflect the real situation. The displacement of the electron cloud is depicted by arrows:



The symbol δ- (delta minus) indicates where the electron density is the highest. Obviously, it is precisely these carbons (in the *ortho* and *para* positions) to which the nitro group is drawn. Let us consider possible substitution positions of σ-complexes. The positive charge is conventionally ascribed to a specific carbon atom, rather than uniformly distributed over the ring. The structure of a σ-complex with an *ortho* substituent is



Pay attention to the fact that the methyl group somehow "quenches" the positive charge on the neighbouring atom. As a result, the σ-complex becomes more stable. Here substitution proceeds more easily. Observe what results when the nitro group is in the *meta* position:



In this case, the carbon atom with the positive charge is separated from the methyl group by two single bonds, and, therefore, the methyl group cannot quench this positive charge. Substitution of a nitro group in the *para* position is similar to that in the *ortho* position described above (try to prove this using the structural formula). Indeed, it has been experimentally established that nitration predominantly involves the *ortho* and *para* positions. The mixture of isomers produced as a result of nitration of toluene consists of 60% *ortho*-nitrotoluene, 36% *para*-nitrotoluene, and only 4% *meta*-nitrotoluene.

We have already discovered that nitration of benzene occurs through a chain of intermediate transformations. But how do scientists know which transformations occur and which intermediate substances are produced in the course of the reaction? In contrast to those formed during the intermediate stages, the reactants (benzene, nitric and sulphuric acids) and the product (nitrobenzene) can be handled, weighed, or analyzed. This situation reminds us of a "black box", where we know for sure only which objects are placed into the box and which are taken out at a certain time. The transformations that occur inside the box and the intermediate substances that are produced can often be established only from indirect data. Suppose that you perform a reaction and measure the concentrations of the initial substances and products. Sometimes, it turns out that after a period of time there are already very small amounts of reactants remaining in the reaction mixture, i.e. the reactants have been almost completely spent, but the amount of the product is still very small. This means that some intermediate substance is present in the reaction mixture.

How can the structure of this compound, whose concentration is often very small, be established? Physical methods of investigation, such as nuclear magnetic resonance, infrared and electron spectroscopy, and electron paramagnetic resonance, can be used for this purpose. These methods provide information about the groups present in the substance and the sequence in which the atoms are bonded in the molecules. Sometimes, however, the intermediate compounds can be established visually.

Put a drop of concentrated sulphuric acid on a glass slide and add naphthalene or phenol, and then, a grain of sodium nitrate (potassium nitrate or silver nitrate can be used instead). The resulting solution acquires an intense yellow or green colour. It is believed that the colour is due to the intermediate σ-complexes formed during nitration. It should be noted here that some Soviet scientists recently discovered that these coloured compounds form as a result of the transfer of an electron from the aromatic compound to the NO_2^+ ion. This leads to the formation of the so-called cation-radical of the aromatic hydrocarbon and the $NO_2^{\bullet}$ radical. These radicals combine to form the σ-complex, which we have already been introduced to. As you can see, the mechanism involving the π-complex and the σ-complex is much more complicated. Scientists must still investigate the details of nitration—a reaction that was discovered long ago and considered to have been sufficiently investigated.

Chemical Puzzles and Paradoxes

Before they begin dissolving, filtering, triturating, or evaporating (i.e. before starting "real" chemical work), chemists quite often turn to molecular models to predict a reaction course. Indeed, it is modelling, rather than a chemical experiment alone, that more often results in great and unexpected discoveries. And how many nontrivial ideas these "chemical toys" can suggest!

At the beginning of the 1950s, the English biologist Watson and the physicist Crick set about to establish the structure of deoxyribonucleic acid (DNA). They assumed that this substance was responsible for the transmission of the hereditary characteristics of an organism. The scientists used the same approach that was used by Linus Pauling in establishing the structure of protein molecules many years before. They began to build models of the component parts of the DNA molecule using balls, wire, and cardboard, and then they combined these parts into a chain. While building the models, Watson and Crick often consulted chemists about the structure of heterocycles in the DNA molecule and about the possible chemical bondings. Numerous variants were suggested and much effort was spent before a simple and elegant solution was found: the DNA molecule consists of two chains that are coiled around each other into a double helix such that the heterocycles are located inside the helix and the phosphoric acid residues are outside the helix. The significance of this great discovery made by "playing with chemical toys" can hardly be overestimated.

Let us also make models of some molecules. Very simple "equipment" will be required: a box of matches, cardboard, and plasticine (modelling clay). First, construct a model of a methane molecule, CH_4. Make a small ball the size of a cherry out of black plasticine: it will represent the carbon atom. Stick four matches into the ball so that their heads are at the angles of a right tetrahedron. The heads of the matches represent the hydrogen atoms, while the match sticks themselves stand for the chemical bonds between the carbon and hydrogen atoms. The model of the methane molecule can easily be transformed into an ethane molecule. CH_3CH_3. To this end, make one more methane molecule, but use only three matches. The fourth match will come from the first methane molecule; it is connected to the second molecule by sticking the head of the match into the second carbon atom. If another $—CH_3$ fragment is added to this ethane molecule in the same way, a molecule of propane, $CH_3CH_2CH_3$, will result.

Now, let us construct a model of propyl chloride using the propane model. One of the hydrogen atoms of propane should be replaced by a chlorine atom. A chlorine atom can be made from white plasticine, and then the head of one of the matches of the propane model should be stuck into the white chlorine atom. But here a question arises: Which match should be chosen, the one that is at the end carbon or that which is at the central carbon? It turns out that when a hydrogen at the end carbon is replaced by chlorine, normal propyl chloride, which boils at 45°C, is obtained. When a hydrogen at the central carbon is replaced by chlorine, isopropyl chloride forms, whose boiling point is 35°C (Fig. 13*a*). Substances that have the same general formula (in our case C_3H_7Cl) but a different sequence in which their atoms are bonded to each other are called isomers. Now construct an ethylene molecule, in which two carbon balls are connected by two matches (double bond) and two more matches are stuck in each carbon so that they lie in the plane of the double bond. A chlorine derivative of ethylene, dichloroethylene, in which chlorine atoms are attached to

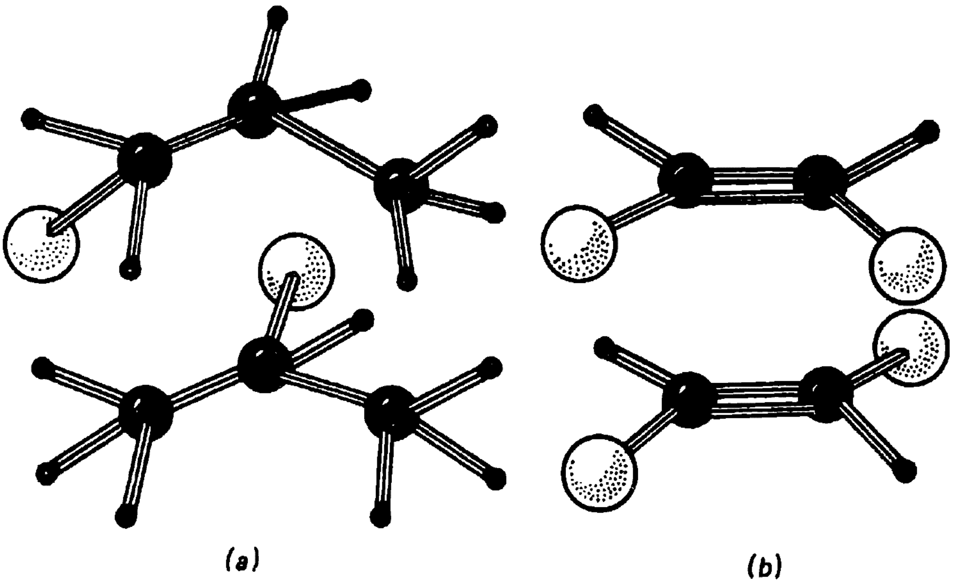


Fig. 13 Models of isomers of propyl chloride (*a*) and of dichloroethylene (*b*)

different carbon atoms can have two possible structures. When both chlorine atoms are on one side of the double bond, the *cis*-isomer is formed; and when the chlorine atoms are on different sides of the double bond, the *trans*-isomer is obtained (Fig. 13*b*). This type of isomerism is called geometric *cis-trans* isomerism. *Cis*-dichloroethylene boils at 60°C, but *trans*-dichloroethylene boils at 48°C. It can be seen that the isomers considered here differ in their physical properties, i.e. boiling points.

Again, take the methane model and replace three of its hydrogens by the following groups: carboxyl, —COOH (let it be represented by a large white plasticine ball), hydroxyl, —OH (it can be made from plasticine of any other colour), and methyl group, $—CH_3$ (large black ball). Place the constructed model in front of a mirror and make a precise copy of its reflection while looking at its mirror image. Now you have models of two molecules, which, though they seem very much alike, are different (Fig. 14*a*). The point is that they do not coincide when superimposed, just as one's left hand does not coincide with one's right hand when superimposed, or the glove for the left hand cannot be put on the right hand.

Do the substances that consist of the "left" and "right" molecules differ? They do, though their boiling points and most

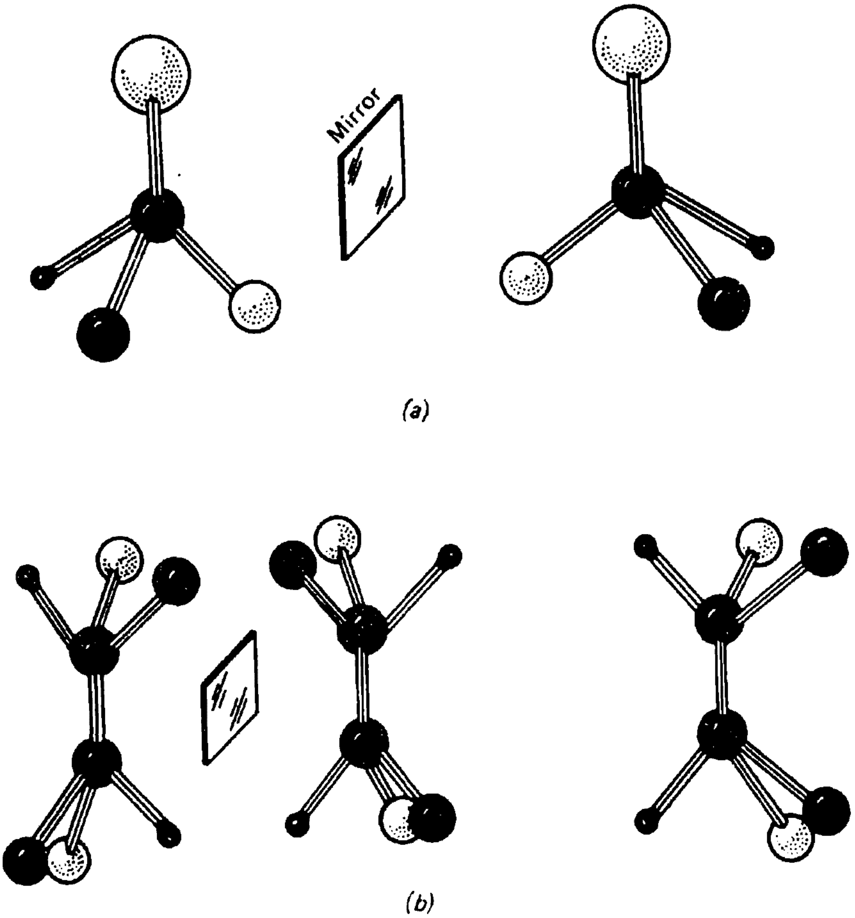


Fig. 14 Models of optical antipodes of chiral molecules of: *a*—lactic acid and *b*—tartaric acid

chemical properties are the same. There is one property, however, that can be used to distinguish them, i.e. their relation to polarized light. It is known that light is the flux of electromagnetic waves. Usually, the vectors of electric and magnetic fields are perpendicular to the line of propagation of the light ray, independent of its direction. When a beam of light passes through special filters, the vector of the magnetic (and electric) field becomes parallel to the line of light propagation and the light is said to be polarized. If a beam of light polarized in one plane is passed through a solution of left-handed and right-handed molecules, the plane of polarization will rotate through a certain angle. It is remarkable that the plane of polarization rotates to the left for molecules of one type and through the same angle but to the right for their antipodes.

When you constructed a model by replacing three of the methane hydrogens and then made its mirror image, you obtained two varieties of lactic acid, $CH_3CH(OH)COOH$. These varieties are mirror images of each other and are called optical antipodes or enantiomers. When a model of a molecule or any other geometrical figure does not coincide with its mirror image, this molecule is said to have the property of chirality. This word comes from the Greek *cheir*, meaning hand, and was used to designate this phenomenon, because the examples with the right and left hands explain it best of all. For a molecule to exist in the form of two antipodes, it must contain, for example, a carbon atom bonded to four different substituents (in our case $-H$, $-CH_3$, $-OH$, and $-COOH$). This carbon atom is called asymmetric or a chiral centre. One can form a great variety of optically active compounds because different substituents can be attached to the carbon atom in a different way. And what happens when a molecule contains two asymmetric carbon atoms? Take, for example, the simplest case, i.e. tartaric acid, HOOCCH(OH)CH(OH)COOH. Construct models for this molecule and its antipodes and you will see that three variants are possible for this substance (Fig. 14*b*). A substance that consists of molecules of one type rotates the plane of polarization to the right, and a solution of their mirror antipodes rotates it to the left. Finally, a third variant is possible, one when the substance does not rotate the plane of polarization. This occurs when one part of a molecule rotates the plane to the right, while the other part rotates it to th left.

Optical isomerism is a phenomenon that is widely encountered in nature. All the amino acids contained in a living organism are in the form of one enantiomer. Only under this condition can the protein molecules, which consist of amino acids, form a proper double helix. Sugar and glucose also exist in the form of optical isomers, and the molecules that occur naturally are those of only one antipode. This is not accidental, because the enzymes that catalyze chemical reactions in a cell can easily distinguish between the relative positions of substituents around asymmetric carbon atoms. It is noteworthy that our tongue is a perfect tool for distinguishing between enantiomers. For instance, one of the antipodes of aspartic acid tastes sweet, although the other antipode has no flavour. Stereoisomers of the amino acid isoleucine differ from each other still more: one isomer is sweet, but the other one is bitter.

The presence of a classically asymmetric carbon atom is not the necessary condition for optical isomerism or optical activity of a substance. It is only necessary that a molecule and its mirror image do not coincide when superimposed, i.e. a molecule must be chiral. Cut two hexagonals out of a piece of cardboard; they will represent benzene molecules. Attach one match to each of the three neighbouring vertices of one hexagonal. Put a white and a black plasticine ball on the two end matches and attach a similarly substituted benzene hexagonal to the central match. You will see that two antipodes can be constructed (Fig. 15*a*). Indeed, optical isomerism in such diphenyls (a white ball represents, for example, a —COOH group, and a black ball is a nitro group, $—NO_2$) was discovered in 1922. And here are examples of new substances produced in the last decades. Cut two regular pentagonals out of a piece of cardboard and make a "sandwich" with a plasticine ball inside.

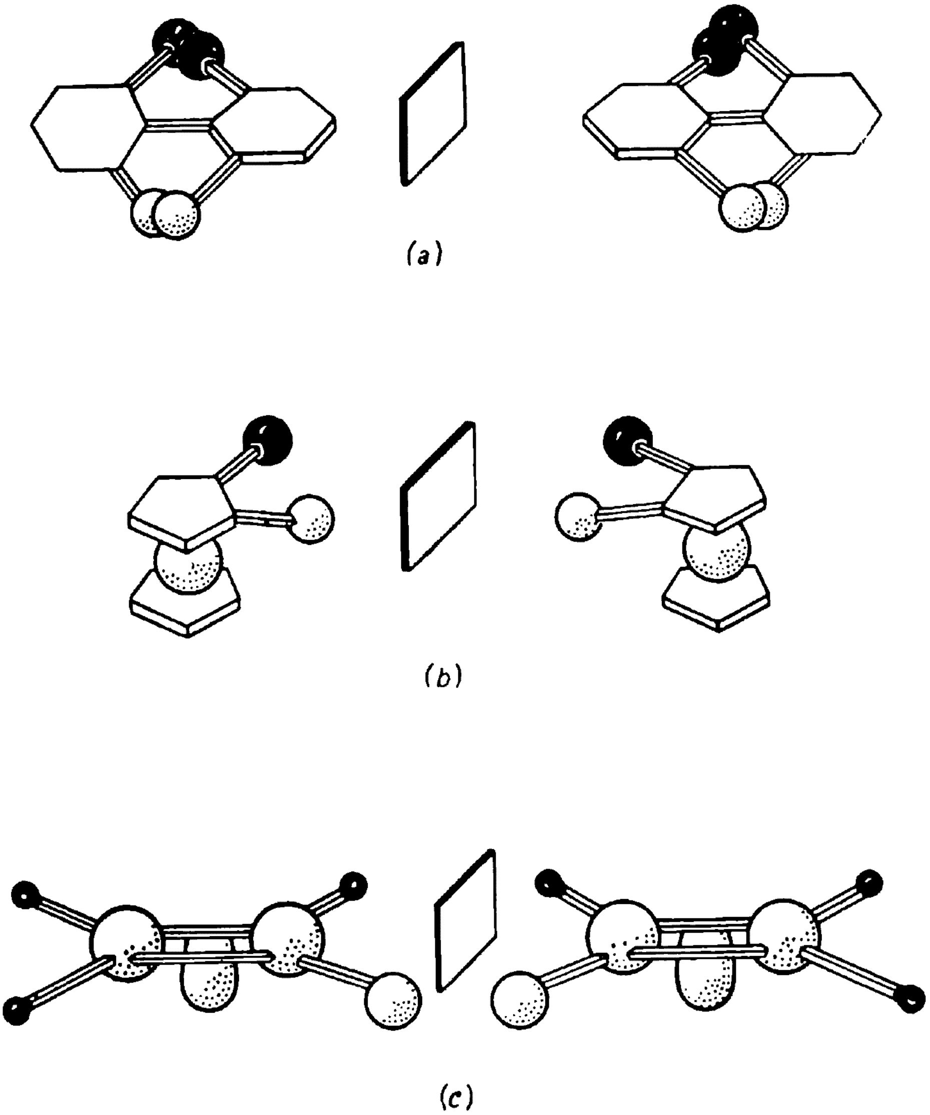


Fig. 15 Models of isomers of chiral diphenyls (*a*), ferrocenes (*b*) and of ethylene π-complex (*c*)

This model represents a molecule of ferrocene, in which the pentagonals are hydrocarbon rings, C_5H_5, and the ball between them is an iron atom. "Substitute" black and white balls for the two hydrogens at the vertices of the pentagonal. It follows from Fig. 15*b* that two enantiomers can exist for this substance. Construct a molecule of acrylic acid by substituting a white ball (—COOH, a carboxyl group) for one of the hydrogens in the ethylene model. Then, attach a lump of plasticine to a double bond, which will represent an $Fe(CO_4)_2$ group. Again, two enantiomers are possible for this substance (Fig. 15*c*).

