**MINISTRY OF HIGHER EDUCATION, SCIENCE AND INNOVATION OF THE REPUBLIC OF UZBEKISTAN**

**NAMANGAN STATE UNIVERSITY**

Department of Inorganic Chemistry

# Training and metodology complex
by subject
# PHYSICAL CHEMISTRY

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|---|---|
| Field of knowledge : | 500000 - Gumanitar subjects |
| Field of study : | 530000 – Natural subjects |
| Direction of study : | 60530100- Chemistry (daytime) |

**Namangan – 2023**

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# 1. Educational materials

## 1-Lecture.

## Introduction to physical chemistry.

Introduction to physical chemistry. Stages of development of thermodynamics, tasks, limits of application and development prospects.

Basic concepts: Thermodynamic systems; insulating systems, closure of the system, homogeneous and heterogeneous systems, non-peripheral systems, state of the system, thermodynamic parameters, state of the function.

Thermodynamic processes: cyclic, isobaric, isochoric, isothermal, adiabatic, isobaric-isothermal, isochoric-isothermal, reversible and irreversible, intensive and extinctive factors.

In the development of physical chemistry, Uzbek scientists.

From the very name of the discipline it follows that it is a border science between chemistry and physics. The main task of physical chemistry is to study the relationship between various physical and chemical phenomena. Since every real phenomenon is complex, the identification of individual aspects in it - physical or chemical - is quite arbitrary. Therefore, it is sometimes difficult to draw a line between the issues studied by physical chemistry and individual branches of physics and chemistry. As a science, physical chemistry began to take shape in the second half of the 19th century, although the name and general definition of the content of physical chemistry was first given by M.V. Lomonosov (1752):

"Physical chemistry is a science that must, on the basis of physical principles and experiments, explain the reason for what happens through chemical operations in complex bodies." Physical chemistry is engaged in a multilateral study of chemical processes and accompanying physical phenomena, using theoretical and experimental methods of both sciences, as well as its own. This makes it possible to predict the course of a chemical process and its result, and, therefore, control it in order to obtain an optimal result.

The field of application of physical chemistry covers all issues of chemical and phase transformations, the influence of physical parameters on chemical processes, and chemical composition on physical properties. Based on a multifaceted study of the various properties of substances and the characteristics of various processes with their participation, physical chemistry solves two most important problems - it establishes the possibility of the process occurring and its speed, and determines the factors that allow it to be controlled.

Metallurgy has long relied on the achievements of physical chemistry, which made it possible to develop the theory of processes occurring in metallurgical units. By justifying the possibility of various processes under given conditions, the scientific approach allows us to identify the conditions for their most complete occurrence, calculate the rates of these processes, take into account the amount of heat absorbed or released during their occurrence and, as a result, optimize the technological regimes for producing high-quality metal.

The production of metals and alloys is a complex and multi-stage process, at each stage of which, including the liquid state, the necessary structure and required properties of the future structural material are formed. Methods of physical chemistry are used to substantiate the chemical composition of an alloy with given properties and determine ways to obtain it, optimize the processes occurring during its crystallization, determine the cooling rate of the ingot, which contributes to the formation of a given phase composition and structure, and in the analysis of many other processes in metallurgy. Thus, physical chemistry is the theoretical basis for the production of metals, alloys and other materials with specified properties.

Currently, physical chemistry is an independent discipline with its own research methods and is the theoretical basis for a number of applied disciplines.

Physical chemistry plays a leading role in the formation of the scientific worldview of a metallurgist, allowing from the most general positions to analyze and predict the course of processes for obtaining and processing metals and alloys.

The purpose of studying physical chemistry is to familiarize students with the basic laws of this scientific discipline and their consequences, some theoretical and experimental methods for studying the parameters of the equilibrium state of systems and the kinetics of ongoing processes, developing the skills and abilities of physical and chemical analysis necessary for an in-depth study of metallurgical processes and technologies in special courses.

**sections** within it, of which the following can be considered the main ones.

**Chemical thermodynamics** deals with the consideration of energy balances, issues of chemical and phase equilibria, as well as elucidation of the direction of processes in systems where there is no equilibrium.

**The structure of matter** includes the study of the structure of atoms, molecules and their interaction in various aggregate states of matter.

**The theory of solutions** aims to explain and predict the properties of solutions and their components based on the properties of the pure substances from which the solution is composed.

**Chemical kinetics** studies the rate and mechanism of chemical reactions, their dependence on conditions.

**Surface phenomena** examines the specific properties of the surface layers of liquids and solids and their influence on the characteristics of the system as a whole.

**Electrochemistry** studies chemical processes in which charged particles - ions - participate. There are no clear boundaries between the listed sections. When studying any phenomenon, one has to use ideas from various sections.

Research in the field of physical chemistry is based on three main methods, each of which has its own range of concepts, laws and experimental methods of research.

### Methods of physical chemistry

**Thermodynamic method .** All concepts and laws obtained with its help are formulated as the result of a description of experience, without penetration into the molecular mechanism of processes. Because of this, this method is formal, which somewhat limits its scope of application. However, this also makes practical calculations easier.

**Statistical method .** The basis is the consideration of bodies as large ensembles of particles, which makes it possible to substantiate the concepts and laws of thermodynamics and expand the range of described phenomena. This method relates the macroscopic properties of substances to the microscopic properties of molecules.

**Molecular kinetic method .** Allows you to describe the properties of substances and the characteristics of processes involving them, including speed, based on the laws of motion and interaction of the particles that make up these substances.

The nature of the phenomena studied by physical chemistry is complex, therefore their theoretical description, despite the steady improvement of theoretical and experimental research methods, cannot be considered exhaustive. A comprehensive understanding of the essence of phenomena follows the path of creating model representations with their gradual complication and detail as new experimental facts accumulate.

Any model is a more or less simplified, obviously idealized image of reality. The most famous simplest abstractions, widely used in physical chemistry, are the models of an ideal gas, an ideal crystal, an ideal solution, etc.

Mathematical expressions that describe phenomena and processes based on the simplest models do not contain difficult-to-define quantities, which simplifies calculations. As a rule, calculations based on them do not provide satisfactory agreement with experimentally measured values of the properties of real systems. However, even such a comparison is useful. It allows one to identify the features of a real object that are not taken into account in the idealized model and introduce additional parameters into more advanced versions of the model theory by the nature and magnitude of deviations of theoretical predictions from experimental data.

## 2-Lecture.

**Basic concepts of thermodynamics.** Basic concepts of thermodynamics. Mathematical apparatus of thermodynamics.

***Basic concepts and definitions***

The basic branch of physical chemistry is chemical thermodynamics. The conceptual apparatus introduced within its framework is also used in other branches of physical chemistry

**A thermodynamic system** is a body or a set of bodies separated from the surrounding space by means of an imaginary or real interface. The mass of a thermodynamic system is constant, and its interaction with the environment occurs only through the exchange of energy in the form of heat and work. In the case of the exchange of a system with a medium by matter, it is called open. We will consider only those thermodynamic systems that exchange energy with the environment, but do not exchange matter (closed), calling them simply "system".

**Energy** is a characteristic of the movement of matter, both from a quantitative and qualitative point of view, i.e. the measure of this movement. Any system has energy, and its forms are diverse, just like the forms of motion of matter.

A system is called **closed** , or **isolated** , if it does not exchange energy with the environment either in the form of heat or in the form of work. If energy exchange occurs only in the form of work, then the system is called **adiabatically closed** . A system is called **homogeneous** if each of its properties has the same value in different parts of the system or changes continuously from point to point.

A system **is heterogeneous** if it consists of several parts separated from each other by physical interfaces, during the transition through which the properties and structure can change abruptly. The homogeneous part of the system, separated from the remaining parts by a physical interface, is called **a phase** . An example of a heterogeneous system is a liquid with steam above it in a closed vessel. This system consists of two parts (phases), and when crossing the boundary between them, for example, the density changes abruptly.

The totality of all physical and chemical properties of a system characterizes its **state** . Changing any properties leads to a change in its state. However, not all properties of the system are independent. Some of them can be expressed through others. For example, the state of an ideal gas can be specified by three of its properties: temperature T, volume V and pressure P. It is enough to select two of them to determine the third from the well-known equation of state of an ideal gas - the Mendeleev-Clapeyron **equation** :

$$\mathbf{PV = nRT}$$

Where: *R is the universal gas constant (R = 8.314 J/(mol · K)), n is the number of moles of gas.*

However, for most real systems, the general equations of state $\mathbf{f(P,V,T) = 0}$ are unknown, or are too complex and not accurate enough, which forces the use of partial relationships of individual properties while others are constant.

Typically, independent variables are those whose values under given conditions are easier to determine and change. Very often these are temperature and pressure. In multicomponent systems, concentrations of components are added to them.

**extensive** properties , i.e. depending on the amount of substance, or the mass of the system (for example, volume), and **intensive** , independent of mass (for example, temperature).

Many intensive properties are easily obtained from extensive ones. Thus, the molar (or molar) volume Vm, which is an intensive property, can be obtained by dividing the total volume of the system (extensive property) by the number of moles of its constituent substances. **Density** - the mass per unit volume of a substance - is also an intensive property. In thermodynamics, they mainly operate on molar properties, because their values in equilibrium are the same for the entire system and for any part of it.

Independent intensive properties of a system are called **parameters states**. Other properties are considered as functions of these parameters.

The value of any property of the system does not depend on the states in which it was previously, i.e. does not depend on the thermodynamic path along which the system came to this state. Any change that occurs in a system and is associated with a change in its properties is called **a process** . Thus, ***the change in property does not depend on the process path, but is determined only by the initial and final states of the system.*** In what follows, we will use the Greek letter Δ (for example, ΔV) to represent a finite change in a property, and the Latin letters d or ∂ (in partial derivatives) to represent an infinitesimal change in this property.

The process in which the system, having left the initial state and having undergone a number of changes, returns to it, is called **circular** . It is obvious that changes in the properties of the system in a circular process are equal to zero. Processes occurring at a constant temperature (T = const) are called **isothermal** , at a constant pressure (P = const) - **isobaric, or isobaric** , at a constant volume of the system (V = const) - **isochoric, or isochoric** .

Processes during which the exchange of energy between the system and the environment occurs only in the form of work are called **adi-abatic** .

The state of the system in which all its parameters at any point have assumed constant values and do not change over time is called **equilibrium** . The process in which a system passes through a series of equilibrium states is called **an equilibrium process** . It can only be an infinitely slow process. The concept of “equilibrium” in this case coincides with the concept of “reversible”. **Reversible** is a thermodynamic process that allows the system to return to its original state without any changes remaining in the environment. Any equilibrium process is reversible and, conversely, during a reversible process the system passes through a series of equilibrium states. After **an irreversible process occurs** , the system cannot independently, i.e. without external influence, return to its original state.

All real, spontaneous processes are irreversible and can only to one degree or another approach the concept of a reversible process.

As noted above, a thermodynamic system can exchange energy with its environment in two forms: work (macrophysical form) and heat (microphysical form).

**Work** is a quantitative measure of this type of transfer of motion (energy), which is carried out by moving finite masses, i.e. the system as a whole or its parts under the influence of any forces.

The most commonly used units of energy and work, particularly in thermodynamics, are the SI joule (J) and the non-systemic unit calorie (1 cal = 4.18 J).

As an example of a process accompanied by work, consider the expansion of a gas located in a cylinder under a piston, which is subject to pressure P (Figure 1).

If a gas under a piston (moving without friction) expands from a state with a volume $V_1$ to a state with a volume $V_2$, it does work A against external pressure. Force F with which the gas acts on the piston

$$F=PS,$$

Where: S is the cross-sectional area of the cylinder. Infinitesimal work δA performed during ascent

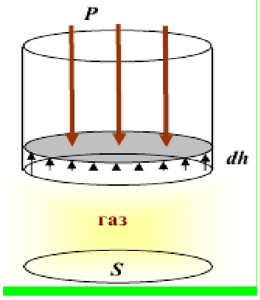


Figure 1 – The work done by gas under pressure during the expansion of the piston to a height dh is

$$\delta A = Fdh = PS\,dh,$$

but because

$$Sdh = dV\,,$$

That

$$\delta A = PdV\,.$$

For a finite change in gas volume, integrating the resulting equation, we obtain:

$$A = \int_{V_1}^{V_2} PdV\,.$$

The considered example can be illustrated graphically for two different paths (a and b) of the system transition from state 1 to state 2 (Figure 2).

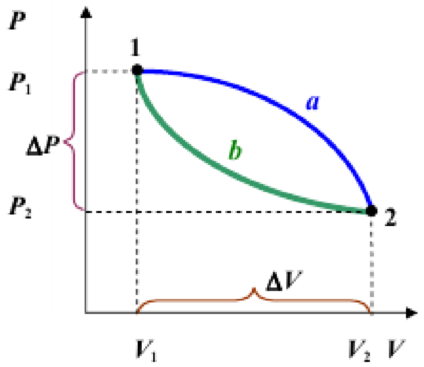


*Figure 2 - Difference in the amount of work done by a gas expanding from volume* $V_1$ *to volume* $V_2$ *in processes occurring along path a and along path b*

Since the work is numerically equal to the area under the curve, which is the graph of the integrand function (P), it is obvious that $A_a \neq A_b$, although the initial and final states of the system in both cases, as well as changes in properties ($\Delta P$ and $\Delta V$), are the same same. ***Therefore, work depends on the path of the process, and therefore is not a property of the system. Work is a characteristic of a process .*** Therefore, in contrast to changes in properties (Δ, d and ∂), the notations A and δA are adopted for work and its infinitesimal amount, respectively.

If a gas expands at a constant external pressure (P = const), then, as shown in Figure 3, the work is calculated by multiplying the pressure by the change in volume as a result of the transition of the system from the initial state to the final state.

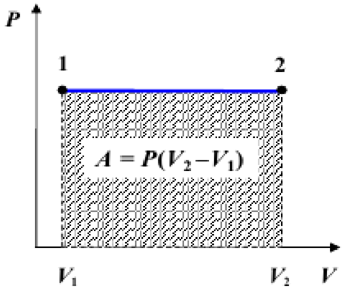


*Figure 3 – Work of gas expansion in an isobaric process*

**Heat** is a quantitative measure of this type of transfer of motion (energy), which is carried out through the chaotic collision of molecules of two contacting bodies.

***Heat, like work, is not a property of the system, but is a characteristic of the process and depends on its path.*** Therefore, we cannot talk about the heat reserve in the system.

The designation of heat is Q or for an infinitely small amount of it - δQ. The system can both absorb and release heat due to the processes occurring in it. Absorption of heat, conventionally considered positive ($Q > 0$), occurs in **endothermic** processes. The release of heat by the system, taken into account with a minus sign ($Q < 0$), is associated with the occurrence of **exothermic** processes (Figure 4). The work done by the system is regarded as positive (A >

0). The work done on the system under the influence of external forces is considered negative (A < 0).

*Figure 4 – Sign rule adopted in thermodynamics for heat and work*

One of the most important quantities in thermodynamics is **the internal energy** (U) of the system, which is its property. It characterizes the energy reserve of the system, including the energy of translational and rotational motion of molecules, the energy of intramolecular vibrational motion of atoms, the energy of electron motion, and internal nuclear energy. The internal energy does not include the kinetic energy of motion of the system as a whole and the potential energy of its position.

Internal energy is a function of the temperature and volume of the system. The dependence of U on temperature is due to the dependence of the kinetic energy of molecular motion on it. The influence of the volume occupied by the system on the value of internal energy is due to the fact that the potential energy of interaction of molecules depends on the distances between them.

The absolute value of the internal energy of the system cannot currently be calculated or measured, since there is no information about the value of intranuclear energy. However, it is possible to calculate changes in internal energy in various processes:

$$\Delta U = U_2 - U_1 .$$

## Mathematical apparatus of thermodynamics.

The mathematical apparatus of thermodynamics is based on the combined equation of the first and second laws of thermodynamics for reversible processes . For systems with constant composition.

**Mathematical apparatus of thermodynamics.**

# 3-Lecture.

# Ideal gas laws .

Ideal gas laws. Poisson's equations.

Equations of state and thermal coefficients. Heat, temperature, pressure, internal energy, work, intensity factors, thermometric scale, absolute temperature, thermometers. Basic equation of kinetic theory of gases (Boltzmann level). Heat capacity of gases. The relationship between heat capacity and degrees of freedom.

## 1. Elements of molecular kinetic theory

Science knows four types of aggregate states of matter: solid, liquid, gas, plasma. The transition of a substance from one state to another is called **a phase transition.** Water, as is known, exists in three states of aggregation: liquid (water), solid (ice), gaseous (steam). This difference between the three states of aggregation is determined by the intermolecular interaction and the degree of proximity of the molecules.

**Gas** is a state of aggregation of a substance in which molecules move chaotically and are located at a great distance from each other. In **solids** , the distances between particles are small, the force of attraction corresponds to the force of repulsion. **Liquid** – state of aggregation, intermediate between solid and gaseous. In a liquid, particles are located close to each other and can move relative to each other; A liquid, like a gas, has no definite shape.

Each of these states can be described by a set of certain parameters: for example, the state of a gas is quite fully described by three parameters: volume, pressure, temperature.

The combination of three parameters, quite easily measured, already from the middle of the 17th century, when barometers and thermometers were created, well describes the state of the gas system. That is why the study of complex polyatomic systems began with gases. R. Boyle stood at the origins of the sciences of chemistry and physics.

## 2. Equation of state of an ideal gas

The study of empirical gas laws ***(R. Boyle, J. Gay-Lussac)*** gradually led to the concept of an ideal gas, since it was found that the pressure of a given mass of any gas at a constant temperature is inversely proportional to the volume occupied by this gas, and the thermal coefficients of pressure and volume c coincide with high accuracy for various gases, amounting, according to modern data, to 1/273 deg $^{-1}$ . Having invented a way to graphically represent the state of a gas in pressure-volume coordinates, ***B. Clapeyron*** obtained a unified gas law connecting all three parameters:

$$\boldsymbol{PV = R\,T}$$

where coefficient ***R*** depends on the type of gas and its mass.

Only forty years later ***D.I. Mendeleev*** gave this equation a simpler form, writing it not for mass, but for a unit amount of a substance, i.e. 1 kmole.

$$\boldsymbol{PV = RT} \qquad (1)$$

where $R$ is the universal gas constant.

Physical meaning of the universal gas constant. $R$ is the work of expansion of 1 kmol of an ideal gas when heated by one degree, if the pressure does not change. In order to understand the physical meaning of $R$ , imagine that the gas is in a vessel at constant pressure, and we increase its temperature by $\Delta T$ , then

$$\boldsymbol{PV_1 = RT_1} \qquad (2)$$

And

$$\boldsymbol{PV_2 = RT_2} \qquad (3)$$

Subtracting equation (2) from (3), we obtain

$$\boldsymbol{P\,(V_2 - V_1) = R\,(T_2 - T_1)}$$

If the right side of the equation is equal to one, i.e. we have heated the gas by one degree, then

$$\boldsymbol{R = \mathrm{P}\Delta\mathrm{V}}$$

Since $P = F / S$ , and $\Delta V$ is equal to the area of the vessel $S$ , multiplied by the height of its piston $\Delta h$ , we have

$$R = \frac{F}{S} S\Delta h = F\Delta h.$$

Obviously, on the right we obtain an expression for the work, and this confirms the physical meaning of the gas constant.

## 3. Kinetic theory of gases

The idea of the molecular structure of matter turned out to be very fruitful in the middle of the 19th century. When A. Avogadro’s hypothesis was accepted that a kilomole of any substance contains the same number of structural units: 6.02 x $10^{26}$ kmol = 6.02 x $10^{23}$ moles, since the molar mass of water is M($H_2O$) = 18 kg/kmol, therefore, in 18 liters of water there are the same number of molecules as in 22.4 $m^3$ of water vapor. This makes it easy to understand that the distance between the molecules of gaseous water (steam) is much greater, on average by one order of magnitude, than in liquid water. It can be assumed that this holds for any substance. Assuming that molecules move chaotically in gases, we can derive the so-called **basic equation of kinetic theory** :

$$P = \frac{1}{3} \times \frac{Na}{V_M} mv^2, \qquad (4)$$

where $N_a$ – 6.02 x 10 $^{26}$ kmol = 6.02 x 10 $^{23}$ mol – Avogadro’s number;

$V_M$ – molecular volume = 22.4 $^{m3}$;

*m* is the mass of one molecule;

*v* is the speed of the molecule.

Let's transform equation (4):

$$PV_M = \frac{1}{3} N_A mv^2 = \frac{2}{3} N_A \frac{mv^2}{2} = \frac{2}{3} N_A E_k,$$

where $E_k$ – energy of one molecule.

It can be seen that on the right is the total kinetic energy of all molecules. On the other hand, comparing with the Mendeleev–Clapeyron equation, we see that this product is equal to *RT*.

This allows us to express the average kinetic energy of a gas molecule:

$$\overline{E} = \frac{3}{2} \times \frac{R}{N_A} T = \frac{3}{2} kT, \qquad (5)$$

where *k = R / Na is* Boltzmann’s constant, equal to 1.38 ґ 10–23 $^{kJ}$ /kmol. Knowing the kinetic energy of a molecule, we can calculate its average speed

$$\begin{aligned} \frac{3}{2}\kappa T &= \frac{mv^2}{2}, \\ v^2 = \frac{3kT}{m} &= \frac{3RT}{M}, \qquad (6) \\ v = \sqrt{\frac{3kT}{m}} &= \sqrt{\frac{3RT}{M}}. \end{aligned}$$

Around 1860, ***D.K. Maxwell*** derived a function describing the velocity distribution of gas molecules. This function has the form of a characteristic curve on the graph with a maximum near the most probable speed of approximately 500 m/s. It is important to note that there are molecules with velocities exceeding this maximum. On the other hand, equation (6) allows us to conclude that the proportion of molecules with high velocities increases when the gas is heated. After almost 60 years, D.K. Maxwell's brilliant guess was confirmed in the experiments of ***O. Stern*** .

## Real gases.

Real gases. Van der Waals equation. Condensation of gases. Critical point. Differences between steam and gases. Reduced pressure, temperature and volume.

As a result of studying the material of the chapter, the student must:

***know*** basic concepts: state of real gases, condensation and critical phenomena;

***be able*** to use the van der Waals equation to consider deviations of the properties of real gases from ideal ones;

***own*** methods for calculating fugacity.

## State of real gases

The properties of real gases differ significantly from the ideal gas. Many of the founders of thermodynamics pointed out these differences.

Thus, back in 1745, M.V. Lomonosov, in his work “Reflections on the Elastic Force of Air,” outlined the conclusions of Boyle’s equation from the point of view of kinetic theory, for the first time in the history of thermodynamics, pointing out the deviations of this equation for real gases.

Great successes in the study of real gases were achieved by D. I. Mendeleev. In his work “Fundamentals of Chemistry” (1871), Mendeleev first established and studied the “critical state” of real gases. Back in 1860, D.I. Mendeleev studied in sufficient detail and experimentally proved the existence of a temperature above which a gas cannot be converted into a liquid at any pressure. D.I. Mendeleev called this temperature “absolute boiling temperature,” and now it is called the critical temperature.

In 1869, T. Andrews, conducting experiments on the isothermal compression of carbon dioxide, came to similar conclusions. Nowadays, there are numerous works devoted to the study of the thermodynamics of real gases.

So, firstly, a real gas does not retain ideality conditions (there are interaction forces between molecules, molecules have a finite volume, etc.); secondly, a real gas (or steam) is an unstable working fluid that can change its state of aggregation during a thermodynamic process.

As is known, the equation of state establishes a functional relationship between pressure $p$ , volume $V$, temperature $T$ and the number of moles $n$ of gas in a state of equilibrium. This relationship can be expressed not only in the form of an equation, but also graphically or in the form of tables, which are often used, especially for practical purposes. The simplest and most famous equation of state is the equation of state of an ideal gas

$$pV = nRT, \qquad (1)$$

where $R$ *is* the universal gas constant.

Real gases are described only approximately by the ideal gas equation of state, and deviations from ideal behavior become noticeable at high pressures and low temperatures, especially when the gas is close to condensation.

Thus, for gases with low liquefaction temperatures (He, H2 , Ne and even N2 , 02 , Ar, CO, CH4 ) at pressures up to 50 atm, deviations do not exceed 5%, and at pressures up to 10 atm - 2% . Easily condensing gases ($C0_2$, $S0_2$, $C1_2$, $CH_3$ C1) already at 1 atm show deviations of up to 2-3%.

One of the clear characteristics of the deviations of real gases from ideal behavior is the molar volume of the gas *V„= V/n.* For an ideal gas it is equal to 22.414 l at 1 atm and 273 K. The values of $V_m$ for some real gases are presented in table. 1.

*Table 1*

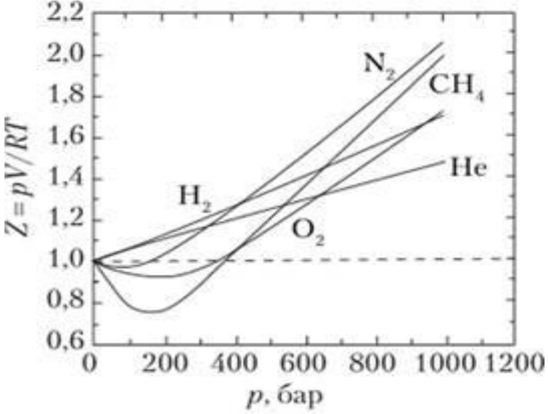
Molar volumes of gases at 1 atm and 273 K

| **Gas** | ***Vm*** **_ , l · mol** $^{-1}$ | **Gas** | ***Vm*** **_ , l · mol** $^{-1}$ |
|---|---|---|---|
| $H_2$ | **22.43** | $CO_2$ | **22.26** |
| **Not** | **22.43** | **N2O**<br>_ – | **22.25** |
| **Ne** | **22.42** | **H2O**<br>_ – | **22.14** |
| $F_2$ | **22.42** | $NH_3$ | **22.08** |
| $N_2$ | **22.40** | $C1_2$ | **22.02** |
| **CO** | **22.40** | **SO2** _ | **21.89** |
| **O2** _ | **22.39** | $C_4H$<br>\|0 | **21.50** |
| $CH_4$ | **22.36** | $O_3$ | **21.60** |

The most convenient measure of nonideality is the compressibility factor $Z = pV_m/RT$, since for an ideal gas $Z = 1$ under any conditions.

In Fig. Figure 1 shows the compressibility factors for some real gases as a function of pressure at 298 K (for comparison, the behavior of an ideal gas is shown by the dotted line). At high pressures for all gases Z > 1, i.e. they are more difficult to compress than an ideal gas because intermolecular repulsive forces dominate in this region. It is obvious from the figure that at lower pressures for some gases $Z < 1$, which is explained by the predominance of intermolecular attraction. When $p \to 0$, the effect of intermolecular attraction disappears, because the distance between molecules tends to infinity and for all gases Z -> 1, i.e. under these conditions, all gases behave almost ideally.

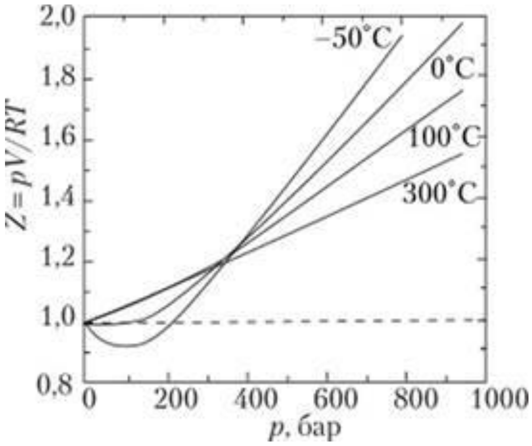
In Fig. Table 2 shows the compressibility factors for nitrogen at different temperatures. As the temperature decreases, the effect of intermolecular attraction increases (which is manifested in the formation of a minimum in the curves in the pressure region of about 100 bar). A minimum in the curves is found for all gases if the temperature is low enough.



***Rice. 1. Dependence of the compressibility factor of some gases on pressure at 298 K.***

For hydrogen and helium, which have very low boiling points, this minimum is observed only at temperatures well below 0°C.

From the data presented, it is obvious that at low pressures real gases can be more compressible (Z< 1) than an ideal gas, and at high pressures they can be less compressible (Z > 1). It is obvious that the main reasons for deviations in the properties of real gases from the properties of an ideal gas are the mutual attraction of molecules and the presence of their own volume. Intermolecular attraction in real gases is most clearly manifested in their ability to condense— transition into the liquid state.



***Rice. 2.*** *Dependence of the N $_2$* ***compressibility factor on pressure at different temperatures.***

At point *E,* the entire sample is a liquid, and further reduction of the volume of the sample requires significant pressure, since liquids are very difficult to compress compared to gases, which is manifested by a sharp rise in the curve to the left of point *E.*

### Critical phenomena

The isotherm at temperature *Tc* plays a special role in the theory of the state of matter . The isotherm corresponding to a temperature below $T_c$ > behaves as already described: at a certain pressure, the gas condenses into a liquid, which can be distinguished by the presence of an interface. If compression is carried out at $Tc$ , *then the surface separating the two phases does not appear, and the condensation point and the point of complete transition to liquid merge into one critical point* of the gas. At temperatures above $Tc$ *, gas* cannot be converted into liquid by any compression. The temperature, pressure and molar volume at the critical point are called critical temperature $Tc$ , critical pressure $pc$ *and* critical molar volume $Vc$ *of the* substance. Collectively, the parameters $p_c$, $V_c$, and $T\,c$ *are* called the critical constants of a given gas (Table 2).

At $T>T_{C,}$ the sample is a phase that completely occupies the volume of the container containing it, i.e. by definition is a gas. However, the density of this phase can be much greater than is typical for gases, so the name "supercritical fluid" is usually preferred . When points $T_c$ and *P c coincide, liquid and gas are indistinguishable* ·

***table 2***

***Critical constants and Boyle temperatures***

| **Gas** | ***To* K** | **$R_s$, bar** | **$V_c$, ml• mol$^{-1}$** | **Zc** | **$T_B$ K** | **$t_B/t_s$** |
|---|---|---|---|---|---|---|
| Not | 5.21 | 2.27 | 57.76 | 0.305 | 22.64 | 4.35 |
| Ne | 44.44 | 26.9 | 41.74 | 0.307 | 122.1 | 2.75 |
| Ag | 150.72 | 48.0 | 75.25 | 0.292 | 411.5 | 2.73 |
| Kg | 209.4 | 54.3 | 92.24 | 0.291 | 575.0 | 2.75 |
| Heh | 289.75 | 58.0 | 118.8 | 0.290 | 768.0 | 2.65 |
| $H_2$ | 33.3 | 13.0 | 65.0 | 0.306 | 110.0 | 3.30 |
| N 2 | 126.1 | 34.0 | 89.5 | 0.292 | 327.2 | 2.60 |
| $O_2$ | 154.4 | 50.5 | 73.4 | 0.292 | 405.9 | 2.63 |
| CO2 | 304.2 | 73.8 | 94.0 | 0.274 | 714.8 | 2.35 |
| $CH_4$ | 190.7 | 46.0 | 99.0 | 0.287 | 510.0 | 2.67 |
| $C_2$ H, | 282.4 | 50.4 | 129.0 | 0.277 | 624 | 2.21 |

At the critical point, the isothermal compressibility coefficient

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

equals infinity because

$$\left(\frac{\partial p}{\partial V}\right)_{T=T_c} = 0.$$

Therefore, near the critical point, the compressibility of the substance is so great that the acceleration of gravity leads to significant differences in density in the upper and lower parts of the vessel, reaching 10% in a column of substance only a few centimeters high. This makes it difficult to determine densities (specific volumes) and, accordingly, *p - V isotherms* near the critical point. At the same time, the critical temperature can be defined very precisely as the temperature at which the surface separating the gaseous and liquid phases disappears when heated and reappears when cooled. Knowing the critical temperature, you can determine the critical density (and, accordingly, the critical molar volume) using the empirical rule of rectilinear diameter (Calete Mathias rule), according to which the average density of liquid and saturated vapor is a linear function of temperature:

$$\bar{\rho} = \frac{\rho_ж + \rho_п}{2} = A + BT, \quad (2)$$

where *A* and *B* are constant quantities for a given substance.

By extrapolating the straight line of average density to the critical temperature, the critical density can be determined. The high compressibility of matter near the critical point leads to an increase in spontaneous density fluctuations, which are accompanied by anomalous light scattering. This phenomenon is called critical opalescence.

## Van der Waals equation

The equation of state and transport phenomena in real gases and liquids are closely related to the forces acting between molecules. The molecular statistical theory, which relates general properties to intermolecular forces, is now well developed for rarefied gases and, to a lesser extent, for dense gases and liquids. At the same time, measuring macroscopic properties makes it possible, in principle, to determine the law according to which forces act between molecules. Moreover, if the type of interaction is determined, then it becomes possible to obtain an equation of state or transfer coefficients for real gases.

For ideal gases, the equation of state $pV = RT$ or $pV/RT = 1.$

This relationship is absolutely accurate in the case when the gas is very rarefied or its temperature is relatively high. However, already at atmospheric pressure and temperature, deviations from this law for real gas become noticeable.

Many attempts have been made to take into account deviations of the properties of real gases from the properties of an ideal gas by introducing various corrections into the equation of state of an ideal gas. Due to its simplicity and physical clarity, the most widely used equation is the van der Waals equation (1873).

Van der Waals made the first attempt to describe these deviations by obtaining equations of state for a real gas. Indeed, if the equation of state of an ideal gas $pV = RT$ is applied to real gases, then, firstly, by the volume that can change to a bullet, it is necessary to understand the volume of intermolecular space, since only this volume, like the volume of an ideal gas, can decrease to zero with an unlimited increase in pressure.

The first amendment in the equation of state of an ideal gas considers the intrinsic volume occupied by the molecules of a real gas. In Dupre's equation (1864)

$$p(V - nb) = nRT \qquad (3)$$

the constant $b$ takes into account the intrinsic molar volume of the molecules.

As the temperature decreases, intermolecular interaction in real gases leads to condensation (formation of liquid). Intermolecular attraction is equivalent to the existence of some internal pressure in a gas (sometimes called static pressure). Initially, the quantity was taken into account in general form in the Girn equation (1865)

$$(p + \pi)(V - nb) = nRT. \qquad (4)$$

J. D. Van der Waals in 1873 gave a functional interpretation of internal pressure. According to the van der Waals model, the attractive forces between molecules (van der Waals forces) are inversely proportional to the sixth power of the distance between them or the second power of the volume occupied by the gas. It is also believed that the forces of attraction are added to external pressure. Taking these considerations into account, the equation of state of an ideal gas is transformed into the van der Waals equation:

$$(V - nb)\left(p + \frac{n^2a^2}{V^2}\right) = nRT \qquad (5)$$

or for 1 mole

$$(V_m - b)\left(p + \frac{a^2}{V_m^2}\right) = RT. \qquad (6)$$

The values of the van der Waals constants *a and b,* which depend on the nature of the gas, but do not depend on temperature, are given in table. 3.

Equation (6) can be rewritten to explicitly express the pressure

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \qquad (7)$$

or volume

$$V_m^3 - \left(b + \frac{RT}{p}\right)V_m^2 + \left(\frac{a}{p}\right)V_m - \frac{ab}{p} = 0. \qquad (8)$$

***Table - 3***

***Van der Waals constants for various gases***

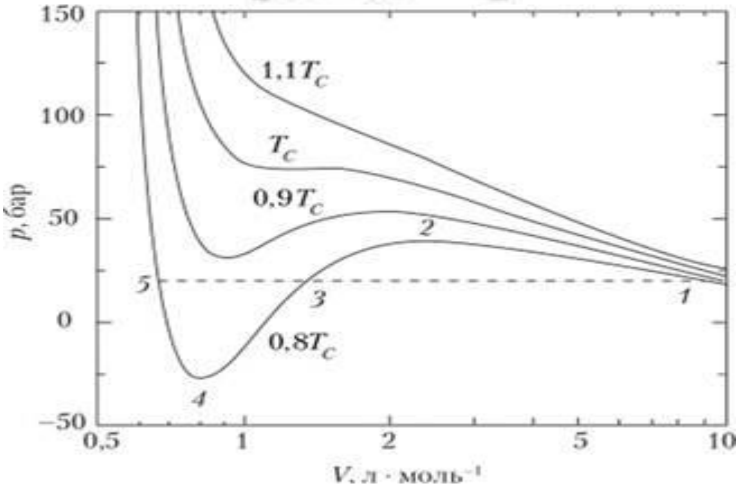
| Gas | *A*, $l^{2} \bullet bar \bullet mol^{-2}$ | *b*, $cm^{3} \bullet mol^{-1}$ | Gas | *A*, $l^{2} \bullet bar \bullet mol^{-2}$ | *b*, $cm^{3} \bullet mol^{-1}$ |
|---|---|---|---|---|---|
| Not | 0.03457 | 23.70 | N0 | 1.358 | 27.89 |
| Ne | 0.2135 | 17.09 | $no_2$ | 5,354 | 44.24 |
| Ag | 1,363 | 32.19 | $n_2o$ | 5.536 | 30.49 |
| Kg | 2,349 | 39.78 | $H_2S$ | 4,490 | 42.87 |
| Heh | 4,250 | 51.05 | $NH_3$ | 4.225 | 37.07 |
| $H_2$ | 0.2476 | 26.61 | $so_2$ | 6,803 | 56.36 |
| $N_2$ | 1,408 | 39.13 | joint venture, | 2,283 | 42.78 |
| O2 _ | 1.378 | 31.83 | $C_2Hi$ | 4,530 | 5,714 |
| $C1_2$ | 6,579 | 56.22 | C2He _ _ _ | 5,562 | 63.80 |
| With O | 1.505 | 39.85 | $C_3H_8$ | 8,779 | 84.45 |
| $CO_2$ | 3,640 | 42.67 | $C_6H_6$ | 18.24 | 115.4 |

Equation (8) contains volume to the third power and therefore has three real roots, or one real and two imaginary.