Make a ring with a strip of paper, but before gluing its ends, rotate one of the ends 180° around the strip axis. The figure thus obtained is called a Möbius band, and it is widely known to mathematicians. It has a remarkable property: if you want to paint both sides of the band, you can do this without lifting the brush from the strip. It turns out that the strip has only one side. But the Möbius band has one more peculiarity: it can be made from a strip of paper in two ways. The resulting two figures do not coincide when they are superimposed, and they are mirror images of each other. In other words, the Möbius band is chiral. If before gluing the ends, the strip is rotated 360°, figures will be produced that are also chiral and possess an interesting feature (Fig. 16, at the top). To reveal this feature, cut the strips with scissors along their axes. The result is two interwoven Möbius bands, both of which are chiral (Fig. 16, bottom part).

What do these strips have to do with chemistry? Suppose that the edges of the strips are the chains of carbon atoms, or, more precisely, $—CH_2—$ groups. These chains are connected, at intervals, by, for example, sulphur atoms, so that something that resembles a circular rope ladder

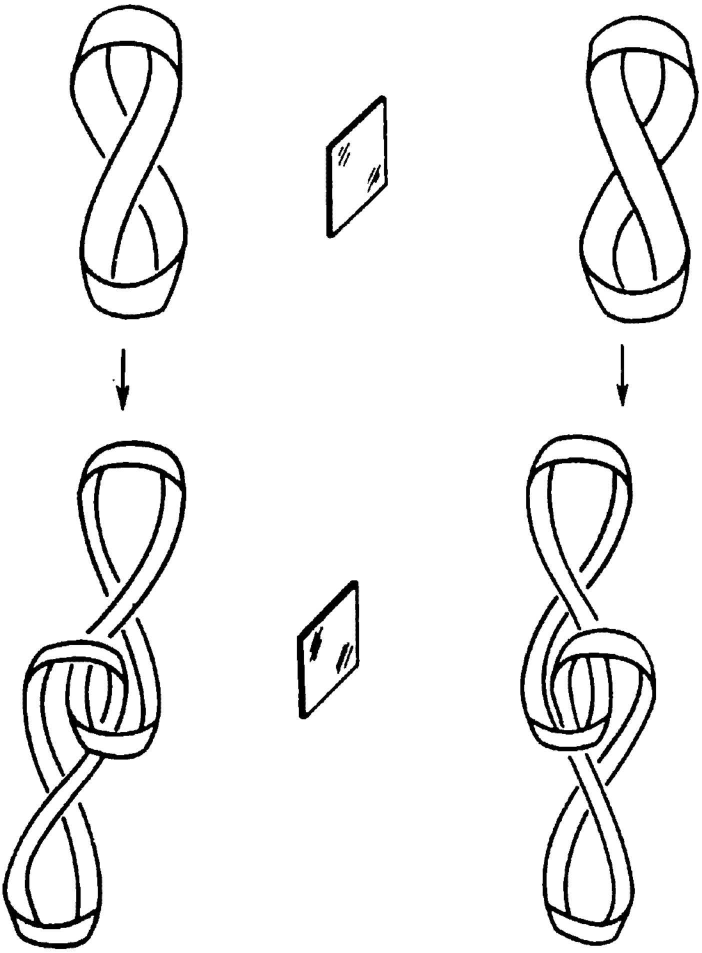
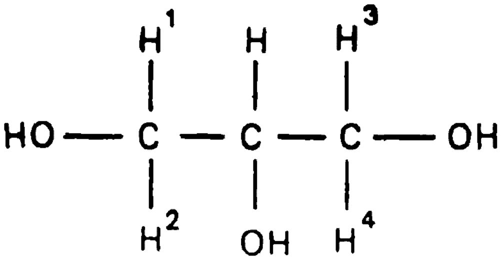


Fig. 16 Models of molecules in the form of chiral bands

is formed. Now, remove the "steps" of the ladder, i.e. the sulphur atoms, and you will obtain a molecule that consists of two coupled rings and is called a catenane (from the Latin *catena*, meaning a chain). Catenanes have been known of for twenty years, but their preparation is time-consuming and labour-intensive. Unfortunately, the idea that was described above has not yet been realized. Only recently, a molecule has been synthesized whose structure is similar to a Möbius band.

The possibility of cutting band molecules is still a chemist's fantasy. But when you carefully examine models of well-known substances, you can discover properties that were unknown to you before. Take, for example, common glycerine. Its structure is simple and "symmetric"



$$\begin{array}{ccccccccc} & & H^1 & & H & & H^3 & & \\ & & | & & | & & | & & \\ HO & - & C & - & C & - & C & - & OH \\ & & | & & | & & | & & \\ & & H^2 & & OH & & H^4 & & \end{array}$$

It seems obvious that two hydrogen atoms, H^1 and H^2, as well as H^1 and H^3 at the end carbons are identical. However, this is not so. Let us first consider more simple examples of models of ... more complex compounds. Cut several equilateral triangles out of a piece of cardboard and push spokes or matches into their centres vertically. Consider a model in which all the triangle vertices are identical; let them be white in colour (Fig. 17*A*). The vertices can easily be interchanged by simply rotating the triangle 60° around the match. Therefore,

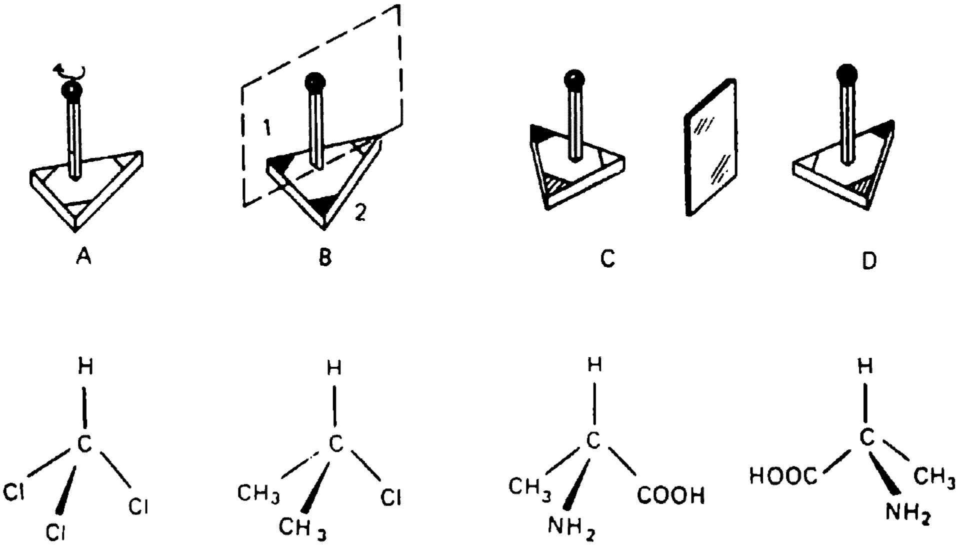


Fig. 17 Models and the corresponding molecules that are used to explain enantiotopy and enantiomerism phenomena

we shall call such interchangeable vertices equivalent. Now, colour two vertices of the triangle black on both sides. Now, the vertices numbered *1* and *2* in model *B* (Fig. 17*B*) cannot be interchanged by rotation; however, if you place a mirror vertically on a white vertex and along the dividing line between sides *1* and *2*, you can obtain vertex *2* in place of vertex *1*.

Hence, in this case vertices (and in general, all sites on the triangle) are interchangeable by reflecting them with a mirror. We call them enantiotopic (from Greek *enantios*, meaning opposite and *topos*, meaning place).

Having discussed two cases (in the first one, the three vertices were identical; and in the second, two vertices were identical and black in colour and one vertex was of another colour), we can now take a third case. Here all the vertices are different. Let them be white, black, and gray in colour. These three colours can be combined in two ways, and both structures are mirror images of each other. Therefore, such structures (see Fig. 17*C* and *D*) can be called enantiomers (either of two compounds exhibiting enantiomorphism).

Before we start analyzing more complex models, we should point out that the cardboard triangles considered above have prototypes among real and well-known substances. For example, structure *A* corresponds to a molecule of chloroform, while the chiral "toys" *C* and *D* reflect the properties of alanine, which is a vitally important amino acid. Not only an atom, but a group, for example, a methyl group ($—CH_3$), can be "coded" by a vertex of a specific colour. Although these molecules have a tetrahedral shape, they can easily be modelled by a triangle with a match attached, i.e. by a pyramid.

Now, we shall pair our structures, but in different combinations by stringing the triangles on the spokes. The combinations *A* and *B*, and *C* and *D* are, most obviously, of little interest. In these combinations, *A* can represent a methyl group. The vertices in the triangle (hydrogen atoms in $-CH_3$) will be equivalent independent of the neighbour on the spoke. You can verify this by exchanging the neighbours of the triangle for white vertices and rotating the triangles around the spoke in all directions. The white triangle will also have no effect on its neighbour on the spoke. Such molecules have already been considered above, for example, CH_3-CH_3, CH_3-CH_2Cl, and $CH_3-CHBrCl$. Next, make the model *E* from two *B* structures (Fig. 18). *E* represents the dichloroethane molecule, CH_2Cl-CH_2Cl. Let us examine how the black vertices are located with respect to each other. By the rules of our game, the triangles can be rotated around the spoke, which corresponds to the rotation, for example, in a molecule of dichloroethane, around the C—C bond. It is impossible to find a position where a mirror could be placed in relation to *E* structure such that the two black vertices of both triangles become interchangeable. But when you rotate one triangle relative to the other to obtain structure *E*′, you will see that it is now possible to place a mirror

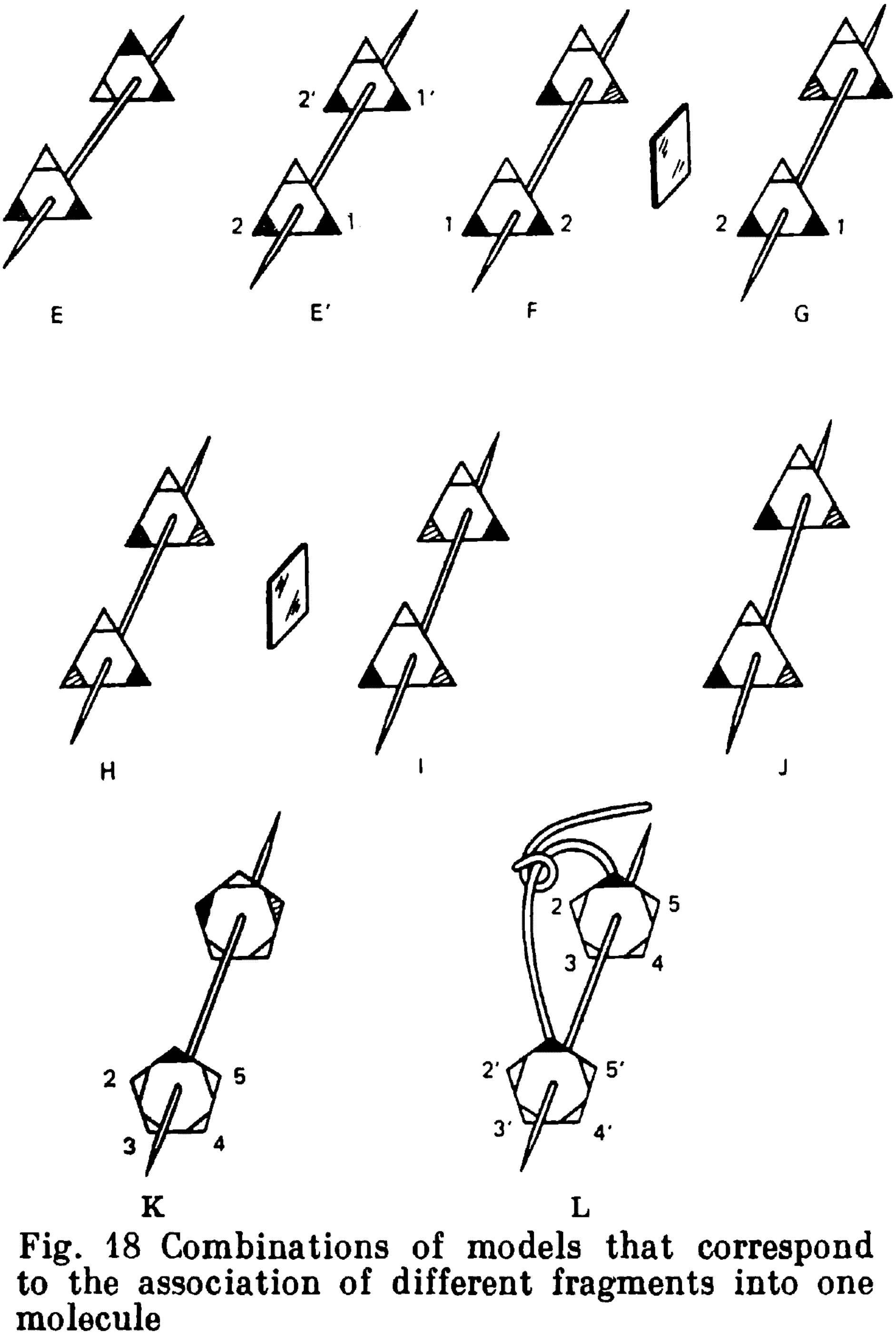


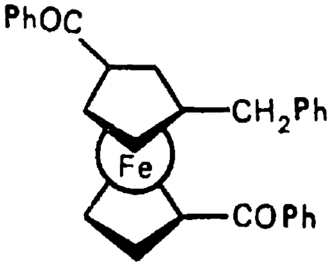
Fig. 18 Combinations of models that correspond to the association of different fragments into one molecule

as we did for structure *B*. This means that the black vertices (*1* and *2*, as well as *1′* and *2′*) in each triangle are enantiotopic. In addition, the mirror can be placed perpendicular to the spoke in the centre of the triangle. Hence, two more pairs, *1* and *1′*, and *2* and *2′*, are also enantiotopic.

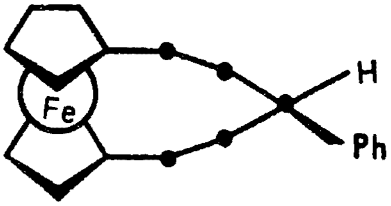
Next, we take more complicated variants: combinations $B + C = F$ and $B + D = G$. This time, no matter how the triangles are rotated, it is impossible to "position" the mirror so that vertices *1* and *2* become interchangeable. It should be pointed out, however, that structures *F* and *G* are enantiomers, and each of them contains corresponding vertices numbered by the same figures. Pairs of "identical" vertices such as *1* and *2*, which are not interchangeable under any conditions, are called diastereotopic (from Greek *dia*, meaning through, across and *stereo*, meaning solid). And the last variants, i.e. combinations of two chiral structures, which are probably three in number: $C + C = H$, $D + D = I$, and $C + D = J$. Structures *H* and *I* are chiral and mirror images of each other; hence they are also enantiomers. Structure *J* is not chiral. Pairs that are not enantiomers, for example, *J-H* and *J-I* are called diastereomers. The reader should understand that all these models correspond to real molecules. For instance, structures *H*, *I*, and *J* are the models of tartaric acid.

Structures composed of pentagonals have much in common with triangular structures. Structure *K* (Fig. 18) is chiral; moreover, the white vertices *2* and *5* (as well as *3* and *4*) are diastereotopic. Connect two vertices of pentagonals in structure *L* with a wire bridge and attach another wire in the form of a loop to the bridge so that it can easily move along the bridge (see Fig. 18*L*). This model will help us clarify one interesting feature. Move the loop towards one of the pentagonals, and you will obtain a chiral structure, in which the pairs of vertices, *2* and *5*, and *3* and *4* of one pentagonal, and *2'* and *5'*, as well as *3'* and *4'*, of the other pentagonal are diastereotopic. However, when the wire loop is placed in the middle of the bridge, at equal distances from each pentagonal, the model no longer remains chiral (a mirror can be placed in the plane of the loop perpendicular to the spoke). The vertices, however, remain diastereotopic.

The reader, probably, has many questions, and we shall try to answer them. First, what molecules correspond to the constructed pentagonal structures? The derivatives of ferrocene, which has already been mentioned, are considered to be the prototypes of structures *K* and *L*. The formulas of these compounds (Ph stands for the phenyl radical, C_6H_5) are given below:



(K)



(L)

Several years ago, the diastereotopy of these molecules was discovered experimentally. The second question is: How does diastereotopy manifest itself in the properties of substances? It can easily be noticed that each of the four terms, enantiomerism, enantiotopy, diastereoisomerism, and diastereotopy, consists of two parts. It turns out that molecules (in this case the root *merism* is used) and molecular fragments, separate atoms or groups (this is denoted by the root *topy*) can be mirror images of each other (here the root *enantio* is applied). Such molecules or their parts have the same properties, the only difference between them arises when they react with chiral substances. The enzymes in organisms only react with one of the enantiomers or with one of the enantiotopic atoms. Diastereoisomers are different substances with different boiling or melting point, and they react with different substances in different ways. Similarly, diastereotopic atoms or groups have different physical properties and reactivities. Diastereoisomers cannot be superimposed, neither by rotation nor by reflection in a mirror. The same is true for the diastereotopic parts of molecules. Quite often, it is difficult to identify diastereotopy, and for this purpose the following test is used. Replace one in the pair of atoms, which are supposed to be diastereotopic, by some other atom, for example, replace hydrogen by chlorine. If this pair of atoms were enantiotopic, then two enantiomers are obtained. If the atoms were diastereotopic, then one or another diastereomer will be produced.

Now, we can return to glycerine. Carry out the following procedure: “replace” H^1 or H^2 in this molecule by Cl, and denote the right-hand group $—CH^3H^4OH$ by the letter R. If you want to construct models for this transformed molecule, you will obtain structures *H*, *I*, and *J*. In other words, they will be diastereoisomers. Hence, atoms H^1 and H^2 in the glycerine molecule are diastereotopic, which was not at all obvious at first.