At high temperatures, equation (8) has one real root, and as the temperature increases, the curves calculated using the van der Waals equation approach hyperbolas corresponding to the ideal gas equation of state.

In Fig. Figure 4 shows isotherms calculated using the van der Waals equation for carbon dioxide (the values of the constants *a* and *b* are taken from Table 3). The figure shows that at temperatures below critical (31.04°C), instead of horizontal straight lines corresponding to the equilibrium of liquid and vapor, wavy curves *1 -2 -3 -4 -5* are obtained with three real roots, of which only two, at points *1* and 5 are physically feasible. The third root (point *3)* is not physically real, since it is located on the section of the curve *2 -3 -4,* which contradicts the condition of stability of the thermodynamic system -

$$\left[\left(\frac{\partial p}{\partial V}\right)_T < 0\right].$$



***Rice. 4. Van der Waals isotherms for CO*** $_2$

The states in sections *1 - 2* and *5 - 4* , which correspond to supercooled steam and superheated liquid, respectively, are unstable (metastable) and can only be partially realized under special conditions. So, by carefully compressing the steam above point *1* (see Fig. 4), you can rise along the curve *1 -2.* This requires the absence of condensation centers, and primarily dust, in the pair. In this case, the steam turns out to be supersaturated, i.e. supercooled state. Conversely, the formation of liquid droplets in such vapor is facilitated, for example, by ions entering it. This property of supersaturated vapor is used in the famous Wilson chamber (1912), used to detect charged particles. A moving charged particle, entering a chamber containing supersaturated vapor and colliding with molecules, forms ions along its path, creating a foggy trail - a track that is recorded photographically.

According to Maxwell's rule *(the Maxwell construction* ), which has a theoretical justification, in order for the calculated curve to correspond to the experimental equilibrium isotherm, it is necessary to draw a horizontal line 1-5 instead of the curve *1-2-3-4-5 so that the areas 1-2 -3 -1* and *3 -4 -5 -3* were equal. Then the ordinate of the straight line *1-5* will be equal to the saturated vapor pressure, and the abscissas of points *1* and 5 will be equal to the molar volumes of vapor and liquid at a given temperature.

As the temperature rises, all three roots come closer together, and at the critical temperature $T_c$ become equal. At the critical point, the van der Waals isotherm has an inflection point

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0$$

with horizontal tangent

$$\left(\frac{\partial p}{\partial V}\right)_T = 0,$$

Those.

$$\left(\frac{\partial p}{\partial V}\right)_{T_C} = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} = 0; \qquad (9)$$

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_{T_C} = \frac{2RT}{(V-b)^3} - \frac{6a}{V^4} = 0; \qquad (10)$$

The joint solution of these equations gives

$$V_C = 3b; \qquad \text{(eleven)}$$

$$p_C = \frac{a}{27b^2}; \qquad (12)$$

$$T_C = \frac{8a}{27Rb}, \qquad (13)$$

which makes it possible to determine the constants of the van der Waals equation from the critical parameters of the gas. Accordingly, according to the van der Waals equation, the critical compressibility factor $Z_c$ for all gases should be equal to

$$Z_c = \frac{p_C V_C}{RT_C} = \frac{3}{8} = 0{,}375. \qquad (14)$$

From the table 2 it is obvious that although the value of $Z_c$ for real gases is approximately constant (0.27-0.30 for non-polar molecules), it is still noticeably less than that resulting from the van der Waals equation. For polar molecules, an even greater discrepancy is observed.

The fundamental significance of the van der Waals equation is determined by the following circumstances:

1) the equation was obtained from model concepts of the properties of real gases and liquids, and was not the result of an empirical selection of the function /(/?, *V T)* describing the properties of real gases;

2) the equation has long been considered as a certain general form of the equation of state of real gases, on the basis of which many other equations of state were constructed (see below);

3) using the van der Waals equation, for the first time it was possible to describe the phenomenon of the transition of gas into liquid and analyze critical phenomena. In this respect, the van der Waals equation has an advantage even over more accurate equations in virial form - see expressions (1), (2).

The reason for the insufficient accuracy of the Van der Waals equation was the association of molecules in the gas phase, which cannot be described, taking into account the dependence of the parameters *a* and *b* on volume and temperature, without using additional constants. After 1873, Van der Waals himself proposed six more versions of his equation, the last of which dates back to 1911 and contains five empirical constants. Clausius proposed two modifications of equation (5), and both of them are associated with a complication of the form of the constant *b*. Boltzmann obtained three equations of this type by changing the expressions for the constant *a*. In total, more than a hundred similar equations are known, differing in the number of empirical constants, degree of accuracy and scope of applicability. It turned out that none of the equations of state containing less than five individual constants turned out to be accurate enough to describe real gases in a wide range of *p, V ', T,* and all these equations turned out to be unsuitable in the region of gas condensation. Of simple equations with two individual parameters, the Diterici and Berthelot equations give good results.

### *Virial equation of state*

The behavior of a real gas can be described with high accuracy using a virial equation (or an equation with virial coefficients). The idea is to abandon the minimum number of parameters and use infinite series - expansions in powers of reciprocal volume

$$p = \frac{RT}{V}\left(1 + \frac{B_2}{V} + \frac{B_3}{V^2} + \ldots\right) \qquad (15)$$

or pressure

$$p = \frac{RT}{V}\left(1 + B'_2 p + B'_3 p^2 + \ldots\right), \qquad (16)$$

where ***$B_g B'$ are the ic*** virial coefficients, which depend on temperature.

The equation of state in the form of an infinite series (15) was proposed by P. A. Thiessen in 1885. However, the virial equation received its main development in 1901 in the work of X. Kamerlingh Onnes, who considered several variants of this equation and proposed calling its coefficients virial .

If we approach the virial equation only as an empirical equation of state, then it has a number of disadvantages. For example, as experimental data show, the convergence of the series is not very good, especially in the high-density region. In addition, at high densities, to satisfactorily describe the experimental data, it is necessary to use a large number of terms of the series, and for this it is necessary to experimentally determine a large number of virial coefficients. Moreover, often the same set of experimental data can be more accurately described by other empirical equations with fewer parameters. However, the exceptional importance of the virial equation of state lies in the fact that it is the only known equation of state that has a strict theoretical basis. Moreover, each virial coefficient can be expressed through the forces of intermolecular interaction. Thus, the second virial coefficient reflects pair interactions, the third - triple ones, etc. Thus, the virial equation of state makes it possible to explain the properties of a gas from the position of intermolecular interactions.

In Fig. Figure 5 shows the dependence of the second virial coefficient on temperature for some gases. At low temperatures **$B_2$** $< 0$, with increasing temperature its value passes through zero, then becomes positive, reaches a maximum and then decreases very slowly. At high temperatures, **$B_2$** and all subsequent virial coefficients tend to zero. The temperature at which **$B_2$** $= 0$ is called ***the Boyle temperature $T_{in}$*** .

The meaning of this name is explained as follows. Let's consider the value ***dZ/dp,*** i.e. slope of the curve of compressibility factor ***Z*** versus ***p.*** For an ideal gas ***dZ/dp*** = 0 (since Z = 1 at all pressures), but for a real gas ***p*** -> 0.

$$\frac{dZ}{dp} = B_2' + 2pB_3' + \ldots \to B_2'. \qquad (17)$$

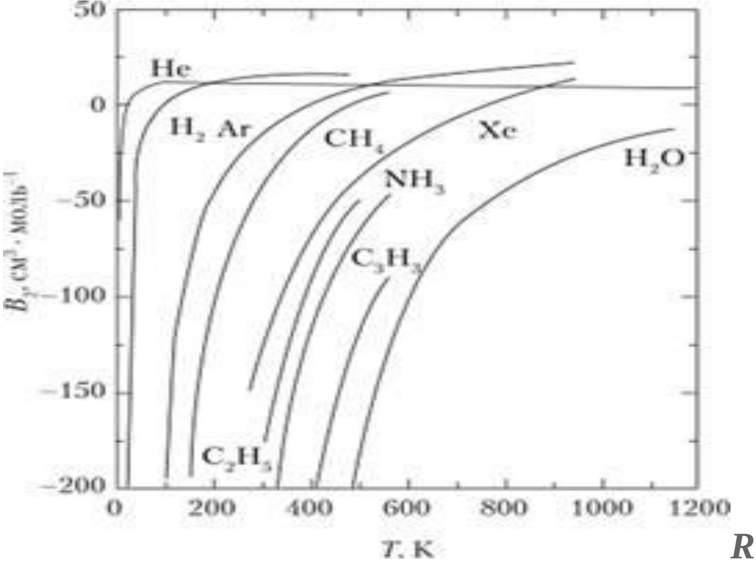
However, since $B_2$ is not necessarily zero, the slope of the curve ***Z*** with respect to ***p*** is not zero, as for an ideal gas. Since some properties of gases depend on derivatives, the behavior of real gases may differ from the ideal even at low pressures

Boyle temperatures for some gases are given in table. 2.

The van der Waals equation constants ***a*** and ***b*** can be approximately related to the coefficients of the virial equation of state. To do this, the van der Waals equation needs to be expanded into a series (see problem 1 for an independent solution to Chapter 10, p. 328). According to the van der Waals equation, the second virial coefficient is

$$B_2 = b - \frac{a}{RT}, \qquad (18)$$

and the remaining coefficients do not depend on temperature: ***B„ = b"~K*** Thus, the van der Waals equation qualitatively correctly conveys the temperature dependence of the second virial coefficient at low temperatures (at low temperatures $B_2 < 0$, increases with increasing temperature, passes through zero, then becomes positive).The van der Waals equation is not suitable for determining the third and subsequent virial coefficients.



***Rice. 5. Dependence of the second virial coefficient of some gases on temperature***

From equation (18) we can obtain an expression for the Boyle temperature according to the van der Waals equation:

$$T_B = \frac{a}{Rb}. \qquad (19)$$

From equations (13) and (19) we obtain the relationship between the Boyle temperature and the critical temperature:

$$\frac{T_B}{T_c} = \frac{27}{8} = 3{,}375. \qquad (20)$$

This value can be compared with real data for various gases (see Table 2).

Sometimes the equations of state of real gases are written through the so-called reduced variables, which are determined through the parameters of the critical state of gases:

$$p_r = p/p_{кр},\ V_r = V/V_{кр},\ T_r = T/T_{кр},$$

where the critical parameters are defined as the coordinates of the inflection point on the isotherm of a real gas:

$$\begin{cases} \left(\frac{\partial p}{\partial V}\right)_{T=T_{кр}} = 0, \\ \left(\frac{\partial^2 p}{\partial V^2}\right)_{T=T_{кр}} = 0. \end{cases} \qquad (21)$$

where *g* and g $_{cr}$ are points corresponding to the state of real gas (g) and real gas in a critical state (g $_{cr}$ ).

### Law of Corresponding States

Since critical constants are characteristic properties of gases, they can be used to create the corresponding relative scale by introducing dimensionless reduced variables: reduced pressure $p_{q}$, reduced volume $V_{g}$ *and* reduced temperature *Tr*

$$p_r = \frac{p}{p_c},\ V_r = \frac{V_m}{V_c},\ T_r = \frac{T}{T_c}. \qquad (22)$$

*corresponding* . According to the law of corresponding states, if for the substances under consideration the values of two reduced variables are the same, the values of the third reduced variable must also be the same. Thus, the equations of state of various substances written in the given variables must coincide. This statement is equivalent to the postulate about the existence of a general universal reduced equation of state

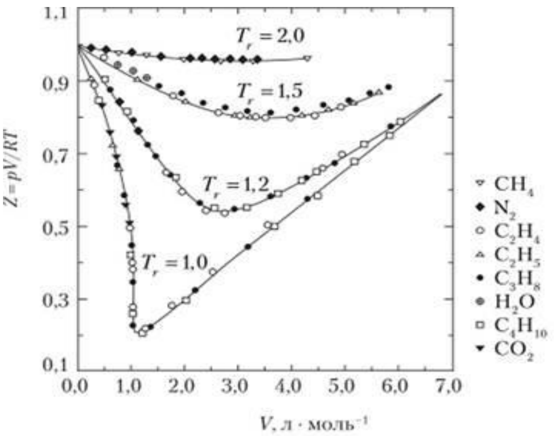
$$F(p_r, V_r, T_r) = 0. \qquad (23)$$

Since this given equation does not explicitly contain individual constants, it should be applicable to any substance. The law of corresponding states is a general statement not related to a specific type of equation of state. In practice, the law of corresponding states is approximately satisfied for substances of the same type, which allows, for example, the use of generalized compressibility diagrams for real gases (Fig. 6).

The van der Waals equation is also consistent with the law of corresponding states. Substituting the constants *a* , *b* and *R into the original equation (5)* , expressed through the critical parameters of equations (11) - (13), and passing to the reduced variables, we obtain the van der Waals equation in the reduced form

$$\left(p_r + \frac{3}{V_r^2}\right)(3V_r - 1) = 8T_r. \qquad (24)$$

It can be shown that any equation of state containing three parameters can be represented in the reduced form. The absence of a universal equation $F(p_r, V_r, T_r) = 0$ does not indicate the incorrectness of the law on corresponding states, but rather the insufficiency of two individual constants and ***R*** in the equation of state.



***Rice. 6. Dependence of the compressibility factor of some gases on reduced pressure at different reduced temperatures***

At present, it is clear why in the equations of state of real gases two individual parameters are generally missing, but in a first approximation this is sufficient. The cause of all deviations from the equation of state of an ideal gas is intermolecular interactions in gases. The dependence of the potential of intermolecular interaction ***on*** the distance between particles ***r*** is quite accurately described by equations containing at least four parameters - ***n*** , ***m, A*** and ***B:***

$$u(r) = \frac{A}{r^n} - \frac{B}{r^m}. \qquad (25)$$

Statistical calculations show that the presence of individual constants in the equation of intermolecular interaction always leads to the appearance of individual constants in the equation of state of gases. Therefore, in the range of values ***p*** , ***V*** and T, for which in real gases the contribution of intermolecular interactions is quite large, individual constants appear in the equations of state, depending on the parameters in the equation of intermolecular interaction. At the same time, for spheroidal molecules the equation cn = 12m = 6 gives fairly good results. Therefore, it is often sufficient to use two individual constants in approximate equations of state.

## 4-Lecture.

## Subject: First law of thermodynamics.

**First law of thermodynamics. Internal energy of the system. Drawing up the energy balance of the system. Thermal and caloric coefficients.**

First law of thermodynamics.

The first law (first law) of thermodynamics is, in fact, the law of conservation of energy. He states that the energy of an isolated system is constant. In a non-isolated system, energy can change due to: a) doing work on the environment; b) heat exchange with the environment.

To describe these changes, a state function is introduced - internal energy U *and* two transition functions - heat $Q$ and work $A$. Mathematical formulation of the first law:

$$dU = \delta Q - \delta A \text{ (differential form) } (2.1)$$

$$\Delta U = Q - A \text{ (integral form) } (2.2)$$

The letter $\delta$ in equation (2.1) reflects the fact that $Q$ and $A$ are transition functions and their infinitesimal change is not a total differential.

In equations (2.1) and (2.2), the signs of heat and work are chosen as follows. **Heat** is considered positive if it ***is transferred to the system* .** On the contrary, work is considered positive if it is performed ***by the system*** over the environment.

There are different types of work: mechanical, electrical, magnetic, surface, etc. Infinitesimal work of any kind can be represented as the product of a generalized force and an increment of a generalized coordinate, for example:

$\delta A_{fur} = p \cdot dV$ ;$\delta A_{el} = \varphi \cdot de$ ;$\delta A_{pov} = \sigma \cdot dW$ (2.3)

( $\varphi$- electric potential, $e$ - charge, $\sigma$- surface tension, W - surface area). Taking into account (2.3), the differential expression of the first law can be represented as:

$dU = \delta Q - p \cdot dV \pm \delta A_{nemech}$ (2.4)

In the further presentation, we will, by default, neglect non-mechanical types of work.

The mechanical work produced during expansion against external pressure $p_{ex}$ is calculated by the formula:

$$A = \int_{V_1}^{V_2} p_{ex} dV \quad (2.5)$$

If the expansion process is reversible, then the external pressure differs from the pressure of the system (for example, gas) by an infinitesimal value: $p_{ex} = p_{in} - dp$ and the pressure of the system itself, which is determined from the equation of state, can be substituted into formula (2.5).

The easiest way is to calculate the work done by an ideal gas, for which the equation of state $p = nRT / V$ *is known* (Table 1).

Table 1. Work of an ideal gas in some expansion processes $V_1 \rightarrow V2$ : _

| Process | $A$ |
|---|---|
| Expansion into vacuum | 0 |
| Expansion against constant external pressure $p$ | $p(V_2 - V_1)$ |
| Isothermal reversible expansion | $nRT \ln(V_2 / V_1)$ |
| Adiabatic reversible expansion | $nC_V(T_1 - T_2)$ |

In a reversible process, the work done is maximum.

**Heat** can be transferred into the system when heated. To calculate heat, use the concept of ***heat capacity* ,** which is defined as follows:

$$C = \frac{\delta Q}{dT} \quad (2.6)$$

If heating occurs at a constant volume or pressure, then the heat capacity is indicated by the corresponding subscript:

$C_V = \left(\frac{\delta Q}{dT}\right)_V$; $C_p = \left(\frac{\delta Q}{dT}\right)_P$. (2.7)

From definition (2.6) it follows that the final heat received by the system during heating can be calculated as an integral:

$Q = \int_{T_1}^{T_2} C dT$ (2.8)

**Heat capacity** - experimentally measured extensive quantity. The thermodynamic tables show the values of heat capacity at 298 K and coefficients describing its dependence on temperature. For some substances, the heat capacity can also be estimated theoretically using statistical thermodynamics methods (Chapter 12). Thus, at room temperature for monatomic ideal gases the molar heat capacity is $C_V = 3/2\,R$, for diatomic gases $C_V = 5/2\,R$.

Heat capacity is determined through the heat transferred to the system, but it can also be associated with a change in internal energy. Thus, at a constant volume, no mechanical work is performed and heat is equal to the change in internal energy: $\delta Q_V = dU$, so

$C_V = \left(\frac{\partial U}{\partial T}\right)_V$. (2.9)

At constant pressure, heat is equal to the change in another state function called enthalpy:

$\delta Q_p = dU + pdV = d(U + pV) = dH$, (2.10)

where $H = U + pV$ is *the enthalpy* of the system. From (2.10) it follows that the heat capacity $C_p$ determines the dependence of enthalpy on temperature.

$C_p = \left(\frac{\partial H}{\partial T}\right)_P$. (2.11)

From the relationship between internal energy and enthalpy it follows that for a mole of ideal gas

$C_p - C_V = R$. (2.12)

Internal energy can be considered as a function of temperature and volume:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \qquad (2.13)$$

For an ideal gas, it was experimentally discovered that the internal energy does not depend on the volume, $\left(\frac{\partial U}{\partial V}\right)_T = 0$ from which the caloric equation of state can be obtained:

$dU = C_V dT$,

$U = \int C_V dT + const$ (2.14)

In isothermal processes involving an ideal gas, the internal energy does not change, and the expansion work occurs only due to absorbed heat.

A completely different process is also possible. If during the process there is no heat exchange with the environment ($\delta Q = 0$), then such a process is called *adiabatic* . In an adiabatic process, work can only be done due to the loss of internal energy. Work of reversible adiabatic expansion of an ideal gas:

$A = -\Delta U = nC_V(T_1 - T_2)$ (2.15)

($n$ is the number of moles, $C_V$ is the molar heat capacity). This work can also be expressed in terms of the initial and final pressure and volume:

$$A = \frac{p_1V_1 - p_2V_2}{\gamma - 1} \quad (2.16)$$

where $\gamma = C_p / C_V$ .

In the reversible adiabatic expansion of an ideal gas, pressure and volume are related by the relation ( *adiabatic equation* ):

$$pV^{\gamma} = \text{const.} \quad (2.17)$$

Two points are important in equation (2.17): firstly, this is a process equation, not a state equation; secondly, it is valid *only for a reversible* adiabatic process. The same equation can be written in equivalent form:

$$TV^{\gamma-1} = \text{const,} \quad (2.18)$$

$$T^{\gamma} p^{1-\gamma} = \text{const.} \quad (2.19)$$

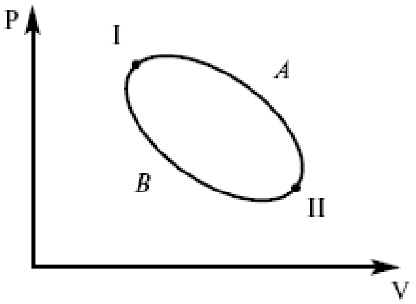
## First law of thermodynamics. Caloric coefficients. Relationship between functions $C_P$ and $C_v$

**Formulations of the first law of thermodynamics.**

1. The total energy supply in an isolated system remains constant.
2. Different forms of energy transform into each other in strictly equivalent quantities.
3. It is impossible to build a perpetual motion machine of the first kind, which would provide mechanical energy, without spending a certain amount of molecular energy on it.
4. The amount of heat supplied to the system is spent on changing $U_{\text{in}}$ and the work performed.
5. $U_{ext}$ *is* a state function, i.e. it does not depend on the process path, but depends on the initial and final state of the system.

Proof:

Let the TDS be considered under two parameters of pressure and volume; there are two states of the system, I and II. It is necessary to transfer the system from state I to state II either along path A or along path B (Fig. 3).



*Rice. 3*

Let us assume that along the path *A* the change in energy will be $\Delta U_A$ , and along the path *B* - $\Delta U_B$ . Internal energy depends on the path of the process

$\Delta U_A = \Delta U_B$ ,

$\Delta U_A - \Delta U_B$ *? 0.*

According to paragraph 1 of the formulation of the first law of thermodynamics, the total energy supply in an isolated system remains constant

$\Delta U_A = \Delta U_B$ ,

$U_{\text{ext}}$ – the state function does not depend on the process path, but depends on the state of system I or II. $U_{\text{ext}}$ – state function, is a total differential

$Q = \Delta U + A$ –

integral form of the equation of the first law of thermodynamics.

$\Delta Q = dU$ + ? *A*–

for an infinitesimal process, ? *A is* the sum of all elementary works.

Caloric coefficients

$$U = l(V_1 T),$$

$$\delta Q = du + pdv,$$

$$\left(\frac{du}{dv}\right)_T + p = l.$$

Heat of isothermal expansion:

$$l = \left(\frac{\delta Q}{\partial V}\right)_T,$$

$$dU = \left(\frac{\partial U}{\partial v}\right)_T dv + \left(\frac{\partial U}{\partial T}\right)_v dT,$$

$$dQ = \left(\frac{\partial U}{\partial v}\right)_T dv + \left(\frac{\partial U}{\partial T}\right)_v dT + pdv,$$

$$\left(\frac{dU}{dT}\right)_v = Cv.$$

Equation of the first law of thermodynamics in caloric coefficients
d $Q = ldv + C_v dT$,
where $l$ is the isothermal expansion coefficient;
$C_v$ *is* the heat capacity at constant volume.

## 5-Lecture.

## Topic: Thermochemistry. Enthalpy.

Thermochemistry. Enthalpy. Hess's law and its conclusions.

**Thermochemistry**

Thermochemistry studies the thermal effects of chemical reactions. In many cases, these reactions occur at constant volume or constant pressure. From the first law of thermodynamics it follows that under these conditions heat is a function of state. At constant volume, heat is equal to the change in internal energy:

$$\delta Q_V = dU \text{ , } Q_V = \Delta U \text{ , } (3.1)$$

and at constant pressure - the change in enthalpy:

$$\delta Q_p = dH \text{ , } Q_p = \Delta H \text{ . } (3.2)$$

These equalities, when applied to chemical reactions, constitute the essence of *Hess's law* :

The thermal effect of a chemical reaction occurring at constant pressure or constant volume does not depend on the reaction path, but is determined only by the state of the reactants and reaction products.

In other words, the thermal effect of a chemical reaction is equal to the change in the state function.

In thermochemistry, unlike other applications of thermodynamics, heat is considered positive if it is released into the environment, i.e. If $\Delta H < 0$ or $\Delta U < 0$. The thermal effect of a chemical reaction is understood as the value $\Delta H$ (which is simply called the "enthalpy of reaction") or $\Delta U$ reactions.

If the reaction occurs in solution or in the solid phase, where the change in volume is negligible, then

$$\Delta H = \Delta U + \Delta(pV) \approx \Delta U. \text{ \_ } (3.3)$$

If ideal gases participate in the reaction, then at constant temperature

$$\Delta H = \Delta U + \Delta(pV) = \Delta U + \Delta n \cdot RT, \quad (3.4)$$

where $\Delta n$ is the change in the number of moles of gases in the reaction.

In order to facilitate comparison of the enthalpies of different reactions, the concept of a “standard state” is used. *The standard state is the state of a pure substance at a pressure of 1 bar (= 10 $^5$ Pa) and a given temperature* . For gases, this is a hypothetical state at a pressure of 1 bar, having the properties of an infinitely rarefied gas. The enthalpy of a reaction between substances in standard states at temperature $T$ is denoted $\Delta_r H_T^0$ ( $r$ stands for "reaction"). Thermochemical equations indicate not only the formulas of substances, but also their aggregate states or crystalline modifications.

Important consequences follow from Hess's law, which make it possible to calculate the enthalpies of chemical reactions.

**Corollary 1.** Standard enthalpy of a chemical reaction

$$\sum_i \nu_i \mathrm{A}_i = \sum_j \nu_j \mathrm{B}_j$$

equal to the difference between the standard enthalpies of formation of reaction products and reagents (taking into account stoichiometric coefficients):

$$\Delta_r H_T^0 = \sum_j \nu_j \Delta_f H_T^0(\mathrm{B}_j) - \sum_i \nu_i \Delta_f H_T^0(\mathrm{A}_i) \quad (3.5)$$

*The standard enthalpy (heat) of formation of a substance* $\Delta_f H_T^0$ ( $f$ means “formation”) at a given temperature is the enthalpy of the reaction of formation of one mole of this substance *from elements* in the most stable standard state. According to this definition, the enthalpy of formation of the most stable simple substances in the standard state is 0 at any temperature. Standard enthalpies of formation of substances at a temperature of 298 K are given in reference books.

The concept of “enthalpy of formation” is used not only for ordinary substances, but also for ions in solution. In this case, the $H^+$ ion is taken as the reference point , for which the standard enthalpy of formation in an aqueous solution is assumed to be zero: $\Delta_f H_T^0(\mathrm{H}^+) = 0$

**Corollary 2 .** Standard enthalpy of a chemical reaction

$$\sum_i \nu_i \mathrm{A}_i = \sum_j \nu_j \mathrm{B}_j$$

equal to the difference between the enthalpies of combustion of the reactants and reaction products (taking into account stoichiometric coefficients):

$$\Delta_r H^0 = \sum_i \nu_i \Delta_c H^0(\mathrm{A}_i) - \sum_j \nu_j \Delta_c H^0(\mathrm{B}_j) \quad (3.6)$$

( $c$ stands for "combustion"). The standard enthalpy (heat) of combustion of a substance is the enthalpy of the reaction of complete oxidation of one mole of a substance. This consequence is usually used to calculate the thermal effects of organic reactions.

**Corollary 3.** The enthalpy of a chemical reaction is equal to the difference in the energies of breaking and forming chemical bonds.

*bond energy* is the energy required to break a bond and separate the resulting particles over an infinite distance:

$AB_{(g)} \rightarrow A_{(g)} + B_{(g)}$ .

Communication energy is always positive.

Hess's law allows us to solve many practically important problems. First of all, we note that this law allows us to express the thermal effects of reactions through **the enthalpies** of formation of substances participating in the interaction.

***Enthalpy of formation** is the change in enthalpy of the system during the synthesis of one mole of a substance from simple substances.* This value is denoted by the symbol $\Delta H_f$. If the process occurs under standard conditions, the enthalpy of formation is called standard ( $\Delta H^{\circ}_{f,\,298}$ ). The standard enthalpies of formation for various compounds are given in thermodynamic reference books.

The enthalpies of simple substances are, by definition, zero. If an element forms several simple substances, then the value for that allotropic modification that is most stable under standard conditions (for example, graphite in the case of carbon) is taken equal to zero $\Delta H^{\circ}_{f,\,298}$ .

Let us consider the relationship between the thermal effect of the reaction and the enthalpies of formation of reagents and reaction products. Let for the reaction

$aA + bB = cC + dD$ ; $\Delta H$ (4)

+ the enthalpies of formation of the substances involved in the interaction are equal to $\Delta H_f$ (A), $\Delta H_f$ (B), $\Delta H_f$ (C) and $\Delta H_f$ (D). In the enthalpy diagram (Fig. 1), the occurrence of reaction (4) corresponds to the thermal effect $\Delta H$. Let's carry out reaction (4) in a different way: we convert compounds A and B into the corresponding simple substances with a thermal effect $\Delta H_{decl}$ , and then from these simple substances we synthesize compounds C and D with a thermal effect $\Delta H_{syn}$ . The thermal effect $\Delta H_{synth}$ corresponds to the synthesis from simple substances of moles of compound C and d moles of compound D. Therefore

$\Delta H_{sint} = c\Delta H_f(C) + d\,\Delta H_f(D)$

Most thermochemical data in reference books are given at a temperature of 298 K. To calculate thermal effects at other temperatures, use ***the Kirchhoff equation*** **:**

$$\frac{d\Delta H}{dT} = \Delta C_p \quad \text{(differential form) (3.7)}$$

$$\Delta H_{T_2} = \Delta H_{T_1} + \int_{T_1}^{T_2} \Delta C_p(T)\,dT \quad \text{(integral form) (3.8)}$$

Where $\Delta C_p$ is the difference between the isobaric heat capacities of the reaction products and the starting substances. If the difference $T_2 - T_1$ is small, then we can accept $\Delta C_p$ = const. If there is a large temperature difference, it is necessary to use the temperature dependence $\Delta C_p(T)$ type:

$$\Delta C_p(T) = \Delta a + \Delta bT + \Delta cT^2 + \Delta c'/T^2 \text{, (3.9)}$$

where the coefficients are *a* , *b* , *c*, etc. for individual substances they are taken from the reference book, and the sign $\Delta$ indicates the difference between the products and reagents (taking into account the coefficients).

**EXAMPLES.**

Example -1. The standard enthalpies of formation of liquid and gaseous water at 298 K are -285.8 and -241.8 kJ/mol, respectively. Calculate the enthalpy of vaporization of water at this temperature.

*Solution* . Enthalpies of formation correspond to the following reactions:

$H_{2\,(g)} + SO_{2\,(g)} = H_2O_{(l)}$ , $\Delta H_1^0 = -285.8$;

$H_{2\,(g)} + SO_{2\,(g)} = H_2O_{(g)}$ , $\Delta H_2^0 = -241.8$.
The second reaction can be carried out in two stages: first, burn hydrogen to form liquid water according to the first reaction, and then evaporate the water:
$H_2O_{(l)} = H_2O_{(g)}$ , $\Delta H^0{}_{isp} = ?$
Then, according to Hess's law,
$\Delta H_1^0 + \Delta H^0{}_{isp} = \Delta H_2^0$ ,
where $\Delta H^0{}_{isp} = -241.8 - (-285.8) = 44.0$ kJ/mol.
*Answer* . 44.0 kJ/mol.

Example -2. Calculate enthalpy of reaction
$6C_{(g)} + 6H_{(g)} = C_6H_{6\,(g)}$
a) by enthalpies of formation; b) by binding energies, under the assumption that the double bonds in the $C_6H_{6\ molecule}$ are fixed.
*Solution* . a) Enthalpies of formation (in kJ/mol) are found in the reference book (for example, PWAtkins, Physical Chemistry, 5th edition, pp. C9-C15): $\Delta_f H^0 (C_6H_{6\,(g)}) = 82.93$, $\Delta_f H^0 (C_{(g)}) = 716.68$, $\Delta_f H^0 (H_{(g)}) = 217.97$. The enthalpy of reaction is:
$\Delta_r H^0 = 82.93 - \times 6{,}716.68 - \times 6{,}217.97 = -5525$ kJ/mol.
b) In this reaction, chemical bonds are not broken, but only formed. In the approximation of fixed double bonds, the $C_6H_{6\ molecule}$ contains 6 C-H bonds, 3 C-C bonds and 3 C=C bonds. Bond energies (in kJ/mol) (PWAtkins, Physical Chemistry, 5th edition, p. C7): $E$ (C-H) = 412, $E$ (C-C) = 348, $E$ (C=C) = 612. Enthalpy reaction is equal to:
$\Delta_r H^0 = -(6{,}412 \times + 3{,}348 \times + 3{,}612 \times) = -5352$ kJ/mol.
The difference with the exact result -5525 kJ/mol is due to the fact that in the benzene molecule there are no single C-C bonds and double C=C bonds, but there are 6 aromatic C C bonds ÷.
*Answer* . a) -5525 kJ/mol; b) -5352 kJ/mol.

## 6-Lecture.

## Topic: Heat capacity. Dependence of heat capacity on temperature.

# 2. Theory of heat capacity of heterogeneous systems.

## 2.1. Types of heat capacities.

*homogeneous* if the properties of their different parts are the same.

*Heat capacity* is the amount of heat required to change the temperature of a unit amount of a substance by 1 degree.

$$¢\ ¿\frac{dQ}{dT}$$

Depending on what is the unit of measurement for the amount of a substance. There are:

1. mass (specific) heat capacity $c = \left[\frac{Дж}{кг \cdot К}\right]$;
2. molar (molar) heat capacity $c_м = \left[\frac{Дж}{Кмоль \cdot К}\right]$

Note: 1 kmol is the amount of substance in kg, numerically equal to its molecular weight;

3. volumetric heat capacity Cw, $\left[\frac{Дж}{м^3 K}\right]$ because Since the volume occupied by a gas depends on its pressure and temperature, volumetric heat capacities in reference literature are usually given for normal physical conditions.

NFU: pH=101325 Pa (760 mmHg)

Tn=273.15 K

Volumetric heat capacity and mass heat capacity are related by the following relationship:

$c_{W\,норм}=c\,ж$ ,

Where $\rho_{norm}$ = $\frac{P_н}{RT_н}=\frac{101325}{R*273,15}$ is the density of the substance at NFU

From the definition of heat capacity we have (59) $c=\frac{dQ}{dt}$, it follows that each process has its own heat capacity, that is, to change the temperature of a unit amount of a substance by one degree, different processes will require different amounts of heat.

Thus, according to the types of processes, they distinguish: isochoric, isobaric, isothermal, adiabatic heat capacity, as well as the heat capacity of a polytropic process.

Then for an isochoric process they distinguish:

*Cv* - mass isochoric heat capacity

$c_{\mu v}$ – molar (molar) isochoric heat capacity;

$c_{Wv}$ – volumetric isochoric heat capacity.

For an isobaric process (p=const) we have:

$c_p$ – mass isobaric heat capacity.

$c_{\mu p}$ – (molar) molar isobaric heat capacity;

$c_{Wp}$ – volumetric isobaric heat capacity.