And finally, we shall answer the most important question: Why are we discussing all these concepts about diastereotopy, Möbius bands, and chains of real atoms? The point is that most organic substances in nature exist in the form of chiral molecules. Take, for example, amino acids, which constitute proteins: only one of the enantiomers is used to build a protein. Enzymes, which function as catalysts during the synthesis of proteins, recognize these features of the molecular structure quite well. Before carrying out various molecular transformations in a flask, a chemist must also be aware of these peculiarities in the structures of molecules. Even such exotic substances as the ferrocene derivative of type (*K*) prove to be effective components of catalysts that favour the synthesis of only one desired enantiomer of an amino acid without impurities. As far as the interwoven paper strips are concerned, we should only note that DNA molecules, which have the structure of two chains coiled around each other many times, sometimes roll up into rings. Maybe those cardboard models will also help solving this riddle.

We have covered only a few aspects of stereochemistry. For more detailed studies in this field of chemistry, the reader should refer to the special literature on the subject.

Plasticine Electron Clouds

Working in the field of chemistry usually involves flasks, test tubes, other types of equipment, and various chemicals. For many years chemists could well manage with these "accessories". However, fifty years ago, a new branch of chemistry appeared in which the working tools are a pencil, paper, and computers. The new branch is called quantum chemistry. It developed at the interface of quantum mechanics and chemistry. Quantum chemistry greatly affects other branches of chemistry, because it can describe chemical bonds and the structures and configuration of electrons in molecules. Therefore, today it is hardly possible to solve the problems of molecular transformations without quantum chemistry.

Modern concepts about the chemical bond, which unites separate atoms to form molecules, rely upon the concept of the electron. It is a negatively charged particle that is thousands of times lighter than the atomic nucleus. In the 1920s, scientists began to treat the electron as something that is simultaneously a particle and a wave. Indeed, some of the properties of electrons (for example, diffraction) are similar to those of light waves and X rays.

Let us try to model certain electron properties. For this purpose, you will need either a rope or a pan with water. Fix one end of the rope and, holding the other end, induce vibrations in it in a vertical plane. The vibrations can be simple (as shown in Fig. 19*a*) or more involved (see Fig. 19*b*). Similar vibrations, called standing waves, can be induced in water when they are produced by lowering a teaspoon into water. Can the standing wave be described mathematically? Yes, it can. To this end, let us introduce function $\psi(x)$ which is the

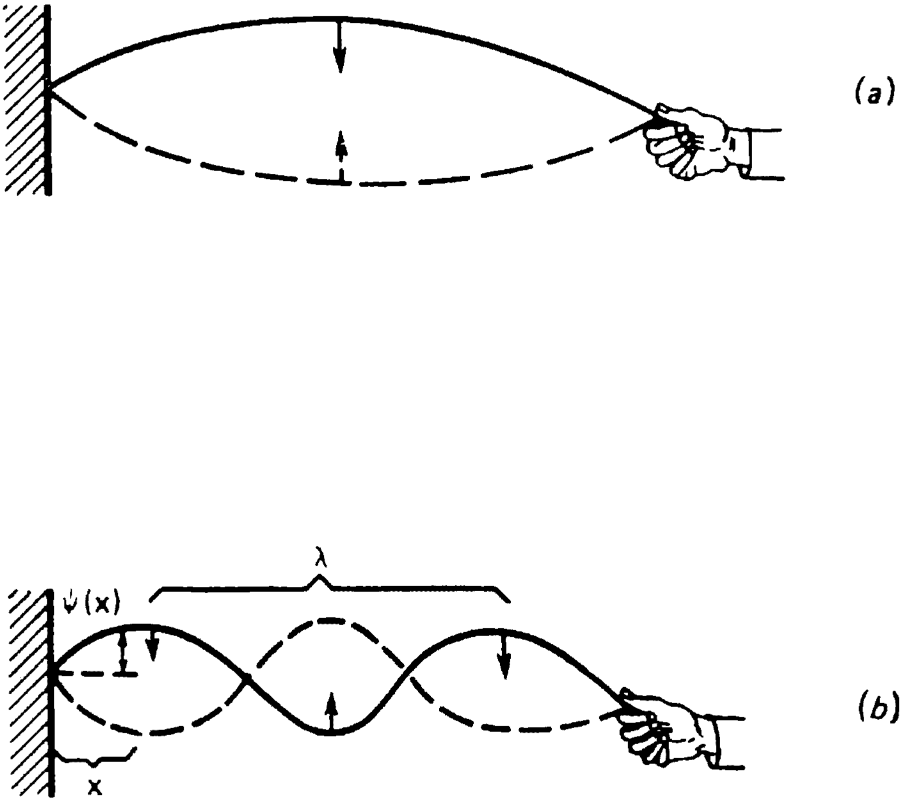


Fig. 19 Vibrations of the rope and the formation of standing waves

wave amplitude and depends on x, i.e. on the distance from the "wall" along the wave. All types of vibration have already been described by classical mechanics, according to which the form of our function $\psi(x)$ can be found by solving a second-order differential equation

$$\frac{d^2\psi(x)}{dx^2} = -\frac{4\pi^2}{\lambda^2}\psi(x)$$

where λ is the wavelength, and π is the well-known constant.

We shall not discuss here what differentiation is, which is denoted by operator d^2/dx^2. We shall only note that this operator signifies a mathematical procedure, which must be performed for function $\psi(x)$. As a result, function $\psi(x)$ transforms into another function. Suppose, you have found a solution for $\varphi(x)$. If, after substitution of the solution into the equation, the latter transforms into identity, we can say that the solution obtained is a mathematical description of the vibration in question. In other words, our task is to find function $\psi(x)$ which has the following property: a second derivative of the function equals the product of the function itself and $-4\pi^2/\lambda^2$, for any x values. It turns out that there can be several such functions and they only "fit" for specific λ values. In our case, ψ is expressed mathematically by a sine.

Next, we shall assume that ψ describes not a wave in the rope, but a wave that is an electron. We call it a wave function. Since an electron rotates in a three-dimensional space, this function should depend on three variable coordinates, i.e.

$\psi(x, y, z)$. We already know how to write an equation for such a function. As in the case of rope vibrations, for the ψ function we introduce an operator $\hat{H}$, which is called the Hamiltonian operator and includes repeat differentiation. The corresponding operations are performed. Then, the obtained function is equated to ψ multiplied by the energy of the electron E. It is known that the energy of the electron is related to "its" wavelength, that is, the shorter the wavelength, the greater is the energy. As a result, the following expression is obtained: $\hat{H}\psi = E\psi$, which is known as Schrödinger's equation. It should be noted that it is impossible to cancel ψ from this equation, because it is contained in the product on the right-hand side of the equation, while the $\hat{H}$ symbol preceding ψ on the left-hand side denotes an operation that should be performed on the ψ function.

It is not necessary here to solve Schrödinger's equation even for the simplest system, i.e. for the hydrogen atom, since this requires fundamental knowledge of the theory of differential equations, whereas for atoms with more involved structures this equation has no strict solution at all. We shall only limit ourselves to a discussion of ψ functions obtained after the solution of the equation for a proton-electron system. But what is the physical meaning of ψ function itself? For a standing wave in a rope, a one-dimensional ψ function is a wave amplitude along the rope. As can be seen from Fig. 19*b*, ψ can take negative values, while at certain points it becomes zero.

Let us now make a sufficiently arbitrary assumption: the wave function ψ determines the electron location in the atom. How can this be understood? In fact, if an electron is a wave, it cannot be present at a definite point in space, whereas if an electron is a particle, then the coordinates of this particle must depend on time, but the latter is not included in Schrödinger's equation. And what if we "disperse" the electron throughout the atom, i.e. transform it into a cloud, and consider that the wave function determines the degree of thickness, i.e. the density of the cloud? Then, the quantity of time will not be required for Schrödinger's equation. Unfortunately, one more difficulty appears: the ψ function can be negative which after all is meaningless. This obstacle can be overcome if we denote the cloud density, or in other words, the probability of finding an electron, by ψ^2, which is always positive.

Now that we know that ψ is a function of three coordinates, x, y, z, and its square is equal to the probability density of finding an electron at a point with the given coordinates x_1, y_1, z_1, but the form of the function is unknown, we can establish some of its properties. If a function does not satisfy these requirements, it will be rejected. First, ψ should become zero at a very great distance from a nucleus. Indeed, it is difficult to imagine a cloud of infinite dimensions. Second, since the electron always exists somewhere, the total probability of its detection must be unity.

Usually, differential equations have several solutions. For example, two graphical solutions for the equation of a standing wave are shown in Fig. 19. They correspond to different values of λ. Similarly, several functions satisfy Schrödinger's equation and a particular value of energy corresponds to each of them. Denote these functions by conventional symbols in the order of increasing energy values as follows: *1s*, *2s*, *2p*, *3s*, *3p*, *3d* ... We shall not discuss here why precisely these notations were chosen. Function *1s* corresponds to the minimal energy, i.e. to the most stable state of the hydrogen atom, and is written as $\psi(1s) = e^{-r}/\sqrt{\pi}$. Here, e is the base of a natural logarithm, and r is the distance from the atomic nucleus expressed in the so-called atomic units of length. The reader may investigate for himself the behaviour of this function, its square, and, finally, of $r^2 [\psi(1s)]^2$ using a calculator and graph paper. Since r^2 is proportional to the area of the sphere around the nucleus, the last function is a measure of probability that an electron is located at a distance r from a nucleus. Note that the expression for the function $\psi(1s)$ does not contain the arguments x, y, and z. The only variable here is radius r, which means that function 1s must uniformly encircle the nucleus. It is said that the function has sphere symmetry.

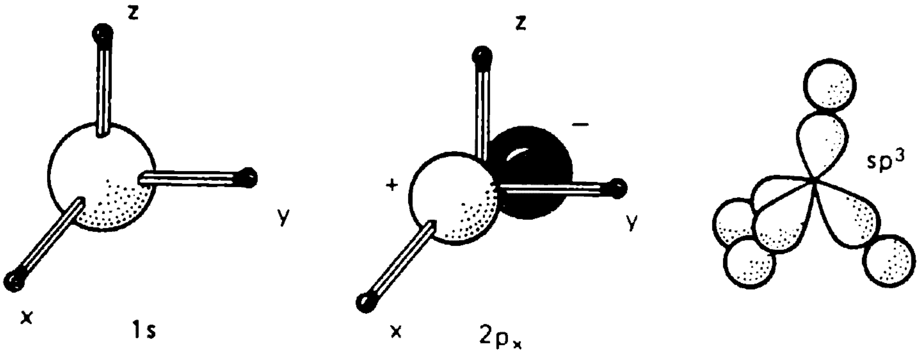


Fig. 20 Models of orbitals made from the plasticine

Take some white plasticine and make a model of an electron cloud, which is described by function $\psi(1s)$ and is called orbital 1s. To indicate the location of the orbital in space, stick three matches into the plasticine ball at right angles. The matches will correspond to the x-, y-, and z-axes (Fig. 20).

Orbital 2s (next in the energy sequence) has a more complicated analytical expression

$$\psi(2s) = -\frac{1}{4\sqrt{2\pi}}(2-r)\,e^{-r/2}$$

The behaviour of this function is more involved (plot its dependence on r), though it is obvious that it also has a spherical symmetry. Therefore, the model for the 1s orbital can also serve as a model for the 2s orbital.

Advancing through the energy sequence, one can arrive at the ψ (2p) function. And here, an unexpected situation occurs. It appears that three functions satisfy Schrödinger's equation simultaneously, all of them containing the common term

$$\frac{re^{-r/2}}{4\sqrt{2\pi}}$$

multiplied by x/r, y/r, or z/r. We specify these functions as $\psi(2p_x)$, $\psi(2p_y)$, and $\psi(2p_z)$ according to the second multiple. The first component of the function depends on r alone, and, like the s orbital, determines only the spherically symmetric part of the ψ function, but this is not what counts. The multiple x/r presents quite another case. To analyze its behaviour, let us move from the Cartesian coordinate system to the spherical one, in which the coordinates of point M are given by three parameters: length of vector r, i.e. the distance from the origin to point M, and two angles, ϑ and φ (Fig. 21). It is apparent that $x = r\sin\vartheta\cos\varphi$, $y = r\sin\vartheta\sin\varphi$, and $z = r\cos\vartheta$. Taking these relations into account, one can write:

$\psi(2p_x) \sim \sin\vartheta \cos\varphi$

$\psi(2p_y) \sim \sin\vartheta \sin\varphi$

$\psi(2p_z) \sim \cos\vartheta$

The functions thus obtained are independent of r. Using a calculator and a protractor, plot the first function on graph paper for different values of ϑ and φ. Firstly, compile tables for the values of the function in planes xz ($\varphi = 0°$), xy ($\vartheta = 90°$), and yz ($\varphi = 90°$). The greater the number of points obtained, the more accurately the functions will be depicted.

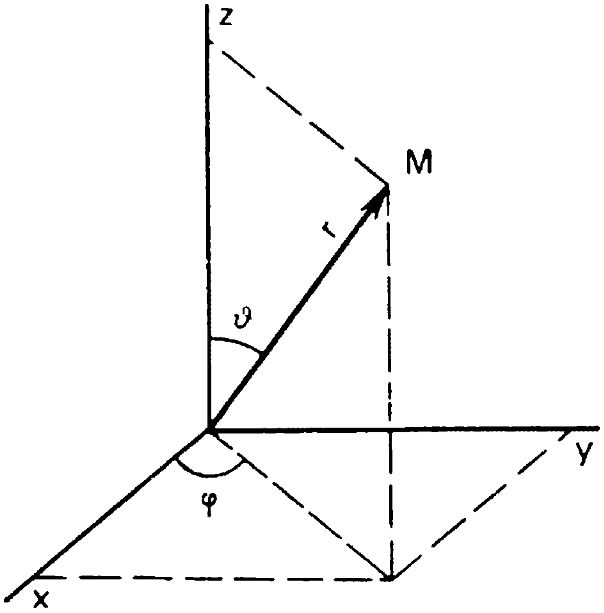
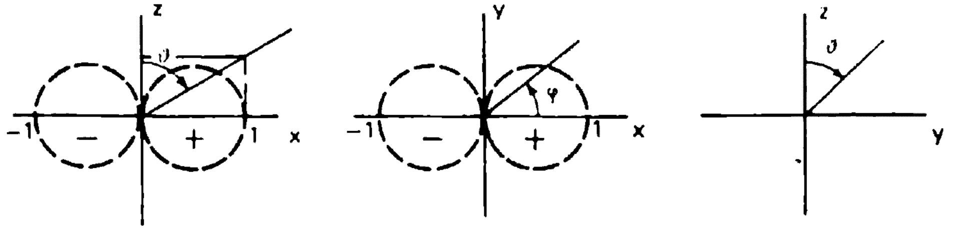


Fig. 21 Transition from the Cartesian coordinates to the polar ones

	$\varphi = 0°$		$\vartheta = 90°$		$\varphi = 90°$
ϑ	$\sin\vartheta\cos\varphi$	φ	$\sin\vartheta\cos\varphi$	ϑ	$\sin\vartheta\cos\varphi$
0	0	0	1	0	0
45	0.7	45	0.7	45	0
90	1	180	−1	...	...
...	...	...	...		

Next, plot "cross sections" of the orbital by three planes, by rotating a vector around the origin through different ϑ and φ angles and by marking the corresponding values of the function along the vector (Fig. 22).



$\varphi = 0°$ $\vartheta = 90°$ $\varphi = 90°$

Fig. 22 Cross sections of the ψ ($2p_x$) function

Thus the component ψ ($2p_x$) of the function, which does not depend on r (but determines the orbital form), represents two spheres whose centres are on the x-axis. The spheres come into contact at the origin, where the atomic nucleus is located. One important thought should be noted here: one sphere contains the positive values of $\sin\vartheta\cos\varphi$ function, the other sphere, the negative values. This does not mean, however, that the vector, which was used to "describe" the sphere, has a negative length, or that the probability of finding an electron in this region is negative. Since the probability density to find an electron is equal to ψ^2, the electron is smeared over the two spheres with equal "desire". However, the signs of separate parts of the orbitals must be taken into account further. Construct a model of a $2p_x$ orbital by joining together two plasticine balls—a white ball (positive part) and a black one (negative part of ψ), and make axes by sticking them from matches (Fig. 20).

The reader may think that, while constructing a model of the orbital, we forgot about the second component of the ψ function that depends on r. No, we haven't, but nothing can be done here, because it is impossible to combine the two components in a three-dimensional space. However, since it is precisely the second component that determines the shape and orientation of the orbital in space, it is considered in many cases that this component determines the entire orbital.

It is suggested that the reader determines the form and orientation of the $2p_y$ and $2p_z$ orbitals for himself. After this, one can examine the structure of the simplest organic molecule—methane—which has a carbon atom at the centre and four hydrogen atoms around it. It is believed that a chemical bond between two atoms arises when their orbitals overlap. The carbon atom has four orbitals that can be overlapped ($2s$, $2p_x$, $2p_y$, and $2p_z$), while each hydrogen atom has one $1s$ orbital. The task is to overlap four hydrogen orbitals with the orbitals of the carbon atom so that

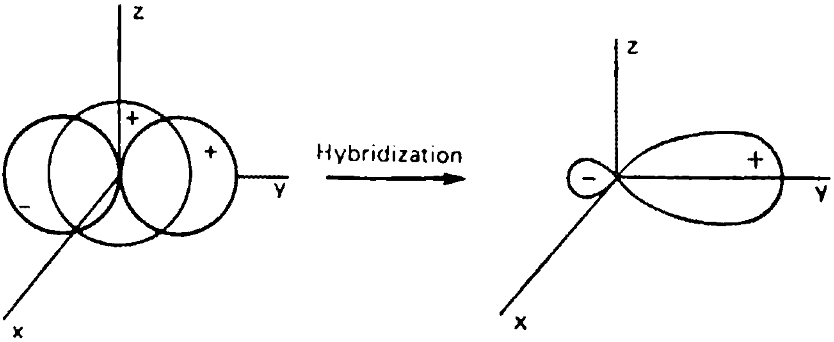


Fig. 23 Hybridization of s and p_y orbitals

all the hydrogen atoms are spaced at equal distances from each other and from carbon, taking into account that the $2s$ orbital forms a sphere and the p orbitals are shaped like dumbbells oriented along the x-, y-, and z-axes. For simplicity, let us assume that the orbitals are averaged in some way and, as a result, hybrids are formed. Figure 23 shows how sp hybridization is realized. In this process, the functions are summarized. Since the s function is positive everywhere, while p_y has both positive and negative values, one has to subtract the wave functions in one part of space. Therefore, the obtained hybrid orbital has the form of an irregular dumbbell with a long positive and a short negative part. Now, you can construct a model of electron clouds in a methane molecule. Four sp^3 hybrid orbitals (since they are formed by one s and three p orbitals) are directed at the vertices of a tetrahedron and are overlapped at their ends by the spheres of the 1*s* orbitals of hydrogen (see Fig. 20).

Theoretical Predictions

Chemistry, like physics, geology, and genetics, is an experimental science. However, if what concerns us is the synthesis of substances, then it is in chemistry that the experiment plays a greater role than in other sciences. This means that there are many experimental observations in chemistry that cannot yet be theoretically confirmed, and that in many cases theory cannot successfully predict the existence of new substances and the possibility of new reactions. Consequently, one often has to rely upon pure chance. Of course, there is something delightful about this. On no account, however, should one think that synthesis is a "blind" science, and that chemists perform their experiments randomly. Scientists of the last century worked out the principles that could be used to predict the courses of many reactions on the basis of generalizations of numerous experiments. According to Markovnikoff's rule, which is the best known principle in organic chemistry, when a hydrogen halide (e.g. HCl) reacts with a substituted ethylene (e.g. $RCH{=}CH_2$), hydrogen goes to the carbon having the greater number of hydrogen atoms bonded to it. In our case, the hydrogen of HCl goes to $=CH_2$.

Today, chemists use many methods and theories that allow one not only to predict whether a given reaction will occur, or which products will be formed, but also to calculate the reaction parameters, such as the reaction rate. Electrophilic substitutions in aromatic compounds, particularly in benzene derivatives, are well known and thoroughly studied. The products of these reactions are important substances, such as acetylsalicylic acid, sulphamide compounds, dyes, etc. Nitration is a typical electrophilic substitution reaction. In the previous chapter titled "The Yellow Dye from the Black Carbon", we considered the method for preparing nitrophenol. Perform a similar experiment with benzene, and add a few drops of benzene to dilute nitric acid in a test tube. After several minutes, pour the contents of the test tube into a glass of water, and carefully smell it. There will not be the odour of bitter almond that is characteristic of nitrobenzene. Hence, the reaction did not occur under these conditions (benzene, however, does react with concentrated nitric acid in the presence of sulphuric

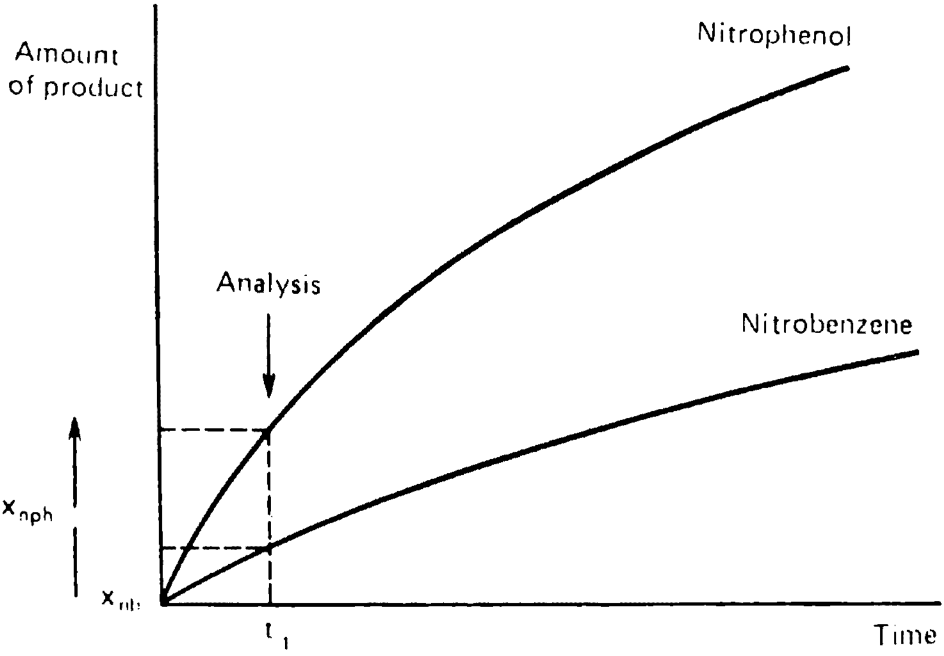


Fig. 24 Kinetic curves for the accumulation of nitrophenol and nitrobenzene

acid). Thus, one may conclude that phenol enters an electrophilic substitution reaction more readily than benzene. It is possible to compare the quantities of phenol and benzene that have reacted with nitric acid. To do this, mix benzene and phenol and add a small amount of nitric acid. First, nitrobenzene and nitrophenol will quickly accumulate in the reaction mixture; then, the accumulation of the reaction products will diminish with time. Naturally, the amount of nitrobenzene produced will be much lower than that of nitrophenol. If we stop the reaction at the beginning (at time t_1 in Fig. 24), when the accumulation of the products follows nearly a straight line, and determine the amounts of the obtained nitrobenzene and nitrophenol, then the ratio of these amounts (x) will show the ratio of the corresponding reaction rates:

$$W = \frac{x_{\mathrm{nph}}}{x_{\mathrm{nb}}}$$

Thus, one can determine the relationship between the nitration rates for benzene or any of its derivatives. For example, toluene is nitrated twenty-five times more quickly than benzene, while chlorobenzene reacts with nitric acid thirty times slower than benzene itself. How can this difference be explained? We have already explained that the hydroxyl group —OH in phenol, or the methyl group —CH_3, in toluene is shifted towards the benzene ring. Thus, the electron density of the ring increases, and the ring readily reacts with the electrophile. Conversely, a chlorine atom attached to the benzene ring somehow "pulls back" the electron density. The "head" developed by the substituents is significantly lower than one electron, but it is enough to change the reaction rate so drastically. Let us try to determine the "power" of our electron pumps. We shall consider benzoic acid containing different substituents X. Such substituted acids dissociate with a loss of a proton as follows:

The established equilibrium is described by the equilibrium constant K. The more the substituent "pumps out" the electrons from the ring, the greater is the value of K. This is obvious because the bond with a proton becomes weaker

$$K_X = \frac{[XC_6H_4COO^-][H^+]}{[XC_6H_4COOH]}$$

Here, the expressions in the brackets indicate the concentrations of the ions and undissociated molecules. The logarithm of the ratio of this constant to the dissociation constant of unsubstituted benzoic acid (i.e. when $X = H$) is designated by σ and characterizes the power of electron pump X

$$\sigma = \log \frac{K_X}{K_H}$$

The reader can easily guess that σ is negative for substituents that supply electrons, and positive for substituents that pump out the electrons. The logarithms of the rates of electophilic substitution prove to be linearly dependent on the relevant values of σ. It is said that in this case, the Hammett relation is valid: $\log W = \rho\sigma$.

Let us analyze a reaction that was discovered not long ago. If metallic platinum is lowered in a solution of aqua regia, it will dissolve to form chloroplatinic acid, H_2PtCl_6. This acid readily reacts with substituted benzenes when heated in the presence of acetic acid. As a result, a substituted benzene C_6H_5X forms a derivative $H_2[XC_6H_4PtCl_5]$. Below are the experimental data on the rate of a reaction between aromatic compounds and chloroplatinic acid. In addition, the values of σ are cited for the corresponding substituents X:

X	W	σ
OCH_3	8.5	−0.27
CH_3	3	−0.17
H	1	0
F	0.3	0.06
COOH	0.09	0.36
Cl	0.08	0.37

On a piece of graph paper, plot the values of σ along the x-axis and the corresponding $\log W$ values along the y-axis, and you will see that the obtained points lie on a straight line with sufficient accuracy. Then, determine the value of ρ from the slope of the line. You will obtain the following Hammett's relation for the reaction under consideration: $\log W = -3\sigma$. The fact that ρ is negative indicates that the reaction with chloroplatinic acid is a typical electrophilic substitution. The rate of the reaction with phenol (where X = OH) was not determined above, therefore the reader can use the value of σ for OH which is equal to —0.37 to determine graphically, or from the equation, how much faster phenol reacts with chloroplatinic acid than benzene does.

It is still more tempting to learn to predict chemical transformations when experimental data are not available and only theoretical considerations are taken into account. Quantum chemistry is of great assistance in this problem, particularly the method called the molecular orbital method. We shall get acquainted with the general idea of this method, and to better understand it shall again use white and black plasticine and thick copper wire.

The main property of atomic orbitals is the ability to overlap each other. This overlapping results in a bond between atoms. Electron clouds can overlap in two ways: first, when the atomic nuclei and the regions of overlapping lie along one axis, and second, when the region of overlapping is not intersected by the line that connects the atomic nuclei. In the latter case, the plasticine balls cannot be freely rotated about the y-axis made from the wire. The first type of bonding is called a σ bond, and the second type is called a π bond (Fig. 25). Now, consider the structure of the ethylene molecule $CH_2{=}CH_2$.

Each carbon atom has four electrons, one of which is in an *s* orbital, while the remaining three electrons are in *p* orbitals. Two *p* orbitals and one *s* orbital form three sp^2 hybridized orbitals. Two hybridized orbitals are engaged in bonding with two

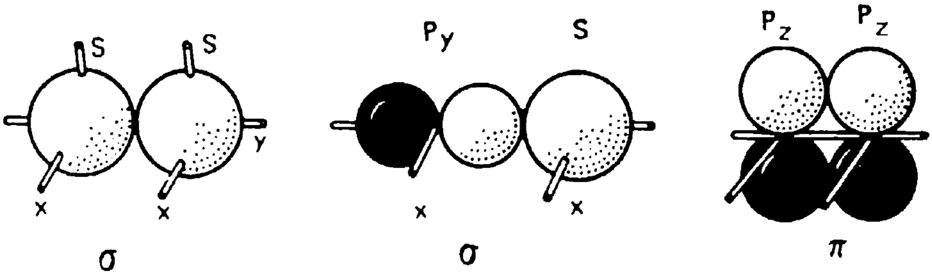


Fig. 25 The overlapping of plasticine models of orbitals according to the σ- and π-type

hydrogen atoms, while the third orbital is overlapped by a similar orbital of the second carbon atom. All these overlaps correspond to a σ type and form the σ core of the molecule. The latter can be made from some plasticine and a wire (Fig. 26), but the core will not subsequently be required, and therefore it can be replaced by a length of wire. Next, attach the remaining two p_z orbitals to the wire. The reader should be reminded that plasticine balls represent electron clouds, which are described by the wave functions ψ. As was already noted, ψ functions have different signs in different halves of the *p* orbital. The positive half will be made out of white plasticine; while

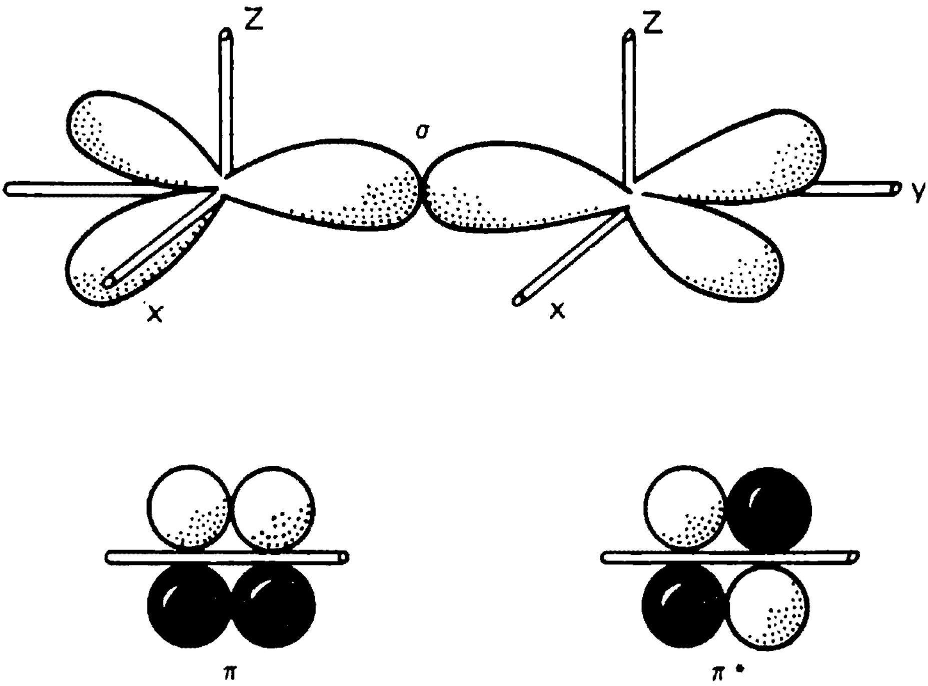


Fig. 26 Plasticine models of the σ-core of ethylene molecule and of the π-orbitals

the negative half, out of black plasticine. It turns out then that the two p_z orbitals can be located in two different ways (Fig. 26). Which of the structures should be preferred, and, in general, how do they differ? The combination, i.e. overlap of clouds, can be described mathematically by the summation of the corresponding ψ functions. Thus, as a result of overlap of two atomic orbitals (AO) of atoms A and B, the molecular orbitals (MO) are formed, for which $\psi_{AB} = \psi_A + \psi_B$. However, if parts of electron clouds with opposite signs are overlapped (in this case the orbital is marked with an asterisk), then it is assumed that $\psi^*_{AB} = \psi_A + (-\psi_B) = \psi_A - \psi_B$. This means that in the second case, the functions are subtracted.

Let us calculate the electron density between atoms C_A and C_B for both cases. In the first case, it is equal to the square of MO: $(\psi_{AB})^2 = (\psi_A + \psi_B)^2 = \psi^2_A + \psi^2_B + 2\psi_A\psi_B$. In the second case, the square of the difference, as is well known, equals: $(\psi^*_{AB})^2 = (\psi_A - \psi_B)^2 = \psi^2_A + \psi^2_B - 2\psi_A\psi_B$. It follows then that in the second case of the formation of MO, the electron density between the atoms is reduced. Moreover, the electron density for ethylene equals zero, because $\psi_A = \psi_B$, and such MO ψ^* is called antibonding. On the contrary, the MO in the first case is efficient for bond formation and is called a bonding MO. It is not without reason that the energy of this molecular orbital is much lower than the energy of each AO (Fig. 27). Since only two electrons can be arranged in each orbital (in MO or AO), it becomes obvious that in ethylene, the two π electrons are located in a more advantageous bonding orbital. The electrons are depicted in Fig. 27 by the arrows.

We now go over to a more complex substance—butadiene—and make its σ core from a piece of wire (prepare four such cores). Distribute 16 plasticine models of p orbitals over all carbon atoms. This can be done in four ways (Fig. 28). The most advantageous orbital is ψ_1, because its energy is minimal (it is therefore located at the bottom), and all the four clouds interact here, i.e. are overlapped according

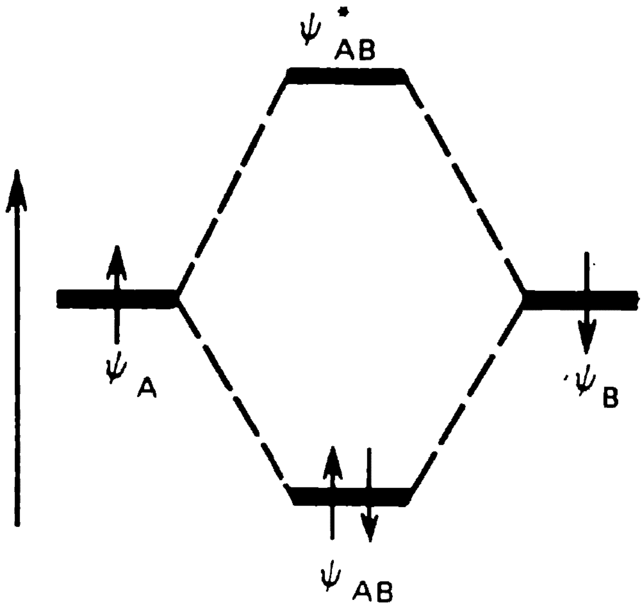


Fig. 27 Energies of atomic orbitals (AO) for atoms A and B and of molecular orbitals (MO) ψ and ψ^* formed from these atoms

to the π type. Orbital ψ_2 represents a combination of two noninteracting ethylenes. The third orbital describes a molecule with a double bond; and, finally, the last orbital is the least advantageous. All these structures can be depicted conventionally as follows:


ψ_1


ψ_2


ψ_3


ψ_4

All the four π electrons of butadiene are located in two lower bonding orbitals, while the orbitals ψ_3 and ψ_4 are antibonding and do not accommodate electrons. The reader may think that antibonding orbitals are useless, because they do not accommodate electrons and do not participate in the formation of a bond. The fact is that in many compounds, separate antibonding orbitals are often occupied. Then, when a molecule is illuminated by light,

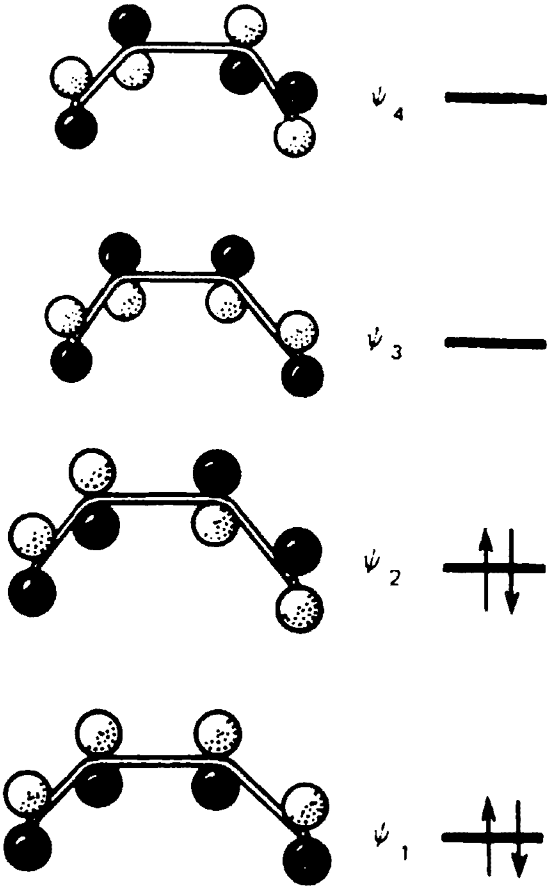


Fig. 28 Models of molecular orbitals of butadiene

the electrons can jump from the bonding to the antibonding orbitals and remain there for a certain period of time. And finally, there is a rule that can be used to predict a chemical reaction. It states that dimerization of two unsaturated hydrocarbons into a cycle is possible in the dark when the highest orbital occupied by the electrons of one reactant is overlapped by the lowest free orbital of the other reactant according to the principle "plus with plus, and minus with minus". Let us see how this rule can be applied when an ethylene molecule is added to a butadiene molecule. According to the first variant, the lowest free orbital of ethylene (it is the antibonding π^* orbital) is overlapped with the highest occupied orbital of butadiene (it is the bonding orbital ψ_2). In the second variant, the lowest free orbital of butadiene (the antibonding ψ_3 orbital) is overlapped by the occupied orbital of ethylene (bonding π orbital). Both variants are shown in

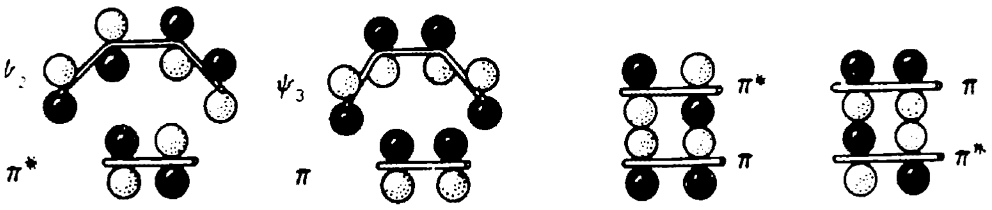
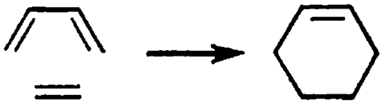


Fig. 29 The overlapping of orbitals during cyclodimerization of butadiene with ethylene and during dimerization of ethylene

the left part of Fig. 29. However, the dimerization of ethylene, no matter how the models are placed, can be represented in only two ways (see the right part of Fig. 29). In the second case, there is no way to avoid the "zebra" where the orbitals of both molecules join. It can thus be concluded that the reaction between butadiene and ethylene is possible in the dark and can be represented by the scheme



However, dimerization of two ethylene molecules cannot be realized in the dark. When ethylene molecules are illuminated by light, one electron can be transferred to π^*, therefore the following transformation becomes possible:

The method considered above allows one to predict whether or not reaction is possible. The quantum-chemical theory of chemical reactions was developed by the American and Japanese scientists R. Hoffmann and K. Fukui who were awarded the Nobel Prize.