+The reference literature contains only the values of isochoric and isobaric heat capacities. There are no isothermal and adiabatic heat capacities in reference books, because it is known in advance that:

$c_T = c_{\mu T} = c_{WT} = \infty$

that is, all isothermal heat capacities are equal to ∞, and adiabatic heat capacities are equal to 0, this result follows from formula (59).

There are true and average heat capacities. True heat capacity is equal to the amount of heat that must be supplied to the body in order to increase its temperature by a differentially small amount. It is determined by the ratio:

$$C_p = \frac{dH}{dT}, \quad C_v = \frac{dU}{dT}, \quad C_v = \frac{dU}{dT}$$

The average heat capacity in the temperature range from T $_1$ to T $_2$ is equal to the amount of heat that must be supplied to the body in order to increase its temperature by 1 degree:

$$\bar{C} = \frac{q}{T_2 - T_1}$$

The relationship between true and average heat capacities is expressed by the equation:

$$\bar{C} = \frac{1}{T_2 - T_1}\int_{T_1}^{T_2} C dT$$

The dependence of heat capacity on temperature in the temperature range 298 – T for practical calculations is usually expressed by empirical equations in the form of average series:

$$C = a_0 + a_1 T + a_2 T^2 + a_{-2} T^{-2}$$

+ where: a $_0$, a $_1$, a $_2$ and a $_{-2}$ are coefficients that depend on the nature of the substance.

The amount of heat in processes at constant V and P, spent on heating n-moles of a substance from T $_1$ to T $_2$ is determined from the relations:

$$q_v = \Delta U = n\int_{T_1}^{T_2} C_v dT, \quad q_p = \Delta H = n\int_{T_1}^{T_2} C_p dT$$

Taking into account the dependence of heat capacity on temperature, we can write:

$$q_p = \Delta H = n[a_0(T_2 - T_1) + \frac{a_1}{2}(T_2^2 - T_1^2) + \frac{a_2}{3}(T_2^3 - T_1^3) + a_{-2}\frac{T_2 - T_1}{T_1 \cdot T_2}] \quad (1\text{-}3)$$

## 7-Lecture.

## Subject: Krichhoff's law.

Krichhoff's law. Heat capacity, integral equations. Temperature dependence of the heat capacity of the reaction.

**Dependence of the thermal effect of the reaction on temperature. Kirchhoff's law.**
In general, the thermal effect of a chemical reaction depends on the temperature and pressure at which the reaction is carried out. The influence of pressure on ΔH and ΔU reactions is usually neglected. The influence of temperature on the magnitude of thermal effects is described by **Kirchhoff's law:**
***The temperature coefficient of the thermal effect of a chemical reaction is equal to the change in the heat capacity of the system during the reaction.***
Let us differentiate ΔH and ΔU by temperature at constant pressure and temperature, respectively:

$$\left(\frac{\partial(\Delta H)}{\partial T}\right)_P = \left(\frac{\partial H_2}{\partial T}\right)_P - \left(\frac{\partial H_1}{\partial T}\right)_P \quad (I.2)$$

$$\left(\frac{\partial(\Delta U)}{\partial T}\right)_V = \left(\frac{\partial U_2}{\partial T}\right)_V - \left(\frac{\partial U_1}{\partial T}\right)_V \quad (I.3)$$

The derivatives of enthalpy and internal energy of a system with respect to temperature are the heat capacities of the system under isobaric and isochoric conditions $C_p$ and $C_v$, respectively:

$$\left(\frac{\partial H_i}{\partial T}\right)_P = C_{p,i} \quad (I.4)$$

$$\left(\frac{\partial U_i}{\partial T}\right)_V = C_{v,i} \quad (I.5)$$

Substituting expressions (I.4, I.5) into (I.2, I.3), we obtain a mathematical representation of Kirchhoff's law:

$$\left(\frac{\partial(\Delta H)}{\partial T}\right)_P = C_{P,2} - C_{P,1} = \Delta C_P \quad (I.6)$$

$$\left(\frac{\partial(\Delta U)}{\partial T}\right)_V = C_{V,2} - C_{V,1} = \Delta C_V \quad (I.7)$$

For a chemical process, the change in heat capacity is specified by a change in the composition of the system and is calculated as follows:

$$\Delta C_P = \sum(\nu_i C_{P,i})_{прод} - \sum(\nu_i C_{P,i})_{исх} \quad (I.8)$$

$$\Delta C_V = \sum(\nu_i C_{V,i})_{прод} - \sum(\nu_i C_{V,i})_{исх} \quad (I.9)$$

If we integrate expressions (I.6, I.7) from $T = T_1$ to $T = T_2$, considering $\Delta C_p$ ($\Delta C_v$) independent of temperature, we obtain the integral form of Kirchhoff's law:

$$\Delta H_{T2} = \Delta H_{T1} + \Delta C_P (T_2 - T_1) \quad (2.1)$$

$$\Delta U_{T2} = \Delta U_{T1} + \Delta C_V (T_2 - T_1) \quad (2.2)$$

$_{298}$ and $\Delta U^\circ_{298}$ are usually known , we transform expressions (2.1, 2.2):

$$\Delta H^\circ_T = \Delta H^\circ_{298} + \Delta C^\circ_P (T - 298) \quad (2.3)$$

$$\Delta U^\circ_T = \Delta U^\circ_{298} + \Delta C^\circ_V (T - 298) \quad (2.4)$$

When calculating the change in the thermal effect of a reaction over a wide temperature range, it is necessary to take into account the dependence of the heat capacity on temperature, which is expressed by the power series $C^\circ_p = aT + bT^2 + cT^3$; coefficients a, b, c are given in reference books.

## 8 -Lecture.

### **Subject:** Second law of thermodynamics.

Second law of thermodynamics. Caratedori's principle and the Carnot cycle.

The second law of thermodynamics, in contrast to the first law of thermodynamics, studies all processes that occur in nature, and these processes can be classified as follows.

Processes can be **spontaneous, non-spontaneous, equilibrium, nonequilibrium.**

Spontaneous processes are divided into **reversible** and **irreversible.**

The second law of thermodynamics is called the law of direction of a process in an isolated system (law of growth S). The word “entropy” was created in 1865 ***by R. Yu. E. Clausius*** - “trope” from Greek means transformation. In 1909, Professor ***P. Auerbach*** called **internal energy the queen of all functions,** and *S* the **shadow** of this queen. **Entropy** is a measure of the disorder of a system.

Second law of thermodynamics. The first law of thermodynamics states that when one form of energy is converted into another, the total energy of the system does not change, but does not indicate any restrictions on the possibility of this process. Therefore, the first law of thermodynamics allows us to calculate the energy effect of the process, but does not answer the questions about whether the process will proceed spontaneously, about the direction and depth of the process. A spontaneous process is a process that can occur without the expenditure of work from the outside, and as a result, work can be obtained in an amount proportional to the change in the state of the system that has occurred.

A spontaneous process can occur either reversibly or irreversibly. Although the definition of a reversible process has already been given, it is worth considering this concept in more detail. In order for a spontaneous process to proceed reversibly, it is necessary to apply such resistance from the outside that the transition is very slow and with an infinitesimal change in the opposing force, the process can go in the opposite direction. In the case of a reversible change in the state of the system, the maximum amount of work is performed. Every real process is irreversible to some extent, and the work produced is less than the theoretical maximum possible.

A forced process is a process that requires external work in an amount proportional to the change in the state of the system.

The second law of thermodynamics makes it possible to determine which of the processes will occur spontaneously, how much work can be obtained in this case, and what is the limit for the spontaneous course of the process. Further, the second law of thermodynamics makes it possible to determine what the conditions must be for the desired process to proceed in the required direction and to the required extent, which is especially important for solving various applied problems.

Like the first, the second law of thermodynamics is derived directly from experiment. At the same time, the second law of thermodynamics has a limited scope: it is applicable only to macroscopic systems.

**Statements of the second law of thermodynamics:**

**Heat** cannot spontaneously transfer from a less heated body to a more heated one.

A process is impossible whose only result is the conversion of heat into work.

It is impossible to build a machine, all of whose actions would be reduced to producing work by cooling a heat source (a perpetual motion machine of the second kind).

Let us consider the operation of a heat engine, i.e. a machine that produces work due to heat absorbed from a body called a heater.

A heater with a temperature $T_1$ transfers heat $Q_1$ to a working fluid, for example, an ideal gas performing expansion work A; in order to return to its original state, the working fluid must transfer a certain amount of heat $Q_2$ to the body having a lower temperature T2 ( refrigerator), and

$A = Q_1 - Q_2$ (I.)

The ratio of the work A performed by a heat engine to the amount of heat $Q_1$ received from the heater is called the thermodynamic efficiency factor (efficiency) of the machine η:

$$\eta = \frac{A}{Q_1} = \frac{Q_1 - Q_2}{Q_1} \qquad (I.35)$$

**Рис. 1.1** Схема тепловой машины

To obtain a mathematical expression for the second law of thermodynamics, let us consider the operation of an ideal heat engine (a machine that operates reversibly without friction and heat loss; the working fluid is an ideal gas). The operation of the machine is based on the principle of a reversible cyclic process - the thermodynamic Carnot cycle (Fig. 1.2).

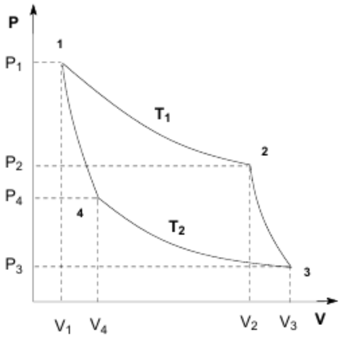


**Рис. 1.2** Цикл Карно

Let's write expressions for working in all sections of the cycle:

Section 1-2: Isothermal expansion.

$$A_1 = Q_1 = RT_1 \ln\left(\frac{V_2}{V_1}\right) \qquad (I.36)$$

Участок 2-3: *Адиабатическое расширение.*

$$A_2 = -\Delta U = C_V(T_1 - T_2) \qquad (I.37)$$

Участок 3-4: *Изотермическое сжатие.*

$$A_3 = -Q_2 = RT_2 \ln\left(\frac{V_4}{V_3}\right) \qquad (I.38)$$

Участок 4-1: *Адиабатическое сжатие.*

$$A_4 = -\Delta U = C_V(T_2 - T_1) \qquad (I.39)$$

Общая работа в цикле равна сумме работ на всех участках:

$$A = A_1 + A_2 + A_3 + A_4 \qquad (I.40)$$

Having carried out a number of simple transformations, we obtain for the efficiency of an ideal heat engine operating according to the Carnot cycle:

$$\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1} \qquad (I.41)$$

$$\eta < \frac{T_1 - T_2}{T_1} \qquad (I.42)$$

thermodynamics.

$$\eta < \frac{T_1 - T_2}{T_1} \qquad (I.42)$$

For the general case we can write:

$$\eta = \frac{Q_1 - Q_2}{Q_1} \leq \frac{T_1 - T_2}{T_1} \qquad (I.43)$$

Based on an analysis of the operation of an ideal Carnot heat engine, we can draw the following conclusion, which is also one of the formulations of the second law of thermodynamics:

Any form of energy can be completely converted into heat, but heat is only partially converted into other forms of energy. Thus, we can conditionally accept that the internal energy of the system consists of two components: “free” X and “bound” Y energies, and “free” energy can be converted into work, and “bound” energy can only be converted into heat .

$U = X + Y$ (I.44)

The smaller the temperature difference, the greater the amount of bound energy, and at $T = \text{const}$ the heat engine cannot produce work. The measure of bound energy is a new thermodynamic function of state called entropy.

Let us introduce the definition of entropy based on the Carnot cycle. Let us transform expression (I.41) to the following form:

$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1} \qquad (I.45)$$

## 9 -Lecture.

## Topic: The concept of entropy.

The concept of entropy. Changes in entropy in various processes.

**Entropy.** **Entropy** (from other Greek. ἐν "in" + τροπή "appeal; transformation") - widely used in natural and exact sciences term (first introduced in thermodynamics as a function of state thermodynamic system ), denoting a measure of the irreversible dissipation of energy , or the uselessness of energy (because not all of the system's energy can be used to convert into any useful work ). For the concept of entropy in this section, physicists use the name *thermodynamic entropy* ; thermodynamic entropy is usually used to describe equilibrium (reversible) processes .

Although the concepts of thermodynamic and information entropy are introduced within the framework of various formalisms, they have a common *physical meaning - the logarithm of the number of available microstates of the system* . The relationship between these concepts was first established by Ludwig Boltzmann . In non-equilibrium (irreversible) processes, entropy also serves as a measure of the proximity of the system state to equilibrium : the greater the entropy, the closer the system is to equilibrium (in a state of *thermodynamic equilibrium ,* the entropy of the system is maximum).

In the broad sense in which the word is often used in everyday life, entropy means a measure of the complexity, chaos or uncertainty of a system: the less the elements of the system are subject to any order, the higher the entropy.

opposite quantity of entropy is called *negentropy* or, less commonly, *extropy* . The concept of entropy was first introduced by Clausius in thermodynamics in 1865 to define the measure of irreversible energy dissipation , a measure of the deviation of a real process from an ideal one. Defined as the sum of reduced heats, it is a function of state and remains constant in closed reversible processes , whereas in irreversible closed ones, its change is always positive. In an open system, a decrease in the entropy of the system under consideration may occur due to the loss of energy, for example in the form of radiation, while the total entropy of the environment increases.

a measurement scale for it based on the first , second and third principles of thermodynamics.

In the thermodynamic formalisms of Clausius [1] and Carathéodory [2], entropy is introduced simultaneously with absolute thermodynamic temperature . The mathematical apparatus of Gibbs thermodynamics [3] is based on the use of entropy as an independent thermodynamic variable, while temperature, a natural candidate for this role, is introduced as a function of internal energy and entropy. Finally, in rational thermodynamics , entropy is expressed in terms of internal energy and temperature, which are considered as the main indeterminate variables of the theory.

### Second law of thermodynamics.

The second law of thermodynamics establishes the criteria for the irreversibility of thermodynamic processes. There are many formulations of the second law that are equivalent to each other. We will present here only one formulation related to entropy.

There is a state function - entropy $S$ , which has the following property: $dS \geq \frac{\delta Q}{T}$ , (4.1) where the equal sign refers to reversible processes, and the greater sign refers to irreversible ones.

For isolated systems, the second law states: $dS$ i 0, (4.2) i.e. the entropy of isolated systems in irreversible processes can only increase, and in a state of thermodynamic equilibrium it reaches a maximum ( $dS = 0$, $d 2 S < 0$).

Inequality (4.1) is called *the Clausius inequality* . Since entropy is a function of state, its change in any cyclic process is equal to 0, therefore for cyclic processes the Clausius inequality has the form:

$$\oint \frac{\delta Q}{T} \leq 0 , \quad (4.3)$$

where the equal sign is placed if the whole cycle is completely reversible.

Entropy can be determined using two equivalent approaches - statistical and thermodynamic. *The statistical definition* is based on the idea that irreversible processes in thermodynamics are caused by a transition to a more probable state, so entropy can be related to probability:

$$S = k \ln W , \quad (4.4)$$

where $k = 1.38 \times 10^{-23}$ J/K is *Boltzmann's constant* ( $k = R / N_A$ ), $W$ is the so-called thermodynamic probability, i.e. the number of microstates that correspond to a given macrostate of the system (see Chapter 10). Formula (4.4) is called *Boltzmann's formula* .

From the point of view of strict statistical thermodynamics, entropy is introduced as follows:

$$S = k \ln \Gamma(E) , \quad (4.5)$$

where G( $E$ ) is the phase volume occupied by the microcanonical ensemble with energy $E$.

*The thermodynamic definition* of entropy is based on the consideration of reversible processes:

$$dS = \frac{\delta Q_{\text{обр}}}{T} . \quad (4.6)$$

This definition allows us to represent elementary heat in the same form as various types of work:

$\delta Q_{arr} = TdS$ , (4.7)

where temperature plays the role of a generalized force, and entropy plays the role of a generalized (thermal) coordinate.

Calculation of entropy change for various processes

Thermodynamic calculations of entropy changes are based on definition (4.6) and on the properties of partial derivatives of entropy with respect to thermodynamic parameters:

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}, \quad \left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T},$$

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p, \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V . \quad (4.8)$$

The last two identities are *Maxwell's relations* (see Chapter 5 for the derivation).

1) *Heating or cooling at constant pressure* .

The amount of heat required to change the temperature of the system is expressed using heat capacity: $\delta Q_{arr} = C_p dT$ .

$$\Delta S = \int_{T_1}^{T_2} \frac{\delta Q_{\text{обр}}}{T} = \int_{T_1}^{T_2} \frac{C_p}{T} dT \quad (4.9)$$

If the heat capacity does not depend on temperature in the interval from $T_1$ to $T_2$ , then equation (4.8) can be integrated:

$$\Delta S = C_p \ln \frac{T_2}{T_1} . \quad (4.10)$$

If the temperature change occurs at a constant volume, then in formulas (4.9) and (4.10) $C_p$ must be replaced by $C_V$ .

2) *Isothermal expansion or contraction* .

To calculate the entropy in this case, you need to know the equation of state of the system. The calculation is based on the use of the Maxwell relation:

$$\Delta S = \int_{V_1}^{V_2} \left(\frac{\partial S}{\partial V}\right)_T dV = \int_{V_1}^{V_2} \left(\frac{\partial p}{\partial T}\right)_V dV \quad (4.11)$$

In particular, for isothermal expansion of an ideal gas ( $p = nRT / V$ )

$$\Delta S = nR \ln \frac{V_2}{V_1} \quad (4.12)$$

The same result can be obtained if we use the expression for the heat of isothermal reversible expansion of an ideal gas: $Q_{arr} = nRT \ln( V_2 / V_1 )$ .

3) *Phase transitions* .

During a reversible phase transition, the temperature remains constant, and the heat of phase transition at constant pressure is equal to $\Delta H_{fp}$ , so the change in entropy is equal to:

$$\Delta S = \frac{1}{T}\int \delta Q_{ф.п.} = \frac{\Delta H_{ф.п.}}{T_{ф.п.}} \quad (4.13)$$

During melting and boiling, heat is absorbed, so the entropy in these processes increases: $S_{tv} < S_l < S_g$. In this case, the entropy of the environment decreases by the amount $\Delta S_{f.p.}$, therefore the change in the entropy of the Universe is 0, as expected for a reversible process in an isolated system.

4) *Mixing of ideal gases at constant temperature and pressure* .

If $n_1$ moles of one gas occupying a volume $V_1$ are mixed with $n_2$ moles of another gas occupying a volume $V_2$, then the total volume will be equal to $V_1 + V_2$, and the gases expand independently of each other and the total change in entropy is equal to the sum of the changes entropy of each gas:

$$\Delta S = n_1 R \ln \frac{V_1 + V_2}{V_1} + n_2 R \ln \frac{V_1 + V_2}{V_2} = -(n_1 + n_2) R (x_1 \ln x_1 + x_2 \ln x_2), \quad (4.14)$$

where $x_i$ is the mole fraction of *the i* -th gas in the resulting gas mixture. The change in entropy (4.14) is always positive, because all $\ln x_i < 0$, so ideal gases always mix irreversibly.

## 10 -Lecture.

## Subject: Direction of the process and equilibrium criteria.

Direction of the process and equilibrium criteria. Criteria and conditions for process equilibrium in isolated, closed and open systems.

The change in entropy unambiguously determines the direction and limit of spontaneous occurrence of the process only for the simplest systems - isolated ones. In practice, most of the time we have to deal with systems that interact with the environment. To characterize the processes occurring in closed systems, new thermodynamic functions of state were introduced: *isobaric-isothermal potential* ( *Gibbs free energy* ) and *isochoric-isothermal potential* ( *Helmholtz free energy* ) .

The behavior of any thermodynamic system in the general case is determined by the simultaneous action of two factors - *enthalpy* , which reflects the system's desire for a minimum of thermal energy, and *entropy* , which reflects the opposite tendency - the system's desire for maximum disorder. If for isolated systems (ΔH = 0) the direction and limit of the spontaneous occurrence of the process is uniquely determined by the magnitude of the change in the entropy of the system ΔS, and for systems located at temperatures close to absolute zero (S = 0 or S = const) the criterion for the direction of the spontaneous process is the change enthalpy ΔH, then for closed systems at temperatures not equal to zero, it is necessary to simultaneously take into account both factors. The direction and limit of spontaneous occurrence of the process in any system is determined by the more general principle of minimum free energy:

***Only those processes that lead to a decrease in the free energy of the system can occur spontaneously; the system reaches a state of equilibrium when the free energy reaches a minimum value.***

For closed systems under isobaric-isothermal or isochoric-isothermal conditions, free energy takes the form of isobaric-isothermal or isochoric-isothermal potentials (the so-called Gibbs and Helmholtz free energy, respectively). These functions are sometimes called simply thermodynamic potentials, which is not entirely strict, since internal energy (isochoric-isentropic) and enthalpy (isobaric-isentropic potential) are also thermodynamic potentials.

Thermodynamics as a science was formed in the first half of the 19th century. As its name implies, thermodynamics studies thermal motion and related processes and phenomena. Developed to explain various physical processes, thermodynamics has also found application in chemistry. Many chemical reactions are accompanied by thermal effects, and in the early stages of the development of chemistry it was assumed that their study could serve as the key to unlocking the secrets of the chemical affinity of elements - the property that determines the ability of atoms and molecules to combine with each other in various combinations.

Indeed, when substances with high chemical affinity interact, the reactions, as a rule, proceed violently and are accompanied by the release of a large amount of heat. Not all reactions, however, proceed this way. Sometimes, instead of releasing heat, it is absorbed. The question turned out to be difficult. The situation changed decisively when D. W. Gibbs introduced the concept of free energy into chemical thermodynamics, later called Gibbs energy. He showed that the behavior of closed thermodynamic systems at constant pressure is exhaustively described by the state function *G:*

$$G = H - TS. \qquad (1)$$

Josiah Willard Gibbs (1839-1903) - American mathematician, physicist and physical chemist, one of the creators of vector analysis and the mathematical theory of thermodynamics, which largely predetermined the development of all modern exact sciences and natural sciences in general; whose image is captured in the "Gallery of Fame of Great Americans." His name is given to many quantities and concepts of chemical thermodynamics: Gibbs energy, Gibbs paradox, Gibbs-Helmholtz phase rule, Gibbs-Rozebohm triangle, Gibbs-Duhem equations, etc.

From formula (1) it follows that the change in Gibbs energy at constant pressure and temperature is equal to

$$\Delta G = \Delta H - T\Delta S. \qquad (2)$$

Regardless of Gibbs, G. Helmholtz came to a similar expression for the free energy of systems limited by a constant volume, introducing the state function $A$ (Helmholtz energy):

$$A \equiv U - TS, \qquad (2.26)\,(3)$$

the change of which for processes occurring at constant volume and temperature has the form

$$\Delta A = \Delta U - T\Delta S. \qquad (2.27)\ (4)$$

Functions $G$ and $A$ have the dimension of energy and are expressed in joules. Both functions have found application in various fields. The system of equations (2) and (4) is called the Gibbs-Helmholtz equations.

Born on August 31, 1821 (Potsdam) in the family of a teacher. He studied medicine at the Royal Medical-Surgical Institute in Berlin.

Hermann von Helmholtz (1821-1894) - German physicist, physician, physiologist, psychologist, acoustician. Formulated the laws of conservation of energy in chemical processes and introduced the concept of free energy. Helmholtz contributed to the recognition of the theory of three-color vision, invented an ophthalmoscope for studying the fundus of the eye and an ophthalmometer for determining the radius of curvature of the eye cornea. By establishing the laws of behavior of vortices in non-viscous liquids, Helmholtz laid the foundations of hydrodynamics and scientific meteorology.

Gibbs energy has become more widespread in practical calculations because technological processes are more often carried out at constant pressure than at constant volume. In biological systems, both pressure and volume are usually constant, $AH = \Delta U$ and, accordingly, $\Delta G$ = DA. In what follows we will operate mainly with the *G function.*

Within the framework of chemical thermodynamics, based on the first and second laws of classical thermodynamics, it is strictly proven (we omit the system of evidence) that for closed systems operating at constant pressure and constant temperature, the only criterion for the spontaneity of the process is the change in $\Delta G$ . The negative or positive sign *of* $\Delta G$ allows us to judge whether the reaction can proceed spontaneously or not. Approaching equilibrium (at $P, T$ = const) is inevitably accompanied by a decrease in G, i.e. the difference $\Delta G$ must be negative. When equilibrium is reached, $G$ takes a minimum value, $\Delta G$ = 0. Thus:

- • if $\Delta G$ or ΔA is equal to a negative value, then the reaction or other process can occur spontaneously;
- • if $\Delta G$ or ΔA is equal to a positive value, then the reaction or other process cannot proceed spontaneously or, more precisely, will proceed in the opposite direction;

• if $\Delta G$ = 0 or ΔA = O, then the system is in equilibrium and can neither gain nor lose energy.

Therefore, to answer the question whether a reaction can occur or not, one should calculate $\Delta G$ (at $P$ and $T$ = const) or ΔA (at $V$ and G = const). For example, if it turns out that ΔG < 0, then the reaction proceeds spontaneously (from left to right). If ΔG > 0, then the reaction proceeds spontaneously in the opposite direction (from right to left).

The expression for ΔG and ΔA combines the mathematical expressions for the first and second laws of thermodynamics:

$$Q = \Delta U + W \text{ и } T\Delta S \geq Q.$$

Hence, at constant volume:

$$T\Delta S \geq \Delta U + P\Delta V.$$

Since V = const, $P\Delta V$ - 0 and $T\Delta S > \Delta U$, or $0 > \Delta U - T\Delta S$. As a result, at equilibrium $\Delta U - T\Delta S = 0$, and in a spontaneous process O > $\Delta U - T\Delta S$.

For isolated systems $\Delta U$ - 0 and $\Delta H$ - 0. Then ΔG = -$T\Delta S$ and ΔA = -$T\Delta S$. Consequently, the only criterion for the spontaneity of a process is entropy:

- • if ΔS is equal to a negative value, then the reaction or other process cannot proceed spontaneously;
- • if $\Delta S$ is equal to a positive value, then the reaction or other process can occur spontaneously;
- • if $\Delta S$ = 0, then the system is in equilibrium.

To calculate D$_r$G?$_{98}$ different reactions and thereby solutions to the question of their spontaneity introduced the concept of the Gibbs energy of formation of substances Δ/G§$_{98}$. By analogy with the calculation of thermal effects through the heat (enthalpy) of formation of substances $\Delta_r G$ ? $_{98}$ reactions equal to the sum D *fG%* $_{98}$ products minus the sum D/G? $_{98}$ starting materials (taking into account stoichiometric coefficients):

$$\Delta_r G^0_{298} = \sum b_j \Delta_f G^0_{298}(\text{продуктов}) - \sum a_i \Delta_f G_A(\text{реагентов}). \qquad (2.28)$$

(5

)

The values of the standard Gibbs energies of formation of substances Δ *fG°* $_{98}$ *(P* - *1* atm) are given in reference literature, indicating the temperature of the process (usually 298 K). There are no reliable data only for complex organic compounds. Nevertheless, some estimated calculations of Δ *fG %* $_{98}$ based on semi-empirical laws are still possible. As an example in table. Table 2.2 shows the Δ/Gf $_{98 \text{ values}}$ of some substances.

Let us analyze expression (2) using the data in table. 2.2, i.e. considering the formation reactions of the given substances. It is obvious that the change in the Gibbs energy of the system has two components: the thermal effect of the reaction (RDG) and the change in entropy (D, D). An ideal option for the process would be a simultaneous increase in entropy (Δ,.S > 0) and a decrease in enthalpy *(A,H* <0 - exothermic reaction). In practice, such cases are quite rare. The fact is that an increase in disorder in a system is, as a rule, associated with a weakening of chemical bonds, i.e. with an endothermic process.

## 11 - 12 Lecture.

## Topic: Thermodynamic potentials. Characteristic functions .

Thermodynamic potentials. Characteristic functions. Concepts of free energy and bound energy.

*(Isaboric-isothermal and isochoric-isothermal potentials. Gibbs and Helmholtz energies. Gibbs-Helmholtz energy. Chemical potential.)*

Thermodynamic potentials, or characteristic functions, are thermodynamic functions that contain all the thermodynamic information about the system. The four main thermodynamic potentials are of greatest importance:

**1)** ***internal energy U ( S , V ),***

**2)** ***enthalpy H ( S , p ) = U + pV ,***

**3)** ***Helmholtz energy F ( T , V ) = U - TS ,***

**4)** ***Gibbs energy G ( T , p ) = H - TS = F + pV*** .

Thermodynamic parameters, which are called natural variables for thermodynamic potentials, are indicated in brackets. All these potentials have the dimension of energy and all of them do not have an absolute value, since they are determined to within a constant, which is equal to the internal energy at absolute zero.

The dependence of thermodynamic potentials on their natural variables is described by the basic *equation of thermodynamics* , which combines the first and second principles. This equation can be written in four equivalent forms:

***dU = TdS - pdV*** **(5.1)**

**$dH = TdS + Vdp$ (5.2)**
**$dF = - pdV - SdT$ (5.3)**
**$dG = Vdp - SdT$ (5.4)**

These equations are written in a simplified form - only for closed systems in which only mechanical work is performed.

Knowing any of the four potentials as a function of natural variables, you can use the basic equation of thermodynamics to find all the other thermodynamic functions and parameters of the system (see Example 5-1).

Another important meaning of thermodynamic potentials is that they allow one to predict the direction of thermodynamic processes. So, for example, if the process occurs at constant temperature and pressure, then the inequality expressing the second law of thermodynamics:

$$dS \geq \frac{\delta Q}{T}$$

is equivalent to the inequality $dG_{p,T} \leq 0$ (we took into account that at constant pressure $\delta Q_p = dH$ ), where the equal sign refers to reversible processes, and inequalities - to irreversible ones. Thus, during irreversible processes occurring at constant temperature and pressure, the Gibbs energy always decreases. The minimum Gibbs energy is achieved at equilibrium.

Similarly, any thermodynamic potential in irreversible processes *at constant natural variables* decreases and reaches a minimum at equilibrium:

| **Potential** | **Natural variables _** | **Spontaneity condition** | **Equilibrium conditions** |
|---|---|---|---|
| ***U*** | **$S$ = const, $V$ = const** | **$dU < 0$** | **$dU = 0$, $d2U$ $^{>}$ 0** |
| ***H*** | **$S$ = const, $p$ = const** | **$dH < 0$** | **$dH = 0$, $d2H$ $^{>}$ 0** |
| ***F*** | **$T$ = const, $V$ = const** | **$dF < 0$** | **$dF = 0$, $d^2F > 0$** |
| ***G*** | **$T$ = const, $p$ = const** | **$dG < 0$** | **$dG = 0$, $d2G$ $^{>}$ 0** |

The last two potentials are of greatest importance in specific thermodynamic calculations - the Helmholtz energy $F$ and the Gibbs energy $G$ , because their natural variables are most convenient for chemistry. Another (outdated) name for these functions is isochoric-isothermal and isobaric-isothermal potentials. They have an additional physical and chemical meaning. The decrease in Helmholtz energy in any process at $T$ = const, $V$ = const is equal to the maximum mechanical work that the system can perform in this process:

$F_1 - F_2 = A_{max}$ (= $A_{arr}$ ).

Thus, the energy $F$ is equal to that part of the internal energy ( $U = F + TS$ ) that can be converted into work.

Similarly, a decrease in the Gibbs energy in any process at $T$ = const, $p$ = const is equal to the maximum useful (i.e., non-mechanical) work that the system can do in this process:

$G_1 - G_2 = A_{floor}$ .

The dependence of the Helmholtz (Gibbs) energy on volume (pressure) follows from the basic equation of thermodynamics (5.3), (5.4):

$$\left(\frac{\partial F}{\partial V}\right)_T = -p, \quad \left(\frac{\partial G}{\partial p}\right)_T = V \qquad . (5.5)$$

The dependence of these functions on temperature can be described using the basic equation of thermodynamics:

$$\left(\frac{\partial F}{\partial T}\right)_V = -S, \quad \left(\frac{\partial G}{\partial T}\right)_p = -S \qquad (5.6)$$

or using the Gibbs-Helmholtz equation:

$$\left(\frac{\partial (F/T)}{\partial T}\right)_V = -\frac{U}{T^2}, \quad \left(\frac{\partial (G/T)}{\partial T}\right)_p = -\frac{H}{T^2} \qquad (5.7)$$

Calculation of changes in functions *F* and *G* in chemical reactions can be carried out in different ways. Let's consider two of them using the Gibbs energy as an example.

1) By definition, $G = H - TS$ . If the reaction products and starting materials are at the same temperature, then the standard change in Gibbs energy in a chemical reaction is equal to:

$$\Delta_r G_T^0 = \sum G(\text{продукты}) - \sum G(\text{реагенты}) = \Delta_r H_T^0 - T\Delta_r S_T^0 \text{ , } (5.8)$$

where the thermal effect can be calculated using standard enthalpies of formation, and the standard entropy change can be calculated using the absolute entropies of reaction participants.

2) Similar to the thermal effect of a reaction, the change in Gibbs energy can be calculated using the Gibbs energies of formation of substances:

$$\Delta_r G_T^0 = \sum \Delta_f G_T^0(\text{продукты}) - \sum \Delta_f G_T^0(\text{реагенты}) \text{ . } (5.9)$$

Thermodynamic tables usually give absolute entropies and values of thermodynamic functions for the formation of compounds from simple substances at a temperature of 298 K and a pressure of 1 bar (standard state). For calculation$\Delta_r G$ and$\Delta_r F$ under other conditions, use relations (5.5) - (5.7).

All thermodynamic potentials are functions of state. This property allows us to find some useful relations between partial derivatives, which are called *Maxwell's relations* .

Let us consider expression (5.1) for internal energy. Because *dU* - total differential, partial derivatives of internal energy with respect to natural variables are equal to:

$$\left(\frac{\partial U}{\partial S}\right)_V = T, \quad \left(\frac{\partial U}{\partial V}\right)_S = -p$$

If we differentiate the first identity by volume, and the second by entropy, we obtain cross second partial derivatives of the internal energy, which are equal to each other:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \qquad (5.10)$$

Three other relations are obtained by cross-differentiating equations (5.2) - (5.4).

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p \qquad (5.11)$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \qquad (5.12)$$

$$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T \qquad (5.13)$$

## 13 -Lecture.

## Subject: chemical potential.

chemical potential. Special properties and versatility of the isobaric-isothermal potential.

The number of moles of components of a thermodynamic system can change during a chemical or physical process. In a homogeneous chemical reaction, the number of moles of reactants decreases, and the number of moles of reaction products increases. In a physical process, for example during the evaporation of a substance, a transition of molecules from one phase to another is observed. At the same time, their number in the liquid and gaseous phases changes. This circumstance must be taken into account in the thermodynamic description of physicochemical reactions. Let us consider an isobaric-isothermal process (ideal gas). The value of the Gibbs free energy will be determined by the pressure, temperature and number of moles ( ni ) of the participants in the process:

$$G = f(p, T, n_1, n_2, ..., n_i).$$

The total differential of this function through partial derivatives can be represented as follows:

$$dG = (\partial G/\partial T)_{p,ni} dT + (\partial G/\partial p)_{T,ni} dp + (\partial G/\partial n_1)_{p,T,ni} dn_1 + (\partial G/\partial n_2)_{p,T,nj} dn_2$$

*where $n_i$ is the number of moles of all components; $n_j$ is the number of moles of all components, except for the one whose change is being considered.*

The third and subsequent terms of this equation differ from each other only in the component under consideration, the number of moles of which changes during the process.

The partial derivative of the Gibbs free energy with respect to the number of moles of the i -th component at constant pressure, temperature and the number of moles of the remaining components of the system is called the chemical potential. This quantity was introduced into chemical thermodynamics by Gibbs. The chemical potential is denoted by the symbol μ.

In the general case, the expression for the chemical potential of the ith component has the form

$\mu_i = (\partial G/\partial n_i)_{p,T,nj}$

The chemical potential of a pure substance is equal to its Gibbs free energy:

$$\mu_i = G_i$$

At constant temperatures and pressures, the total Gibbs free energy differential is written as follows:

$$dG = \mu_1 dn_1 + \mu_2 dn_2 + \ldots + \mu_i dn_i.$$

For the equilibrium state of the thermodynamic system ( dG = 0) we obtain

$\mu_1 dn_1 + \mu_2 dn_2 + \ldots + \mu_i dn_i = 0$ or $\sum (\mu_i dn_1)_{\mathbf{pT}} = 0.$

A similar expression is obtained at constant volume and temperature:

$$dF_{v,T} = \sum (\mu_i dn_1)_{\mathbf{vT}} = 0.$$

When equilibrium is reached, the total Helmholtz energy differential is also zero:

$$\sum (\mu_i d n_1)_{\mathbf{vT}} = 0.$$

Thus, for thermodynamic systems with a variable number of moles of substances, the criteria for spontaneity and equilibrium can be expressed in terms of the chemical potentials of the reactants and reaction products. If the dependence of the chemical potential on temperature and pressure is known, then the equilibrium properties of pure gases and their mixtures can be expressed through state parameters.