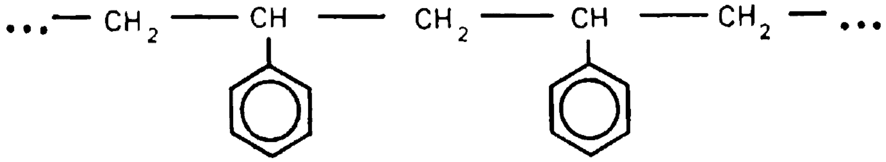
Types of Polymers

There once was a stone age, a bronze age, and an iron age, but today, we live in the age of polymers. One cannot imagine life without polymers, i.e. without plastics that substitute for wood and metal, without fibres used to make fabrics and ropes, without organic glass and polyethylene. But what are polymers? They are not just very long or very large molecules. For example, the hydrocarbon molecule $C_{80}H_{162}$ is quite long, but this paraffin is not classified as a polymer. Polymers are substances whose molecules consist of alternating monomer units, with the number of these units being large and indefinite. What does an indefinite number of units mean? This means that one molecule of a substance may consist of three thousand units, while another molecule of the same substance is made up of three thousand and five hundred such units, and still another molecule has two thousand and five hundred units.

Today great variety of polymers are known, and to differentiate between them requires a classification system. According to one system, all the polymers can tentatively be divided into three classes: natural polymers (isolated from natural products), artificial polymers (produced by the action of chemical reagents on natural polymers), and synthetic polymers (synthesized from monomers). Each polymer class can be further subdivided according to the structure of the polymer chains. The structures of natural and synthetic polymers can be similar, therefore, the properties of the synthetic polymers are often similar to those of natural polymers. It is also possible to classify polymers based on other characteristics, for example, they can be divided into fibres and films, or differentiated on the basis of their thermal stability, etc.

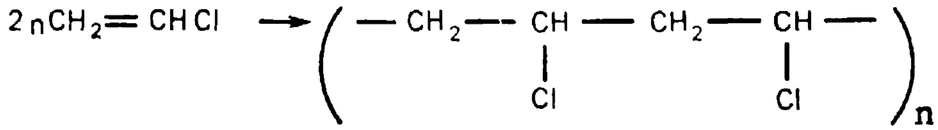
Let us consecutively discuss the best known polymers and apply a classification system based on their chemical structure. Polymers with the simplest structure are included in the class of carbon-chain compounds, in which the chain consists of carbon atoms alone. Carbon atoms can only be connected to hydrogen atoms or other carbon atoms. Here, the polymers are saturated hydrocarbons, such as polyethylene or polypropylene. Polyethylene is formed from ethylene according to the reaction: $n\mathrm{CH_2{=}CH_2} \rightarrow [\mathrm{-CH_2-CH_2-}]_n$. It is widely used in the household in the form of transparent films for wrapping food, insulating materials for radio-engineering devices, and impregnants of fabrics and paper. A strong fibre can be produced from polypropylene. At ordinary temperatures, these materials do not dissolve in any solvent, but at 80°C they swell and can then be dissolved in carbon tetrachloride or toluene. Polyethylene can easily be distinguished from other polymers by introducing a piece of polyethylene film into the flame of a gas burner. First, it will melt and liquefy, and then it will burn with first a blue and then a yellow flame. You can smell the odour of paraffin, because polyethylene and paraffin have a similar composition.

If one of the hydrogen atoms in ethylene is replaced by a phenyl ring, styrene will be produced, which can easily be polymerized to form polystyrene



Polystyrene already becomes soft at 80°C, and when introduced into the flame of a burner or a match, it quickly ignites and burns with a yellow sooty flame. The evolving vapours have a characteristic sweet odour. You can verify this by heating a piece of polystyrene in a test tube over a gas burner. When polystyrene is heated, it undergoes depolymerization as a result of which styrene is obtained. Polystyrene is a good dielectric and is used to produce a light-weight foam plastic.

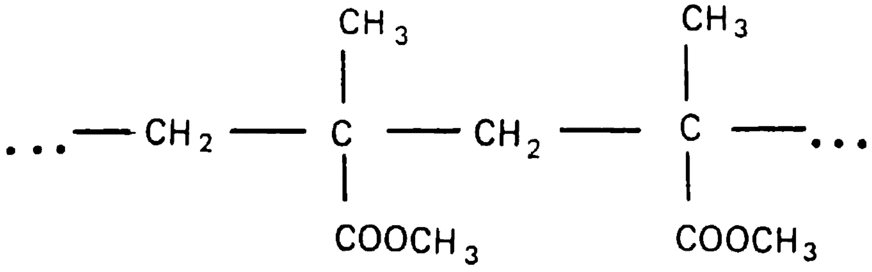
If some of the hydrogen atoms in a long chain of polyethylene are replaced by halogen atoms or by oxygen or nitrogen, new polymers are formed with new valuable properties. However, it is very difficult or even impossible to replace hydrogen atoms directly in polyethylene, therefore the process is conducted as follows: one or several hydrogens are replaced in ethylene, and the product is then polymerized. The simplest way is to replace one ethylene hydrogen with a chlorine atom, and to polymerize the resulting vinyl chloride:



$$2n\mathrm{CH_2{=}CHCl} \longrightarrow \left(-\mathrm{CH_2}-\underset{\mathrm{Cl}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\underset{\mathrm{Cl}}{\underset{|}{\mathrm{CH}}}-\right)_n$$

The polyvinyl chloride thus formed is widely used as an insulator for electric wires. This polymer is soluble in acetone, chloroform, and ethyl acetate, while a mixture of acetone and benzene dissolves it best of all. Polyvinyl chloride can easily be identified and distinguished from the other polymers that do not contain chloride atoms. Calcine a copper wire in the flame of a gas burner, touch a polymer with a hot wire, and then again introduce the wire into the flame. If the polymer contains chlorine atoms, the flame will be coloured green. This means that the polymer under investigation is polyvinyl chloride or it is a copolymer of vinyl chloride, i.e. a compound whose long molecules contain fragments of polyvinyl chloride, polyvinyl acetate, or polyacrylonitrile (Orlon). Polyvinyl chloride burns with difficulty, and the flame has a greenish colour.

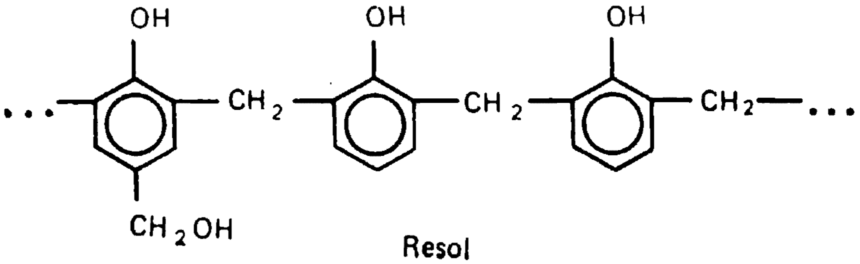
Polymerization of tetrafluoroethylene yields a valuable product, polytetrafluoroethylene, or Teflon: $n\mathrm{CF_2 = CF_2} \rightarrow [\mathrm{-CF_2-CF_2-}]_n$. It is a white substance that does not dissolve in any solvent; it is inert to temperature as low as —100°C or as high as +250°C. Teflon is stable to the action of hydrochloric, sulphuric, or nitric acids. It is used in electrical equipment, in radio engineering, in the manufacture of chemically resistant pipes and pumps, and in the synthesis of fibres. Polytetrafluoroethylene can be distinguished by its white colour; it is "greasy" to the touch like a piece of marble. Teflon is an opaque substance, which does not resemble glass, while polyethylene can transmit light: if a printed text is covered by a polyethylene film, the text can be easily read. Nevertheless, polyethylene does not look like glass. At a large distance it appears slightly opaque, and nothing can be seen through it. But if in a polyethylene chain one hydrogen at each second carbon atom is replaced by a methyl group and the other hydrogen is replaced by an ester group, $\mathrm{-COOCH_3}$, a transparent polymer called polymethyl methacrylate is formed



$$\ldots-\mathrm{CH_2}-\underset{\mathrm{COOCH_3}}{\underset{|}{\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}}}-\mathrm{CH_2}-\underset{\mathrm{COOCH_3}}{\underset{|}{\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}}}-\ldots$$

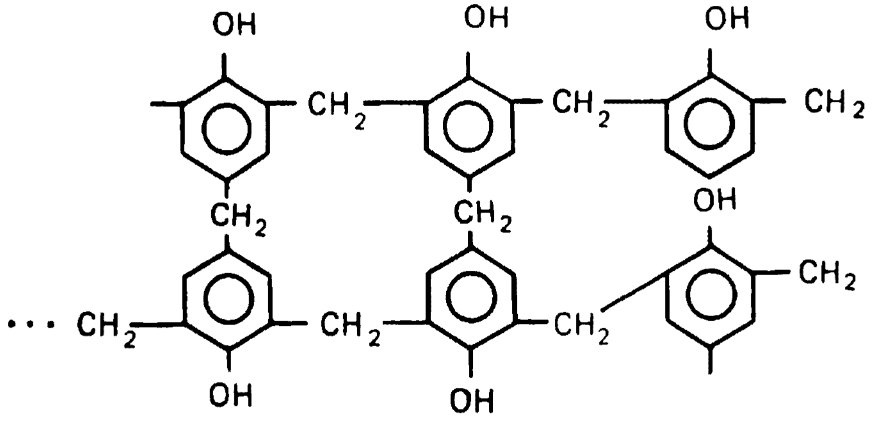
Polymethyl methacrylate is a well known organic glass which readily dissolves in acetone, chloroform, and ethyl acetate.

Benzene rings can also be incorporated into the hydrocarbon chain of a polymer molecule. Place a teaspoon of crystalline phenol in a test tube or a glass and add the same volume of a 40% aqueous solution of formaldehyde. Stir the mixture with a glass rod and then add a few drops of concentrated hydrochloric acid. Cool the test tube in cold water and, using a glass rod, transfer a small amount of the obtained viscous mass into another test tube with alcohol. The polymer thus formed dissolves in the alcohol. What polymer has been produced? Under the action of the acid, formaldehyde CH_2O displaces hydrogen atoms from the ortho positions of the phenol and resol is formed:



Resol

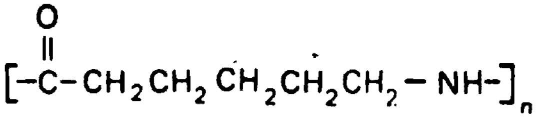
Remove the test tube from the cold water and put it into a boiling water bath. In a few minutes the polymer will solidify, and the resulting resin can only be removed from the test tube if the latter is broken. Treat a piece of the resin with alcohol and make sure that it does not dissolve. What has happened? The polycondensation of phenol with formaldehyde has followed an advanced course, and formaldehyde molecules "sewed together" the long chains of resol. As a result, a spatial network of resite (C-stage resin) is formed:



Resite

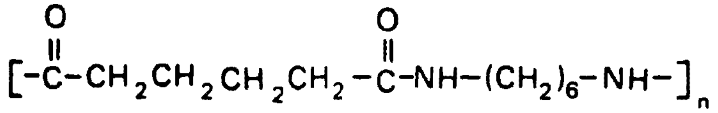
When the alcohol was added to the resite, its molecules could not tear off one chain of the polymer molecule from another one, and therefore the resite did not dissolve in the solvents. The obtained phenol-formaldehyde resin is widely used in the manufacture of insulating materials, plastics, buttons, etc.

Now, let us consider heterochain polymers that include, in addition to carbon atoms, atoms of nitrogen, oxygen, and other elements. The following three heterochain polymers are used to produce fibres:



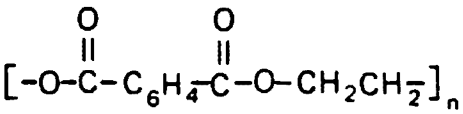
$$\left[-\overset{O}{\overset{\parallel}{C}}-CH_2CH_2CH_2CH_2CH_2-NH-\right]_n$$

Nylon 6



$$\left[-\overset{O}{\overset{\parallel}{C}}-CH_2CH_2CH_2CH_2-\overset{O}{\overset{\parallel}{C}}-NH-(CH_2)_6-NH-\right]_n$$

Nylon 66



$$\left[-O-\overset{O}{\overset{\parallel}{C}}-C_6H_4-\overset{O}{\overset{\parallel}{C}}-O-CH_2CH_2-\right]_n$$

Dacron

The first two polymers are amides, which contain a —CONH— group, while the third polymer is an ester. Introduce a piece of fabric made of polyamide fibre into the flame of a gas burner. The fibre will melt and separate drops will run down the fabric. You will also sense an unpleasant characteristic odour. In a few minutes the fabric transforms into a brownish-black solid. Polyamide fibre can be dissolved in glacial acetic acid upon heating. When polyester fibre is introduced into a gas burner, it burns slowly with a yellow flame, and brown vapours and soot are evolved. Unlike polyamide fibre, polyester fibre does not dissolve in boiling concentrated hydrochloric acid. However, polyester fibre is soluble in boiling concentrated nitric acid. The reaction with the acid is used to identify the type of fibre.

Natural fibres—silk, wool, flax, and cotton—are also heterochain polymers. Wool and silk consist of proteins, which are made up of amino acids. Thus, wool and silk are polyamide fibres. Wool is composed of keratin protein, which contains considerable amounts of sulphur, while the proteins of silk do not contain practically any sulphur. Therefore, silk can be distinguished from wool by a characteristic odour, which appears when the tested fibre is placed in a flame. When wool burns, there is a pungent unpleasant odour of burnt hair. Put a white wool thread in a test tube with concentrated nitric acid and carefully heat the test tube. The wool will acquire a bright yellow colour. This is a characteristic test for protein. Then rinse the thread with water and immerse it in a concentrated solution of aqua ammonia. You will see that the wool turns orange. Flax and cotton, like paper, consist of cellulose, therefore, when they burn, they smell like burnt paper. Cellulose is a polysaccharide, in which the alternating unit is a six-membered ring containing an oxygen atom. A natural polysaccharide—cotton wool—can be modified chemically to form artificial products. To do this, first prepare a nitrating mixture: carefully add a small amount of concentrated sulphuric acid into a glass with concentrated nitric acid that has been placed in a cold water bath. Immerse a small piece of cotton wool in the prepared mixture for 2 or 3 minutes (not longer). Catch the wool with a glass rod and rinse it under a jet of tap water. In a few minutes, squeeze out the wool, spread it on a filter paper and dry in the air. You have obtained dinitrate of cellulose by replacing the hydrogen atoms of the hydroxyl groups in the cellulose molecule with nitro groups. After the cellulose dinitrate is dried, dissolve it in a mixture of ether and alcohol (2 : 1). The obtained viscous solution called collodion is used to make airtight stoppers for the bottles with various liquids. Small wounds on the skin can also be treated with collodion. Run another experiment by adding dinitrate of cellulose wetted with alcohol in small portions to an alcohol solution of camphor (spirit of camphor can be used instead). Thoroughly stir the obtained mixture and distribute it in a thin layer over a metallic plate. In a short time, the alcohol will evaporate and a film will remain that is called celluloid. Nitrates of cellulose are used in the production of films, lacquers, and plastics. When acetic acid is used instead of nitric acid, cellulose acetates are formed that are utilized in the manufacture of incombustible motion picture films and acetate fibres.

Why Is Rubber Elastic?

Try to bend or stretch out an iron nail with your hands and you will see that your attempts will fail. But when you take a rubber band and repeat your test, the results will be quite different. Indeed, in order to stretch a rubber band by only a one-hundredth fraction of its length, a force must be applied that is 100 000 times less than that required to stretch an iron nail by the same amount. However, the force that must be applied is not the only thing that makes these materials different. The rubber band can be stretched to ten times its original length, and the band will not break. The ability of rubber to experience tension is 1000 times greater than the extensibility of solids under normal conditions. What is responsible for this remarkable property? Surely, the answer must lie in the molecular structure of the substance.

People began to use rubber articles a long time ago, but the theory that could explain its elasticity was only developed in 1932 by the Swiss scientist Mayer. Rubber is formed from caoutchouc (crude rubber), which had formerly been cured over a fire into a solid, dark mass. This substance consists of long polymer molecules, in which certain carbon atoms are connected by double bonds. Each molecule of caoutchouc includes several thousands of units, and therefore the molecular mass of the substance reaches hundreds of thousands. What is the length of the polymer molecule? If the polymer molecule is stretched out to form a thread, its length will equal about a micron. A silk thread that is one-half metre long can be a "model" of such a molecule because it reflects the relationship between the width of the molecule and its length. We used the expression "stretch out" most appropriately because in reality the molecules of solid or liquid polymers are shaped like a zigzag. When placed on the surface of water, the thread, i.e. the model of the molecule, will acquire the form of an unusual curve. The form of the molecule can be predicted theoretically. Run an experiment that resembles blind man's buff. Cover your friend's eyes with a kerchief, turn him around several times and then ask him to take a step. Plot the direction of his motion on paper. Then, repeat everything once more and you will obtain a broken curve—a mathematical model of a polymer molecule. The more times the experiment is run, the more the form of the sketch will approach an average statistical molecule. One can determine the dimensions of such a ball. It should be mentioned, however, that real molecules occupy a three-dimensional space, while the experiment was run in a plane. Nevertheless, the principle of analysis is the same. The distance between the ends of the molecule r, as well as the distance between the start and the end of your friend's path, can be expressed by the formula

$$r = l\sqrt{n}$$

where l is the length of a step and n is the number of steps. Of course, this doesn't mean that if you measure the distance r with a ruler (in metres), the result will coincide with the value calculated from the formula. But the more times you repeat the game, the closer r will approach the calculated value. Therefore, r is called an average statistical quantity. The length of a molecule, i.e. the path covered by your friend, is expressed by $h = ln$. The ratio h/r shows the degree of "convolution" of the molecule or the degree of "futility" of your friend's wanderings. It is equal to $h/r = \sqrt{n}$, i.e. the longer the molecule, the more it is coiled up.

One can assume that the reason for the elasticity of rubber is that when it is stretched out, the coiled molecules become straightened. The assumption is correct, except for one "but". Let us model the following process: place several threads on a water surface so that they do not contact. Take the ends of two threads and move the threads apart. The threads will not return to the initial positions, and reversible elasticity will not be observed. We have thus created a model soft plastic paraffin, rather than rubber. Now, tie nine threads together into a regular network and place this chain on the water surface. Carefully pull on one end of the network, while holding the other end. When you release the ends of the network, it will return to its initial position. This is a model of rubber. The "ties" that bind together separate caoutchouc molecules in the rubber are the bridges of sulphur atoms. These bridges are introduced during the vulcanization of caoutchouc when it is treated with sulphur at elevated temperatures.

Several questions may have arisen during this explanation.

What makes the stretched network return to the initial state after the tensile force is removed? The fact is that molecules possess kinetic energy and therefore they are always in motion. In rubber, cross-links do not permit large molecules to move relative to one another under the action of heat. However, thermal motion "pushes apart" separate parts of the molecules and coils up long molecules. It is precisely this thermal motion that returns the network to its initial position. If a piece of rubber is stretched and then freezed at a very low temperature, its molecules lose a considerable part of their kinetic energy, and the stretched rubber cannot return to its initial state. But when heated to room temperature, it shrinks again. Rubber has another remarkable property. It is known that all "normal" bodies and liquids expand when they are heated. Rubber, on the contrary, shrinks when heated. You can check this by running the following experiment. Hammer two nails into a stick and connect them with a metallic spring and a rubber band. If the rubber band is placed in hot water, it shrinks, which can be seen from the extension of the spring. When the temperature is raised, the kinetic energy of the molecules is increased, and the network tends to shrink.

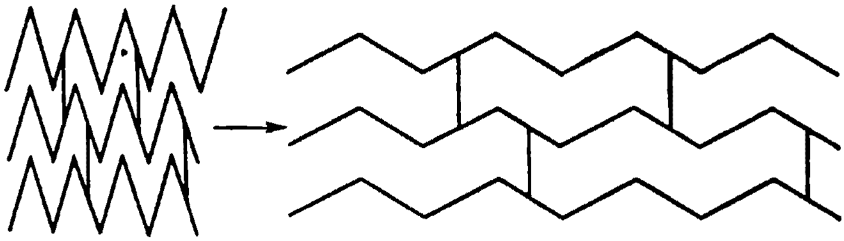
Caoutchouc does not contain sulphur cross-links and therefore separate molecules are not connected to each other. Nevertheless, caoutchouc can be reversibly extended (though it resembles paraffin). This occurs because there are "ties" in the caoutchouc that connect long molecules together. The "ties" are formed when these molecules are entangled or interwoven like separate fibres in a piece of cotton wool. Since there are no strong "ties" that can bind separate caoutchouc molecules, the latter is less elastic than rubber, and can dissolve in benzene, while rubber only swells (you can check this experimentally).

Why can many polymers, such as polyethylene, be extended irreversibly, i.e. why don't they shrink when the tensile force is removed? The point is that unlike caoutchouc molecules, the molecules of polyethylene are arranged as in a crystal. Such molecules can only slide relative to one another.

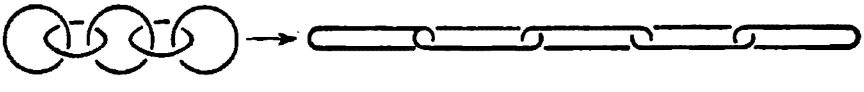
We mentioned that the molecular masses of polymers are very large and have been determined for all polymers; we also noted that the real length of the polymer molecule is smaller than the length of the stretched molecule. How do scientists determine these quantities? Since even large, long polymer molecules cannot be seen under a microscope, indirect methods are used. The simplest way to determine the molecular mass of a substance is to measure the increase in the boiling point of a solution. Dissolve some table salt in water and heat the solution to boiling. Heat the same volume of pure water under the same conditions, and you will see that the solution boils at a higher temperature than the pure water. In the same way, a salt solution freezes at a lower temperature than pure water. This can be verified by placing two liquids in a refrigerator. The difference between the boiling and freezing points of solution and pure solvent depends on the concentration of solute and its molecular mass.

How can the shape of molecules be determined? The shape of molecules in solution can be established by measuring the viscosity of the solution. The longer the molecules and the more they are stretched into a chain, the easier they become entangled and the greater the resistance they exert against the "flowing" water molecules. The following rough analogy can be drawn: the sand from the bottom of a river, which consists of fine particles, can easily be passed through a conical funnel. A piece of cotton wool, however, is drawn through the funnel with difficulty because the wool consists of long entangled fibres.

In concluding this discussion, let us express an idea from the realm of science fiction. The principle of rubber elasticity can be expressed as follows



And now imagine that a substance is synthesized, whose molecules consist of a variety of rings coupled together to form a chain. Scientists already know how to connect two or three rings into a chain. But if a molecule consists of hundreds or even thousands of such rings, the stretched molecule will be represented as



Thus, it becomes obvious that the extensibility of such a polymer should be thousands of times greater than the extensibility of common rubber.

Our Food

A human organism can, in a sense, be compared to an internal-combustion engine, because it converts the chemical energy of substances taken in with the food into motion and heat. The components of food—proteins, carbohydrates, fats, vitamins, salts, and water—are vitally important and necessary for an organism, and each of them has a specific function. Carbohydrates are a "fuel" for humans and animals. These substances have the general formula $C_x(H_2O)_y$ and this is why they are called carbohydrates. For example, the formula of the most well-known and important carbohydrate, glucose, is $C_6H_{12}O_6$ or $C_6(H_2O)_6$. The structure of a glucose molecule reveals that this substance can be simultaneously regarded as an alcohol with five hydroxyl groups OH and an aldehyde that contains a CHO group. Glucose molecules can exist in three forms that are in a dynamic equilibrium, i.e. two cyclic and one opened forms. Hydroxyl and aldehyde groups in the glucose can be identified by the following test. Add 2 or 3 drops of sodium hydroxide to a few drops of an aqueous glucose solution in a glass, and then add a copper sulphate solution dropwise until a persistent turbidity forms. When the glass is heated in a pan with hot water, the solution turns yellow and a precipitate is formed. This reaction is the oxidation of the glucose aldehyde group to an acid group —COOH. The oxidant—copper(II) hydroxide—is thus reduced to copper oxide Cu_2O, which settles as a yellow precipitate.

In another test, a small amount of silver nitrate is dissolved in a few drops of water in a glass and ammonium hydroxide solution is added until the precipitate thus obtained is dissolved. Then, a small amount of glucose is added. When the glass is heated in a hot water bath, silver is reduced and separates in the form of a black precipitate. These two tests can be used to identify the aldehyde group. Now conduct the reactions for the hydroxyl group. Place a few drops of copper sulphate in a glass or on a glass slide and add sodium hydroxide solution. A precipitate of copper hydroxide will result, to which glucose solution is added by drops. A blue compound is formed in which copper is connected to the oxygen of the hydroxyl groups of the glucose.

Glucose is widely encountered in nature, but most frequently it is found in a bound state. Let us discuss the best-known derivatives of glucose. A molecule of ordinary cane sugar (succharose) consists of two parts: glucose and fructose. However, they are arranged in such a way that the glucose aldehyde group cannot reduce copper hydroxide (you can check this with the reaction for an aldehyde group). On the contrary, the hydroxyl groups can easily be identified by the corresponding reaction. Sugar decomposes into its main components (glucose and fructose), when it is boiled with an acid. Place a small amount of glucose solution and a few drops of dilute sulphuric acid into a test tube and boil for 2 or 3 minutes. After neutralization with an alkali solution, the glucose can be identified in the resulting solution.

Cane sugar is a disaccharide (dimer) whose molecule consists of two units of the simplest carbohydrates. Glucose can form long polymer chains and, depending on the way the units are connected, starch or cellulose is obtained. When iodine tincture is added to a starch solution (or starch paste), a blue colour appears, because a starch molecule represents a long hollow cylinder, which absorbs iodine molecules to form insertion compounds. Add an excess amount of ammonium hydroxide solution to a small amount of copper sulphate solution in a glass and drop a piece of cotton wool into the obtained solution: in a few minutes the wool dissolves. If dilute hydrochloric acid is added to the contents of the glass, cellulose will again separate from the solution. When starch and cellulose are heated with acid solutions, they decompose to form glucose molecules.

Thus, food is a source of energy. But how does this "fuel" burn and how is the energy contained in it utilized? Suppose you have boiled rice, boiled potato, sweet tea, and bread for your breakfast. Bread contains about 50% starch; potato contains 20%; and rice, 80%. Therefore, after such a breakfast, you have been supplied with a portion of carbohydrates. The digestion of food begins already in the mouth. Under the action of organic catalysts (enzymes), starch, cellulose, and sugar are broken down in the organism to glucose units. Enzymes accelerate this reaction so that it takes only a few seconds, while under normal conditions prolonged heating with an acid is required for this reaction to occur. Each chain of starch or cellulose decomposes into many thousands of glucose molecules. The decomposition of polysaccharides terminates in the stomach under the action of gastric juice. Glucose is then absorbed through the walls of the intestine and is carried with the blood throughout the entire organism. Each cell therefore obtains glucose with the blood. But the cells do not consume glucose uniformly, because the energy expenditures during hard work are greater than during a state of rest. If the concentration of the glucose in the blood is greater than the amount required for the cells at a given moment, the glucose excess is carried with the blood to the liver where it again polymerizes to form the reserve, nonreducing polysaccharide glycogen. But how does blood "know" that excess glucose should be stored for future use? This is controlled by a special hormone called insulin, which is produced by the pancreas. If the cells require additional energy, glycogen is decomposed, and the glucose thus formed is delivered by the blood to the cells.

What happens to a glucose molecule when it enters a cell? These transformations are complex and occur in many stages, but scientists today have unravelled them in general form. Here, special enzymes and an energy accumulator—adenosine triphosphate (ATP)—are involved. The latter is a complex compound, which, after the separation of a phosphate group, transforms into adenosine diphosphate (ADP) liberating energy that is required by the cell. At the first stage, the molecule of glucose reacts with the enzyme glucosidase and the ATP molecule, which loses its energy and transforms into ADP. Further, a chain of transformations occurs in which the glucose molecule splits into smaller fragments, and all these processes yield ATP, which is utilized by a cell. An intermediate substance in the transformations of glucose is pyroracemic (pyruvic) acid $CH_3COCOOH$, which is involved in new reactions and while reacting with oxygen (delivered to the cell by the haemoglobin of blood), transforms into citric, oxalic-succinic, succinic, and malic acids and, at last, into carbon dioxide and water that are carried from the cell with the blood. The entire process of glucose oxidation by oxygen obtained by breathing consists of 22 consecutive chemical reactions and requires the participation of two dozen enzymes. The cell obtains 38 ATP molecules (formed from ADP molecules) for every glucose molecule that is "burned". The efficiency of cell is 45%.

Where is this energy spent? First of all, it is used to maintain the normal temperature of the body, because many processes in the cell cannot occur at low temperatures. Every reaction that proceeds in a cell requires energy, and it is released during the transformation ATP → ADP. For example, the muscle protein myosin splits the ATP molecule and as a result the protein molecule becomes shorter and the muscle contracts. This is the mechanism by which the chemical energy of the carbohydrates contained in food is transformed into the motion of the muscles.

Pyroracemic acid, which is an intermediate in the oxidation reaction, can be completely oxidized to carbon dioxide and water when oxygen is in excess. On the other hand, if there is not enough oxygen, pyroracemic acid is reduced to a lactic acid, $CH_3CH(OH)COOH$. This is why sportsmen have increased lactic acid levels in their muscles immediately after intense exercise, because there is too little oxygen in the organism to oxidize all the glucose and their energy requirements were large.

Finally fungus microorganisms (yeasts) transform glucose into pyroracemic acid, as in the case of breathing, and then the pyroracemic acid is decomposed into carbon dioxide and acetaldehyde CH_3CHO. The acetaldehyde reacts with ethanol dehydrogenase and a special reducing agent to yield ethyl alcohol (Fig. 30).

Carbohydrates are not the only substances that provide energy for our body. The second type of "fuel" for a living organism is fat. Fats are esters of organic acids and trihydric alcohol—glycerin. They are deposited in body tissues and are similar in function to glycogen. When treated with alkalies, fats decompose into glycerin and the salts of organic acids, which are used as soaps. Add a small amount of an alcohol to a few drops of vegetable oil in a glass and place there a small quantity of sodium hydroxide. Heat the mixture in a hot water bath until it becomes homogeneous. You have thus obtained a soap solution. If you then add dilute sulphuric acid to the solution, drops of organic acids will appear on the surface of the solution. Vegetable oils contain glycerides of unsaturated acids, which can easily be identified using potassium permanganate. The permanganate reacts at the site of a double bond and becomes colourless. Add a small amount of washing soda solution and a few drops of potassium permanganate to a glass con-

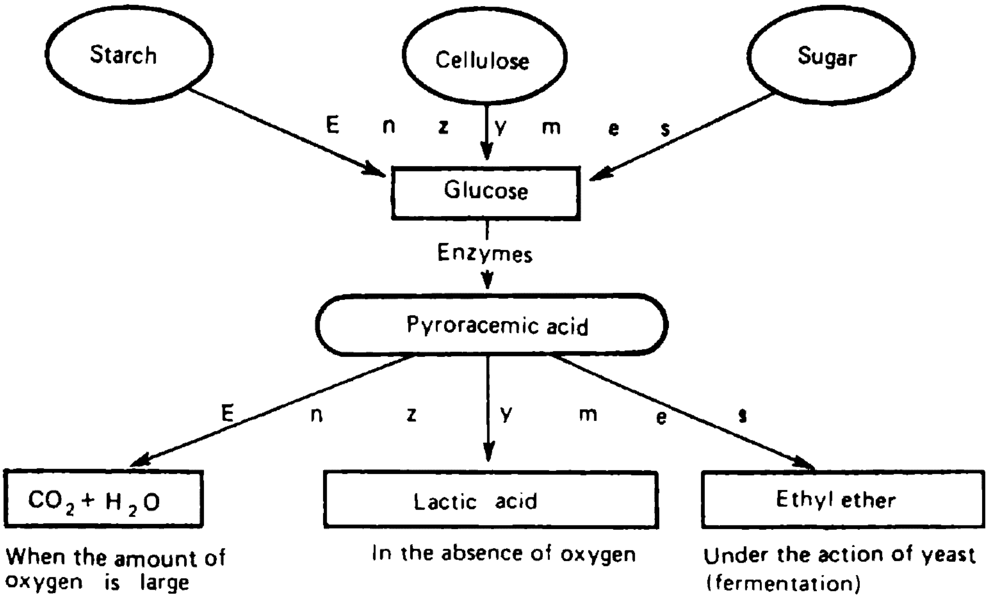


Fig. 30 The oxidation of hydrocarbons in organisms

taining a few drops of vegetable oil. When the mixture is stirred, the crimson colour of potassium permanganate vanishes.

Proteins constitute another component of food, which are used as a construction material for the body and to produce other proteins in the organism. When the organism needs more energy than is available, it "burns" the amino acids of proteins. This can be compared to kindling a fire with a costly species of wood. Of course, walnut or beech can be used as firewood, but it is more rational to use them in the manufacture of fine furniture.

There are a vast number of proteins, but they all consist of similar residues of amino acids. An amino acid molecule contains two groups, which have opposite properties; namely, a carboxyl group with acid properties and an amino group with basic properties. Due to these groups, amino acid residues can be connected into long chains: $\mathrm{H_2N{-}\underset{|}{CH}{-}COOH + H{-}NH{-}\underset{|}{CH}{-}COOH \rightarrow H_2N{-}\underset{|}{CH}{-}CO{-}NH{-}\underset{|}{CH}{-}COOH + H_2O}$. A protein molecule usually contains dozens of amino acid residues.

Isolate an egg white, beat it thoroughly and add a tenfold amount of water. Now filter the obtained mixture through a double layer of gauze. The filtrate contains a protein called albumin, while a protein called globulin remains in the precipitate.

The globulin can be dissolved in a solution of common salt. Put a few drops of albumin solution in a glass or onto a glass slide and add a few drops of the alkali and copper sulphate solution: a violet colour appears. The oxygen and nitrogen atoms attached by peptide bonds to the protein react with the copper to form a violet complex.

The sequence of amino acid residues in a protein molecule is called its primary structure. Although scientists can now establish the primary structures for very intricate protein molecules, the procedure is tedious and time-consuming. In order to establish the primary structure of a protein, special reagents are used to split the protein into residues containing only a few amino acids. The structure of these residues can then be identified more easily. Then, a map is compiled from which the structure of the whole protein molecule can be reproduced. Scientists can now also synthesize many proteins. This is achieved by gradually adding to a chain of amino acid until the required structure is produced.