For a pure gas at constant temperature, the total Gibbs free energy differential is

$dG = d\mu = v\,dp$ .

Integrating the last equation results in the expression

$\mu = \text{const} + \int v dp$ ,

*where v is the volume of one mole of pure gas; const – integration constant depending on pressure.*

Taking into account the Mendeleev–Clapeyron equation for one mole of an ideal gas $pv = RT$ we write

$$d\mu = RTp^{-1}\,dp\ .$$

When the pressure changes from $p_1$ to $p_2$ we get

$\Delta\mu = RT \ln ( p_2 / p_1 )$.

At $p_1 = 1$ atm and $p_2 = p$, the expression for the chemical potential of an ideal gas will take the form

$\mu = \mu^\circ + RT \ln p$ ,

where $\mu^\circ$ is the standard chemical potential of an ideal gas at $p = 1$ atm.

In a mixture of ideal gases, the chemical potential of some gas ($\mu_i$) will be equal to

$\mu_i = \mu_1{}^\circ + RT \ln p_i$ ,

*where: $\mu_1{}^\circ$ – standard chemical potential of the i-th ideal gas;*
*$p_i$ is the partial pressure of the i-th ideal gas.*

### Special properties and versatility of the isobaric-isothermal potential.

Closed and open systems are real. They exchange energy with the environment, so when searching for a criterion for the spontaneous occurrence of a process, one should take into account not only the change in entropy, but also the change in energy.

That processes occur spontaneously that involve the release of heat, i.e. exothermic processes, in other words, the system tends to minimize energy, and on the other hand, it tends to increase disorder, i.e. to maximum entropy.

A parameter that takes into account both opposing tendencies of the system - during spontaneous processes is another thermodynamic function - the isobaric-isothermal potential or Gibbs energy, G. The change in Gibbs energy is calculated using the equation

$$\mathbf{\Delta G = \Delta H - T\,\Delta S} \quad (1)$$

*where ΔH is the enthalpy term. It reflects the tendency of the system to a - minimum of energy .*

According to the first law of thermodynamics, ΔH characterizes the total energy reserve of a system at constant pressure and temperature: $\mathbf{Q_1 = \Delta H}$.
T·ΔS is *the entropy term* ; it characterizes the system's tendency toward maximum disorder. According to the second law of thermodynamics at T = const, this is the part of the heat received by the system that is wasted uselessly , bound heat: $\mathbf{Q_2 = T \cdot \Delta S}$.

+Δ *G is called free energy* - part of the remaining energy, $\Delta G = Q_1 - Q_2$, which can be converted into work, i.e. when it is consumed, a spontaneous process can occur and decrease. Consequently , ΔG is *a criterion for the possibility of a spontaneous process* at constant pressure and temperature (P = const, T = const).

***Equation (1) is called the combined equation of the first and second principles of thermodynamics .***

**, only such processes can spontaneously occur as a result of which the Gibbs energy decreases**

$$\mathbf{\Delta G < 0} \quad (2)$$

***This mathematical expression of the second law of thermodynamics is a - universal criterion for the spontaneous occurrence of a reaction and any process.***

If ΔG > 0, then under these conditions the reaction cannot proceed spontaneously .
If ΔG = 0, then the system is in a state of equilibrium, the Gibbs energy has reached its minimum value and does not change anymore.

To determine the possibility of a spontaneous reaction:

a) *under standard conditions,* the change in the Gibbs energy of the reaction is calculated using Hess's law, as in the case of other thermodynamic functions (ΔH and ΔS):

$$\Delta G^\circ\text{reaction} = \Sigma\, i \cdot \Delta G^\circ_{298}\,\text{products} - \Sigma\, i \cdot \Delta G^\circ_{298}\,\text{starting substances} \quad (3)$$

*where ΔG° kJ/mol are the tabulated values of the standard Gibbs energy of - substance formation.*

b) *for non-standard conditions,* ΔG reactions are calculated using the combined equation of the first and second laws of thermodynamics. To do this, the enthalpy of the reaction ΔH° and the entropy of the reaction ΔS° are preliminarily calculated.
Analyzing the combined equation, we can conclude that reactions can occur spontaneously (i.e. $\Delta G^\circ < 0$):

***- exothermic ($\Delta H°<0$), if |ΔHreactions| > |T·ΔSreaction|, i.e. at low temperatures, when the enthalpy term is greater than the entropy term.***

***- endothermic ($\Delta H°>0$), if |ΔHreactions| < |T·ΔSreaction|, i.e. at high - temperatures, when the entropy term is greater than the enthalpy term.***

## 14 -Lecture.

## Subject: Thermodynamics of chemical equilibrium.

Thermodynamics of chemical equilibrium. Isothermal, isobaric and isochoric equations of chemical reactions. Equilibrium constants.

### Dependence of the equilibrium constant on temperature. Isobar equation for a chemical reaction.

It was shown above that the equilibrium constant of the reaction depends only on temperature. The form of this dependence can be found using the Gibbs-Helmholtz equation, presented in the form (21)

$$\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}=-\frac{\Delta H}{T^2}$$

The equation is valid for any change in the Gibbs energy, including the standard one

$$\frac{\partial\left(\frac{\Delta G^\circ}{T}\right)}{\partial T}=-\frac{\Delta H^\circ}{T^2}.$$

Using the relationship between ΔG° and the equilibrium constant ($\Delta G° = –RT\ln K$), we obtain the equation for the isobar of the chemical reaction

$$\left(\frac{\partial \ln K}{\partial T}\right)_p=\frac{\Delta H^\circ}{RT^2} \quad (36)$$

This differential equation is used to qualitatively analyze the dependence of the equilibrium constant on temperature. The sign of the derivative on the left side of the equation is determined by the sign of the right side, which, in turn, depends on the sign of ΔH°.

If $\Delta H° > 0$, then with increasing temperature the equilibrium constant also increases.

If $\Delta H° < 0$, then with increasing temperature the equilibrium constant decreases.

If $\Delta H° = 0$, then the equilibrium constant does not depend on temperature.

The greater the absolute value of ΔH°, the stronger the dependence of Ka on temperature. Note that the qualitative conclusions will not change if we take the value ΔH° or

ΔH under these conditions (P ≠ 1 atm), since ΔH weakly depends on pressure. Therefore, in writing the isobar equation of a chemical reaction, the symbol “°” for the thermal effect is sometimes omitted.

To quantify the K(T) dependence, equation (36) must be integrated. Direct integration leads to the so-called. the Gibbs-Helmholtz equation to calculate the equilibrium constant. This equation is accurate within the accuracy of the empirical characteristics used, but is inconvenient for practical use. Another method for calculating the equilibrium constant was proposed by M.A. Temkin and L.A. Shvartsman. It is also accurate, but more convenient to use. There are also approximate equations, but their use is advisable only in the absence of the necessary reference data on the reagents.

### Calculation of the equilibrium constant of a chemical reaction at various temperatures using the Temkin-Schwartzman method using reference data.

Let us write the above equation (32) in the form:

$$\ln K = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

and substitute into it instead of ΔH° and ΔS° expressions that reflect the dependence of these quantities on temperature, including reference data on the heat capacity of the reagents:

$$\Delta H^\circ = \Delta H^\circ_{298} + \Delta a(T - 298) + \frac{\Delta b}{2}(T^2 - 298^2) - \Delta c'\left(\frac{1}{T} - \frac{1}{298}\right),$$

$$\Delta S^\circ = \Delta S^\circ_{298} + \Delta a \ln\frac{T}{298} + \Delta b(T - 298) - \frac{\Delta c'}{2}\left(\frac{1}{T^2} - \frac{1}{298^2}\right).$$

As a result of substitution and grouping of terms, we obtain:

$$\ln K = -\frac{\Delta H^\circ_{298}}{RT} + \frac{\Delta S^\circ_{298}}{R} + \frac{\Delta a}{R}\left(\ln\frac{T}{298} + \frac{298}{T} - 1\right) + \frac{\Delta b}{R}\left(\frac{298^2}{2T} - \frac{T}{2} + T - 298\right) +$$
$$+ \frac{\Delta c'}{R}\left(1 - \frac{1}{298T} - \frac{1}{2T^2} + \frac{1}{2 \cdot 298^2}\right)$$

or

$$\ln K = -\frac{\Delta H^\circ_{298}}{RT} + \frac{\Delta S^\circ_{298}}{R} + \frac{\Delta a}{R}M_0 + \frac{\Delta b}{R}M_1 + \frac{\Delta c'}{R}M_{-2}, \quad 37)$$

where $M_0$, $M_1$ and M-2 are temperature functions calculated by Temkin and Shvartsman and given in reference books.

## 15 -Lecture.
## Subject: Third law of thermodynamics.

## Third law of thermodynamics. Expression of the concept of heat capacity from the point of view of quantum mechanics. Berthelot's principle.

**Third law of thermodynamics. The concept of chemical affinity.** It is known that many substances react with each other easily and quickly, other substances react with difficulty, and still others do not react. Based on this, it was assumed that there is some kind of chemical affinity between substances.

1st assumption - the measure of chemical affinity was the reaction rate.

2nd assumption - ***M. Berthelot*** and ***H. Thomson*** stated that the measure of chemical affinity is **the thermal effect** .

3rd assumption – max A (van't Hoff). If *max A* > 0, then chemical affinity between substances exists, and the reaction proceeds from left to right. If $A_{\max} <$ 0 >, then there is no chemical affinity between the substances, and the reaction proceeds from right to left. If $A_{\max} = 0$, then the reaction proceeds both back and forth. Based on this, the third law of thermodynamics was created; ***M. Berthelot*** and ***H. Thomson*** , studying the behavior of thermodynamic systems at low temperatures, in 1906 discovered that at low temperatures there is a so-called chemical affinity between substances, which they defined as the thermal effect, they established that the thermal effect $Q_v – A_{\max}$ in condensed systems at low temperatures, where $A_{\max}$ – maximum work.

$$A_{\max} = Q_V - T\left(\frac{\partial \Delta F}{\partial T}\right)_{V_1 T},$$

but in fact it is not max, based on the Helmholtz equation.

In order for the work to be max, it must be equal to the thermal effect $A_{\max}$ \u003d $Q_v$, you need to calculate:

$$\lim_{T\to 0}\left(\frac{\partial \Delta F}{\partial \delta}\right)_{V,T} = 0,\ T \to 0,$$

$\Delta F = Q_v$.

**Analytical expressions of the third law of thermodynamics:**

$$\lim_{T\to 0}\left(\frac{\partial \Delta F}{\partial T}\right) = \lim_{T\to 0}\left(\frac{\partial Q_V}{\partial T}\right) = \lim_{T\to 0}\left(\frac{\partial \Delta U}{\partial T}\right) = 0 \ -$$

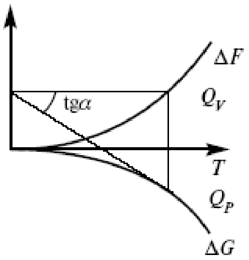
these are isochoric-isothermal conditions.

If $A_{\max} = Q_P$, ? $G$ , $Q_p$, ?H – functions

$$\lim_{T\to 0}\left(\frac{\partial \Delta G}{\partial T}\right) = \lim_{T\to 0}\left(\frac{\partial Q_P}{\partial T}\right) = \lim_{T\to 0}\left(\frac{\partial \Delta H}{\partial T}\right) = 0 \ -$$

These are isobaric-isothermal conditions.

**Nernst's thermal theorem** (third law of thermodynamics) (Fig. 16)



*Rice. 16*

Energy ( $\Delta U$, $\Delta H$, $QV$ , $QP$ , $\Delta F$, $\Delta G$), $tg\alpha$ the angle of inclination of a straight line - gives the temperature coefficient of any function.

For reactions occurring in **condensed systems** as the temperature approaches absolute zero, the max work and thermal effect curves are connected and have one large tangent parallel to the temperature axis.

**Corollaries from the third law of thermodynamics:**

1. Properties of entropy near absolute zero – Planck's postulate:

$\Delta F = \Delta U - T\Delta S.$

Продифференцируем по $T \rightarrow \left(\frac{\partial \Delta F}{\partial T}\right) = \frac{\partial \Delta U}{\partial T} - T\left(\frac{\partial \Delta S}{\partial T}\right) - \Delta S$

$$\lim_{T\to 0}\left(\frac{\partial \Delta F}{\partial T}\right) = \lim_{T\to 0}\left(\frac{\partial \Delta U}{\partial T}\right) - \lim_{T\to 0}\left(\frac{\partial \Delta S}{\partial T}\right) - \lim_{T\to 0}(\Delta S),$$

$$\lim_{T\to 0}\Delta S^0 = 0 \text{ —}$$

absolute entropy.

2. Heat capacity $C_p$, $C_v$

$$\Delta C_P = \frac{\Delta H}{\Delta T},$$

$$\lim_{T \to 0} \frac{\partial \Delta H}{\partial T} = 0,$$

$$\lim_{T \to 0} \Delta C_P = 0,$$

$$\Delta C_V = \frac{\Delta U}{\Delta T},$$

$$\lim_{T \to 0} \frac{\partial \Delta U}{\partial T} = 0,$$

$$\lim_{T \to 0} \Delta C_V = 0.$$

3. The coefficient of thermal expansion of the body and thermal pressure.

$$\gamma = \lim_{T \to 0} \left( \frac{\partial V}{\partial T} \right) = 0,$$

$$v = \lim_{T \to 0} \left( \frac{\partial P}{\partial T} \right) = 0.$$

Ideal gases do not obey the third law of thermodynamics, since a gas near absolute zero is called degenerate.

$C_P - C_V = R$ near absolute zero – Mayer’s equation does not work.

4. About the impossibility of reaching absolute zero. The third law of thermodynamics is an approximate law. Used for perfect crystal of any substance.

## 16 -Lecture.

## Topic: Nernst's theorem and Planck's postulate.

Nernst's theorem and Planck's postulate. Methods for calculating equilibrium constants using thermodynamic functions.

Solving the problem of determining the conditions of chemical equilibrium was greatly facilitated after the discovery of the thermal theorem by Nernst in 1906 .

Using Nernst's thermal theorem, it is possible to determine the numerical value of the integration constant I, provided that T = 0 K and the reaction proceeds between substances in a condensed state.

Nernst's thermal theorem is a statement that as T -> 0 for any processes, the change in entropy tends to zero. The former name The Third Law of Thermodynamics is no longer used due to the development of statistical methods for calculating entropy.

The third law of thermodynamics , or heat theorem, was formulated by Nernst in 1906 and is therefore often called by his name. The works of M. Planck (1911) were of great importance in the development of this theorem. Nernst's thermal theorem has the following formulation: at absolute zero, the entropy of any homogeneous body is equal to zero.

Properties of matter near absolute zero . From the third law of thermodynamics a number of consequences can be obtained concerning the properties of substances near absolute zero. The third law of thermodynamics (W. Nernst's theorem taking into account M. Planck's postulate) states that in an isolated system at T=OK, entropy tends to some constant value 3 8, independent of the nature of the influence on the system. In particular, if at T = OK the system is in stable equilibrium , then 8 = 0. This means that at absolute zero the heat capacity of the system is Cy = O, which means that it is impossible to carry out such a process as a result of which the system reaches absolute zero , although this value can be approached as close as desired. Therefore, the third law is known as the principle of the unattainability of absolute zero temperatures.

Unlike internal energy $U$and enthalpy, $H$entropy can be defined in absolute terms S. This possibility does not directly follow from the second law of thermodynamics, but appears only when using Planck's postulate, also called the third law of thermodynamics. Experimental data show that the heat capacities Cp $_{of}$ all substances at T→0K sharply drop to negligible values (for crystals Cp $_{decreases}$ in proportion to T3 $_{)}$. The ratio $\frac{C_p}{T}$ decreases sharply, because C $_p$ decreases faster than T.

The result of the generalization of experimental data was the thermal theorem of Nernst (1906), which states: near 0, all processes occur without a change in entropy (or with a negligible change). The mathematical expression of Nernst's theorem is as follows:

$$\lim \Delta S = 0,$$

T → 0K.

Planck (1911) expanded Nernst’s thermal theorem, considering that at T $_0$= 0K, not only ΔS = 0, but also S = 0, then

$$\lim S = 0,$$

T → 0K.

According to Planck's postulate, the entropy of a perfect crystal at OK is zero.

This provision does not apply to defective crystals, glasses, solid solutions, etc. For them, entropy at 0K is negligible, but not equal to 0 (S>0). In real crystals there are negligible impurities, defective structures are observed, and the entropy is low, but S>0.

Thus, Planck's postulate is valid only for correctly formed crystals. Therefore, we can take S $_0$ $_{=0}$ as the reference point . Planck's postulate turned out to be very important for chemists, because an initial reference point has appeared (S $_0$ =0 at T $_0$ =0) and the absolute value of S can be calculated at any temperature. Typically, the value of S is calculated for a substance in the standard state (p $_0$ = 1 atm, T = 298 K), expressed in S ° $_{298}$ ( ) or ( ) and tabulated.

The equation for calculating the absolute value of entropy S is:

To calculate entropy, data on heat capacity are required, determined in the range of low temperatures and the heat of phase transitions of substances. If a substance has more than one modification in the solid state, you need to add the corresponding terms to the right side of the equation.

The value of entropy in a complex way reflects the entire set of properties of a compound in a given state of aggregation. It depends on the molecular weight - for related substances it increases with its growth; from the state of aggregation – increases during the transition from solid→liquid→gas; on the crystal structure (for example, graphite, diamond); on the isotopic composition ($H_2$ and $D_2$, $H_2O$ and $D_2O$), on the structure of the molecules (n-butane and isobutane).

If entropy values are needed under other conditions (different from standard ones), S is recalculated using special equations.

The change in entropy can be calculated by knowing the entropies of all substances participating in the reaction (taking into account stoichiometric coefficients):

The magnitude of the change in entropy is used to determine the possibility of a process occurring spontaneously (in isolated systems), as well as to calculate chemical equilibria.

## 17-Lecture.

## Topic: Basic concepts of statistical thermodynamics.

Macro and micro conditions and thermodynamic probability. Boltzmann equation. Amount depending on circumstances.

It is necessary to connect the concepts of phenomenological thermodynamics with atomic-molecular theories. In a narrow sense, the task is to express thermodynamic quantities in terms of molecular parameters. The macrostate of the system is characterized by thermodynamic parameters: temperature, pressure, volume. The macrostate corresponds to internal energy, entropy, Gibbs energy, etc. To set the microstate of the system, it is necessary to accurately characterize the instantaneous state of each of the particles included in the system (momentum, coordinates of each particle). One macrostate can correspond to many microstates. Let us denote the number of microstates of a given macrostate by the letter W. W is the thermodynamic probability of the state. Unlike ordinary probability, thermodynamic probability is not normalized, i.e. $W \geq 1$. Qualitative relationship between entropy and the number of microstates of the system. An increase in the number of microstates means an increase in chaos. It is intuitively clear that chaos grows during equilibrium melting, evaporation and sublimation. The gaseous state is more chaotic, etc. We know that the entropies of melting and evaporation, calculated using the formulas of phenomenological thermodynamics, are positive quantities. So, an increase in chaos is, as a rule, an increase in the number of microstates and an increase in entropy. Entropy as a function of W. What form does the functional dependence S have? f W =( ) ? Let our system consist of two loosely coupled parts (for example, a piece of iron and neon gas above it). The entropy of the system as a whole will be the sum of the entropies of the two parts. The thermodynamic probability of the system as a whole will be equal to the product of the thermodynamic probabilities of the subsystems, since any microstate of iron can combine with any of the microstates of neon. So:

$S = f(W)$.

$$S_{Ne}+S_{Fe}=f(W_{Fe})+f(W_{Ne})=f(W_{Ne}\times W_{Fe})=S_{Fe+Ne} \quad (1)$$

Relation (1) will be satisfied if the function f is a logarithm. That's why

$$S=f(W)=k\ln W \quad (2)$$

$k=\dfrac{R}{N_A}$ – множитель, имеющий размерность энтропии.

Equation (2) defines a quantity that can be called a statistical analogue entropy. The choice of k as a multiplier should ensure that the statistical analogous to phenomenological entropy defined in Lecture 4.

Let's consider a system with constant energy, constant number of particles (we used to say "number of moles") and constant volume. The system has not reached equilibrium, but it is moving towards it.

At the moment of equilibrium, entropy should reach a maximum. The equilibrium state must correspond to the maximum number of microstates. To count the number of microstates, a model of the system is needed.

## Boltzmann cell method.

In a system of N particles, the total energy U=E and volume V are given.

The system has r energy levels at which particles can be located. Values the particle energies at the levels, εi, are given. The energy of the system, E, consists of the energies individual particles:

$$N=n_1+n_2+n_3+\ldots n_r$$

$$E=n_1\varepsilon_1+n_2\varepsilon_2+n_3\varepsilon_3+\ldots n_r\varepsilon_r \quad (3) \qquad V = \text{const}$$

The macrostate is specified by indicating the number of particles at each energy level.

The microstate is specified by indicating the numbers of particles located at each level. In Boltzmann's method, the particles are distinguishable and each can be assigned a number.

Let's count the number of microstates for a system of three particles located at three energy levels,

$E=6,\ \varepsilon_1=1,\ \varepsilon_2=2,\ \varepsilon_3=4$. Рассмотрим макросостояния *1* $(n_1=2,\ n_2=0,\ n_3=1)$ и *2* $\left(n_1=0,\ n_2=3,\ n_3=0\right)$ (см. рис. 1)

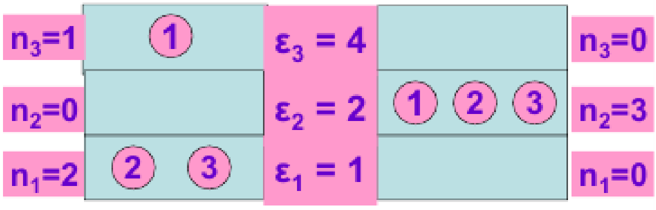
**The number of microstates (thermodynamic probability of a macrostate) can be calculated using the formula:**

$$W = \frac{N!}{n_1!\,n_2!\,n_3!}, \quad W(1) = 3,\ W(2) = 1$$

The first macrostate has three microstates, the second has one.

General formula for counting the number of microstates ( N particles, r levels)

$$W = \frac{N!}{n_1!\,n_2!\,n_3!\ldots n_r!}$$



$$W = \frac{3!}{1!0!2!} = 3 \qquad W = \frac{3!}{0!3!0!} = 1$$

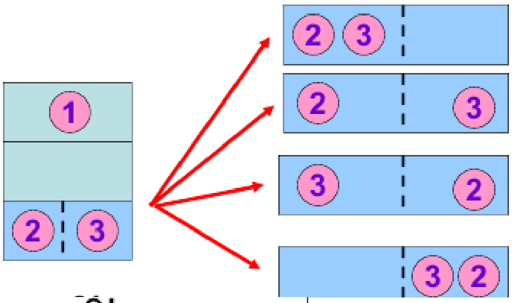
Rice. 1. Counting the number of microstates in the Boltzmann cell method.

Accounting for degeneracy.

Level degeneracy (number!) is the number of levels with the same energy. Let in our example, the degeneracy of level 1 is 2. Level 1 is, as it were, split into two

compartments with the same energy ε 1. Then each of the previous microstates of macrostate 1 will be divided into 4 (see Fig. 2):

$z^{n_1} = 4$ ( z – degeneracy, n 1 – number of particles at the level).



$$W = \frac{3!}{1!0!2!} \times 2^2 = 12$$

Fig.2. Counting the number of microstates taking into account degeneracy.

General formula for W :

$$W = \frac{N!}{n_1!n_2!\ldots n_r!} \times \prod_{i=1}^{r} z_i^{n_i}$$ (5)

$$\ln W = \ln(N!) - \ln(n_1!) - \ln(n_2!) \ldots - \ln(n_r!) + \sum_{i=1}^{r} n_i \ln z_i$$ (6)

Let us find the maximum of W when the values of ni change and conditions (3) are met.
The energy structure of the system is given. The number of particles at levels changes.
The maximum W (the state with the maximum number of microstates) must correspond to the maximum entropy, i.e. equilibrium state of the system. We use the Stirling formula (it is valid for large N):

$$\ln N! = N \ln N - N$$ (7)

$$\ln W = N \ln N - N - n_1 \ln n_1 - n_2 \ln n_2 \ldots - n_r \ln n_r +$$

$$+ \sum_{i=1}^{r} n_i + \sum_{i=1}^{r} n_i \ln z_i$$ (8)

**Let us find the maximum ln W, considering the number of particles at levels ni as variables**

$$d \ln W = 0$$

$$d\ln W = -(\mathrm{Ln}\, n_1 + 1)dn_1 - \ldots(\mathrm{Ln}\, n_r + 1)dn_r + \sum_{i=1}^{r} \ln z_i dn_i =$$

$$-(\mathrm{Ln}\, n_1 + 1 - \ln z_1)dn_1 - \ldots(\mathrm{Ln}\, n_r + 1 - \ln z_r)dn_r = 0$$ (9)

Поскольку $\sum dn_i = dN = 0$ , единицы в скобках исчезают. Получаем

$$-(\mathrm{Ln}\, n_1 - \ln z_1)dn_1 - \ldots(\mathrm{Ln}\, n_r - \ln z_r)dn_r = 0$$ (10)

It is necessary to find a set of ni that satisfy relation (10) and additional conditions (3). In differential form, conditions (3) have the form

$$\sum_{i=1}^{r} dn_i = 0$$ (eleven)

$$\sum_{i=1}^{r} \varepsilon_i dn_i = 0$$ (12)

Finding the conditional extremum ln W by Lagrange method. Let's multiply equation (10) by (-1), condition (11) by a constant ( α ), and condition (12) by ( β ) and add (10), (11) and (12):

$$(\ln n_1 + \alpha + \beta\varepsilon_1 - \ln z_1)dn_1 + (\ln n_2 + \alpha + \beta\varepsilon_2 - \ln z_2)dn_2 +$$

$$\ldots..(\ln n_r + \alpha + \beta\varepsilon_r - \ln z_r)dn_r = 0$$ (13)

Let us assume that the extremum has been reached, and the values of the variables n1, n2 in the first two
brackets correspond to it.

Let us select the constants α and β in such a way that the first two brackets become zero.
This can always be done, since there are two constants, and there are also two brackets (equations).
The remaining brackets must be equal to zero, since the remaining ni are independent variables.
Now additional conditions (3) are taken into account, (r-2) variables can be considered as independent and for the left side to be equal to zero, each of the (r-2) brackets must be equal to zero

$$\left(\ln n_i + \alpha + \beta\varepsilon_i - \ln z_i\right) = 0 \qquad n_i = z_i e^{-\alpha-\beta\varepsilon_i} \text{ для любого i.}$$

Просуммируем $n_i$:

$$\sum_{i=1}^{r} n_i = N = \sum_{i=1}^{r} z_i e^{-\alpha-\beta\varepsilon_i} = e^{-\alpha}\sum_{i=1}^{r} z_i e^{-\beta\varepsilon_i} \tag{14}$$

$$e^{-\alpha} = \frac{N}{\sum\limits_{i-1}^{r} z_i e^{-\beta\varepsilon_i}} = \frac{N}{Q}; \quad Q = \sum_{i=1}^{r} z_i e^{-\beta\varepsilon_i} \tag{15}$$

$$n_i = \frac{N}{Q} z_i e^{-\beta\varepsilon_i} \tag{16}$$

The quantity Q is called the sum over states for an individual particle or the molecular sum over states. The summation is carried out over all levels accessible to our particle. In the exponent, the exponents are the level energies, εi . Size

$$\rho_i = \frac{n_i}{N} = \frac{z_i e^{-\beta\varepsilon_i}}{Q} \tag{17}$$

или

$$\rho_i = \frac{n_i}{N} = \frac{z_i}{N}\frac{1}{e^{\alpha+\beta\varepsilon_i}} \tag{18}$$

let's call it the probability of finding a particle at level i . This concludes our consideration of the Boltzmann cell method. Note, however, that the way is open for calculating thermodynamic probability and entropy. Substituting expressions (16) for ni into formula (8) for lnW , we obtain an expression relating entropy to the sum by state:

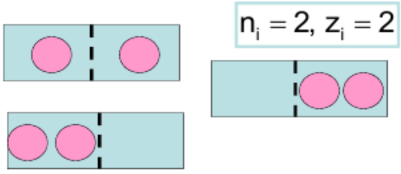
$$S = k\ln W = -k\sum_i n_i \ln\left(e^{-\beta\varepsilon_i}\right) + kN\ln Q = k\beta E + kN\ln Q \tag{19}$$

The Boltzmann model can only be applied to an ideal gas (a system of non-interacting particles).
Disadvantages of Boltzmann statistics: distinguishability of particles, use of the Stirling formula, impossibility of application to systems with interacting particles.

Bose-Einstein statistics.

This model uses a method for calculating the number of microstates that differs from formula (5). The laws of quantum physics are taken into account.

The particles are indistinguishable (the disadvantage of Boltzmann statistics is eliminated). Exchange between levels does not lead to the emergence of new microstates. Different microstates arise due to degeneracy at the same level. We need to distribute ni particles into zi boxes. Example: ni =2, zi = 2. Wi =3 (see Figure 3).



$$W_i = \frac{(n_i + z_i - 1)!}{n_i!(z_i - 1)!} = 3$$

Rice. 3. Counting the number of microstates at one level according to Bose-Einstein.

Number of microstates of the system

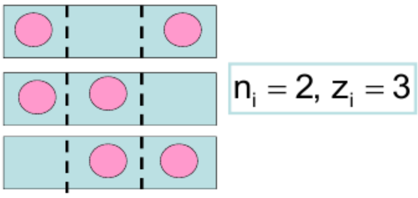
$$W = \prod_i W_i$$

## Fermi-Dirac statistics.

Another version of quantum statistics.

The particles are indistinguishable (the disadvantage of Boltzmann statistics is eliminated). Different microstates arise due to degeneracy. We need to decompose ni particles into zi boxes. Each box can only contain 1 or 0 particles (a limitation imposed by the Pauli principle!).

To solve the problem, you need to select ni occupied boxes from the total number zi . In our example , ni =2, zi = 3, ( see Fig. 4):



$$W_i = \frac{z_i!}{n_i!(z_i - n_i)!} = 3, \quad z_i > n_i$$

Число микросостояний системы $W = \prod_i W_i$

Больцмана:

$$n_i = \frac{z_i}{e^{\alpha + \beta\varepsilon_i}} \tag{20}$$

Бозе:

$$n_i = \frac{z_i}{e^{\alpha + \beta\varepsilon_i} - 1} \tag{21}$$

Ферми – Дирака

$$n_i = \frac{z_i}{e^{\alpha+\beta\varepsilon_i}+1} \qquad (22)$$

При больших значениях экспоненты $(e^{\alpha+\beta\varepsilon_i} \gg 1)$ формулы (20)-(22) неразличимы.

$$dw = \rho(p,q)dpdq \qquad (23)$$

$$\rho(p,q) \geq 0, \quad \int_{\Gamma} \rho(p,q)dpdq = 1 \qquad (24)$$

## 19 -Lecture.

## Subject: Basic law of phase equilibrium.

Basic law of phase equilibrium. Principles of succession and conformity.

### Phase equilibrium

The concept of phase, component (component), degree of freedom. Gibbs phase rule. One-component systems. Diagram of the state of water and sulfur. The Claperon-Clayusis equation and its integral and differential form .

An illustration of the practical application of the second law of thermodynamics is the Gibbs phase rule (1878), which gives a qualitative characteristic of heterogeneous multiphase equilibrium systems. This rule has received numerous confirmations and various applications.

### 1. Basic concepts and definitions.

Thermodynamic systems, represented by a body or group of bodies, isolated from the environment and in continuous motion, are homo- and heterogeneous.

Homogeneous systems are systems within which there are no interfaces separating parts of the system that differ in properties from each other.

Heterogeneous systems have interfaces within them that separate parts of the system that differ in properties.

It was previously indicated that the state of the system is determined by a set of state parameters (P, T, V ).

Phase ( f ) is a state of matter that is everywhere homogeneous not only in chemical composition, but also in physical properties - this was the definition of this concept given by D. W. Gibbs. The phases are solid, liquid and gaseous.

A component of the system (p) is chemically individual substances that represent the system and are capable of independent existence outside the system.

For example, a system formed by three chemical compounds $NH_4Cl_{(TB)}$, $NH_{3\,(G)}$ and $HCl_{(G)}$ consists of three components.

System component ( k ) - chemical individuals, the smallest number of which is necessary and sufficient for the formation of all phases of a given system.

The number of components is equal to the number of components minus the number of equations ( r ) connecting the components. In the system under consideration. consisting of three components, a reaction of the form is possible:

$$NH_4Cl_{(TV)} \Leftrightarrow NH_{3\,(G)} + HCl_{(G)},$$

therefore the number of components will be equal to two:

$$k = p - r = 3 - 1 = 2.$$

The number of degrees of freedom (c) is the number of independent thermodynamic parameters that determine the state of the system.

Independent are those parameters that can be arbitrarily set or changed without this entailing a change in other independent state parameters, and when changing independent state parameters, the number of phases in the system should not change.

To calculate the number of degrees of freedom of the system, you need to subtract the number of equations connecting them from the total number of state parameters.

## 2. Phase rule equation.

Let the system under consideration consist of *f* - phases and k - components, and each of the k - components is present in some quantity in each of *the f* - phases.

Pressure and temperature are the same for all phases of a given system, i.e. There are two general status parameters.

Since each component is in each phase, the possible concentrations of the components in all phases are:

$C'_{I}, C'_{II}, C'_{III}, ..., C'_{f}$ - for the first component;

$C''_{I}, C''_{II}, C''_{III}, ..., C''_{f}$ - for the second component;

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$C^{k}_{I}, C^{k}_{II}, C^{k}_{III}, ..., C^{k}_{f}$ - for the k -th component. (6.1)

The number of possible concentrations of components will be $k \cdot f$. In total, for the system under consideration, the total number of state parameters is equal to ( $k \cdot f + 2$), where the figure takes into account the number of common parameters for all phases of this system - pressure and temperature.

Each phase has its own equation of state.

For example, for the first phase this equation is:

$$\varphi\left(P, T, C'_{I}, C''_{I}, C'''_{I}, ..., C^{k}_{I}\right) = 0 . \quad (6.2)$$

There are as many such equations as there are phases in the system, i.e. *f* - pieces.

The system is in a state of thermodynamic equilibrium, which means the equality of the chemical potentials of the components ( $\mu_i$ ) in all phases of the system, i.e.:

$\mu'_{I} = \mu'_{II} = \mu'_{III} = ... = \mu'_{f}$ - for the first component;

$\mu''_{I} = \mu''_{II} = \mu''_{III} = ... = \mu''_{f}$ - for the second component;

\- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -

$\mu^{k}_{I} = \mu^{k}_{II} = \mu^{k}_{III} = ... = \mu^{k}_{f}$ - for the kth component. (6.3)

The number of rows in the matrix is equal to the number of components ( k ), and the number of columns is ( *f* - 1), then the total number of equations will be:

$$k\,(f - 1).$$

Thus, the total number of equations relating the values of the chemical potentials of the components will be calculated as

$$f + k\,(f - 1).$$

According to the definition, the number of degrees of freedom is equal to the difference between the total number of state parameters and the number of equations connecting these parameters:

$$c = (k \cdot f + 2) - [f + k(f - 1)]$$

or

$$c = k - f + 2. \quad (6.4)$$

i.e. the number of degrees of freedom is equal to the difference between the number of components and phases plus two .

In systems without the participation of a gaseous phase in equilibrium, one of the parameters common to all phases of the system, namely pressure, does not affect the equilibrium in the system if it changes within small limits and is therefore excluded from the general parameters of state. This position applies, in particular, to metal melts and therefore the phase rule equation is written as:

$$c = k - f + 1. \quad (6.5)$$

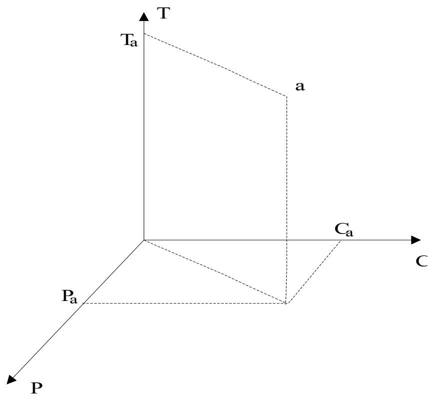
Equilibrium is invariant (variantless) if c = 0, monovariant (single-variant) if c = 1 and divariant (two-variant) if c = 2.

### 3. Geometric image of the equation of state.

It was previously indicated that the state of the system is uniquely determined by an equation of state of the form $\varphi(P, T, C) = 0$. At the same time, the numerical values of the parameters of a particular state determine the position of a certain point (figurative point) in the three-dimensional coordinate system P - T - C (Fig. 6.1).

However, in practice there is no need to always use three-dimensional space to determine the state of the system; it is enough to set only two parameters, since the third will be determined from the equation of state. In other words, to unambiguously determine the state of the system, it is enough to determine the position of a figurative point in a two-dimensional coordinate system, for example P - T or T - C. Such a graphical representation of the equation of state of the system is called state diagram .

It is important to note that, despite the widespread use of equations of state in thermodynamics, they are very approximate, and all attempts to refine them lead to cumbersome formulas, which are difficult to work with. Therefore, state diagrams are of great interest. With their help, using experimental data, it becomes possible to clearly and clearly depict in the form of geometric images the real relationship of thermodynamic parameters that determine the state of the system.



Rice. 6.1. Scheme for determining the state of the system.

### 4. One-component systems.

An example of an on-component system is any substance (element or chemical compound) that has a strictly defined chemical composition in all states of aggregation.

From the equation of state $\varphi(P, T, C) = 0$ it follows that at c = const , the state diagram of a one-component system is constructed on a plane in the P - T coordinate system. Most often, as an example of a diagram of a one-component system, the state diagram of water in the region of low pressures is given (Fig. 6.2).

Curves OM, O N and O Q divide the coordinate field into three regions. Each of them denotes a specific state of aggregation of water:

S - region corresponds to the solid (crystalline) state;

L - region corresponds to the liquid state;
G - region corresponds to the gaseous state;

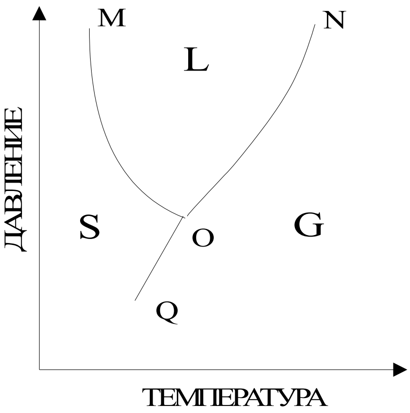
For any point lying inside a particular region, the phase rule determines:

$$c = k - f + 2 = 1 - 1 + 2 = 2,$$

that is, the system has two degrees of freedom. This means that a simultaneous change in pressure and temperature within a given region will not cause a violation of phase equilibrium.

ON line is the geometric location of the points that determine the values of P and T, which ensure the equilibrium coexistence of two phases - liquid and vapor:

$$L \leftrightarrow G.$$



Rice. 6.2. Diagram of the state of water.

At the same time, this curve expresses the dependence of saturated vapor pressure on temperature or the dependence of the boiling point of a liquid on pressure. In this regard, the ON curve is called the evaporation curve .

Line OM - the boundary between region S and region L , which is a set of points corresponding to the state of two-phase equilibrium between the solid and liquid phases:

$$L \leftrightarrow S.$$

Line OM is called melting curve , since it depicts the dependence of the melting temperature of ice on pressure.

Line O Q - sublimation or sublimation curve. The points on this curve correspond to the equilibrium state of the solid and gaseous phases:

$$S \leftrightarrow G.$$

This line establishes the dependence of vapor pressure above the solid phase on temperature and, on the other hand, establishes the influence of pressure on the sublimation temperature.

According to the phase rule equation, the number of degrees of freedom for any point on any curve will be:

$$c = k - f + 2 = 1 - 2 + 2 = 1,$$

that is, the system has one degree of freedom. This means that without disturbing the equilibrium state, you can arbitrarily change only one parameter. In this case, the other parameter must also change in accordance with the equation of the corresponding curve.

The lines ON , OM and OQ have one common point, point O, called the triple point. It determines the parameter values at which liquid, vapor and crystals are in a state of equilibrium. According to the phase rule, the number of degrees of freedom of the system at the triple point is:

$$c = k - f + 2 = 1 - 3 + 2 = 0,$$

which determines the conditions for the equilibrium coexistence of three phases at strictly fixed values of P and T. For water:

$P_0$ \u003d $0.006 \cdot 10^5$ Pa and $T_0$ \u003d 273.0075 K.

## 20 -Lecture.

## Topic : Phase transitions of the first type .

Differential and integral types of Clapeyron-Clausius equations. Calculation of evaporation, liquefaction and sublimation temperatures.

**Phase equilibrium conditions. Phase diagrams.**

Experience shows that the same homogeneous substance, depending on external conditions, can be in different states, i.e. have different macroscopic properties (for example: density, viscosity, conductivity, etc.), and vice versa, under given external conditions in thermal equilibrium, a substance can not exist as a homogeneous body, but disintegrate into two or more contacting homogeneous parts located in different macroscopic states. Such states are called phase states of matter. From the point of view of thermodynamics, a phase is any homogeneous system whose macroscopic properties are the same at all points. Examples of such states can be aggregate states of matter - gaseous, liquid, solid, homogeneous states differing in chemical composition, various amorphous and crystalline modifications of a solid. The concept of a phase state is much broader than the concept of the aggregate state of a substance. We can say that a phase state is a concept based on the difference in the nature of the structural organization of a substance at the molecular level. For example, polymorphic crystalline modifications of a certain substance are different phase states that differ in the nature of the relative arrangement of atoms and molecules. Strictly speaking, the concept of a state of aggregation is not precisely defined. We can say that the aggregate - gas, liquid and solid states of matter primarily differ in the nature of the thermal movement of atoms and molecules.

The conditions for the equilibrium existence of a multiphase system (without taking into account the features associated with the properties of the phase interface) are reduced to the constancy of intensive parameters throughout the entire system under consideration. These conditions are easily derived from the principle of maximum entropy for an isolated equilibrium system. For example, from the requirement for the maximum entropy of a two-phase system $S = S_1 + S_2 = \max$ (that is, the variation $d S = 0$), with the state of all parts of the system unchanged, the condition follows that the derivative is equal to zero

$$\frac{\partial S}{\partial N_1} = \frac{\partial S_1}{\partial N_1} + \frac{\partial S_2}{\partial N_2}\frac{\partial N_2}{\partial N_1} = 0 ,$$

where $N_1$ and $N_2$ are the numbers of particles in the first and second phases, respectively. Under the condition of constancy of the total number of particles $N_1 + N_2 = N = \text{const}$, i.e.

$$\frac{\partial N_2}{\partial N_1} = -1 ,$$

we get:

$$\frac{\partial S_1}{\partial N_1} = \frac{\partial S_2}{\partial N_2}$$

From the basic thermodynamic equation

$$dE = TdS - PdV + \mu dN$$

presented as

$$dS = \frac{dE}{T} + \frac{P}{T}dV - \frac{\mu}{T}dN$$

it follows that for constant E and V

$$\frac{\partial S}{\partial N} = -\frac{\mu}{T}.$$

Thus, the phase equilibrium condition reduces to the equation

$$\frac{\mu_1}{T_1} = \frac{\mu_2}{T_2}$$

and since in equilibrium $T_1 = T_2$, we finally get

$$\mu_1(T,P) = \mu_2(T,P) \quad (3.1)$$

Consequently, the two phases can be in equilibrium only at such values of temperature and pressure that satisfy equation (3.1). When the pressure changes, the coexistence temperature of the phases changes. This dependence P = P(T) can be depicted graphically on a phase diagram.

In Fig. 3.1 shows an example of such a diagram, depicted in coordinates P,T . Curve 1, determined by the equality of the chemical potentials of the liquid and gaseous phases, separates the regions of existence of the liquid and gaseous phases on the phase diagram. Similarly, curves 2 and 3 correspond to liquid-solid and gas-solid equilibrium. The common point of all three equilibrium lines is called the triple point. At this point, all three phases can exist simultaneously. Since three phases of a substance can simultaneously be in equilibrium only at a certain temperature, triple points are a convenient standard for the temperature scale. To reproduce them, you do not need to worry about maintaining a certain pressure, as is required, for example, when choosing the melting point of ice as a standard point. Currently, the triple point of water, equal to 273.16 K, is chosen as the standard for defining the absolute temperature scale.

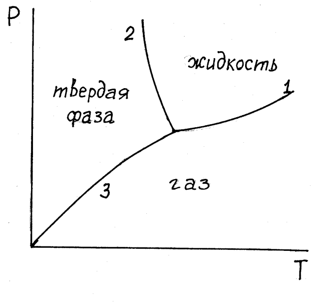


Fig.3.1.

The phase diagram can also be depicted in other coordinates - T,V or P,V, where V is the volume occupied by a certain amount of substance. In such diagrams, states in which two phases coexist, unlike P,T diagrams, fill the entire region of the plane. This is due to the fact that two-phase equilibrium systems always have the same temperatures and pressures, while the specific volumes of these phases differ. Figure 3.2 shows an example of a T,V gas-liquid diagram. The shaded area corresponds to two-phase states when liquid and gaseous phases coexist simultaneously

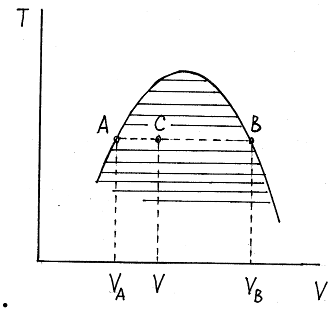


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Fig.3.2.

For example, point C in Fig. 3.2 is a state in which the volumes of gaseous and liquid phases Vq + V $_1$ = V are related in accordance with the so-called lever rule

$$\frac{V_q}{V}=\frac{AC}{AB}\ \frac{V_l}{V}=\frac{BC}{AB}\ .$$

The phase diagram looks similar in coordinates P,V

**Clayperon-Clausius equation.**

. It is very difficult to find a universal analytical expression for the phase equilibrium curve, since there are often no analytical relationships for the chemical potentials of the phases, but it is quite simple to obtain a differential equation for the phase equilibrium curve.

Differentiating equation (3.1), we obtain the relation

$$\left(\frac{\partial \mu_1}{\partial T}\right)_P dT+\left(\frac{\partial \mu_1}{\partial P}\right)_T dP=\left(\frac{\partial \mu_2}{\partial T}\right)_P dT+\left(\frac{\partial \mu_2}{\partial P}\right)_T dP\ ,$$

from which follows

$$\frac{dP}{dT}=\frac{\left(\frac{\partial \mu_2}{\partial T}\right)_P-\left(\frac{\partial \mu_1}{\partial T}\right)_P}{\left(\frac{\partial \mu_1}{\partial P}\right)_T-\left(\frac{\partial \mu_2}{\partial P}\right)_T} \quad (3.2)$$

Equation (3.2) makes sense if the difference of the corresponding derivatives is not equal to zero, that is

$$\left(\frac{\partial \mu_2}{\partial P}\right)_T-\left(\frac{\partial \mu_1}{\partial P}\right)_T=v_2-v_1\neq 0$$

$$\left(\frac{\partial \mu_2}{\partial T}\right)_P-\left(\frac{\partial \mu_1}{\partial T}\right)_P=s_2-s_1\ ,$$

where n 1.2 and s1.2 are the specific volumes and entropies of the corresponding phases. Taking into account that s $_2$ - s $_1$ = q/T, where q is the specific heat of phase transition, we obtain the differential equation of the phase equilibrium curve, which is called the Clausius-Clausius equation:

$$\frac{dP}{dT}=\frac{q(T)}{T(v_2-v_1)} \quad (3.3)$$

Phase transformations in which the first derivatives of the thermodynamic potential undergo a discontinuity are called first-order phase transitions. Sometimes they are also called discontinuous phase transitions, in contrast to continuous phase transitions (or phase transitions of the 2nd order), in which the first derivatives are continuous.

The phase equilibrium curve defined by equation (3.1) is called the binodal, or saturation line. In the space (m ,P,T), the binodal is formed by the intersection of the surfaces m 1(P,T) and m 2(P,T). In Fig. Figure 3.3 shows the trace of these surfaces on the plane P =const and T =const using the example of a gas-liquid phase transition.

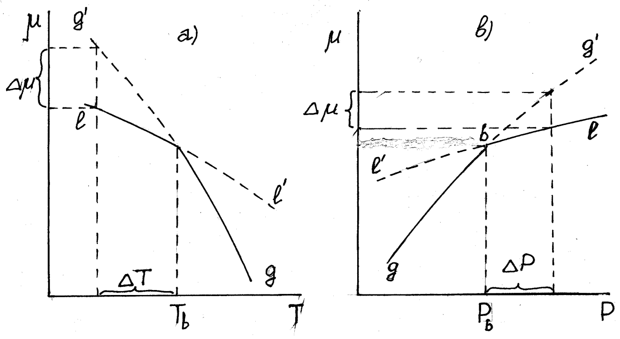


Fig.3.3.

When passing through the binodal, the chemical potential does not undergo any peculiarities, i.e. point b - the trace of the binodal on the corresponding plane - is not a singular point of the functions m 1(P,T) and m 2(P,T). This means that the initial phase state can exist during the transition through the binodal, but it will no longer be thermodynamically stable. For example, at T < Tb in Fig. 3.3a or at P > Pb in Fig. 3.3bmg > m 1 and, therefore, the gaseous phase becomes unstable compared to the liquid phase, but nevertheless can exist as metastable. We will discuss the reason for the existence of metastable phases further. Here we note that such phases are stable only with respect to small changes in the parameters of the system, i.e. in this case, this means that the metastable phase state is stable only to small heterophase fluctuations. The characteristic size of heterophase fluctuations is determined by the degree of deviation of the temperature and pressure of the system from the values set by the binodal and, ultimately, the corresponding difference in chemical potentials (Fig. 3.3).

**Thermodynamic stability of a single-phase state of matter.**

The question arises how far one can advance into the region of metastable states. Let us consider the theory of phase stability with respect to continuously changing thermodynamic parameters. This theory was formulated by Gibbs on the basis of the basic thermodynamic inequality, which we present here in the form

$\Delta T \Delta S - \Delta P \Delta V \geq 0$ (3.4) where D - means finite difference. Let us choose entropy and volume as independent variables and denote their virtual changes by d S and d V.

$$\left(\frac{\partial T}{\partial S}\right)_V (\delta S)^2 + \left(\frac{\partial T}{\partial V}\right)_S \delta V\,\delta S - \left(\frac{\partial P}{\partial V}\right)_S (\delta V)^2 - \left(\frac{\partial P}{\partial S}\right)_V \delta S\,\delta V > 0 \qquad (3.5)$$

Let us express the partial derivatives in (3.5) in terms of the corresponding partial derivatives of the internal energy E. We obtain the following expression:

$$E_{SS}\,(\delta S)^2 + E_{SV}\,\delta V\,\delta S + E_{VV}\,(\delta V)^2 + E_{VS}\,\delta S\,\delta V > 0,$$

which is a quadratic form with respect to the variables d S and d V.

$$E_{SS}\,(\delta S)^2 + 2E_{SV}\,\delta V\,\delta S + E_{VV}\,(\delta V)^2 > 0 \qquad (3.6)$$

As is known, a necessary and sufficient condition for the positive definiteness of a real quadratic form is the fulfillment of the following inequalities:

$$E_{SS} = \left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V} > 0 \qquad (3.7)$$

$$E_{SS}E_{VV} - E_{SV}^2 > 0 \qquad (3.8)$$

from which it also follows that Evv is positive definite:

$$E_{VV} = -\left(\frac{\partial P}{\partial V}\right)_S > 0 \qquad (3.9)$$

Inequality (3.8) is equivalent

$$\frac{T}{C_V}\left(\frac{\partial P}{\partial V}\right)_T < 0$$

and since, according to (3.7), the heat capacity at constant volume is Cv > 0, this is equivalent to the condition:

$$\left(\frac{\partial P}{\partial V}\right)_T < 0 \qquad . (3.10)$$

The expression D =EssEvv - $E^2$sv is called the adiabatic determinant of stability, and the equation

$$E_{SS}S_{VV} - E_{SV}^2 = 0 \qquad (3.11)$$

equivalent to the equation:

$$\left(\frac{\partial P}{\partial V}\right)_T = 0 \qquad (3.12)$$

determines the line of absolute phase instability, which is called the spinodal. Thus, the region of metastable states is limited by the spinodal.

Let's consider the classical vapor-liquid phase diagram in P -V coordinates Fig. 3.4).

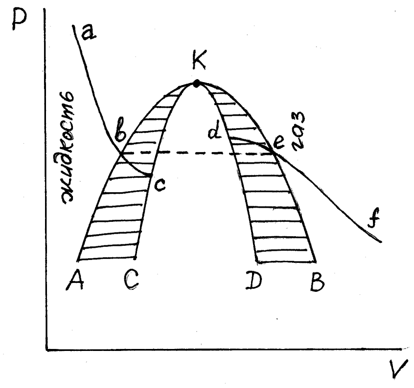


Fig.3.4.

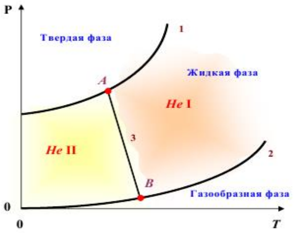
The saturation curve – the AKB binodal limits the region of two-phase vapor-liquid states. To the left of the binodal is the region of the liquid phase, to the right - the gas phase. Consider the abcdef isotherm. Section abc refers to the liquid phase, and all points of section ab represent a sequence of thermodynamically equilibrium states in which inequality (3.10) is strictly satisfied. In section bc, the liquid phase becomes metastable, but inequality (3.10) is also satisfied except for point c, at which isothermal compressibility becomes zero.

Similarly, for the gas isotherm fed, inequality (3.10) is satisfied both for the section fe (thermodynamically equilibrium states) and for the section ed - metastable supersaturated vapor, with the exception of point d. Thus, the CKD line, which is called the spinodal, limits the region where the substance cannot exist as a single-phase substance under any conditions. Shaded in fig. 3.4 regions correspond to single-phase metastable states (on the left - superheated liquid, on the right - supercooled steam). It is interesting to note that the section of the bc isotherm can even cross the x-axis, i.e. superheated liquid may have negative pressure.

At points b and e, not only the specific volumes of liquid V1 and gas Vg differ, but also the compressibility values:

$$\left(\frac{\partial P}{\partial V}\right)_b \neq \left(\frac{\partial P}{\partial V}\right)_e \quad (3.13)$$

As the temperature increases, the isotherms intersect the binodal closer and closer to point K - the so-called critical point. The concept of a critical point was introduced by D.I. Mendeleev in 1860, as a state in which the difference between the liquid and gaseous phases disappears. Indeed, as the critical point is approached, the difference between the specific volumes of liquid and gas decreases and, apparently, the values of isothermal compressibility should approach each other. It can be shown that the following condition is satisfied at the critical point:



$$\left(\frac{\partial P}{\partial V}\right)_T = 0 \quad (3.14)$$

$$P(V,T) = P(V + \delta V, T) \quad (3.15)$$

Expanding the right-hand side of the equality in powers of d V and dividing termwise by d V, we obtain the equation

$$\left(\frac{\partial P}{\partial V}\right)_T + \left(\frac{\partial^2 P}{\partial V^2}\right)_T \frac{\delta V}{2} + \ldots = 0 \quad (3.16),$$

passing in which to the limit d V ® , we arrive at equality (3.14). This also implies another important conclusion that the AKB binodal and the CKD spinodal have a single common point K. The critical point of the vapor-liquid phase transition is a special point in mathematical terms for the thermodynamic potentials of a substance, in particular, at this point it is not only zero isothermal compressibility, but also the second derivative.

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0 \quad (3.17)$$

The latter means that point K is the inflection point of the critical isotherm.

## 21 -Lecture.

### Topic: Phase transitions of the second type .

Monotropic and enantiotropic phase transitions and general graphs expressing them. Ehrenfest equation.

### The concept of phase transitions of the second kind

In the phase diagram of helium (Figure 21), in contrast to the phase diagram discussed above, there is no triple point corresponding to the simultaneous equilibrium existence of solid, liquid and gaseous phases. The melting and evaporation curves of helium do not intersect, since the solid phase is formed only at pressures above 25 atm. Helium has two liquid phases, HeI and HeII, which differ in properties. Helium has two triple points - A and B, in which three phases coexist in equilibrium: two liquid and, accordingly, crystalline helium (point A) and gaseous helium (point B). Point B corresponds to a temperature of approximately 2.2 K. The equilibrium between HeI and HeII corresponds to a second-order phase transition. It is characterized by the fact that the first derivatives of the Gibbs potential (–S and V) with respect to the state parameters P and T do not have jumps, i.e. at the transition point, the entropy and volume of both phases are the same, and $\Delta S = 0$, $\Delta V = 0$, $\Delta H = 0$, but the second derivatives change abruptly (Figure 19).

Figure 21 – Helium phase diagram
1 – melting curve, 2 – evaporation curve, 3 – separation curve of liquid phases HeI and HeII, A and B – triple points

The second derivative of G with respect to pressure is

$$\left(\frac{\partial^2 G}{\partial P^2}\right)_T = \left(\frac{\partial V}{\partial P}\right)_T = \beta_T V,$$

where the magnitude

$$\beta_T = -\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_T$$

the coefficient of isothermal compressibility is indicated. Its value changes abruptly during phase transitions of the second kind. The second derivative of G with respect to temperature is

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_P = -\left(\frac{\partial S}{\partial T}\right)_P = -\frac{c_P}{T}$$

indicates a jump in heat capacity during phase transitions of the second order. mixed derivative with respect to state parameters –

$$\left(\frac{\partial^2 G}{\partial P \partial T}\right) = \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T = \alpha V,$$

where is the value

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

is the coefficient of thermal expansion, reflects the abrupt change in the value of α during phase transitions of the second order.

Most often, phase transitions of the second kind are associated with an abrupt change in some property of the symmetry of the body, caused by a change in the order in the arrangement of particles. For example, the transition from a ferromagnetic state to a paramagnetic state (Curie point)
or from antiferromagnetic - to paramagnetic (Néel point) is accompanied by an abrupt violation of the coordinated orientation of elementary magnets, or disordering of magnetic moments in magnetic domains. The transition of a substance from a superconducting state to a state with normal conductivity also refers to phase transitions of the second kind. Processes of ordering-disordering of solid solutions at certain temperatures and concentrations can also occur as phase transitions of the second order, for example, in β-brass. In this case, ordering may not affect the values of the lattice parameters; therefore, it occurs without volumetric and thermal effects, but it affects the temperature coefficients of these values. The graphs of the dependences of these properties show kinks (Figure 19), and the dependence of the isobaric heat capacity on temperature near the transition point has a λ-shaped form (at the transition point there is not only a jump, but also a maximum). This type gave grounds to call the discussed transitions λ-transformations.

The Clausius-Clapeyron equation is not applicable to these transitions, since the fraction dT/dP turns into an uncertainty 0/0. Expanding it leads to the Ehrenfest equations:

$$\frac{dP}{dT}=\frac{\left(\frac{\partial \Delta S_{\text{фп}}}{\partial T}\right)_P}{\left(\frac{\partial \Delta V_{\text{фп}}}{\partial T}\right)_P}=\frac{\left(\frac{\Delta c_P}{T_{\text{фп}}}\right)}{V\Delta\alpha}=\frac{\Delta c_P}{T_{\text{фп}}V\Delta\alpha}; \qquad \frac{dP}{dT}=\frac{\left(\frac{\partial \Delta S_{\text{фп}}}{\partial P}\right)_T}{\left(\frac{\partial \Delta V_{\text{фп}}}{\partial P}\right)_T}=\frac{-\left(\frac{\partial \Delta V}{\partial T}\right)_P}{-V\Delta\beta_T}=\frac{V\Delta\alpha}{V\Delta\beta_T}=\frac{\Delta\alpha}{\Delta\beta_T}.$$

Equating the right-hand sides of the resulting Ehrenfest equations, we obtain the combined Ehrenfest equation:

$$\frac{\Delta c_P}{T_{\text{фп}}V\Delta\alpha}=\frac{\Delta\alpha}{\Delta\beta_T}, \text{ или} \qquad \boxed{\Delta c_P=\frac{T_{\text{фп}}V(\Delta\alpha)^2}{\Delta\beta_T}}.$$

## Phase transition of the 2nd order. Ehrenfest's theory .

The critical point of the vapor-liquid transition is an example of a continuous phase transition (or, according to P. Ehrenfest’s classification, a phase transition of the 2nd order), in which the first derivatives of the thermodynamic potential are continuous, and the second derivatives change abruptly.

The second derivatives of thermodynamic potentials are the so-called thermodynamic coefficients. Among them, the most important are the following.

Thermal expansion coefficient

$$\alpha_P=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P=-\frac{1}{V}\left[\left(\frac{\partial^2 F}{\partial V^2}\right)_P\right]^{-1} \quad (3.18)$$

Isothermal compression ratio

$$K_T=-\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_T=-\frac{1}{V}\left(\frac{\partial^2 G}{\partial P^2}\right)_T \quad (3.19)$$

Adiabatic compression ratio

$$K_S=-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S=-\frac{1}{V}\left(\frac{\partial^2 F}{\partial P^2}\right)_T \quad (3.20)$$

Heat capacity at constant volume

$$C_V=\left(\frac{\partial Q}{\partial T}\right)_V=T\left(\frac{\partial S}{\partial T}\right)_V=-T\left(\frac{\partial^2 G}{\partial T^2}\right)_V \quad (3.21)$$

Heat capacity at constant pressure

$$C_P=\left(\frac{\partial Q}{\partial T}\right)_P=T\left(\frac{\partial S}{\partial T}\right)_P=-T\left(\frac{\partial^2 G}{\partial T^2}\right)_P \quad (3.22)$$

The differential equation for the line of phase transformation of the 2nd kind, which relates jumps in thermodynamic coefficients with the corresponding derivative of pressure with respect to temperature, can be obtained by differentiating the relations that determine the equality of the first derivatives of the chemical potential of two phases, which reflect the fact that entropy and volume do not change at continuous phase transition.

$$S_1 = S_2 \; V_1 = V_2 \quad (3.23)$$

We obtain the following system of linear equations for the differentials dP and dT:

$$\begin{cases} \Delta\left(\dfrac{\partial S}{\partial T}\right)_T dP + \Delta\left(\dfrac{\partial S}{\partial T}\right)_P dT = 0 \\ \Delta\left(\dfrac{\partial V}{\partial P}\right)_T dP + \Delta\left(\dfrac{\partial V}{\partial T}\right)_P dT = 0 \end{cases} \quad (3.24)$$

Using formulas (3.18) – (3.22) it is possible to express the partial derivatives in equations (3.24) through the corresponding thermodynamic coefficients. We get

$$\begin{cases} -V\Delta\alpha_P dP + \dfrac{\Delta C_P}{T} dT = 0 \\ -V\Delta K_T dP + V\Delta\alpha_P dT = 0 \end{cases} \quad (3.25)$$

The homogeneous system of linear equations (3.25) has a non-zero solution provided that the determinant of the system is equal to zero:

$$(\Delta\alpha_P)^2 - \tfrac{1}{TV}\Delta C_P \Delta K_T = 0 \quad (3.26)$$

Thus, the jumps of the second derivatives are not independent, but are related to each other by relation (3.26). The solution to the system of equations (3.25) under condition (3.26) has the form:

$$\frac{dP}{dT} = \frac{\Delta C_P}{TV(\Delta\alpha_P)^2} \quad (3.27)$$

Formulas (3.26) and (3.27) are called Ehrenfest equations.

Unlike the Clayperon-Claudius phase equilibrium curve, this equation defines the phase transition line, because During phase transitions of the 2nd order, there are no metastable states. The new phase appears immediately in the entire volume of the substance and, accordingly, there is no interphase interface and surface energy.

It is interesting that the assumption about the possibility of metastable phase states during second-order phase transitions leads to the conclusion that second-order phase transitions are not possible at all. Indeed, at the point of a continuous phase transition, the intersection point of m 1 and m 2 must also be a point of tangency (common tangent), but in the case of a simple tangent, m 2 < m 1, both for T > T0 and for T < T0, i.e. e. there can be no transition. Therefore, it is necessary that point T0 be the inflection point of the curves m 1(T) and m 2(T), which means

$$\mu_1'(T_c) = \mu_2'(T_0) = 0$$

in this case, only the third derivative can be a discontinuous function, which corresponds to a third-order phase transition.

Thus, Ehrenfest's theory provides a connection between the jumps in the corresponding thermodynamic coefficients (3.26) and determines the derivative line of the phase transformation (3.27).

However, theoretical and experimental studies have shown that Ehrenfest's theory has a limited scope. It turned out that, as a rule, the corresponding thermodynamic coefficients at the transition point do not experience a jump, but diverge (i.e., tend to infinity).

## 22 Lecture.

## Topic: Two-component systems.

Physico-chemical analysis. Two-component systems. Hard alloys, liquid mixtures and solutions.

### Physico-chemical analysis.

In accordance with the principle of continuity, changes in density, heat capacity, boiling and melting points and other physical and chemical properties of a system deviate from monotonicity when the number and nature of its phases change. Therefore, observing changes in any property of the system under conditions of a given nature of temperature change, it is possible to use the speed deviation

heating or cooling from a given speed, establish at what temperatures phase transformations occur in a system of a given composition and what their nature is. This method of physical and chemical analysis is called thermal analysis.

**Fusibility diagrams.** To construct fusibility diagrams, so-called cooling curves are used, which show how the temperature of the system changes at a constant rate of heat removal to the environment

Wednesday. Figure 16 shows the construction of a fusibility diagram from cooling curves for systems with complete insolubility in each other in the crystalline state. This figure shows curves for pure substances A and B (curves 1 and 5) and for systems containing 20, 41 and 67 mass percent of substance B (curves 2-4, respectively).

While no phase transformations occur in the system (for example, the melt is cooled), the graph of the temperature of the system versus time is a straight line, the angle of inclination of which to the abscissa axis depends only on the rate of heat exchange with the environment. In Figure 16a, the cooling of the melts corresponds to the initial sections of the cooling curves up to the upper inflection point (the point at which crystallization begins).

When the melt is cooled to the temperature at which crystallization begins in the system, then, according to the law of conservation of energy, during this process the same amount of heat will be released as was expended on melting the crystals to obtain the melt. The release of this heat, called the latent heat of crystallization, partially or completely compensates for the heat removal to the environment, and the cooling process of the system slows down (flat sections of curves 2 and 4) or even stops (horizontal sections of the cooling curves). When the last drop of liquid crystallizes in the system (the end point of crystallization), the latent heat of crystallization will no longer be released and the cooling rate of the system will increase, so the last section of the curves again has a greater steepness.

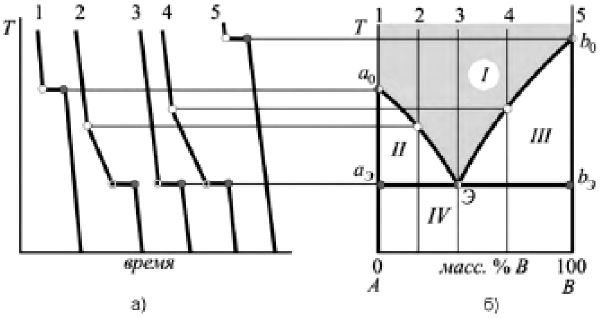


Figure 1 – Construction of a fusibility diagram using cooling curves

○ – точка начала кристаллизации;

⊙ – точка начала кристаллизации расплава эвтектического состава;

● – точка конца кристаллизации.

For pure substances, the start and end temperatures of crystallization are the same. The pure substance crystallizes (and melts) at a constant temperature (horizontal section on cooling curves 1 and 5).

For two-component systems, a similar course of cooling curves (curve 3) is observed only during the crystallization of eutectic (eutektik - well-melting) - a microheterogeneous mixture of solid crystalline phases, simultaneously released from the liquid phase at the so-called eutectic temperature (Te).

From two-component systems of non-eutectic composition (curves 2 and 4), the precipitation of crystals occurs in a certain temperature range and occurs in two stages: first, the component that is in the melt in excess compared to the eutectic composition (sloping section on the cooling curve) passes into the solid phase, and then, when the composition of the liquid phase becomes eutectic, the eutectic crystallizes at a constant temperature (the horizontal section of the cooling curve).

Due to hypothermia and other side effects, the cooling curves obtained experimentally may differ slightly from the dependences presented in Figure 1a. The construction of fusibility diagrams from cooling curves is carried out by transferring points from the temperature - time graph to the temperature - composition graph, as shown in Figure 1.

**Two-component systems**

Two-component systems. Diagrams of the cooling system status. Different types of status chart.

Two-component systems are those formed by two components, which can be either simple substances or chemical compounds. The ratio of components can significantly change the properties of the system.

Based on the principles of constructing the equation of state for a two-component system, the following equation is valid:

$$( \qquad ) = \quad , (6.3)$$

where $C_1$, $C_2$ are the concentrations of the first and second components.

But $C_1 + C_2$ = const, and if p = const, then (6.3) is simplified:

$( \quad ) =$ . (6.4)

Thus, the state diagram of a two-component system is constructed in coordinates T - C. If in a one-component system the Gibbs energy of the phase changes only when P and T change in accordance with equation (4.67), in a two-component system the Gibbs energy is determined not only by the values of P and T, but also phase composition, therefore

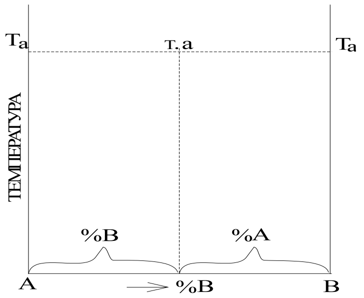
$= \qquad +$

, (6.5)

where is the chemical potential of the i-th component;

$n_i$ is the amount of the i-th component in the phase.

Equation (6.5) is the main equation of chemical thermodynamics, the basis of application



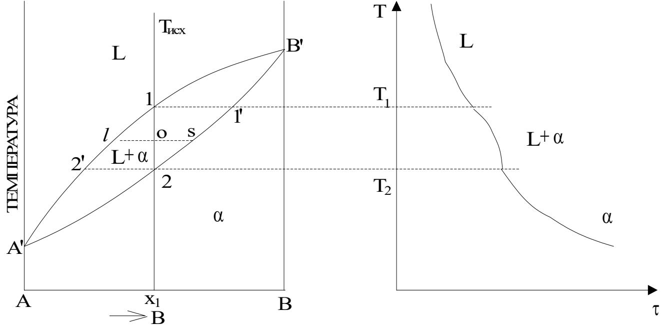
thermodynamics in chemistry and the theory of phase transitions. Systems whose behavior is described on the basis of (6.5) are called open (non-closed).

Any point on the diagram of a two-component system is a carrier of certain information (Fig. 6.3).

So the figurative point (a) indicates that the alloy of composition (%B, %A) is at temperature TA. An alloy is a solid or liquid system formed primarily by the fusion of two or more metals, as well as metals with various nonmetals. Only points characterizing melting or solidification processes, phase transitions, etc. are plotted on the diagram of a two-component system. The lines connecting these points have specific names. The line, which is a set of points at which the crystallization of all alloys of the system begins, is called the liquidus line. The line, which represents a set of points at the end of crystallization, is called the solidus line.

## Systems with unlimited solubility of components in solids and liquid state.

Diagrams of these systems come with and without extreme points on the lines of the diagram (minimum and maximum points). Most often in metal systems there are diagrams without maxima and minima (Fig. 6.4).



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Rice. 6.4. State diagram of a system with unlimited solubility of components (with the formation of a continuous series of solid solutions) (a) and cooling curve of alloy x1 (b).

The diagram consists of three regions: liquid solution (L), solid solution ( ) and the region of two-phase equilibrium (L + ).

An alloy of composition x $_1$ at TISH is a homogeneous liquid, unsaturated relative to the solid phase. For this temperature, the phase rule gives:

$c = k - f + 1 = 2 - 1 + 1 = 2,$

i.e. T and C are two independent state parameters.

At the temperature of point 1, the process of crystallization of the alloy begins: the liquid becomes saturated relative to the crystals - a solid solution of the composition of point 1', which are released from it. Line 1 - 1', connecting the compositions of equilibrium phases, is called a conode.