The hydrogen atoms in the amino groups in a protein chain can form hydrogen bonds with oxygen atoms in the carbonyl groups C=O. Because each hydrogen in each NH group bonds to the CO group three amino acid residues along in the same chain, a long chain of amino acid coils into a regular helix. The general formula of an amino acid is $H_2NCH(R)COOH$, where R stands for hydrogen, methyl, or more complex radical or group, for example, $—CH_2CH_2CH_2CH_2NH_2$. This group distinguishes the amino acids. When the chain of a protein molecule coils into the helix, the radicals protrude from the spiral cylinder, and the resultant helix is called the secondary structure of the protein.

The radicals in one protein molecule can attract groups in another and thus the molecules interact. As a result, the whole protein helix can roll into a ball. However, this rolling is not random event, it follows a plan. This is why proteins need radicals and why a different protein is formed when only one radical is changed in a molecule. The way the molecule is rolled is called the tertiary structure of the protein. But this is not all. Several protein balls can combine to form a quaternary structure. This is the case with the haemoglobin molecule. It is rather difficult to establish the tertiary and quaternary structures of a protein, and to do it protein crystals must be analyzed by X rays.

All four structures of a protein can be modelled. Take a long thin wire. This represents the primary structure of a protein molecule. To obtain the secondary structure, coil the wire into a spiral. The tertiary structure is produced when the spiral is rolled into a ball. Several balls combined together model a synthesized protein in its natural form. Indeed, a protein can only "work" in the organism if it is in its tertiary or quaternary structure. However, this structure can easily be destroyed. Everyone has done this when boiling an egg. What happens to the transparent, liquid, and water-soluble egg albumin when it is heated? It turns out that the hydrogen bonds between the —R groups, which keep the protein molecule in the form of a compact ball, break. After this, the tertiary structure is destroyed and the protein, whose molecules take on the form of long entangled threads, ceases to be soluble. A protein can be denatured, i.e. its tertiary structure destroyed, in other ways. If alcohol or acetone is added to an aqueous solution of egg albumin, the solution becomes turbid. In fact, the protein has not yet been denatured, rather the albumin has been precipitated. When more water is added to the turbid solution, the precipitated albumin redissolves. However, when the turbid solution is allowed to stand for a time, the tertiary structure of the protein gradually breaks down completely.

The proteins eaten as food are broken down in the stomach into separate residues, which are further degraded in the intestine into individual amino acids. Those can then penetrate the intestine walls and are carried by the blood to the body's cells.

Once in the cells, the amino acids are combined into different proteins, i.e. the proteins needed by the cell. The synthesis of a protein in a cell requires energy, and therefore molecules that accumulate ATP, which acquire energy as a result of glucose oxidation, are involved in the synthesis. Proteins with constituents such as valine, leucine, and lysine must always be eaten. They are the essential amino acids (as they cannot be replaced by other amino acids), and everyday some 30 g of these proteins should be consumed. The other amino acids, i.e. alanine, asparagine and glutamine, are not obligatory components of food, because they can be synthesized in the organism if necessary.

Vitamins and Chemistry

Today we know that the normal functioning of the body requires vitamins and that the lack of vitamins in food results in severe diseases. So, what are these substances, how many vitamins are known, and what role do they play in the organism?

The history of vitamins goes back to the end of the last century. At the time, it was known that proteins, fats, carbohydrates, water, and mineral salts were indispensable components of food, and that without them the organism cannot develop normally and will finally die. In 1881, the Russian scientist Lunin carried out an experiment in which he prepared "artificial" milk by mixing purified proteins, fats, carbohydrates and mineral salts in the same proportions they are in natural milk. This "milk" was fed to the experimental animals (mice), and after a certain time, all the animals died. Thus, it was clear that natural food contains something else essential for an animal organism. In 1911, a Polish biochemist C. Funk called these indispensable substances vitamins (from the Latin *vita* meaning life + amine). Although it was later shown that many vitamins are not amines, the name remained.

Dozens of vitamins and their structures are now known. Most vitamins can be synthesized industrially. In an organism, vitamins provide constituents to enzyme molecules. A living organism cannot synthesize vitamins by itself and therefore they must be eaten in food. We shall consider several vitamins. Vitamins are mainly named by the letter of the alphabet, and we shall consider them in the alphabetical order.

A deficiency of vitamin A causes metabolic disturbances, weight loss and one's hair falls out. The main danger of vitamin A deficiency is softening of the cornea and dry eyes, resulting in night blindness. In a molecule of vitamin A, which is also called retinol, double bonds alternate with single bonds in a long chain of carbon atoms that terminates with a hydroxyl group. Retinol is a pale-yellow viscous substance that is soluble in fat and insoluble in water. A derivative of vitamin A called retinene is a pigment (in which $—CH_2OH$ group is replaced by an aldehyde group $—CHO$) and is contained in the retina of the eye. In the rods of the retina, it combines with the protein opsin to form the visual pigment rhodopsin. When light falls on a rod, the rhodopsin decomposes into opsin and *cis*-retinene. Then, *cis*-retinene immediately transforms into *trans*-retinene, which is accompanied by the transmission of a nervous impulse to the brain (Fig. 31). After the impulse has reached the brain, which means that a man has perceived a quantum of light, the *trans*-retinene is again transformed into the *cis*-form. This process can be compared to winding of a film in a camera to take a next picture, bringing unexposed film in front of the lens. This “winding on” in the eye proceeds in the dark according to the following scheme. An enzyme and a biological reducing agent reduce the *trans*-retinene to *trans*-retinol (i.e. to vitamin A), which is then transformed into *cis*-retinol by the enzyme isomerase. Then, the *cis*-retinol is oxidized to *cis*-retinene, and the eye is ready to “photograph” the next picture.

Vitamin A is contained in fish-liver oil, which can be confirmed experimentally. Add five drops of chloroform and a drop of concentrated sulphuric acid to a drop of a fresh fish-liver oil in a glass or on a glass slide: the mixture turns red. Carotene is often found in natural food. A molecule of carotene consists of two parts, i.e. two molecules of vitamin A. Carotene is converted

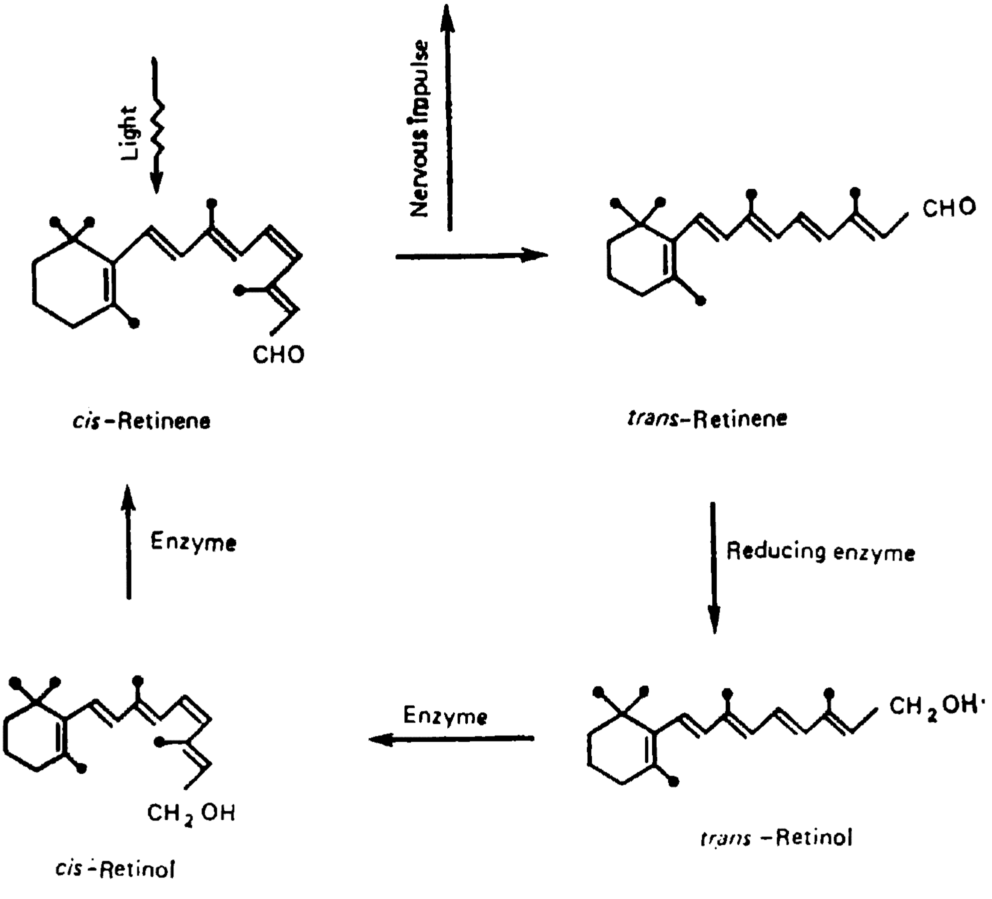


Fig. 31 A simplified scheme of conversions of vitamin A derivatives during light perception by an eye. Black dots are the methyl groups

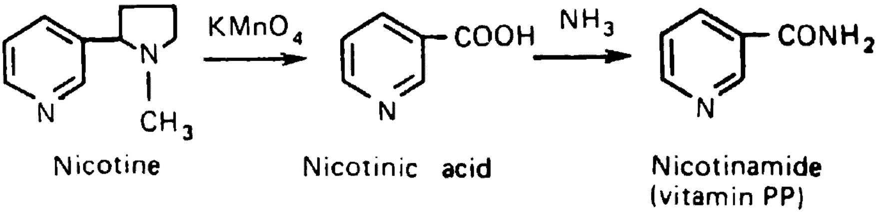
in the body into retinol. Triturate a rose hip with sand in a glass and add several drops of chloroform. The carotene in the rose hip is extracted by the chloroform. Pour the solution into another glass and add several drops of concentrated sulphuric acid. The upper chloroform layer turns green and then blue.

Rose hips also contain another vitamin, i.e. vitamin C (ascorbic acid). This is a colourless, crystalline substance that is readily soluble in water. In aqueous solution it is unstable and it is easily decomposed by heating. Vitamin C is a good reducing agent, and it is this property that is utilized in biological processes. Ascorbic acid is involved in the synthesis of hormones, and it prevents adrenaline, which is an important biological compound, from oxidizing. Ascorbic acid is also a constituent of some enzymes. It is a cure for scurvy, and it should be taken when exercising heavily either physically or mentally. Many reactions are based on the reducing properties of ascorbic acid. Obtain an extract from a rose hip by triturating it with sand and water. Filter the resultant mass through cotton wool or filter paper and use the filtrate in the following experiments. Add a few drops of the filtrate to a few drops of iodine solution in a glass. The iodine solution decolourizes as a result of reduction, while the ascorbic acid is oxidized to dehydroascorbic acid. In a second test, add 1 or 2 drops of sodium carbonate solution and a few drops of the filtrate to a strongly diluted solution of methylene blue dye in a test tube. The dye becomes colourless when the test tube is heated. Finally, if a drop of the filtrate is added to a drop of potassium ferricyanide in a test tube, a precipitate of Prussian blue is formed. These experiments can also be carried out with pure ascorbic acid.

Fish oil, which we have already mentioned, is a useful product. In addition to vitamin A, it contains vitamin D (also known as calciferol). Vitamin D is essential for normal calcium and phosphorus deposition in bones and teeth. Deficiency of vitamin D in children results in rickets. Mix several drops of fish oil, chloroform, aniline and a drop of concentrated hydrochloric acid in a test tube. Heat the test tube over a gas burner and observe how the mixture turns red, which is characteristic of vitamin D. When a mixture of an oil solution of vitamin D, chloroform, and concentrated sulphuric acid is vigorously stirred, it turns red.

In 1936, the Hungarian scientist A. Szent-Györgyi concluded that permeability of small blood vessels is affected by a substance called vitamin P complex. Today it is known that this effect is produced by rutin, hesperidine, and the catechins. Rutin contains phenol hydroxyl groups, and hence produces a characteristic colour with ferric chloride. Mix a saturated solution of rutin (you can buy it in a chemist or pharmacy store) with a few drops of ferric chloride in a test tube or on a glass slide: the liquid turns green. The rutin is reduced when 2 or 3 drops of concentrated hydrochloric acid and a piece of zinc are added to a few drops of vitamin P solution. As a result, the liquid turns red. The catechins, which are the components of vitamin P, are contained in tea. Pour some ethyl alcohol into a glass containing some tea leaves. The solution above the tea leaves turns yellow after some time. Then, pour the solution into another glass and add an alcohol solution of ferric chloride. Observe the green colouration.

Vitamin PP has nothing to do with vitamin P complex. Antipellagric vitamin PP is an amide of nicotinic acid, but one should not conclude from the name that it is as poisonous as nicotine. However, nicotine can be used to produce nicotinic acid, from which vitamin PP can easily be obtained



Dissolve a small amount of nicotinic acid in a few drops of dilute acetic acid in a test tube with heating. Boil the solution and add a few drops of copper acetate. The liquid becomes turbid and turns light blue. After a time, a dark blue precipitate separates from the liquid. Nicotinamide plays an important role in biology. It combines with sugar, ribose, phosphoric and adenylic acids into a complex, which is a component of the hydrogenase enzymes. One of these enzymes takes part in light perception by the rods of the eye retina. The reducing agents nicotinamide adenine dinucleotide (NAD) and nicotinamide adenine dinucleotide phosphate (NADP) convert *trans*-retinene to *trans*-retinol and contain vitamin PP.

Experiments with Medicines

Most human diseases are caused by microorganisms that penetrate the tissue and disturb the normal chemical processes in them. One of ways of controlling these microbes is to "poison" them by bringing into contact with some chemical compounds.

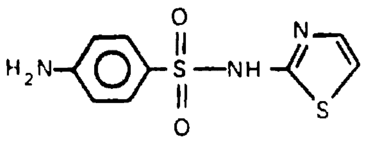
At the beginning of this century *para*-aminobenzene sulphonamide (sulphanilamide) was obtained as an intermediate in the production of dyes. It was noticed that this compound kills the microorganisms responsible for some diseases. After numerous tests, sulphanilamide was used as a medicine and called streptocide. If a tablet of streptocide is heated on a metal plate, a violet melt is formed that smells of ammonia. This test identifies the amino group in the substance. Now, boil a tablet of streptocide in a test tube in a small amount of concentrated nitric acid, dilute the solution with water, and add barium chloride solution. As a result, a white precipitate is produced, which proves the presence of a sulpho group $—SO_2—$.

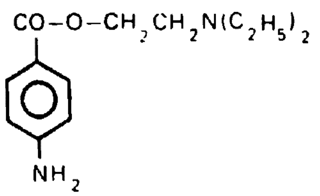
Why can streptocide kill microorganisms? It turns out that the normal function of a bacterium requires *para*-aminobenzoic acid, which is also called H_1 vitamin. *Para*-aminobenzoic acid is a component of folic acid, from which the bacteria produce enzymes. Vitamin H_1 is a growth factor without which bacteria can neither grow nor reproduce. A molecule of streptocide is similar in size and chemistry to a molecule of *para*-aminobenzoic acid. Bacteria utilize the sulphanilamide to form "folic" acid and then their enzymes, but then the forgery comes to light for the enzymes do not function. Thus, the normal bacterium's metabolism is disrupted and the bacterium dies.

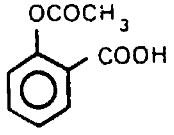
Streptocide is the simplest sulphanilamide. Numerous other sulphanilamide derivatives are now known and they are all used as medicines. They include sulphadimezine (sulphadimedine, sulphamethazine), sulphathiazole (norsulphazole), sulphaguanidine (sulgin), and ethazole (sulphaethidole). For example, phthalyl sulphathiazole is like a molecule of streptocide, but the hydrogen atoms in the amino groups are replaced by the residues of complex organic compounds. These substituents prevent the medicine from penetrating the intestine walls into the blood stream and thus being distributed throughout the organism. Therefore, phthalyl sulphathiazole is effective in controlling disease-carrying microorganisms in the stomach and intestine (Fig. 32).

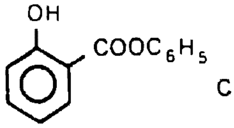
Heat a tablet of sulphathiazole in a test-tube: a dark brown melt is formed which smells of hydrogen sulphide. The latter is due to a sulphur atom in the five-membered ring contained in the sulphathiazole molecule. Now, place sodium hydroxide solution into each of the three test tubes, and add sulphathiazole to the first test tube, ethazole to the second, and sulphadimedine to the third test tube. If copper sulphate solution is then added to each test tube, precipitates of different colours will be formed: a dirty violet precipitate appears in the first test tube, a green compound (which turns dark after a while) precipitates in the second, and a yellow-green compound, which later becomes brown, precipitates in the third test tube.

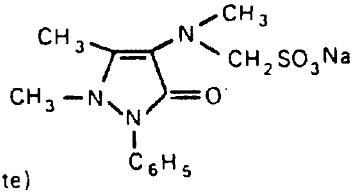
The derivatives of *para*-aminobenzoic acid are widely used in medicine. If the hydrogen atom of its carboxyl group is replaced by an ethyl radical, anesthesin (benzocaine) is obtained, while novocaine (procaine) is formed when the hydrogen atom is replaced by a more complex radical, viz. —$CH_2CH_2N(C_2H_5)_2$. Both compounds are used as local anaesthetics and analgesics. Salicylic acid somewhat resembles *para*-aminobenzoic acid. It is a derivative of benzene, in which two neighbouring hydro-

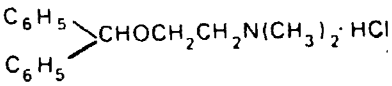

Norsulphazole (sulphathiazole)

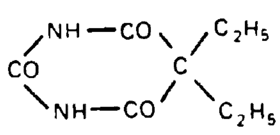

Novocaine (procaine)

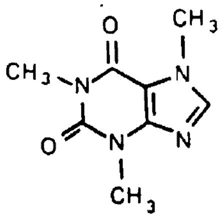

Acetylsalicylic acid


Salol
(phenyl salicylate)


Analgin (dipyrone)


Dimedrol (diphenylhydramine)


Veronal (barbital)


Caffeine
(1,3,7-trimethylxanthine)

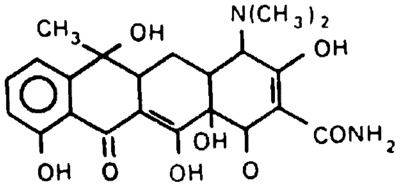

Tetracycline

Fig. 32 Structural formulas of certain medicines gen atoms are replaced by a carboxyl and a hydroxyl group. Salicylic acid is an important medicine; it is used as a bactericide and to treat rheumatism. The sodium salt of salicylic acid is used as an analgesic, antipyretic, antiphlogistic, and antirheumatic agent. The methyl ester of this acid (in which $-COOCH_3$ group substitutes for $-COOH$ group) is used in ointments as antiphlogistic and antirheumatic agent. Everyone is familiar with acetylsalicylic acid, in which the $-OH$ group is replaced by the $-OCOCH_3$ group (it is called aspirin). The phenyl ester of acetylsalicylic acid, i.e. phenyl salicylate (where $-COOH$ group is replaced by $-COOC_6H_5$), which is also called salol, and is a good antiseptic and disinfectant. The sodium salt of *para*-aminosalicylic acid ·(this compound contains two amino groups in the benzene ring) is antitubercular agent.