Number of degrees of freedom of the system for point 1:

$c = k - f + 1 = 2 - 2 + 1 = 1,$

i.e. T = f (C).

Indeed, the equation T = f (C) is the equation of the liquidus line.

Temperature interval (T1 - T2) - crystallization interval. The crystallization process is accompanied by a change in the composition of the equilibrium phases and can be described by an equation of the form:

. (6.6)

Equation (6.6) is the equation for the process of primary crystallization. For point 2 the number of degrees of freedom will be:

$c = k - f + 1 = 2 - 2 + 1 = 1,$

i.e. T = f (C) and determines the position of the solidus line.

Thus, the composition of the first crystals is determined by the projection of point 1' onto the concentration axis, and the composition of the last drops of liquid is determined by the projection of point 2'.

The relative mass fractions of phases (R.M.D.) of a crystallizing alloy at a temperature of point O are determined from the relations (lever rule):

= — = —
, . (6.7)

The change in the temperature of the alloy x1 during its cooling is depicted by the corresponding cooling curve (Fig. 6.4), plotted in “temperature - time” coordinates.

## 23-Lecture.

## Topic: State diagrams of two-component systems.

Thermal analysis. Amorphous and crystallizing substances. Cooling and state diagrams of two-component systems. The concepts of liquidus, solidus, eutetics, figurative point. Leverage rule.

Two-component systems are those formed by two components, which can be either simple substances or chemical compounds. The ratio of components can significantly change the properties of the system.

Based on the principles of constructing the equation of state for a two-component system, the following equation is valid:

$( \qquad ) =$ , (6.3)

where $C_1$, $C_2$ are the concentrations of the first and second components.

But $C_1 + C_2 =$ const and if p = const , then (6.3) simplifies:

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Thus, the state diagram of a two-component system is constructed in coordinates T - C. If in a one-component system the Gibbs energy of the phase changes only when P and T change in accordance with equation (4.67), in a two-component system the Gibbs energy is determined not only by the values of P and T, but also phase composition, therefore

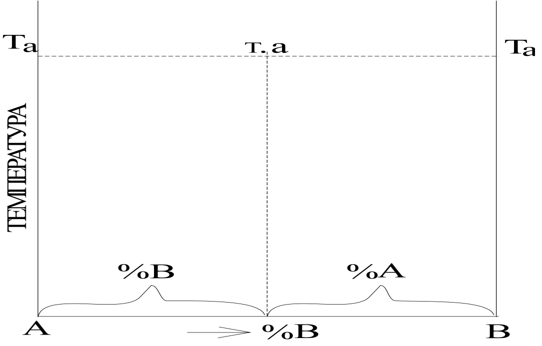
$= \qquad +$

, (6.5)

where is the chemical potential of the i -th component;

$n_i$ - the amount of the i -th component in the phase.

Equation (6.5) is the main equation of chemical thermodynamics, the basis of application thermodynamics in chemistry and the theory of phase transitions. Systems whose behavior is described on the basis of (6.5) are called open (non-closed).



Any point on the diagram of a two-component system is a carrier of certain information (Fig. 6.3).

So the figurative point (a) indicates that the alloy of composition (%B, %A) is at temperature TA. An alloy is a solid or liquid system formed primarily by the fusion of two or more metals, as well as metals with various nonmetals. Only points characterizing melting or solidification processes, phase transitions, etc. are plotted on the diagram of a two-component system. The lines connecting these points have specific names. The line, which is a set of points at which the crystallization of all alloys of the system begins, is called the liquidus line. The line, which represents a set of points at the end of crystallization, is called the solidus line.

## 5.1. Systems with unlimited solubility of components in solid and liquid states.

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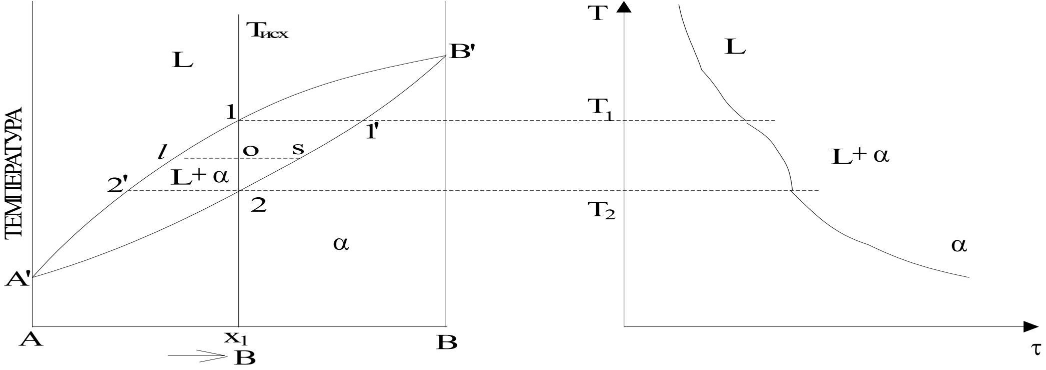

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An alloy of composition $x_1$ at TISH is a homogeneous liquid, unsaturated relative to the solid phase. For this temperature the phase rule gives:

c = k - f + 1 = 2 - 1 + 1 = 2,

i.e. T and C are two independent state parameters.

At the temperature of point 1, the process of crystallization of the alloy begins: the liquid becomes saturated relative to the crystals - a solid solution of the composition of point 1', which are released from it. Line 1 - 1' connecting the compositions of equilibrium phases is called a conode.

Number of degrees of freedom of the system for point 1:

c = k - f + 1 = 2 - 2 + 1 = 1,

i.e. T = f ( C ).

Indeed, the equation T = f ( C ) is the equation of the liquidus line.

Temperature interval (T1 - T2) - crystallization interval. The crystallization process is accompanied by a change in the composition of the equilibrium phases and can be described by an equation of the form:

. (6.6)

Equation (6.6) is the equation for the process of primary crystallization. For point 2 the number of degrees of freedom will be:

c = k - f + 1 = 2 - 2 + 1 = 1,

i.e. T = f ( C ) and determines the position of the solidus line.

Thus, the composition of the first crystals is determined by the projection of point 1' onto the concentration axis, and the composition of the last drops of liquid is determined by the projection of point 2'.

The relative mass fractions of phases (R.M.D.) of a crystallizing alloy at a temperature of point O are determined from the relations (lever rule):

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The change in the temperature of the alloy x 1 during its cooling is depicted by the corresponding cooling curve (Fig. 6.4), plotted in “temperature - time” coordinates.

### 2 4 - Lecture.

### Topic: Systems containing congruent and incongruent diluting chemical compounds.

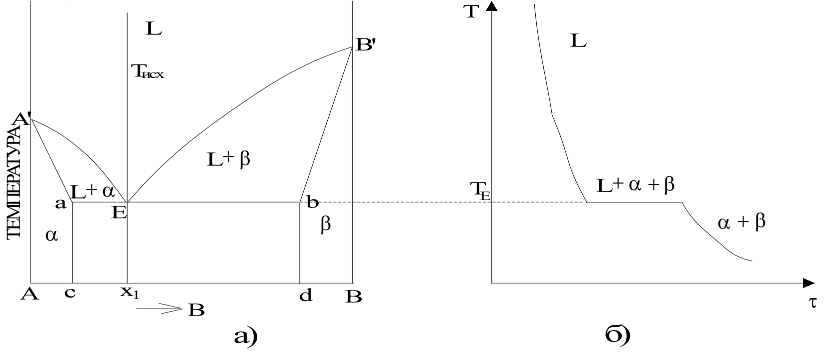
Systems containing congruent and incongruent diluting chemical compounds. Special and peritectic points.

Analysis of the state of the diogram of two-component systems with the concept of lines of liquidus, solidus, eutetic point, eutetic composition, figurative point, connode lines, cooling congruent and incongruent chemical compounds, singular and disthetic points, peretectic points. Shoulder rule. Systems with unlimited solubility of components in the liquid state and limited in the solid state.

There are approximately an order of magnitude more such systems than those previously considered.

*Rice. 6.5. State diagram of a eutectic type system (a) and cooling curve of alloy x1 (b).*

Eutectic type systems.



The eutectic type diagram is shown in Fig. 6.5.

Line A'EB' is the liquidus line, line A'aEbB' is the solidus, line aEb is the eutectic horizontal. Eutectic translated from Greek means easily melting.

Lines ac and bd are solvus lines or lines of maximum solubility of components in each other.

Regions and - regions of solid solutions. Solid solutions are homogeneous crystalline phases of alloys in which atoms of the soluble component replace solvent atoms in its crystal lattice.

In TISC, the alloy of composition x1 is represented by a homogeneous liquid, which, upon reaching the eutectic horizontal temperature (TE), is saturated simultaneously with respect to two solid solutions: - a solution of composition point (a) and - a solution of composition point b, which are released from it. The so-called eutectic transformation occurs, which can be described by an equation of the form:

(6.8)

As a result of the eutectic transformation, a eutectic mixture of two phases is formed: i. The system variation during TE will be determined:

c = k - f + 1 = 2 - 3 + 1 = 0,

i.e., invariant equilibrium in a two-component system is realized at constant temperature (TE) and constant phase compositions

With further cooling, the compositions of the equilibrium phases do not change.

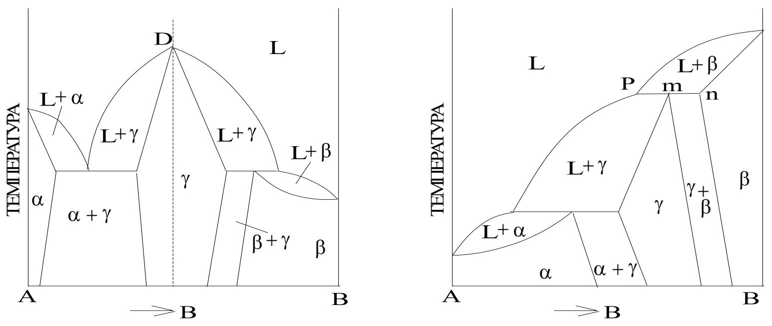
Peritectic type systems.

“Peritektos” - environment (Greek). The peritectic type phase diagram is shown in Fig. 6.6.

A homogeneous liquid is cooled to the temperature of point 1, which at temperature T1 is saturated with a relatively solid solution, which begins to separate. The process of separation of the solid solution continues in the temperature range (T1 - TP) and can be described by an equation of the form:

characterizing the process of primary crystallization.

Rice. 6.6. Diagram of the state of a peritectic type system (a) and cooling curve of alloy x1 (b).



а) б)

(6.9)

At temperature TP (temperature of the peritectic horizontal Pab), the liquid of composition point P becomes unsaturated with respect to the precipitated crystals - solid solution and supersaturated with respect to crystals - solid solution of composition point a. Therefore, crystals dissolve in the liquid, and crystals are released from it.

Equation (6.9) describes the process of peritectic crystallization.

Number of degrees of freedom for the system with TR:

$$c = k - f + 1 = 2 - 3 + 1 = 0.$$

**Systems with intermediate phases.**

Rice. 6.7. Phase diagrams with a congruently (a) and incongruently (b) melting intermediate phase.

Systems with intermediate phases are divided into two groups: with congruently (Fig. 6.7, a) and with incongruently melting intermediate phases (Fig. 6.7, b).

If the compositions of the liquid and solid phases at the melting temperature coincide (point D), then such systems are called systems with a congruently melting intermediate phase (Fig. 6.7, a), and if the compositions of the equilibrium phases at the melting temperature do not coincide (Fig. 6.7, b ), then these are systems with an incongruently melting intermediate phase.

Point D is called the distectic (hard-to-melt) point.

Systems with limited solubility in the liquid state.

State diagrams of systems with limited solubility in the liquid state are represented by diagrams of two types: with monotectic and syntectic transformations (Fig. 6.8 a, b).

Line nkm - dome of separation - line of limited solubility in the liquid state.

When the alloy x $_{\text{1 is cooled}}$ (Fig. 6.8, a) and it reaches the temperature of point 1, the liquid of the composition of point 1 is saturated in relation to another liquid of the composition of point 1'. In the interval ($T_1 - T_2$), the process of separation occurs, accompanied by a change in the composition of the liquids:

. (6.10)

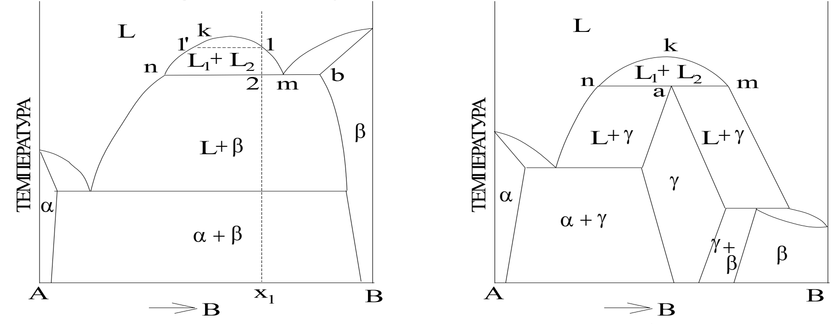
Synthetic type systems are rare in real metallurgical systems. The meaning of syntectic transformation can be represented by a diagram of the form:

, (6.11)

for which

c \u003d k - f + 1 \u003d 2 - 3 + 1 \u003d 0.

Rice. 6.8. State diagrams of systems with stratification.



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Rice. 6.8. State diagrams of systems with races

## 25-Lecture.

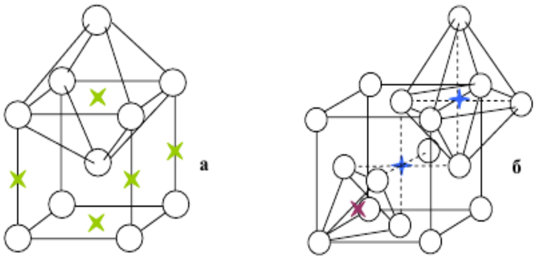
## Topic: Solid solutions.

Solid solutions. Solid solutions resulting from insertion and placement. Systems of solid solutions with infinitely and finally soluble components. Phenomena of isomorphism and polymormism.

Very often, during the crystallization of metal melts, it is not a pure solid that is released, but a solid solution - a homogeneous crystalline phase of variable composition, consisting of two or more components. Substances, mixing with each other, form a common crystal lattice. The following main types of solid solutions are distinguished.

**1. Interstitial solid solutions** .

In solutions of this type, the atoms of the solute are distributed in the voids (interstices) of the crystal lattice of the solvent (Figure-1). To fit into interstices, the solute atoms must have a diameter not exceeding 60% of the diameter of the solvent atom. In solid metals, elements with small atoms ( H , N , C , O , B ) dissolve by interstitial type. As the concentration of the solute increases, the stability of the solvent lattice decreases. In addition, the number of interstices capable of accommodating atoms of a dissolved element in a metal is finite. Therefore, during the formation of interstitial solid solutions, limited solubility occurs. The interstitial solid solution is low-carbon steel - a solution of carbon in iron.



*Picture 1. Possible locations of solute atoms (marked with asterisks) in the interstices of metal crystal lattices: body-centered cubic (a) and face-centered cubic (b)*

**2. Substitutional solid solutions.**

In substitution solutions, atoms of the solute replace some of the solvent atoms at lattice sites (Figure 2). The condition for the formation of such solid solutions is the similarity of the crystal structures and a small difference in the sizes of the component atoms. According to the Hume-Rothery rule, if the radii of atoms differ by no more than 15%, the substitution does not cause strong stresses in the lattice, and it can be stable at any composition, up to unlimited mutual solubility. With a larger difference in atomic sizes, substitutional solid solutions are formed in a limited range of compositions.

Both types of solid solutions can be either disordered - with a random, irregular distribution of atoms of the solute in the solvent lattice - or ordered (Figure 2). Ordering-disordering processes occur with changes in composition and temperature and manifest themselves as phase transitions of the 1st or 2nd order.

**3. Subtraction solid solutions.**

Solutions of this type are formed on the basis of the crystal lattice of a chemical compound when there is a deficiency of atoms of any component. The subtraction solid solution lattice contains vacant sites.

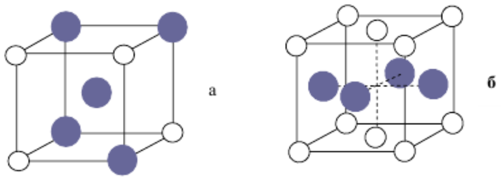


*Figure-2. unit cells of crystal structures of substitutional solid solutions: a – disordered solution based on a body-centered cubic structure; b – ordered substitution solution based on a face-centered structure .*

In solid solutions, static lattice distortions are always present. The contribution of lattice deformation energy to the total Gibbs energy affects the thermodynamic properties of solid solutions. This contribution is different in the ordered and disordered states of the solid solution, which affects its various properties, in particular, strength characteristics.

For metallurgists, the presence of a wide range of solubility in a metal system is of great importance, since solid solutions have higher mechanical properties than pure metals.

Phenomena of isomorphism and polymormism.

## 26-Lecture.

## Topic: Limited soluble systems in the liquid phase.

Limited soluble systems in the liquid phase. Complex state diagrams. Eutonics.

Depending on the nature of solubility, liquid systems are divided into

1) unlimitedly mutually soluble (water - ethyl alcohol $C_2H_5OH$);

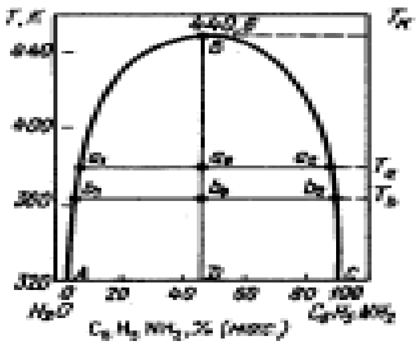
2) practically mutually insoluble (water - mercury);

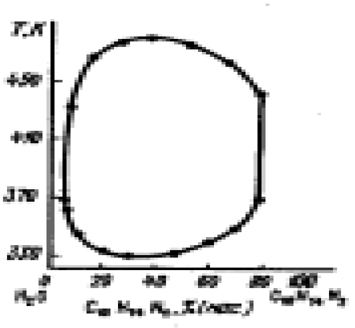
3) limitedly mutually soluble (water - aniline $C_6H_5NH_2$, water - phenol $C_6H_5OH$, water - triethylamine $(C_2H_5)_3N$, water-nicotine $C_{10}H_{14}N_2$, etc.)

If liquids are mutually soluble to a limited extent, then in a certain temperature range they form two liquid phases (two layers).

Phase diagrams showing the dependence of the composition of liquid layers on the temperature of the system are called mutual solubility diagrams.

The figure shows a state diagram of the water – aniline system. Inside the ABC region, two liquid phases coexist; C=2–2+1=1 the system is univariant. Separation curves are curves showing the dependence of the composition of liquid layers on temperature - curves AB and BC - the composition of the aqueous and aniline layers.





In this case, with increasing temperature, the mutual solubility of aniline in water and water in aniline increases. When both layers become identical in composition, the delamination curves converge at the critical point B (at TK = 440.6 K - critical temperature).

**The upper critical** solubility temperature TK is the temperature above which liquids mix with each other without limit.

**Connections** a1a2 and b1b2 indicate the compositions of the equilibrium conjugated layers. Outside the ABC region, the system is single-phase and bivariant.

If the curve limiting the separation region passes through a minimum (for example, in the system water - triethylamine $(C_2H_5)_3N$), then the temperature TK is called the lower critical solubility temperature. There are systems (for example, water - nicotine $C_{10}H_{14}N_2$) that have both upper and lower critical solubility temperatures (see figure).

The existence of critical temperatures explains the Le Chatelier-Brown principle of mobile equilibrium.

If the mutual dissolution of phases is accompanied by the absorption of heat, then with increasing temperature the solubility increases - there is an upper critical solubility temperature.

If dissolution is accompanied by the release of heat, then with increasing temperature the solubility decreases - there is a lower critical solubility temperature.

If the heat of solution changes sign when the temperature changes, this leads to the appearance of upper and lower critical solubility temperatures.

The critical solubility point on the separation curve is determined using Alekseev's straight-line diameter rule: the midpoints of the connodes connecting the figurative points of conjugate solutions lie on a straight line passing through the upper or lower critical solubility point.

## 27-Lecture.

## Topic: Three-component systems.

Three-component systems. Determination of the composition of solid solutions by the Gibbs and Roseboom methods.

**Three-component systems.** Analysis of three-component systems using the Gibbs and Rosembum methods. Analysis of solutions diagrams the state of one name and ions of two salts. Studying the complex state of the diagram during the formation of salt between hydrated, complex and double salt waters.

In practice, along with two-component systems, it is much more common to deal with systems composed of three or more components.

The equation of state of three-component systems connects five parameters and has the following form:

$\varphi(C_1, C_2, C_3, P, T) = 0$ . (6.12)

From (6.12) it follows that the state diagram of a three-component system cannot be depicted on a plane.

Assuming that P = const and C1 + C2 + C3 = 1, if the method of expressing the composition of alloys is mole fractions, a three-component diagram can be constructed in three-dimensional space.

The compositions of three-component alloys are usually depicted on a plane using a concentration triangle. At the vertices of the triangle there are pure components A, B and C, and its three sides reflect the compositions of binary alloys. The axis perpendicular to the plane of the concentration triangle is the temperature axis.

Properties of the concentration triangle.

First property. If from some point M lying in the plane of the triangle we lower three perpendiculars to the sides, then:

MA + MV + MS = const = BD,

where BD is the height of the concentration triangle (Fig. 6.9, a).

If BD is taken as 100%, then each of the perpendiculars is the concentration of each component in the alloy:

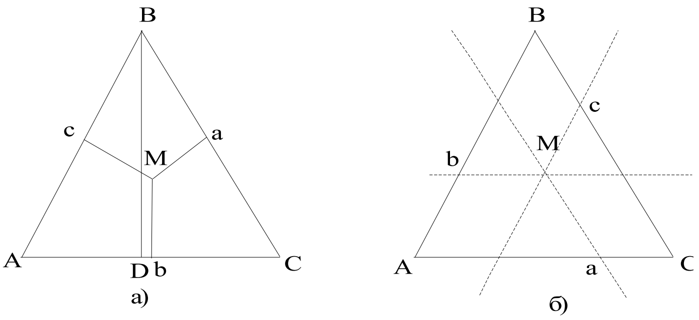
Ma = % A; Mb = %B; Mc = % C.

Second property. If through the point M, which lies in the plane of the triangle, we draw three

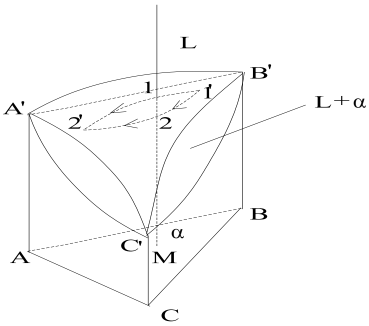
lines parallel to the sides of the triangle, then the sum of the segments Ab, Bc and Ca cut off by these lines on the sides of the triangle is a constant value and equal to the side of the triangle:

A b + Bc + Ca = const = AB .

If AB = % B, Bs = % C, and Ca = % A, then the composition of the three-component alloy is determined.



Rice. 6.9. Properties of an equilateral triangle applied for depicting the compositions of three-component alloys.



Thus, knowing the properties of an equilateral triangle, the position of the figurative point can be used to estimate the composition of the three-component alloy, or, knowing its composition, the position of the figurative point in the plane of the concentration triangle can be found.

As for two-component systems, the complexity of the phase diagrams of three-component systems depends on the mutual solubility of the components and on the possibility of the formation of chemical compounds between them.

The simplest is the state diagram of a three-component system with unlimited solubility of the components in liquid and solid states (Fig. 6.10).

For the diagram in Fig. 6.10 TS(B) > TS(A) > TS(C) m. A', B' and C' are the melting points of the pure components.

Rice. 6.10. State diagram of a ternary system with unlimited solubility of components in liquid and solid states.

The faces of the prism are double systems with unlimited solubility of components in solid and liquid states. The liquidus surface passes through three liquidi. Above the liquidus surface is the volume of liquid solutions (L). The solidus surface passes through three solidus. Below the solidus surface there is a volume of solid solutions ( $\alpha$). The volume of space between the liquidus and solidus surfaces is occupied by an equilibrium two-phase system of liquid and solid solutions (L + $\alpha$). The interval between the surface of liquidus and solidus is the interval of crystallization (melting) of alloys of a three-component system.

The alloy of composition T. M (Fig. 6.10) at T > T1 is in the state of an unsaturated liquid solution. Crystallization of the alloy begins at T1 lying on the liquidus surface. The composition of the first crystals $\alpha$- the solid solution - corresponds to the projection of point 1' onto the plane of the concentration triangle.

With a further decrease in temperature from T1 to T2, the liquid gradually takes on the composition of point 2' and disappears, and the crystals $\alpha$ of the solid solution - point 2. Therefore, the process of crystallization of the alloy is represented by an equation of the form:

$$L_{M-2'} \xrightarrow{T_1-T_2} \alpha_{1'-M} . \quad (6.10)$$

Below the temperature T2, the crystals of the solid solution are cooled $\alpha$.

When working with state diagrams of three-component systems, it is convenient to use their cuts - poly- and isothermal. Isothermal sections characterize phase equilibria in ternary alloys, and polythermal sections are used to establish the temperatures of the beginning and end of crystallization of alloys, etc.

This chapter examines a number of more or less complex systems, the study of which is difficult using only one thermodynamic method. Using state diagrams, it is quite simple to describe the properties of such systems. But only the parallel application of the thermodynamic method and the basic positions of physicochemical analysis, with the help of which state diagrams are constructed, allows one to obtain very deep information about the system being studied. However, it is always necessary to remember that for the most part only equilibrium systems are considered. It is for such systems that the corresponding state diagrams are displayed. The number and specific type of phases of a complex system observed in practice may in fact differ greatly from the equilibrium ones, due to the inhibition of the process of transition to an equilibrium state.

## Lecture -28

## **Topic:** Thermodynamics of solutions.

Collective properties of solutions. Cryoscopy and ebullioscopy.

Issues of solution theory occupy an important place in thermodynamics. Both in nature and in technology one has to deal primarily with solutions rather than with pure substances. Chemically pure substances represent only a limiting state that is not actually achieved. Ultrapure substances obtained by modern purification methods (for example, vacuum and zone melting of metals) still contain negligible (~ 10–6%) amounts of impurities and are essentially solutions.

Chemical reactions during the smelting of iron and steel take place mainly in solutions. Liquid cast iron and steel are solutions of various elements in iron, and slag in blast furnace and steelmaking is a solution of various oxides. Aqueous solutions of salts, acids and bases are used in hydrometallurgy for the extraction of non-ferrous metals from ores.

Solutions are very diverse in their nature and the nature of particle interaction. Thus, a solution of sulfuric acid in water is formed with the release of a large amount of heat and is characterized by significant chemical interaction. On the contrary, the dissolution of sodium hyposulfite (thiosulfate) in water occurs with the absorption of heat, causing a noticeable cooling of the resulting solution. Let's define a solution.

**A solution is** a homogeneous system consisting of two or more substances, the composition of which can vary continuously within certain limits.

When a substance goes into solution, it becomes a component of the solution and, to one degree or another, loses its individuality. Chemical compounds are also homogeneous, but their chemical composition is either unchanged and obeys stoichiometric ratios, or varies within narrow limits. Solid compounds have their own crystal structure, different from the structures of the substances that form them. This is a significant difference between compounds and solid solutions that form a crystal lattice based on one of the components.

From a thermodynamic point of view, all components of the solution are equivalent. Therefore, the division of components into solvent and solutes is arbitrary. Typically, the solvent is the component that is present in the solution in the largest quantity. If a solid or gas is dissolved in a liquid, then regardless of the amount, the liquid is considered a solvent. Let us agree that if we further have to distinguish between a solvent and a solute, then we will denote the first by the index “1”, and the second by the index “2”.

The state of the solution, like other systems, is determined by the parameters T and P, as well as a specific parameter - concentration. The concentration of a component can be expressed in different ways, but you can always move from one method of expression to another.

**Methods of expressing the concentrations of solution components and their relationship**

1) Mass (weight) fraction - the ratio of the mass of the component to the mass of the solution. When the mass fraction is multiplied by 100, the mass percentage is obtained.

2) Volume fraction - the ratio of the volume of the solute to the volume of the solution. Multiplying the volume fraction by 100 gives the volume percentage.

3) Molarity - the number of moles of a component in 1 liter of solution.

4) Normality – the number of gram equivalents of a component in 1 liter of solution.

5) Molality - the number of moles of dissolved substance per 1000 g of solvent.

6) Mole fraction - the ratio of the number of moles of a component to the sum of the numbers of moles of all components of the solution

$$x_i = \frac{n_i}{\sum_{i=1}^{k} n_i},$$

∑

where k is the number of components in the solution. When multiplying the mole fraction of a component by 100, its mole percentage is obtained. The last method of expressing the concentration of components is used in the thermodynamics of solutions. It follows from the definition that

$$\sum_{i=1}^{k} x_i = 1 \text{ и } 0 \le x_i \le 1.$$

1

If the number of moles of all components of a solution is such that

$$\sum_{i=1}^{k} n_i = 1,$$

the solution is present in an amount of 1 mole. In other words, we can say that the mole fraction is the number of moles of a component in 1 mole of solution.

All types of expression of concentration are interconnected. The most commonly used are mass percentage (in technology) and mole fraction (in theory). Let's find the relationship between them.

Let there be 100 g of a binary solution, which consists of 60 g of the 1st component and 40 g of the 2nd component. In this case, the number of moles of the 1st component is n 1 = 60/M1, the number of moles of the 2nd component is n 2 =

40/M2. By definition of mole fraction

$$x_1 = \frac{\frac{60}{M_1}}{\frac{60}{M_1} + \frac{40}{M_2}}, \quad x_2 = \frac{\frac{40}{M_2}}{\frac{60}{M_1} + \frac{40}{M_2}}, \text{ или в общем виде: } \boxed{x_i = \frac{\frac{мас\%i}{M_i}}{\sum_{1}^{k} \frac{мас\%i}{M_i}}}; \; x_2 = 1 - x_1.$$

Let's move from mole fractions to mass percentages. Let's take 1 mole of solution, in which x 1 and x 2 are the mole fractions of the 1st and 2nd components, respectively. Then the mass of the 1st component is m 1 = x 1 M 1, and the mass of the 2nd component is m 2 = x 2 M 2, and

$$мас.\%1 = \frac{m_1}{m_1 + m_2} 100\% = \frac{x_1 M_1}{x_1 M_1 + x_2 M_2} 100\%,$$

$$мас.\%2 = \frac{m_2}{m_1 + m_2} 100\% = \frac{x_2 M_2}{x_1 M_1 + x_2 M_2} 100\%,$$

or in general:

$$\boxed{\text{мас.}\%i = \frac{m_i}{\sum_{1}^{k} m_i}100\% = \frac{x_i M_i}{\sum_{1}^{k} x_i M_i}100\%}.$$

Other methods of expressing the concentrations of components are used in individual cases and do not have universal application. So, for example, the volume percentage is used only in gas solutions, since only in them the volume of the solution consists of the volumes of pure components, normality is convenient in solutions of electrolytes, etc.

The properties of solutions, like pure substances, are characterized by the same thermodynamic quantities: V , G , F , H , S , etc. For one mole of solution, these properties are called molar or molar. However, the properties of the components of the solution are generally different from the properties of these substances in a pure state. It is precisely this circumstance that does not allow one to determine the properties of a solution by adding the properties of pure substances in proportion to their concentrations, i.e., as they say, according to the rule of additivity.

Partial molar properties of solution components and methods for their determination

If we consider the dependence of any property of a solution, for example, molar volume, on its composition, we can see that this dependence is not always expressed by a straight line graph (line 1 in Figure 12), but more often by lines of type 2 or 3. Let us introduce the notation: $\varepsilon$ 11 – energy of interaction between particles (atoms, molecules or ions) of the first component; $\varepsilon$ 22 – energy of interaction between particles of the second component; $\varepsilon$ 12 – energy of interaction between unlike particles. These energies have negative values, since the potential energy of interaction of particles when they move infinitely away from each other is taken to be zero.

If the sizes of particles of the 1st and 2nd grades are close, as is usually the case in metal solutions, the type of dependence V = f ( x2 ), as well as a number of other properties, is determined by the ratio of these energies.

If $|\varepsilon_{12}| = (|\varepsilon_{11}| + |\varepsilon_{22}|)/2$, then the dependence on the composition is additive, that is, linear (line 1 in Figure 12).

If $|\varepsilon_{12}| > (|\varepsilon_{11}| + |\varepsilon_{22}|)/2$, then compression occurs, i.e. reduction in the volume of the solution compared to the total volume of mixed substances. The dependence of the solution volume on the composition is expressed by curve 3.

If $|\varepsilon_{12}| < (|\varepsilon_{11}| + |\varepsilon_{22}|)/2$, then decompression is observed, i.e. an increase in the volume of the solution in relation to the sum of the volumes of mixed pure substances 1 and 2 (curve 2).

Obviously, only in a particular case the volume of the solution consists of the volumes of pure substances. In the general case, V solution $\neq$ $\Sigma$xiVi . This means that the volume and other properties of the solution differ from the properties of the substances that form it in their pure form. Therefore, to describe the properties of the components of a solution, the concept of partial molar properties of the components is introduced. They are determined by a change in the extensive property of a solution when a given component is added to it under certain conditions.

To determine how the addition of a given substance affects the general property of the solution, we add to a solution of a given composition Δ xi moles of substance i . However, the increase in overall property will depend on the composition of the solution. Therefore, it is necessary to add the i -th substance so as not to change the composition of the solution (for example, add a finite amount of the i -th substance to an infinitely large amount of solution, or add an infinitely small amount of this substance to a finite amount of solution). Then the general property will change by the value Δ V total, and this change will be associated only with a change in the number of moles of the i -th substance (with other parameters being constant: temperature, pressure, composition).

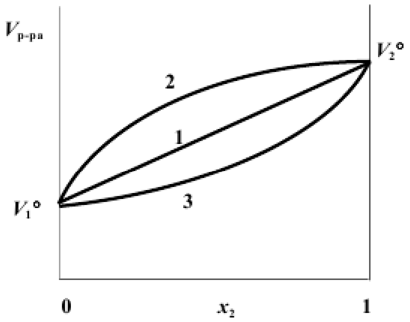


Рисунок 12 – Зависимости объема раствора от состава

Figure 12 – Dependence of solution volume on composition

The limit of the ratio of the increment in the general property of the solution to the increment in the amount of the added component at P , T = const and at Δ ni → 0 is the partial molar property of the i -th component:

$$\lim_{\Delta n_i \to 0} \frac{\Delta V_{общ}}{\Delta n_i} = \left( \frac{\partial V_{общ}}{\partial n_i} \right)_{P,T,n_{j \neq i}} = \overline{V}_i$$

This definition makes sense only for the extensive properties of a solution, since intensive properties, for example, temperature, do not depend on the amount of substance (number of moles of the component).

The partial molar property of a solution component is the partial derivative of the extensive property of a solution with respect to the number of moles of a given component, provided that the temperature, pressure and number of moles of all other components are constant.

Partial molar properties can be written for any extensive property of a solution: Si , Ui , Hi , etc. A special role in the theory of solutions is played by the partial molar Gibbs energy Gi , also called chemical potential: Gi = μ i . This value expresses the tendency of a substance to leave a given phase, and is a measure of its dissipation.

Chemical potential, like other partial molar properties, is obviously an intensive quantity.

There are three ways to determine partial molar properties.

1. Analytical method

If there is a mathematical expression for the dependence of some property of the solution $\Phi$ on $x_i$, then by differentiating $\Phi$ with respect to $x_i$, we can obtain the desired value $\Phi$ i . The disadvantage of the method is that in order to obtain an accurate functional dependence, it is necessary to process a large amount of experimental material and draw up an equation based either on theoretical studies or using an empirical description of experimental data.

2. Graphical method

This method is used more often, however, it is convenient to use only for binary solutions. Using simple geometric constructions, it can be shown that the partial molar properties of the components of a binary solution are determined by drawing tangents to the curve of the dependence of the general property of the solution on the composition at a given concentration (Figure 13). The ends of the tangent (straight lines in red) cut off segments on the ordinate axes (shown in green), the lengths of which correspond to the partial molar properties of the first and second components (left and right, respectively) in a solution of a given composition.