All phenols are turned violet by ferric chloride solution. This can be verified by reacting an alcohol solution of salol with a drop of ferric chloride. When this test is performed with acetylsalicylic acid, no violet colouration is observed. The reason is that the acid has no free hydroxyl group, and the hydrogen is replaced by the acetyl group. However, we can easily obtain salicylic and acetic acids from acetylsalicylic acid by boiling a tablet of the latter in a sodium hydroxide solution in a test tube.

After cooling, the solution is acidified with dilute sulphuric acid. The precipitated salicylic acid can be identified by the violet colouration which appears when a drop of ferric chloride solution is added to the precipitate.

Phenacetin is an effective medicine for fever. A molecule of this compound includes benzene ring with attached $—NHCOCH_3$ and $—OC_2H_5$ groups. Place a small piece of phenacetin tablet into a test tube containing dilute nitric acid. First, the solution turns yellow, and then a yellow precipitate forms. Now, boil a piece of phenacetin tablet in a small amount of dilute hydrochloric acid in a test tube, and after cooling the solution add a drop of potassium dichromate solution. The violet colour which first appears, changes to red.

The derivatives of pyrazolone (ketopyrazoline) comprise another class of antipyretics and analgesics. They include antipyrine (analgesin), amidopyrine (pyramidon), and analgin (novaminsulphon, dipyrone) and have similar formulas. Antipyrine gives red colouration with ferric chloride solution, while with acidified sodium nitrite solution it produces a green nitroderivative. In contrast to antipyrine, amidopyrine reacts with ferric chloride to give a blue solution, from which a brown substance precipitates after some time. If this solution is acidified with hydrochloric acid, a violet colouration is observed. Amidopyrine solution also goes the same colour when treated by silver nitrate solution.

Derivatives of barbituric acid are soporifics. The barbiturates include veronal (barbital), phenobarbital (luminal), barbamyl (sodium amobarbital), nembutal (sodium pentobarbital), and others. Add sodium hydroxide and copper sulphate solutions to a solution of barbital. The solution first turns blue, and then a red precipitate forms. A molecule of barbamyl contains sodium, which can be identified by dipping a wire into the substance and placing the wire into a flame. The flame colours bright yellow.

Finally, a few words about antibiotics. These are produced by certain microorganisms and can kill the causative agents (pathogens) of many diseases. For example, penicillin does not permit pathogenic bacteria to assimilate amino acids from food, and therefore, bacteria cannot construct cell membranes. Terramycin (oxytetracycline) disturbs phosphorylation in a bacterium, i.e. the process by which it releases energy. In the presence of tetracycline or streptomycin (agrimycin, agri-strep), bacteria cannot synthesize individual proteins. Certain antibiotics undergo specific chemical reactions. Add a drop of sodium hydroxide to a few drops of streptomycin and boil the mixture for a few seconds. Then, acidify the liquid with hydrochloric acid and add ferric chloride: a red-violet colouration appears. When an alcohol solution of ferric chloride is added to a solution of terramycin, the solution turns brown. If several crystals of terramycin are dissolved in a drop of concentrated sulphuric acid, a red colouration appears. If a tablet of levomycetin (chloramphenicol) is dissolved in a sodium hydroxide solution with heating. the solution first turns yellow and then red,

Why Are Poisons Toxic?

A human organism is in a sense, a gigantic chemical plant, which produces a great variety of substances. Some chemical compounds (for example, proteins) are used to build the human body, others (carbohydrates) are utilized to provide energy, and others (e.g. hormones) are regulators, by means of which one organ affects others. In a healthy organism the "production" of chemical compounds is a finely adjusted process, and each organ fulfils its own production "plan" for specific compounds. It should be noted that both underproduction and overproduction are undesirable, because an excess of a compound may result in disease or death.

Every living organism is an open system which constantly exchanges substances with the surrounding medium. Some substances are consumed, processed and utilized in the organism, while unnecessary and unutilized ones are excreted. One can only admire how all these processes are accurately balanced in the organism. However, this balance can easily be disturbed by certain chemical compounds. These compounds are called poisons, and unfortunately there are quite a number. So how do poisons affect us, and why do some things not influence the organism, while others, even in minute amounts, have severe consequences? In order to answer these questions in detail, we should have to study the functions of a variety of compounds produced by the organs, as well as the functioning of the organs themselves. Today, scientists know in general the mechanisms by which poisons affect the organism, but the details are still unknown in many cases.

Let us consider the action of poisons frequently encountered in the household and while doing the simplest chemical experiments. It is convenient to divide all poisons into inorganic and organic categories (although the division lacks scientific basis).

The inorganic substances that have a bad effect on the human organism may do so in any state (gas, liquid, or solid). The toxic action of carbon monoxide is, probably, best known. Carbon monoxide easily forms complex compounds with iron ions, which are the components of blood haemoglobin. By reacting with the iron, carbon monoxide blocks the ions, and the organism loses, as it were, its haemoglobin. The oxygen transport in the blood becomes thus impossible, and cells stop receiving oxygen. Carbon monoxide is a product of the incomplete combustion of carbon. The maximum allowable concentration of carbon monoxide is 0.02 mg per litre of air. Of course, the degree of intoxication depends not only on the carbon monoxide concentration, but also on the time a person was exposed to the gas. The symptoms of intoxication are dizziness (vertigo), headache, and fainting. In the case of carbon monoxide intoxication, one should inhale fresh air. Although carbon monoxide binds haemoglobin iron more strongly than oxygen does, the oxygen concentration in the lungs becomes greater upon vigorous inhalation of air, and soon the entire carbon monoxide is gradually displaced by oxygen.

We have discussed the effect of an oxide of a typical nonmetal, i.e. carbon. Certain metal oxides have absolutely no toxicity (for example, aluminium oxide), while others are strong poisons. To quantify the toxicity of a poisonous substance, the DL_{50} test is introduced. This is the dose for which half the experimental animals in the test die within 14 days. Since the dose for animals and humans depends on body weight, the DL_{50} is calculated per kilogram of body weight. If the DL_{50} is less than 15 mg of poison per kilogram of animal weight, then the substance is considered to be extremely toxic. Substances for which the DL_{50} is more than 1500 mg/kg have low toxicity. Toxic oxides are those of mercury, thallium, and lead. In general, the heavier the metal, the more toxic are its compounds. However, there are two exceptions, namely, berillium and copper. These are light metals but their oxides are very poisonous. Metal salts are usually more poisonous than their oxides.

Mercury is one of the most poisonous metals, its vapour being very toxic too. Therefore, when a mercury thermometer is broken, all the mercury should be carefully collected using a copper plate cleaned with a sand paper (the mercury drops stick to the surface of the copper plate). The remaining small drops of mercury should be neutralized with ferric chloride, which converts the metal into a salt. Although mercury salts are not volatile, they are very toxic once inside the organism. Nevertheless, mercury salts are widely used in laboratory practice and medicine. How can mercury salts be distinguished? There are several reactions which are specific to this metal. When a salt of monovalent mercury is treated with an alkali, a dark brown precipitate of mercurous oxide is formed. A salt of divalent mercury reacted with an alkali yields a yellow precipitate of mercuric oxide. Potassium iodide solution precipitates red mercury iodide from a salt of divalent mercury. If then an excess of potassium iodide is added, the precipitate dissolves, and a colourless solution of a complex salt is formed.

One should not think that mercury salts are so toxic that one has only to hold a test tube with a mercury compound to be intoxicated. Mercury salts are used in medicine, e.g. mercurous chloride (calomel) is used as laxative and chologogue (the maximum allowable dose is 0.6 g), while very diluted solutions of mercury bichloride (corrosive sublimate) are used as disinfectants (not more than 0.02 g of corrosive sublimate should get into the organism). Therefore, if a chemist is careful and attentive while working with mercury compounds and then thoroughly washes his utensils and hands, there will be no poisoning. The symptoms of mercury poisoning are a metallic taste in the mouth and the pain in the abdomen, as well as diarrhoea and vomiting. A person poisoned by a mercury salt should drink milk, irrigate the stomach with a suspension of activated carbon in water and to gargle with weak potassium permanganate solution. Hot tea and a hot bath are recommended. On no account should a table salt or salty food be eaten.

Copper salts are less toxic than mercury salts, but when they get into the organism, they can cause severe poisoning. Copper compounds can easily be distinguished by their blue or green colour. An iron article is quickly covered with a layer of copper when it is treated with a solution of a copper salt. If potassium iodide solution is added to a divalent copper salt solution, iodine is evolved (divalent copper is reduced to monovalent copper). The evolved iodine gives a specific blue colouration with a starch solution. Copper sulphate is used in medicine as emetic, antiseptic and cauterant. A single dose of copper sulphate for an adult should not exceed 0.5 g. Arsenic is the best known poison, and its compounds are widely used to combat rodents. Acute arsenic poisoning is accompanied by a collapse and muscle weakness. When the arsenic dose is large, paralysis and death can occur. For acute poisoning, the stomach should be first irrigated to cause vomiting. Taking of water suspension of magnesia will also be of certain help here.

Lead is also said to be a poisonous metal, but, unlike arsenic, lead poisonings are mainly of chronic nature. The first symptom of chronic poisoning in people who deal with lead alloys, for example, in those who work in printing houses, are pains in the abdomen and a grey border on the gum. It is noteworthy that a lead compound, i.e.

tetraethyl lead, is an additive to a petrol. In acute poisoning by a lead compound, which is accompanied by a disorder of the gastro-intestinal tract, a dilute solution of sulphuric acid is taken. Lead is thus transferred to a poorly soluble lead sulphate. The toxic effect of heavy metal compounds arises because ions of these metals form rather stable complexes with proteins in the organism. As a result, the proteins (which include enzymes, hormones, and other vitally important compounds) can no longer fulfil their functions. The ideal balance between the processes in the cell is thus disturbed. Vanadium(V) affects the biosynthesis of cholesterol and violates metabolism of amino acids, while chromium(VI) penetrates and destroys red blood cells.

Metal ions in complexes with proteins are transferred in the organism by the blood stream and deposit in the organs, which contain compounds or groups that can form stronger bonds with the ions. It is interesting that every metal has its “favourite” organ. For example, lead, berillium, barium, and thorium are accumulated in the bone marrow, mercury collects in the kidneys, arsenic is deposited in the thyroid gland, chromium in the pancreas, and cadmium and zinc are accumulated in the testicles. It has been established that metals are deposited in the organs where the content of these metals under normal conditions is higher than normal. For instance, the mercury content in a healthy organism is always greater in the kidneys, while that of the lead in the bones.

The toxicity of an element strongly depends on its valence. For example, arsenic(III) compounds are ten times more toxic than arsenic(V) compounds. Unfortunately, arsenic(V) is reduced in the organism to the more toxic form. By contrast, compounds of chromium and vanadium with higher oxidation states are toxic, while the metals in lower oxidation states are not poisonous. Therefore, in a case of chromium poisoning, e.g. with potassium dichromate (Soviet chemists use it in a mixture with sulphuric acid to wash utensils), ascorbic acid is recommended. The reason can be seen from the following experiment. Add a drop of sulphuric acid and a pinch of ascorbic acid or a tablet of vitamin C to an aqueous solution of potassium dichromate. The yellow colour of potassium dichromate changes to green because the ascorbic acid reduces dichromate to a chromium(III) compound, which is not toxic.

There are vastly more organic poisons than inorganic ones. These include alkaloids extracted from plants (e.g. strychnine and brucine), protein poisons (the toxins made by snakes and scorpions) and almost all the organic solvents in use both in chemical laboratories and in the household. Inhaling any one of a group of chlorine-containing solvents which includes carbon tetrachloride (used to remove greasy spots and in fire extinguishers), chloroform (which is still employed in medicine), vinyl chloride (from which PVC is produced), and dichloroethane (which is a component of plastic glue) leads to a disturbance in the cardiac rhythm, fat degeneration, cirrhosis and atrophy of the liver, and metabolic disturbances. It is thought that when chlorine-containing solvents get into the organism, they react with certain substances in such a way that the carbon-chlorine bond is broken, forming two radicals, e.g. Cl^- and $CCl_3^{\cdot}$, from carbon tetrachloride. These radicals react with unsaturated fatty acids to yield new radicals, which further react with oxygen. As a result, derivatives of hydrogen peroxide are formed, which, in turn, destroy fatty acids, in particular, in the cell membranes. The harmful effect of chloroform is aggravated by light, which transforms chloroform into phosgen. The latter is an acid chloride of carbonic acid, $COCl_2$. Like any acid chloride, phosgen is chemically active, and thus it readily reacts with proteins and other cell molecules.

Benzene is an aromatic hydrocarbon used as solvent and starting material in many organic syntheses. It is highly toxic. If safety measures are not observed when working with this liquid, intoxication can occur. The number of red blood cells and haemoglobin level are lowered and significant changes occur in the nervous system and cardio-vascular system. A first aid measure is to take a suspension of activated carbon in water, after which vomiting should be induced. As compared to benzene, the mixture of saturated hydrocarbons that is called petrol is less toxic. Nevertheless, the nervous system of a person working with petrol for a long time can be affected. Petrol can also gravely affect the genital system and the development of a fetus during pregnancy.

Now let us consider how a nerve cell is constructed, and how a nervous impulse is conducted along the cells. In the 18th century, the Italian scientist Galvani established that the muscles contract under the action of electricity which runs along the nerves. Later, the German physicist Helmholtz measured the rate at which the nervous impulses propagate through the nerve. This rate for a frog is 30 m/s, which is too small to confirm a hypothesis that the nervous impulse is only an electric current. Thus, it was deduced that some chemical reactions are involved in this process.

Like a battery, a living cell has a potential difference. If two small electrodes are attached to the inner and outer sides of a cell, then a galvanometer connected to the electrodes would show a potential difference, which is called the rest potential. A nerve stimulus of any intensity results in a change of the potential difference, which is quickly conducted along the nerve. However, nerves have finite length and there are points at which the nerves touch one another. How does the electric impulse jumps from one nerve to another? Here is where chemical agents come into play.

A point at which nerves come into contact is called a synapse. When the first impulse (called the action potential) passes along the first (presynaptic) nerve cell and reaches the point where the nerve cell contacts the second (postsynaptic) cell, a special substance called acetylcholine is evolved from the presynaptic cell into the synapse. The acetylcholine acts on the postsynaptic cell and induces a new nervous impulse that is transmitted to another cell. A similar process takes place at a point where the nerve cell touches a muscle. The acetylcholine evolved from the nerve cell produces a change in the potential difference in the muscle cells, after which an impulse appears and a muscle contracts. Acetylcholine does not continuously stimulate a nervous impulse in a muscle or postsynaptic cell. Having fulfilled its duty, the chemical agent must immediately quit the stage.

It is destroyed by a special enzyme called cholinesterase, which hydrolyzes the acetylcholine into choline. The latter is biologically active.

Any violation of nervous impulse transmission has dramatic consequences. These violations can be caused by many chemicals. For instance, the poison curare blocks the centres of the nerve cells that are sensitive to acetylcholine. Therefore, an extract from the curare plant produces instantaneous paralysis (South American Indians dipped their arrow tips into curare). It should be noted that only strong impulses are transmitted through a synapse. However, an alkaloid called strychnine (a plant poison) increases the sensitivity of a synapse, so that even weak stimulus can cause muscle convulsions.

There are also chemicals that affect cholinesterase, and, unfortunately, there are many. Organophosphorus compounds, in which the phosphorus atom is directly bonded to the carbon atom, deactivate cholinesterase. They include sarin (isopropylmethyl phosphonofluoridate), soman (1,2,2-trimethyl propyl methyl phosphonofluoridate), tabun (dimethyl phosphoroamido cyanidic acid), and pesticides such as thiophos (parathion), trichlorfon (dipretes), mercaptophos (demeton). Although pesticides affect insects more than they do warm-blooded, some are also toxic to humans. Thiophos is especially toxic, while trichlorfon is moderately toxic, and bromophos is weakly toxic.

When a poison enters an organism and destroys cholinesterase, which means that too much acetylcholine accumulates, and a severe biological effect, i.e. lowering blood pressure and causing convulsions, is produced.

A typical experiment can be carried out with the relatively nontoxic trichlorfon (safety rules should be observed). Dissolve several crystals of trichlorfon in a teaspoon of ethyl alcohol in a glass, then add a teaspoon of acetone and half a teaspoon of an alcoholic solution of sodium hydroxide. In a few minutes, a pink colour appears, which later changes to crimson and orange.

Numerous tests on experimental animals have been performed to find chemicals that neutralize the action of various poisons. For example, a series of substances have been established that restore, or reactivate cholinesterase blocked by an organophosphorus poison. These chemicals are called antidotes and are injected into an intoxicated organism. It should be noted that the intoxicated organism tries to resist the toxin by itself. It employs many biologically active compounds, enzymes and oxygen to accomplish several very complex chemical reactions to transform the toxins into less toxic products that can be further eliminated from the organism. All toxins are eliminated exponentially: the most of the toxin is removed during the first few minutes and hours, while the remainder is eliminated over many days or even weeks. Regrettably, a mild toxin can sometimes be transformed in the organism into a stronger one. An example here is the oxidation of thiophos into the stronger toxin paraoxon. Therefore, natural organisms cannot always cope with all poisons.

In conclusion we would like to remind our readers that all poisons used in the household should be handled with due care. Jars and boxes with poisonous contents must be clearly labelled "Poison" and kept out of the reach of children. Hands and utensils should be carefully washed after handling. If in spite of the precautions symptoms of poisoning appear, a doctor should be called at once. Before the doctor arrives, vomiting should be induced by taking more than five glasses of salt water and by pressing the root of the tongue with two fingers. If the victim is unconscious, vomiting should not be induced. It is recommended that several tablespoons of a suspension of finely crushed activated carbon in water be taken.

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ISBN 5-03-000542-0