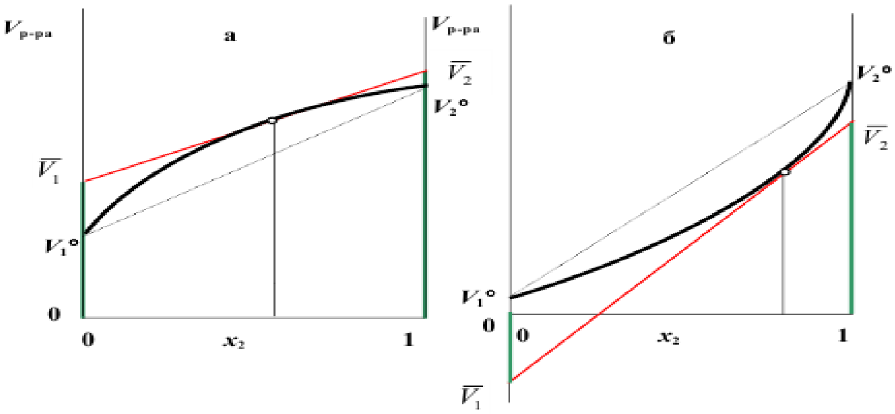


Figure 13 – Determination of partial molar volumes of components of a binary solution by a graphical method for solutions with decompression (a) and solutions exhibiting compression (b)

It can be seen from the figure that since with a change in the composition of the solution the slope of the tangent to the concentration axis will also change, the partial molar properties depend on the concentration of the components. Figure 13, b also shows that the value of the partial molar property, including volume, can also take on negative values (negative partial derivative of the total volume of the solution with respect to the number of moles of the 1st component), in contrast, for example, to the molar volume. The meaning of this is that the partial molar property represents the change in the overall property of a solution when a given component is added to it. Indeed, with a very strong interaction of unlike particles in a solution, it may become compacted when a component is added in a certain composition range.

3. Solution modeling.

Both previous methods cannot be called universal. In addition, they are based on initial experimental data on changes in the general or molar properties of the solution. A more general approach is to create model theories of solutions that make it possible to calculate both partial molar characteristics and the properties of the entire solution. We will look at some examples of the simplest models below. However

It should be noted that the current level of development of science does not allow creating a general theory of the solution due to the too complex nature of the interparticle interaction in many real multicomponent systems.

## Equations of connection between partial molar quantities

Let's consider some property of the solution Θ , depending on P , T , $n_1$ , $n_2$ , ..., $n_k$ . Its differential at P, T = const is determined by the expression:

$$d\Theta = \left(\frac{\partial\Theta}{\partial n_1}\right)_{P,T,i\neq 1} dn_1 + \left(\frac{\partial\Theta}{\partial n_2}\right)_{P,T,i\neq 2} dn_2 + \ldots + \left(\frac{\partial\Theta}{\partial n_k}\right)_{P,T,i\neq k} dn_k ,$$

or, taking into account the definition of partial molar properties

$$d\Theta = \overline{\varphi}_1 dn_1 + \overline{\varphi}_2 dn_2 + \ldots + \overline{\varphi}_k dn_k . \qquad (40)$$

Let's integrate equation (40), assuming the composition of the solution is constant ( $n_1 : n_2 : ...: n_k$ = const ). Since, if the composition of the solution is constant, all ϕi are constant, they can be taken out of the integral sign. After integration (40) we have:

$$\Theta = n_1\overline{\varphi}_1 + n_2\overline{\varphi}_2 + \ldots + n_k\overline{\varphi}_k . \qquad (41)$$

The integration constant is equal to 0, since for all $n_i$ = 0 the property itself is Θ = 0. It follows from equation (41) that the general property of the solution does not consist of the properties of pure substances, but of the partial molar properties of the components. Dividing equation (41) by the sum of the numbers of moles of all components of the solution ( $n_1 + n_2 + ...+ n_k$ ) , we obtain the molar property of the solution

$$\Theta_M = x_1\overline{\varphi}_1 + x_2\overline{\varphi}_2 + \ldots + x_k\overline{\varphi}_k ,$$

or

$$\Theta_M = \sum_1^k x_i\overline{\varphi}_i .$$

This equation shows the importance of partial molar properties for describing a solution: with their use instead of the molar characteristics of the components, an additive equation becomes valid for determining the molar property of a solution.

Next, considering all quantities ni and ϕ $_{\text{i as variables}}$ , we differentiate equation (41) for P , T = const :

$$d\Theta = n_1 d\bar{\varphi}_1 + n_2 d\bar{\varphi}_2 + \ldots + n_k d\bar{\varphi}_k + \bar{\varphi}_1 dn_1 + \bar{\varphi}_2 dn_2 + \ldots + \bar{\varphi}_k dn_k \, .$$

(42)

Let us subtract equation (40) from equation (42), assuming that the change in the general property of the solution in both processes is the same. We get

$$\boxed{n_1 d\bar{\varphi}_1 + n_2 d\bar{\varphi}_2 + \ldots + n_k d\bar{\varphi}_k = 0}\,.$$

(43)

Equation (43) is called the Gibbs-Duhem equation and is the basic equation for the relationship of partial molar properties. In compressed form it can be written like this:

$$\boxed{\sum_1^k n_i d\bar{\varphi}_i = 0}\,.$$

After dividing equation (43) by the value ( n $_1$ + n $_2$ + ...+ n $_k$ ) it refers to 1 mole of solution:

$$\boxed{\sum_1^k x_i d\bar{\varphi}_i = 0}\,.$$

(44)

Consider a binary solution. Fair for him

$$x_1 d\bar{\varphi}_1 + x_2 d\bar{\varphi}_2 = 0 \, .$$

Divide this equation by the value dN 2 and move the second term to the right side:

$$x_1\left(\frac{\partial\bar{\varphi}_1}{\partial x_2}\right) = -x_2\left(\frac{\partial\bar{\varphi}_2}{\partial x_2}\right),$$

или

$$\frac{\left(\dfrac{\partial\bar{\varphi}_1}{\partial x_2}\right)}{\left(\dfrac{\partial\bar{\varphi}_2}{\partial x_2}\right)} = -\frac{x_2}{x_1} = -\frac{x_2}{1-x_2} \, .$$

(45)

From the analysis of the obtained relationship (45) the following conclusions follow.

1. Since x $_1 \geq 0$ and x $_2 \geq 0$, the right side of the equation is always negative, therefore, the left side is also negative. This means that if one derivative is positive, then the other must be negative. In other words, if in some

concentration range the property $\phi_1$ increases with increasing concentration $x_2$, then $\phi_2$ decreases.

2. For $x_1$ \u003d $x_2$ \u003d 0.5, the ratio of derivatives on the left side of the equation is 1. Hence, they are the same in absolute value and opposite in sign.

3. If the concentration dependence of one of the partial molar properties has a maximum, then the dependence of the second has a minimum at the same concentration.

Indeed, if neither $x_1$ nor $x_2$ are equal to zero, then both derivatives are equal to zero, and opposite signs correspond to the maximum and minimum.

4. If $x_2 > x_1$, то $\left|\frac{\partial\bar{\varphi}_1}{\partial x_2}\right| \succ \left|\frac{\partial\bar{\varphi}_2}{\partial x_2}\right|$, i.e. in a solution of a given concentration, the partial molar property of the component whose concentration is lower changes more intensely.

## 29-Lecture.

## Partial molar quantities.

Relationship between partial molar sizes and chemical potential.

### Partial molar quantities and their significance in the thermodynamics of solutions.

To establish the dependence of the properties of solutions on the composition and properties of the components, partial molar quantities are used.

When solutions are formed, the properties of the components forming the solution change. The concept of “partial molar value” was introduced to express the numerical value of any property of one mole of a solution component .

For example, the partial molar volume of a component is the volume of one mole of that component in solution. Depending on how much and in what direction the interaction forces between particles have changed during the formation of a solution, the value of the partial molar volume of a component may be greater or less than the volume that the same mole of this component had before being added to the solution. Thus, the molar volume of water is 18.0 ml (at a density of 1 g/cm $^3$). When a 40% aqueous solution of ethyl alcohol is formed, each mole of water decreases in volume by 0.4 ml and becomes equal to 17.6 ml. This volume should be called the partial molar volume.

*Let*'s consider some extensive (depending on the amount of solution) thermodynamic property ( *Xtotal* ) of the solution. Extensive thermodynamic properties include: Gibbs energy ( *Gtot )* , enthalpy ( *Htot* ), entropy ( *Stot* ), volume ( *Vtot* ) , heat capacity ( *Ctot )* , etc.

*consisting* of a solvent and a solute, its extensive property ( *Xtotal* ) depends on the number of moles *n1* of the solvent, the number of moles *n2 of the dissolved* substance, pressure and temperature:

$$X_{общ} = f(n_1, n_2, p, T) \quad (4.3)$$

Considering that the extensive property of a solution ( *Xtotal* ) is a function of state, let us take the total differential of this expression at *constant p* and *T* :

$$dX_{общ} = \left(\frac{\partial X_{общ}}{\partial n_1}\right)_{p,T,n_2} dn_1 + \left(\frac{\partial X_{общ}}{\partial n_2}\right)_{p,T,n_1} dn_2 \; . \quad (4.4)$$

Let's denote:

$$\overline{X}_i = \left(\frac{\partial X_{общ}}{\partial n_i}\right)_{p,T,n_j} . \quad (4.5)$$

Then

$$dX_{общ} = \overline{X}_1 dn_1 + \overline{X}_2 dn_2 \; , \quad (4.6)$$

where $\overline{X}_i$ is the partial molar value or property *of the i* -th component in the solution.

The partial molar value of the i-th component of a solution is the change in a given extensive property of a solution when 1 mol of *the i* -th component is added to a larger amount of solution at constant temperature and pressure.

A few notes:

1. A larger amount of solution means that the composition of the solution practically does not change after adding one mole of a component.

2. The partial molar value of a pure substance is equal to the property of a pure substance: $\overline{X}_i = X_i^0$ .

3. The partial molar value always refers to some component.

4. Among the partial molar quantities, the most important is the partial molar Gibbs energy ( $\overline{G}_i$ ), which is identical to the chemical potential: $\overline{G}_i \equiv \mu_i$

The practical significance of partial molar quantities is that the same thermodynamic relationships remain between them as between ordinary thermodynamic quantities.

For example: $\overline{G}_i \equiv \overline{H}_i - T\overline{S}_i$, where: $\overline{G}_i$ – partial molar Gibbs energy *of the i* -th component, $\overline{H}_i$ – partial molar enthalpy *of the i* -th component; $\overline{S}_i$ – partial molar entropy *of the i* -th component.

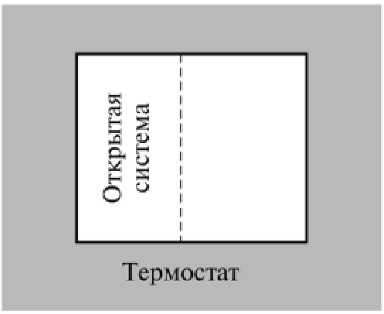
## 30-Lecture.
## Topic: Gibbs-Duhem and Duhem-Margulis equations.

Decision laws for ideal, infinitely dilute and real systems.

### Gibbs-Duhem equation and partial molar quantities.

Let us imagine a homogeneous medium in thermodynamic equilibrium, within which a mental boundary is drawn and an open system is identified (Fig. 2.5). All extensive properties of this open system depend on the position of the mental boundary. Therefore, we can write for it according to (2.22d):

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \sum \mu_i \mathrm{d}n_i.$$



Rice. 2.5. **Open system (to the left of the imaginary boundary)**

Since the intensive properties of *T, p* and all p, are the same in a homogeneous environment, this equation can be easily integrated within the variables corresponding to the initial position of the mental boundary 1 and the final position 2:

$$(U_2 - U_1) = T(S_2 - S_1) - p(V_2 - V_1) + \sum \mu_i (n_{2,i} - n_{1,i}).$$

Since both positions of the boundary are arbitrary, we can choose 0 as the initial volume and all other initial extensive variables, and some variable quantities depending on the final position of the boundary as the final ones:

$$U = ST - Vp + \sum n_i \mu_i .$$

Let's differentiate this equation:

$$\mathrm{d}U = S\mathrm{d}T + T\mathrm{d}S - V\mathrm{d}p - p\mathrm{d}V + \sum n_i \mathrm{d}\mu_i + \sum \mu_i \mathrm{d}n_i$$

and subtract the original Gibbs equation (2.22d) from the resulting equation:

$$0 = S\mathrm{d}T - V\mathrm{d}p + \sum n_i \mathrm{d}\mu_i . \qquad (2.26)$$

This equation is called the Gibbs-Duhem equation. It is often referred to as the fundamental equations of thermodynamics, since it underlies the description of the properties of multicomponent systems (Chapter 6). In addition, it allows you to say how many independent variables an open homogeneous system has.

Let the number of components be equal to C. Then the differential form in (2.26) contains *C +2* differentials of intensive variables, but since it is equal to 0, only C + 1 of them are independent. When the C + 1 intensive variables of a simple system are named, all other intensive variables become defined and depend on them. It is customary to say, therefore, that C + 1 intensive variables determine *the intensive state* of the system, which does not depend on the size of the system.

Let us now consider an arbitrary extensive property *X (X* can be *U, H, S, V, A, G,* $C_p$ , $C_y$ , etc.) as a function of *T, p* and the number of components: *X(T, p* , $p_A$ , I'm $_{\text{in}}$ ,...). The differential of this function has the form:

$$\mathrm{d}X = \sum X_i \mathrm{d}n_i \quad \text{при } T, p = \text{const}, \qquad (2.27a)$$

Where

$$X_i = \left(\frac{\partial X}{\partial n_i}\right)_{T,p,n_{j\neq i}} \qquad (2.27б)$$

called partial molar quantity. Note that the chemical potential is equal to the partial molar Gibbs energy. Note also that in a one-component system the partial molar quantities are equal to the molar quantities:

$$X_i = X_{\mathrm{m}} \quad \text{при } C = 1. \qquad (2.28)$$

Referring to Fig. 2.5 and reasoning in the same way as above - when deriving the Gibbs-Duhem equation, we can write:

$$X = \sum X_i n_i . \qquad (2.29)$$

This equation is called the rule of additivity of partial quantities *XiHj.* The word partial *{partial* ) means *incomplete, forming part of the whole.* The sum of the partial values *X,n,-* over all components constitutes the complete extensive property *X,* and each coefficient *Xj* serves as a partial contribution from a unit amount of the component. Let's differentiate this equation:

$$dX = \sum X_i dn_i + \sum n_i dX_i$$

and subtract equation *(2.21a) from it:*

$$\sum n_i dX_i = 0 \quad \text{при } T, p = \text{const}. \qquad (2.30)$$

This equation is also called the Gibbs-Duhem equation. The reason for this is that the Gibbs energy and chemical potentials are characteristic functions. Any function *X* or *Xj* can be derived from them for *T, p* = const. Consequently, equation (2.30) is derived from the original Gibbs–Duhem equation (2.26).

For example, for a homogeneous system with two components A and B:

$$dG = \mu_A dn_A + \mu_B dn_B \quad \text{при } T, p = \text{const};$$

$$G = \mu_A n_A + \mu_B n_B;$$

$$n_A d\mu_A + n_B d\mu_B = 0 \quad \text{при } T, p = \text{const}.$$

For partial molar quantities, many of the relations between partial derivatives derived earlier for extensive quantities are true, because the order (sequence) of differentiation does not matter. In particular, from (2.11 *a)* it follows:

$$\left(\frac{\partial \mu_i}{\partial T}\right)_p = -S_i; \quad \left(\frac{\partial \mu_i}{\partial p}\right)_T = V_i. \qquad (2.31)$$

Other useful ratios:

$$H_i = \mu_i - T\left(\frac{\partial \mu_i}{\partial T}\right)_p; \quad \left[\frac{\partial(\mu_i/T)}{\partial T}\right]_p = \frac{H_i}{T^2}; \qquad (2.32)$$

$$\left(\frac{\partial H_i}{\partial T}\right)_p = T\left(\frac{\partial S_i}{\partial T}\right)_p = C_{p,i}. \qquad (2.33)$$

## 31-Lecture.

## 32-Lecture.

## 33-Lecture.

## Thermodynamics of volatile liquid mixtures.

Gibbs-Konovalov and Vrevsky laws. Properties of azeotropic mixtures.

***Relationship between the composition of liquid solution and vapor. Konovalov's laws.***

The relative content of components in steam, as a rule, differs from their content in solution - steam is relatively richer in the component whose boiling point is lower. This fact is reflected in Konovalov’s first law:

*Saturated steam, compared to the equilibrium solution, is enriched in the component whose boiling point is lower.*

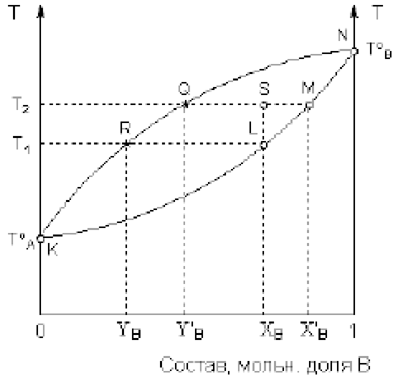
Adding this component to a liquid solution lowers the boiling point of the solution at a certain constant pressure (or, which is the same thing, increases the total vapor pressure above the solution).

The separation of solution components using distillation is based on the difference in the compositions of the solution and the vapor in equilibrium with it. For consideration

equilibrium in such systems, it is convenient to use state diagrams of solution - vapor in the coordinates boiling point - composition or vapor pressure - composition.

Let us consider the phase diagrams of a binary liquid solution, the components of which are unlimitedly soluble in each other and do not form an azeotropic mixture (type 1 systems). (For azeotropic mixtures, see below).

When considering the process of distillation of a solution at constant pressure, a phase diagram is used in the coordinates boiling point - composition *(Fig. 12).*

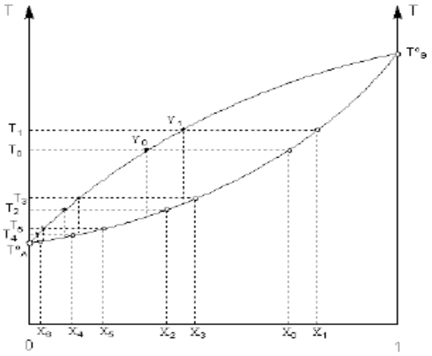


*Rice. 12. Type 1 system state diagram*
*in temperature–composition coordinates (p = const)*

The KLMN curve represents the dependence of the initial boiling point on the composition of the solution; Below the curve there is an area corresponding to the liquid phase. The KRQN curve represents the dependence of the boiling temperature of the solution on the composition of the steam; Above the curve is the region corresponding to the gaseous phase. The area between the curves is the area of heterogeneity of the system.

As can be seen from the diagram, a solution of composition XB begins to boil at T1 (point L), and the vapor that is in equilibrium with it has composition YB (point R), i.e. steam is enriched in comparison with the liquid phase with component A, the addition of which to the solution lowers the initial boiling point of the solution. The phase diagram allows not only to determine the composition of equilibrium phases, but also to calculate their relative quantities. Let us consider a system of general chemical composition located at temperature $T_2$ (point S). The equilibrium liquid phase (point M) will have the composition X'B, and the equilibrium vapor will have the composition Y'B (point Q). The relative amounts of phases are determined by the lever rule: in this case, the amount of the liquid phase (in moles, since the composition is expressed in mole fractions) will relate to the amount of vapor as the length of the segment |QS| refers to the length of the segment |SM|.

Thus, the phase diagram makes it possible to determine the composition of the fraction distilled from a solution of chemical composition in the temperature range from $T_1$ to $T_2$. It is obvious that in this case the composition of the fraction will be between YB and Y'B, i.e. the distilled fraction will be enriched in component A compared to the original solution. If the condensed steam is subjected to repeated distillation, a fraction will be obtained that is even more enriched in component A. As a result of repeated repetition of such operations, pure component A can be obtained. Separation of components of a liquid solution having different temperatures boiling, due to repeated repetition of evaporation - condensation cycles is called rectification. The rectification process is shown schematically in *Fig. 13.*



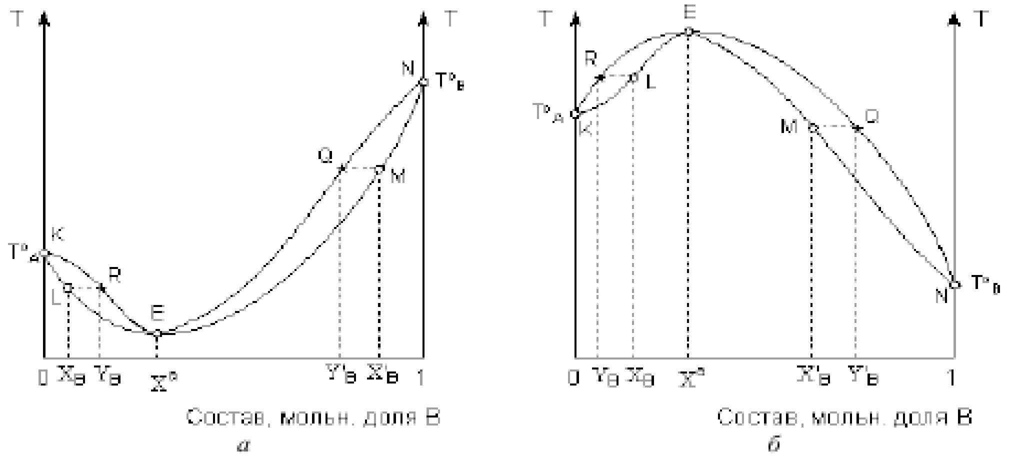
*Composition, mol. share B*

*Rice. 13. Rectification of solutions of volatile liquids.*

When distilling a source solution of composition X0, the composition of the solution continuously changes and the boiling point increases. During distillation in the temperature range from $T_0$ to $T_1$, the composition of the equilibrium vapor also changes from $Y_0$ to $Y_1$; its condensation will produce a liquid fraction of the composition in $X_2$ (composition averaged), boiling at temperature $T_2$. By distilling it in the temperature range from $T_2$ to $T_3$ after condensation of the steam, a fraction of the composition $X_4$ will be obtained, boiling at a temperature $T_4$. By distilling the latter in the temperature range from $T_4$ to $T_5$, a fraction of composition $X_6$ is obtained. The composition and boiling point of this fraction are already quite close to pure component A.

The number of evaporation-condensation cycles required for complete separation of the solution components (the number of theoretical plates of the distillation column) is determined by the nature of the components (primarily the difference in their boiling points) and the desired degree of purity of the resulting rectified product and can be calculated using a state diagram of the system.

Examples of phase diagrams of type 2 mixtures characterized by an extremum are shown in *Fig. 14.*



*Rice. 14. State diagrams of solution - vapor for volatile solutions of the 2nd type in the coordinates boiling point - composition for systems with a minimum (a) and maximum (b) boiling point*

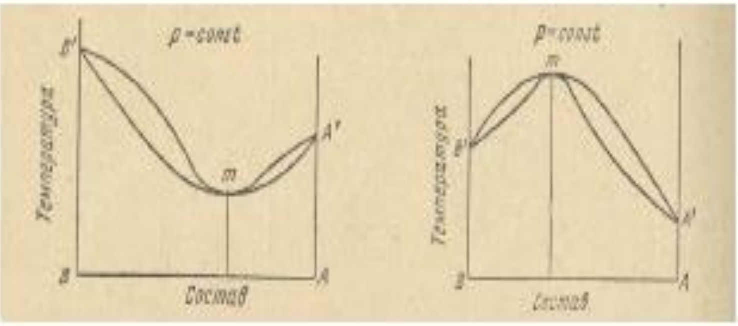
Type 2 solutions are called azeotropic. The composition corresponding to the extremes (minimum or maximum) is called the composition of the azeotropic solution. At the points corresponding to the minimum or maximum, the composition of the vapor coincides with the composition of the liquid (Konovalov’s second law). The boiling point of azeotropic solutions at constant external pressure is unchanged, and the composition of the solution does not change during distillation (as with individual substances). The state diagram of a type 2 system can, in principle, be considered as a set of state diagrams of two systems of type 1, in each of which an azeotropic mixture acts as one of the components. The analysis of the state diagram of such systems is similar to that for type 1 systems.

As can be seen in Fig. 14, complete separation of such systems by distillation is impossible. During fractional distillation of a system with a minimum boiling point (Fig. 14, a), the composition of the distillate gradually approaches ***azeotropic*** . The liquid residue is enriched with the component that was in excess in the initial solution compared to the composition of the azeotropic mixture - component A in the concentration range to the left of the azeotropic composition and component B in the concentration range to the right of the azeotropic composition. In systems with a maximum boiling point (Fig. 14, b), on the contrary, the distillate is enriched with a component that was in excess relative to the azeotropic solution, and the composition of the bottoms gradually approaches azeotropic.

It should, however, be remembered that the identification of an azeotropic mixture with an individual substance is conditional. When the external pressure changes, the extremum on the curve of the dependence of the boiling point on the composition shifts (in some cases, the extremum may disappear). Consequently, the compositions of azeotropic solutions for liquid mixtures of these components at different pressures differ. Thus, for the ethanol-water system, the mole fraction of ethanol in the azeotrope is 0.895 at a pressure of 760 mm Hg. Art., and 0.996 - at 100 mm Hg. Art.

Finally, when the pressure rises to point M//, the last vapor bubble will have composition R. Thus, the liquid composition will change along the QCM// curve, and the vapor composition will change along the PDR curve.

Let us also consider diagrams of systems with maximum and minimum.



According to Konovalov’s II law, at points C the composition of the vapor coincides with the composition of the liquid. Unlike all mixtures, azeotropic mixtures (corresponding to point M) will turn into vapor without change when the pressure decreases.

**These diagrams well illustrate Konovalov's I-law** .

For example, in a diagram with a maximum for mixtures whose composition points lie to the left of the azeotropic point, the vapor will be richer in component A, the addition of which increases the total vapor pressure. And, conversely, for mixtures whose composition lies to the right of the azeotropic point, the vapor will be richer in component B, the addition of which in this case also increases the total vapor pressure above the liquid.

## I-Vrevsky's law

As the temperature of the solution in equilibrium vapor increases, the relative content of the component whose partial molar heat of evaporation is greater increases.

## II-Vrevsky's law

In systems that have a maximum in the vapor pressure curve, with increasing temperature in the azeotropic solution, the concentration of the component whose partial molar heat of evaporation is greater increases.

Composition diagram – boiling point of a binary liquid system with a minimum Composition diagram – boiling temperature of a binary liquid system with a maximum. In systems that have a minimum on the vapor pressure curve, in the azeotropic mixture, as the temperature increases, the concentration of the component whose partial molar heat of evaporation is lower increases.

### III-Vrevsky's law

When the temperature changes, the composition of the azeotropic solution in systems with a maximum on the vapor pressure curve changes in the same direction as the composition of the equilibrium vapor, and in systems with a minimum - in the opposite direction.

## 34-Lecture.

## Basic concepts of electrochemistry.

Theory of electrolytic dissociation and its application. Thermodynamic theory of electrolyte solutions. Theory of electrostatic dissociation of solutions of strong electrolytes.

Electrolytes are substances whose melts or solutions conduct electric current due to dissociation into ions.

### Theory of electrolytic dissociation. Degree of dissociation.

To explain the peculiarities of the properties of electrolyte solutions, S. Arrhenius proposed the theory of electrolytic dissociation, based on the fact that electrolytes in solutions disintegrate into ions - dissociate.

Dissociation of electrolytes in solution occurs under the influence of polar solvent molecules; the presence of ions in a solution determines its electrical conductivity. To assess the completeness of dissociation, the theory of electrolytic dissociation introduces the concept of the degree of dissociation α, which is equal to the ratio of the number of molecules n that disintegrated into ions to the total number of molecules N:

$$\alpha = \frac{n}{N}.$$

The degree of dissociation depends on the nature of the solvent and solute, the concentration of the solution and temperature. Based on the degree of dissociation, electrolytes are divided into three groups: strong ($\alpha \geq 0.7$), medium strength ($0.3 < \alpha < 0.7$) and weak ($\alpha \leq 0.3$). Strong electrolytes include almost all salts (except for $Pb(CH_3COO)_2$, $HgCl_2$, $CdCl_2$), most inorganic acids and alkalis; to weak ones - all organic acids, water, $NH_4OH$, $H_2S$, etc. Some inorganic acids are medium-strength electrolytes: HF, HCN, $H_3PO_4$.

### Weak electrolytes. Dissociation constant.

The process of dissociation of weak electrolytes is reversible. A dynamic equilibrium is established in the system, which can be quantified by the equilibrium constant expressed in terms of the concentrations of the resulting ions and undissociated molecules. This constant is called the dissociation constant. For some weak electrolyte, which disintegrates into ions in solution in accordance with the equation

$$\mathbf{A^{a}B^{b} = aA^{x-} + bB^{y+}}$$

the dissociation constant will be expressed by the following relation:

$$K = \frac{[A^{x-}]^a[B^{y+}]^b}{[A_aB_b]}$$

For a binary (decomposing into two ions) electrolyte, expression (63) can be rewritten as

$$K = \frac{[A^{x-}][B^{y+}]}{[AB]}. \quad (63a)$$

Since the concentration of each ion for a binary electrolyte is equal to the product of the degree of dissociation α and the total concentration of the electrolyte C, expression (63a) in this case can be rewritten as follows:

$$K = \frac{\alpha^2 C^2}{(1-\alpha)C} = \frac{\alpha^2}{(1-\alpha)}C.$$

For dilute solutions we can assume that (1 – α) = 1. Then we get

$$K = \alpha^2 C; \quad \alpha = \sqrt{\frac{K}{C}}. \quad (65)$$

Thus, the degree of dissociation of a weak electrolyte is inversely proportional to the concentration, i.e. is directly proportional to the dilution of the solution. Expression (65) is called Ostwald's dilution law.

The degree of dissociation of a weak electrolyte can be related to the isotonic coefficient i. We will assume that out of N electrolyte molecules, n molecules have dissociated, forming νn ions (ν is the number of ions into which the molecule dissociates). Since the isotonic coefficient shows how many times the total number of molecules and ions in solution is greater than the number of molecules before dissociation, we obtain

$$i = \frac{N + n(\nu - 1)}{N} = 1 + \frac{n}{N}(\nu - 1), \qquad i = 1 + \alpha(\nu - 1). \quad (66)$$

Relation (66) makes it possible, by experimentally determining the isotonic coefficient of a solution, to calculate the degree of dissociation of a weak electrolyte.

## Strong electrolytes

Strong electrolytes in solutions of any concentration completely dissociate into ions and, therefore, the patterns obtained for weak electrolytes cannot be applied to strong electrolytes without appropriate adjustments.

The theory of strong electrolytes was developed by P. Debye and G. Hückel in 1923. For strong electrolytes that completely dissociate into ions, even at low solution concentrations, the energy of electrostatic interaction between the ions is quite large, and this interaction cannot be neglected. The interaction of oppositely and likewise charged ions (attraction and repulsion, respectively) leads to the fact that near each ion there are predominantly ions with opposite charges, forming an ionic atmosphere. The radius of the ionic atmosphere is relatively large, so the ionic atmospheres of neighboring ions intersect; In addition, each ion is surrounded by dipole solvent molecules - a solvation shell.

Thus, in a solution of a strong electrolyte, a semblance of a spatial structure appears, which limits the freedom of movement of ions and leads to a change in the properties of the solution in the same direction as a decrease in the degree of dissociation would act. Therefore, by determining the degree of dissociation of a strong electrolyte solution, the apparent degree of dissociation is obtained, i.e. value α adjusted for inter ionic interaction. The higher the concentration of the solution, the stronger the interaction of the ions, the lower the apparent degree of dissociation of the strong electrolyte.

Quantitative calculations of the characteristics of solutions of strong electrolytes are carried out using the concepts of electrolyte activity ae and the activities of cations and anions $\boldsymbol{a}^{+}$ and $\boldsymbol{a}^{-}$, respectively, which are equal to the product of the activity coefficient and the concentration:

$$a_{\text{э}} = f\,C; \quad a_+ = f_+C_+; \quad a_- = f_-C_-.$$

For a binary electrolyte, the average activity of the electrolyte is related to the activities of the ions by the relation

$$a_{\text{э}} = a_+a_-.$$

The average activity coefficient is related to ionic activity in a similar way:

$$f_{\text{э}} = f_+f_-.$$

Debye and Hückel developed a method for calculating the average activity coefficient of a strong electrolyte. For a binary electrolyte, the equation has the following form:

$$\lg f_{\text{э}} = -0{,}5z^2\sqrt{I}. \quad (67)$$

Here z is the charge of the ion for which the activity coefficient is calculated;
I is the ionic strength of the solution. The ionic strength of the solution is equal to half the amount of contrations of all ions multiplied by the square of their charge:

$$I = 0{,}5\sum(C_iz_i^{\,2}).$$

The Debye–Hückel theory is applicable only at concentrations not exceeding 0.05 mol/l. For more concentrated solutions of strong electrolytes, there is no quantitative theory.

## Electrical conductivity of electrolyte solutions .

Electric current is the ordered movement of charged particles. Electrolyte solutions have ionic conductivity due to the movement of ions in an electric field (in contrast to the electronic conductivity of metal conductors).

The value of the preferential movement of the ion (cm) in the direction one of the electrodes when current passes through the solution, related to a potential gradient of 1 V/cm, is the absolute speed of movement of the ion. The absolute velocities of ion movement are of the order of 0.0005–0.003 cm $^2$ /(V s). The absolute velocities of U + cations and U– anions differ; this results in ions of different signs carrying different amounts of electricity.

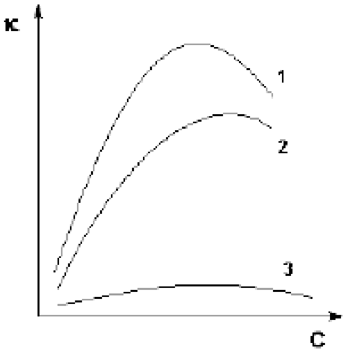
Any conductor through which current flows is characterized by resistance R , which, according to Ohm's law, is directly proportional to the length of the conductor l and inversely proportional to the cross-sectional area S. The proportionality coefficient is the resistivity of the material ρ - the resistance of a conductor having a length of 1 cm and a cross-section of 1 cm $^2$ :

$$R = \rho \frac{l}{S}, \text{ Ом.}$$

As a quantitative measure of the ability of an electrolyte solution To conduct electric current, specific electrical conductivity κ (kappa) is usually used - the reciprocal of resistivity:

$$\kappa = \frac{1}{\rho}, \text{ Ом}^{-1}\text{см}^{-1}.$$

The value of specific electrical conductivity of an electrolyte depends on a number of factors: the nature of the electrolyte and solvent, temperature, concentration solution. The specific electrical conductivity of electrolyte solutions (as opposed to the electrical conductivity of conductors with electronic conductivity) increases with increasing temperature, which is caused by an increase in speed movement of ions due to lowering the viscosity of the solution and reducing the solvation of ions.



Rice. 20. Dependence of the specific electrical conductivity of electrolytes on concentration: 1 – $H_2SO_4$ ; 2 – KOH ; 3 – $CH_3COOH$ .

With increasing concentration, the specific electrical conductivity of solutions first increases, reaching a certain maximum value, and then begins to decrease *(Fig. 20).* This dependence is very clearly expressed for strong electrolytes and much worse for weak ones. The presence of a maximum in the curves is explained by the fact that in dilute solutions of strong electrolytes, the speed of movement of ions depends little on the concentration, and κ first increases almost directly in proportion to the number of ions; As the concentration increases, the interaction of ions increases, which reduces the speed of their movement.

For weak electrolytes, the presence of a maximum in the curve is due to the fact that with increasing concentration the degree of dissociation decreases, and when a certain concentration is reached, the number of ions in the solution increases more slowly than the concentration.

## 35-Lecture.

## Electrical conductivity of electrolyte solutions.

Onsager's theory. Ostwald's law. Conductometric titration.

### Specific electrical conductivity of electrolyte solutions

Electric current is the ordered movement of charged particles. Electrolyte solutions have ionic conductivity (they are so-called conductors of the second kind), i.e. the electrical conductivity of electrolyte solutions is due to the movement of ions in an electric field (in contrast to the electronic conductivity of conductors of the first kind).

The amount of preferential movement of an ion in the direction of one of the electrodes when current passes through a solution, related to a potential gradient of 1 V/cm, is the *absolute speed of movement of the ion* . The absolute velocities of ion movement are on the order of 0.0005 – 0.003 cm $^2$ /(V s). The absolute speeds of movement of U $_{+}$ cations and U $_{–}$ anions differ; this results in ions of different signs carrying different amounts of electricity.

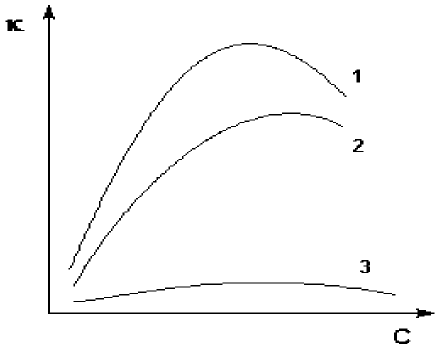
Any conductor through which current flows represents for it a certain resistance R, which, according to Ohm’s law, is directly proportional to the length of the conductor l and inversely proportional to the cross-sectional area S; the coefficient of proportionality is the resistivity of the material ρ - the resistance of a conductor having a length of 1 cm and a cross-section of 1 cm $^2$ :

$$R = \frac{\rho l}{S}\text{, Ohm}$$

As a quantitative measure of the ability of an electrolyte solution to conduct electric current, *specific electrical conductivity* κ (kappa) is usually used - the reciprocal of resistivity (i.e., the reciprocal of the resistance of a solution column between electrodes with an area of 1 cm $^2$ located at a distance of 1 cm):

$$\kappa = \frac{1}{\rho}\text{, Ohm}^{-1}\text{ cm}^{-1}$$

The value of the specific electrical conductivity of the electrolyte depends on a number of factors: the nature of the electrolyte, temperature, and concentration of the solution. The specific electrical conductivity of electrolyte solutions (in contrast to the electrical conductivity of conductors of the first kind) increases with increasing temperature, which is caused by an increase in the speed of movement of ions due to a decrease in the viscosity of the solution and a decrease in the solvation of ions. The dependence of specific electrical conductivity on solution concentration is shown in Fig. 3.9.



**Rice. 2.** Dependence of the specific electrical conductivity of electrolytes on concentration (1 – $H_2SO_4$, 2 – KOH, 3 – $CH_3COOH$) .

As can be seen from the figure, with increasing concentration, the specific electrical conductivity of solutions first increases, reaching a certain maximum value, and then begins to decrease. This dependence is very clearly expressed for strong electrolytes and much worse for weak ones. The presence of a maximum in the curves is explained by the fact that in dilute solutions of strong electrolytes, the speed of movement of ions depends little on the concentration, and κ first increases almost directly in proportion to the number of ions; As the concentration increases, the interaction of ions increases, which reduces the speed of their movement. For weak electrolytes, the presence of a maximum in the curve is due to the fact that with increasing concentration the degree of dissociation decreases, and when a certain concentration is reached, the number of ions in the solution begins to increase more slowly than the concentration. To take into account the influence of their concentration and interaction between ions on the electrical conductivity of electrolyte solutions, the concept of molar electrical conductivity of a solution was introduced.

### Molar electrical conductivity of electrolyte solutions .

*The molar electrical conductivity* of a solution $\lambda$ is the reciprocal of the resistance of a solution containing 1 mole of solute and placed between electrodes located at a distance of 1 cm from each other. The molar electrical conductivity is related to the specific electrical conductivity $\kappa$ and the molar concentration of the solution C by the following relationship:

$$\lambda = \frac{1000\kappa}{C}, \text{ Ohm}^{-1}\text{ cm}^{2}\text{ mol}^{-1}$$

The molar electrical conductivity of both strong and weak electrolytes increases with decreasing concentration (i.e., increasing solution dilution V = 1/C), reaching a certain limiting value $\lambda_0$, called molar electrical conductivity at infinite dilution (Fig. 3 - 4).

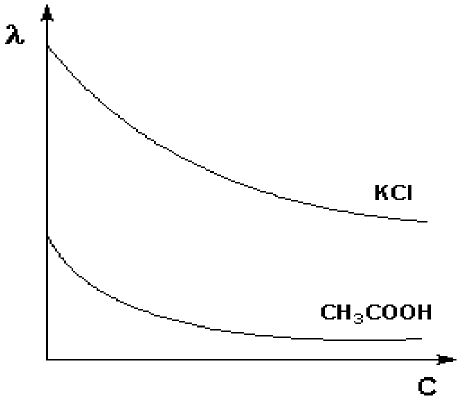


**Fig.3.** Dependence of molar conductivity on concentration.

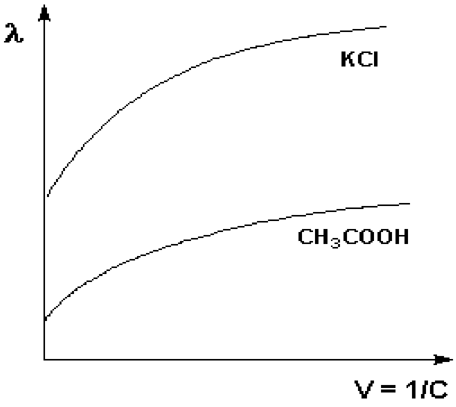


**Fig.4.** Dependence of molar electrical conductivity from dilution

For a weak electrolyte, this dependence of the molar electrical conductivity on concentration is mainly due to an increase in the degree of dissociation with dilution of the solution. In the case of a strong electrolyte, as the concentration decreases, the interaction of the ions with each other weakens, which increases the speed of their movement and, consequently, the molar electrical conductivity of the solution. The latter is associated with the absolute velocities of movement of cations and anions $U_+$ and $U_-$ by the Arrhenius equation :

$$\lambda = \alpha F(U_+ + U_-) \quad 2)$$

F. Kohlrausch showed that each ion makes its own independent contribution to the molar electrical conductivity of infinitely dilute electrolyte solutions, and $\lambda_o$ is the sum of the molar electrical conductivities of the cation and anion $\lambda_+$ and $\lambda_-$ (the so-called *ion mobilities* ), and formulated *the law of independence of motion ions* :

> *The molar electrical conductivity at infinite dilution is equal to the sum of the electrolytic mobilities of the cation and anion of a given electrolyte.*

$$\lambda_o = \lambda_+ + \lambda_- \qquad 3)$$

3 ) into this expression and accepting that at infinite dilution the degree of dissociation α is equal to unity, we obtain:

$$\lambda_o = F(U_+ + U_-) = FU_+ + FU_- \quad 4)$$

From here

$$\lambda_+ = FU_+;\ \lambda_- = FU_- \quad 5)$$

Electrolytic mobility is the most important characteristic of an ion, reflecting its participation in the electrical conductivity of a solution.

### CARRY NUMBER.

Current carriers in electrolyte solutions are ions. Due to the different absolute speeds of movement of the ions, the proportion of electricity carried by them will be different. A larger fraction is always carried by faster ions. The value through which the fraction of electricity transferred by ions can be expressed is called the transfer number and is denoted by the indices t+ for the cation and t– for the anion.

The ion transfer number determines the fraction of electricity transferred by cations and anions:

$$t_+ = \frac{Q_+}{Q_+ + Q_-} \quad \text{и} \quad t_- = \frac{Q_-}{Q_+ + Q_-}$$

where is $Q_i = z_i \cdot F \cdot c_i \cdot u_i^* \cdot S \cdot \tau$ the amount of electricity transferred by ions of the i-th type with charge $z_i$ and absolute speed $u_i^*$, through a section of area S in time τ, $c_i$ – concentration (m), F – Faraday number.

The transfer number also reflects the differences in the absolute rates of movement of the cation and anion, and taking into account the electrical neutrality of the solution (z+ ·c+ = z– ·c–), they can be written as follows:

$$t_+ = \frac{u_+^*}{u_+^* + u_-^*} \quad \text{и} \quad t_- = \frac{u_-^*}{u_+^* + u_-^*}.$$

The transfer number is not a parameter of a given ion, since it depends on the mobility of the ion paired with it and shows the unequal amount of electricity transferred by ions of the opposite sign. The transfer number, for example, of cations ($t_+$) $H^+$, $K^+$ and $Li^+$ in solutions with a concentration of 0.1 mol/l HCl, KCl and LiCl is, respectively, 0.831; 0.490 and 0.317. Thus, the largest share of electricity is carried by protons, and the smallest by lithium cations.

The transfer number $\boldsymbol{t_i}$ determines not the individual property of the ion, but the role of this ion in the migration transfer of charges in a given electrolyte solution. In a binary solution, the transport number depends on the mobility of the second ion.

For example, the transfer number of chloride ion in an HCl solution is less than in a KCl solution of the same concentration, since hydrogen ions are more mobile than potassium ions. In a multicomponent solution, the transfer number also depends on the ratio of the concentrations of the solution components.

As temperature increases, the absolute rates of ion movement increase, but to varying degrees, and the ion transport number will also change. Moreover, if the cation transfer number increases, then by the equality t+ + t–=1 the anion transfer number decreases, and vice versa. For strong electrolytes, absolute rates $(u_i^*)$ are proportional to ion mobility $(F \cdot u_i^* = \lambda_i)$, which allows us to write the electricity transfer number in terms of the ratio of the mobilities of cations and anions:

$$t_+ = \frac{\lambda_+}{\lambda_+ + \lambda_-} \quad \text{и} \quad t_- = \frac{\lambda_-}{\lambda_+ + \lambda_-}$$

Taking into account the Kohlrausch relation $\lambda^\infty = \lambda_+^\infty + \lambda_-^\infty$ and equalities $\mathbf{t_+ + t_- = 1}$, the following relations hold:

$$\lambda_+^\infty = \lambda^\infty \cdot t_+ \quad \text{и} \quad \lambda_-^\infty = \lambda^\infty \cdot t_-$$

Methods for determining the transfer number are based on electrolysis of electrolyte solutions. These methods include the Hittorf method, which is based on determining the change in electrolyte concentration as a result of electrolysis in the cathode or anode space. Another method, the moving boundary method, is based on measuring changes in the position of a moving boundary.

### Fundamentals of the conductometric method of analysis.

Conductometry became one of the first instrumental methods for studying the composition and properties of electrolyte solutions. Conductometric analysis is carried out using special instruments - conductometers that measure the resistance of solutions. The value of resistance determines its inverse value - electrical conductivity. From the electrical conductivity values you can calculate:

- dissociation constant of weak electrolytes, their degree of dissociation;
- product of solubility of poorly soluble compounds;
- instability constant of complex compounds;
- ionic mobility;
- pH of solutions of acids and bases.

Electrolytic dissociation is the process of breaking apart molecules into ions. Let us consider the dissociation equilibrium of a weak binary electrolyte, which gives upon dissociation one cation and one anion, for example, a weak acid:

$$ON \rightleftarrows N^{+} + A^{-}.$$

If the degree of acid dissociation

$\alpha = \frac{C_{H^+}}{C_{HA}} = \frac{C_{A^-}}{C_{HA}},$ That $C_{H^+} = C_{A^-} = \frac{\alpha}{V}$ And $C_{HA} = \frac{1-\alpha}{V},$ где $V = \frac{1}{C_{HA}}$ – – dilution of the solution. Then the concentration dissociation constant

$$K_C = \frac{C_{H^+} C_{A^-}}{C_{HA}} = \frac{\alpha^2}{V(1-\alpha)} = \frac{\alpha^2 C_{HA}}{1-\alpha} \qquad (1)$$

This expression is called ***V.F.'s law of dilution. Ostwald .***

Obviously, the higher KC $_{,}$ the higher the degree of dissociation. Thus, the K $_{C}$ $_{value}$ can serve as a measure of the strength of the electrolyte.

Electrolytes are considered strong if their dissociation constant exceeds 1. Electrolytes of medium strength have a dissociation constant from 10 $^{-4}$ to 1, weak electrolytes have a dissociation constant of less than 10 $^{-4}$ . Like any equilibrium constant, the dissociation constant depends on temperature, so the strength of the electrolyte changes with temperature.

Ostwald's dilution law allows us to determine the dissociation constant weak electrolyte based on its degree of dissociation a at a given concentration. With incomplete dissociation of the electrolyte

$\alpha = \frac{\lambda}{\lambda^{0}}.$

This expression is called ratio S.A. Arrhenius (1859-1927), who received it, believing that everything differences $\lambda$ from $\lambda^{0}$ are caused only by incomplete dissociation of the electrolyte.

Substituting it into expression (1), we get:

$$K_C = \frac{\lambda^2 C}{\lambda^{0}(\lambda^{0} - \lambda)} \qquad (2)$$

This equation, like equation (1), is called Ostwald's dilution law.

If we determine l for electrolyte solutions of different concentrations, then we can find $\lambda_0$ and $K_C$. To do this, expression (2) is transformed into one of the linear forms:

$$\frac{1}{\lambda} = \frac{1}{\lambda^{o}} + \frac{1}{K_C(\lambda^{o})^2}\lambda C \qquad (3)$$

or

$$\lambda C = -K_C\lambda^{o} + \frac{K_C(\lambda^{o})^2}{\lambda} \qquad (4)$$

By constructing dependency graphs $\frac{1}{\lambda} = f(\lambda C)$ или $\lambda C = f\left(\frac{1}{\lambda}\right)$ receive direct from the slope of which and from the segments cut off by them on the ordinate axis, they calculate $\lambda_0$ and $K_C$. However, determining $\lambda_0$ by extrapolating dependencies (3) and (4) is very inaccurate. Therefore, when calculating $K_C$, values are used $\lambda^{o}$, found as sums of limiting mobility $\lambda^{o}_{+}$ и $\lambda^{o}_{-}$ cation and anion, on which the electrolyte under study dissociates.

One of the disadvantages of the conductometry method is its low selectivity, since electrical conductivity is an additive value due to presence of all ions. Therefore, the method is sensitive to the presence foreign electrolyte impurities. However, this method has more advantages than shortcomings. The advantages of the method include high sensitivity, simplicity of the technique, availability of equipment, the ability to study colored and cloudy solutions, automation and speed of analysis. This The method has found application in many industries. It is used for continuous monitoring of food quality, to determine humidity of various materials, to determine the total salt composition of water.

The conductometric titration method has wide analytical capabilities, during which the electrical conductivity of a solution is measured. after adding certain portions of the reagent. Let's consider this method in relation to acid-base titration.

When titrating acids and bases of different strengths, the conductometric curves titration (dependence of the specific electrical conductivity of the titrated solution on volume of added titrant) have their own characteristics. Let a strong base be added to a solution of a strong acid (HCl) (NaOH) *(Fig. 4).*

The specific electrical conductivity of a solution is additively composed of electrical conductivities of the ions present in it. Before adding alkali it due to the mobility of $H^+$ and $Cl^-$ ions. Since HCl is a strong electrolyte, then H+ ions are present in the solution in significant quantities. They have abnormally high mobility, therefore the specific electrical conductivity of the solution acid will be quite high. As NaOH is added, $H^+$ ions are bound into molecules of a slightly dissociated compound - water:

$$H^+ + OH^- \rightarrow H_2O$$

Electrical conductivity decreases as a result. Instead of $H^{+,\ \text{less mobile}}$ $Na^+$ ions appear in the solution , this leads to a decrease in electrical conductivity solution. The concentration of $Cl^{-\ \text{ions}}$ and the resulting electrical conductivity do not change during the titration process (provided that the dilution of the solution caused by the addition of an alkali solution can be neglected). Decrease electrical conductivity of the solution continues to the equivalence point, at which it reaches a minimum value, caused almost exclusively by ions $Na^+$ and $Cl^-$. After reaching the equivalence point, the electrical conductivity grows due to an increase in the total concentration of electrolyte, and the straight line is steep rises upward due to the high mobility of the $OH^{-\ \text{ion}}$. However, the slope of this branches are slightly less than the slope of the first branch of the titration curve, because the mobility of the $OH^{-\ \text{ion}}$ is less than the mobility of the $H^{+\ \text{ion}}$. Dependence of the specific electrical conductivity of the solution on the volume of the added reagent (with the accuracy with which we can neglect the dilution of the solution and assume the ion mobilities to be constant), expressed by straight lines. This allows us to find the equivalence point as a break point on the conductometric titration curve, i.e. like an intersection descending and ascending lines of dependence

$$æ = f(V).$$

(In order for the dilution of the solution to be neglected, the titration should be done with a much more concentrated alkali solution than the acid solution being titrated.)

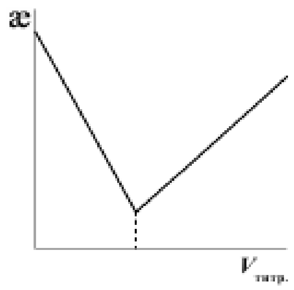


**Рис. 4.** Кривая кондуктометрического титрования сильной кислоты сильным основанием.

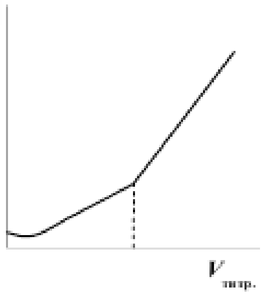


**Рис. 5.** Кривая кондуктометрического титрования слабой кислоты сильным основанием.

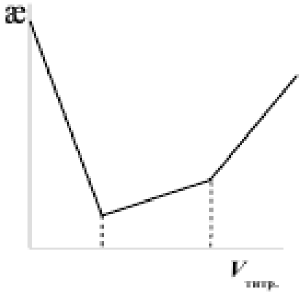


**Рис. 6.** Кривая кондуктометрического титрования смеси сильной и слабой кислот сильным основанием.

When titrating a weak acid (for example, $CH_3COOH$) with a strong base (NaOH) *(Fig. 5)*, the specific electrical conductivity initially decreases slightly, since the small amount of $H^{+\ \text{ions}}$ that was formed during the dissociation of the weak acid disappears. Further addition of NaOH leads to the formation sodium acetate. The small minimum at the beginning of the titration curve is explained by some suppression of the already small dissociation of acetic acid due to the appearance of $CH_3COO$ anions $^-$ from the $CH_3COONa$ salt. Upon reaching the equivalence point, mobile $OH^-$ ions appear , so the titration curve slopes steeply up. When titrating a weak acid, the change in electrical conductivity is complicated hydrolysis of the $CH_3COONa$ salt. As a result, the influence of $OH^{-}$ ions is already felt to the point of equivalence and manifests itself in a deviation from the linear course of the curve near her. The equivalence point is determined by extrapolation of linear sections, but in this case, to achieve the same accuracy as in the previous case, a slightly larger number of points in the linear sections of the titration curve is required.

When titrating a mixture of strong and weak acids (Fig. 6), the strong acid is first neutralized and only after that the weak acid begins to titrate. Depending on the nature of the reaction occurring, the change in electrical conductivity during titration and the nature of the titration curves may be different.

However, all conductometric titration curves have a break at the equivalence point.

## 36-Lecture.

## Classification of electrolytes.

The mechanism of formation of the electrode potential. Standard electrode potentials, redox potential, diffusion potential.

### Electrolyte solutions.

Electrolytes are substances whose solutions or melts conduct electric current (electrolyte - decomposed by electricity).

When studying electrolyte solutions, it was discovered that these substances cause a higher osmotic pressure than follows from Van't Hoff's law for non-electrolytes. Electrolyte solutions freeze at lower temperatures and boil at higher temperatures than non-electrolyte solutions of equal molecular concentrations. For electrolytes, Van't Hoff introduced a correction factor i, called the isotonic coefficient, which shows how many times the observed osmotic pressure $P_{op} > P_{vych}$

$$i = \frac{П_{оп}}{П_{выч}}.$$

Based on this, the Van't Hoff equation, when applied to electrolyte solutions, takes the following form:

$$P_{osm} = iCRT.$$

The reason for the deviation from van't Hoff and Raoult's laws in electrolyte solutions can be explained using the theory of electrolytic dissociation and the theory of strong electrolytes.

### Electrode potentials.

***Electrode*** called an electrochemical system that consists of at least two phases, one of which is a conductor of the first kind, and the other of the second, and an electric current can flow in it; such a system is sometimes also called *a half-element* .

***Electrode process* –** This is a reaction between the components of two phases, as a result of which electric charge passes from one phase to another.

As noted above, in an electrochemical cell the reaction participants are spatially separated and the overall reaction can be represented as the sum of half-reactions occurring at individual electrodes:

$\nu_A$ A + ... + $zF$ L $\nu_L$ L + ...,

$\nu_B$ B + ...L $\nu_M$ M + ... + $zF$ ,

and the EMF of the element is as the sum of the electrode potentials:

$$E = \varphi_1 + \varphi_2 = \frac{RT}{zF}\ln K_1 - \frac{RT}{zF}\ln\frac{a_L^{\nu_L}\ldots}{a_A^{\nu_A}\ldots} + \frac{RT}{zF}\ln K_2 - \frac{RT}{zF}\ln\frac{a_M^{\nu_M}\ldots}{a_B^{\nu_B}\ldots} =$$

$$= \phi_1^o - \frac{RT}{zF}\ln\frac{a_L^{\nu_L}\ldots}{a_A^{\nu_A}\ldots} + \phi_2^o - \frac{RT}{zF}\ln\frac{a_M^{\nu_M}\ldots}{a_B^{\nu_B}\ldots}. \qquad (1)$$

It follows that the equation for the electrode potential has the same form as the equation for the EMF of an electrochemical element, but it includes the activities of only those substances that take part in the electrochemical reaction at a given electrode. The $^o$ values $\varphi$represent ***standard electrode potentials*** , i.e. electrode potentials provided that the activities of all participants in the reaction are equal to unity ( $a_i = 1$). From equation (18.5) it follows that the electrode potential

$$\phi = \phi^o + \frac{RT}{zF}\ln\frac{a_A^{\nu_A}\ldots}{a_L^{\nu_L}\ldots}. \qquad (2)$$

This equation is usually called ***the Nernst equation*** for **electrode potential.**

*table* 18.1

Standard electrode potentials in aqueous solutions at 298.15 K

| Electrode | $\varphi^o$ , B | Electrode | $\varphi^o$ , B |
|---|---|---|---|
| $Li^+$\|Li | – 3.045 | $Cu^{2+}$\|Cu | + 0.337 |
| $K^+$\|K | – 2.925 | $Cu^+$\|Cu | + 0.521 |
| $Na^+$\|Na | – 2.714 | $I^-$\|$I_2$ | + 0.536 |
| $Mg^{2+}$\|Mg | – 2.37 | $Pb^{4+}$\|Pb | + 0.7 |
| $Al^{3+}$\|Al | – 1.66 | $Hg_2^{2+}$\|Hg | + 0.789 |
| $Zn^{2+}$\|Zn | – 0.763 | $Ag^+$\|Ag | + 0.799 |
| $Fe^{2+}$\|Fe | – 0.440 | $Hg^{2+}$\|Hg | + 0.854 |
| $Cd^{2+}$\|Cd | – 0.403 | $Br^-$\|$Br_2$ | + 1.065 |
| $Ni^{2+}$\|Ni | – 0.250 | $OH^-$\|$O_2$ | + 0.401 |

| | | | |
|---|---|---|---|
| $Pb^{2+}$\|Pb | – 0.126 | $Au^{3+}$\|Au | + 1.29 |
| $H_3O^+$\|$H_2$ | 0.000 | $Cl^-$\|$Cl_2$ | + 1.360 |

In reality, it is impossible to determine or calculate the potential of a single electrode, since it is determined by the potential difference between the electrode metal and the solution (galvanic potential). Therefore, a conditional scale of relative values that can be unambiguously measured was introduced. These quantities are called electrode potentials.

**Electrode potential** is defined as the EMF of an element, one of the electrodes of which is the one under study, and the other is a suitable reference electrode. The reference electrode is usually a standard hydrogen electrode at a given temperature. The standard hydrogen electrode is a 1.013 hydrogen pressure electrode $\cdot 10^5$ Pa (1 atm) and the activity of hydrogen ions in solution equal to one. According to international sign convention, the electrode potential is equal to the emf of the circuit composed of the electrode under study and the standard hydrogen electrode written on the left. If the activity of ions in a solution with the electrode under study is equal to unity, then the emf of such a circuit is equal to the standard potential of the electrode. The standard potential of a hydrogen electrode is conventionally assumed to be zero in all solvents and at all temperatures ( $\varphi^o_{H+/H} \equiv 0$). This means that there are many scales of electrode potentials (for each solvent and each temperature), and comparison of electrode potentials in different scales is possible only after bringing the scales to a single reference point. Table 18.1 shows the standard potentials of some electrodes in aqueous solutions at 298 K.

## Redox potentials.

In redox reactions, a special case of which are some electrochemical processes, electrons transfer from one substance, a reducing agent, to another, acting as an oxidizing agent. Oxidizing agents and reducing agents differ in their chemical activity. In this case, oxidized forms of elements act as oxidizing agents, and reduced forms act as reducing agents. Oxidized forms of atoms have a higher oxidation state (Mn+7, Fe3+, Cl0) than reduced forms (Mn2+, Fe2+, Cl-). The stronger the oxidizing agent, the less active the reducing agent is the reduced form of the element. For example, the most powerful oxidizing agent is free fluorine, and its reduced form, the fluoride ion, has virtually no reducing properties. A quantitative characteristic of an oxidizing agent and a reducing agent is the redox potential. It determines the possibility and direction of the redox reaction. The relative value of the redox potential can be determined using a galvanic cell consisting of a platinum electrode and a standard hydrogen electrode, the potential of which is conventionally assumed to be zero.

The platinum electrode does not participate in the redox process, but only plays the role of an electron conductor. The concentration dependence of the equilibrium redox potential (E) is determined by the Nernst equation:

$$E = E^0 + \frac{RT}{nF}\ln\frac{[Ox]^a}{[Red]^b}$$

where E $^o$ is the standard redox potential; aOx, aRed are the activities of the oxidized and reduced forms of the substance, respectively. The most commonly used entry for the Nernst equation is for T = 298 K (t = 25°C):

$$E = E^0 + \frac{0.059}{n}\lg\frac{[Ox]^a}{[Red]^b}$$

If one of the forms (for example, reduced) is a solid, then its activity is taken equal to 1 and then the Nernst equation takes the form:

For example, in the case of the redox reaction $Zn^{2+} + 2e \leftrightarrow Zn^0$

$$E = E^0 + \frac{0{,}06}{n}\lg[Zn^{2+}]$$

**Thus, at a given temperature, the equilibrium redox potential is determined by the nature of the redox couple and the activity of the substances in the solution.**

## Diffusion potentials.

In chains with transfer, a potential jump occurs at the interface of two solutions, associated with the diffusion of salt ions in the solution against the concentration gradient. Between the ion diffusion coefficient $D_i$ and its mobility $U_i$ there is a relationship first obtained by Nernst:

$$D_i = \frac{U_i RT}{zF}.$$

The diffusion coefficient of a salt *D* can be expressed in terms of the mobilities and diffusion coefficients of the ions into which this salt dissociates:

$$D = \frac{2UV}{zF(U+V)}RT = 2\frac{D_+ D_-}{D_+ + D_-}$$

Ions with greater mobility diffuse into a more dilute solution at a higher speed, therefore, at the contact boundary, the dilute solution acquires a charge corresponding in sign to the charge of the diffusing ion, and a more concentrated solution acquires a charge of the opposite sign, i.e. an electrical double layer is formed. The appearance of a potential difference at the boundary leads to the acceleration of the movement of the slower ion and the deceleration of the faster one until the velocities of the ions are equalized. *A stationary state* occurs , in which the dissolved electrolyte diffuses as a single whole, and the potential difference at the boundary ceases to change - ***diffusion potential is established .*** Since the stationary state is not equilibrium, and a potential jump occurs between points lying in two different phases, it is strictly thermodynamically impossible to determine the value of the diffusion potential. The thermodynamic method makes it possible to determine the EMF of the concentration element as a whole with the inclusion of the diffusion potential. Only in some simple cases it is possible to approximately estimate the value of the diffusion potential.

Let us consider the calculation of the value of the diffusion potential using the example of the above concentration chain with transfer (VII). When coulombs of electricity pass through element *F , the following processes occur in the left half-cell: 1) 1 equivalent of silver dissolves;* 2) goes from left to right $t_+$ equivalents of $Ag^+$; 3) comes from the right $t_-$ equivalents $NO_3^-$. As a result, $(1 - t_+) = t_-$ equivalents of $Ag^+$ and $t_-$ equivalents $NO_3^-$ appear in the left half-element . In the right half-cell 1) 1 equivalent of $Ag^{+\text{ is discharged}}$; 2) the half-cell receives $t_+$ equivalents of $Ag^+$ from the left half-cell; 3) goes into the left half-element *of* $t_-$ equivalents $NO_3^-$. In total, $_{\text{the}}$ $t$ equivalents of both ions disappear in the right half-element .

Thus, the overall process in the element consists of the transfer of $t_-$ equivalents of two ions from a solution with higher activity to a solution with lower activity. Change in Gibbs energy in this process

$$\Delta G = t_- RT\ln\frac{a_{Ag^+(I)}}{a_{Ag^+(II)}} + t_- RT\ln\frac{a_{NO_3^-(I)}}{a_{NO_3^-(II)}} = 2t_- RT\ln\frac{a_{\pm AgNO_3(I)}}{a_{\pm AgNO_3(II)}} = -FE$$

EMF of the element

$$E = 2t_- \frac{RT}{F}\ln\frac{a_{\pm AgNO_3(II)}}{a_{\pm AgNO_3(I)}} = 2\frac{V}{U+V}\frac{RT}{F}\ln\frac{a_{\pm AgNO_3(II)}}{a_{\pm AgNO_3(I)}}.$$

This equation differs from equation (01) for the EMF of the circuit, obtained without taking into account the diffusion potential. The difference between these emfs gives the value of the diffusion $\varphi$potential $_{D.}$ If in equation (01) we take $a_{Ag^+} = a_{\pm AgNO_3}$, then

$$\phi_D = \left(2\frac{V}{U+V} - 1\right)\frac{RT}{F}\ln\frac{a_{\pm AgNO_3(II)}}{a_{\pm AgNO_3(I)}} = (2t_- - 1)\frac{RT}{F}\ln\frac{a_{\pm AgNO_3(II)}}{a_{\pm AgNO_3(I)}}. \quad (1)$$

This shows that if the anion mobility is greater than the cation mobility ( $V > U$ ), then $\varphi_D > 0$, i.e. diffusion potential is added to the potential difference of the electrodes, otherwise ( $V < U$ ) $\varphi_D < 0$. If the mobilities of the cation and anion are close ( $U \approx V$ ), then $\varphi_D \approx 0$. This is used to *eliminate* (reduce) the diffusion potential with the help of salt bridges consisting of concentrated solutions of electrolytes with similar mobilities of the cation and anion.

In another special case - when two solutions of the same concentration of different electrolytes come into contact with a common ion - the diffusion potential arises due to the difference in the mobilities of different ions in the two solutions. The diffusion potential at such a boundary can be estimated using the formula:

$$\phi_D = \frac{RT}{F}\ln\frac{U_1 + V_1}{U_2 + V_2}.$$

A more general formula for diffusion potentials in mixed solutions containing *i* types of ions was obtained by Henderson:

$$\phi_D = \frac{RT}{F}\frac{(U' - V') - (U'' - V'')}{(U_1' - V_1') - (U_1'' - V_1'')}\ln\frac{U_1' + V_1'}{U_1'' + V_1''},$$

where for solution ( ′)

$$U' = \sum m_i U_i';\ V' = \sum m_i V_i';\ U_1' = \sum z_i m_i U_i';\ V_1' = \sum z_i m_i V_i'$$

and the same designations for the solution ( ″).

+ It should be noted, however, that the calculation of the diffusion potential using various formulas can give large errors, therefore, in practice, elimination of the diffusion potential using salt bridges is used, and for accurate determinations, chains without transfer are used.

## Types of electrodes .

As follows from the Nernst equation, the potential of any electrode at a given temperature and pressure is determined by the standard potential $\varphi^o$ and the activities of the substances taking part in the electrode reaction. The standard potential is a constant characteristic of each given electrode, while the activities of the substances participating in the reaction can be different and depend on the composition of the reaction medium. The nature of the influence of the activities of the solution components on the value of the electrode potential is directly related to the nature of the electrode reaction. As mentioned earlier, in electrochemistry they use the concept of a reversible electrode - an electrode on which an equilibrium is established between two oppositely directed electrode reactions, the rates of which are quite high from a practical point of view. Depending on the device and nature of the electrode process, several types of reversible electrodes are distinguished. The most common types of electrodes are:

1. ***Electrodes of the first kind*** . These include ***cationic*** electrodes whose potential depends on the activity of cations. On such electrodes, an equilibrium is established between electrically neutral particles (for example, metal atoms) and the corresponding cations in solution - metal (zinc, copper, silver, etc.), amalgam (amalgams of alkali and alkaline earth metals) electrodes, gas hydrogen electrode. On ***anionic*** In electrodes of the first kind, an equilibrium is established between electrically neutral particles and anions - chlorine, bromine, iodine electrodes.

2. ***Electrodes of the second kind*** . These electrodes consist of three phases - the metal, its sparingly soluble salt and a solution containing anions of this salt. On these electrodes, an equilibrium is established between metal atoms and anions in the solution as a result of two partial equilibria: between the metal and the cation of a sparingly soluble salt and between the anion in the solid phase of this salt and the anion in the solution.

3. ***Redox electrodes*** . They are composed of an indifferent metal (usually platinum, sometimes gold or palladium) immersed in a solution that contains oxidized and reduced forms of the same substance.
4. ***Ion-selective electrodes*** on which membrane potentials arise.

## Electrodes of the first kind

The potential of the metal cationic electrode Me $^{z+}$ |Me depends on the activity of the metal ions in the solution:

$$\phi = \phi^{o} + \frac{RT}{z_{+}F} \ln a_{\mathrm{Me}^{z+}} \qquad (3)$$

where $z_+$ is the number of electrons spent on the reduction of one metal ion, i.e. charge of an ion in solution. In the case of an amalgam electrode, the metal is dissolved in mercury; therefore, not only the activity of the metal ions in the solution can change $a_{\mathrm{Me}^{z+}}$, but also the activity of the metal in the amalgam $a_{\mathrm{Me}}$ . Amalgam electrode potential

$$\phi = \phi^{o} + \frac{RT}{z_{+}F} \ln \frac{a_{\mathrm{Me}^{z+}}}{a_{\mathrm{Me}}} \qquad (4)$$

If a component of the electrode is a gas sorbed by the metal surface, then such an electrode is called a gas electrode, and its potential also depends on the gas pressure. The most important electrode for theory of the first kind is the gas hydrogen electrode, which, as indicated above, is the standard reference electrode. It is a platinum plate coated with platinum black. The electrode is then saturated with thoroughly purified and dried hydrogen. Platinum black plays a dual role: on the one hand, it catalyzes the equilibrium reaction at the $H_2$ L2H$^+$ electrode , and on the other, due to its large specific surface area, it ensures the presence of significant amounts of hydrogen. On platinum, an equilibrium is established between hydrogen and its ions in solution:

$2H^+ + 2e$ЛН$_2$

Since the standard potential of the hydrogen electrode is taken equal to zero, its potential

$$\phi_{\mathrm{H}^{+}/\mathrm{H}} = \frac{RT}{F} \ln \frac{a_{\mathrm{H}^{+}}}{p_{\mathrm{H}_2}^{1/2}} \qquad (5)$$

The potential of *an anionic electrode* of the first kind is expressed by the equation

$$\phi = \phi^{o} - \frac{RT}{z_{-}F} \ln a_{\mathrm{A}^{z-}} \qquad (6)$$

If the anionic electrode is a gas electrode, then the gas pressure is also included in the equation for the electrode potential. ,

For example, the potential *of the chlorine* electrode Pt(Cl $_2$ )|Cl $^-$

$$\phi_{\mathrm{Cl/Cl^-}} = \phi^{o}_{\mathrm{Cl/Cl^-}} - \frac{RT}{F} \ln \frac{a_{\mathrm{Cl^-}}}{p_{\mathrm{Cl}_2}^{1/2}} \qquad (7)$$

Anionic electrodes of the first kind are rarely used in practice; It is much more convenient to use electrodes of the second type that are reversible with respect to anions.

## Electrodes of the second kind.

An electrode of the second kind, as already indicated, is a half-cell consisting of a metal, its sparingly soluble compound (salt, oxide, hydroxide) and immersed in a solution containing the same anion as the sparingly soluble compound of the electrode metal. Schematically, an electrode of the second kind can be represented as

And $^{z-}$| MA | M,

and the electrode reaction that occurs on it

MA + $z$ eLM +A $^{z-}$

The equation for the electrode potential of an electrode of the second kind is:

$$\phi = \phi^{o} + \frac{RT}{zF}\ln\frac{a_{\mathrm{MA}}}{a_{\mathrm{A}^{z-}}\,a_{\mathrm{M}}} \text{ . (8)}$$

Considering that the activities of the metal and the solid compound MA are constant, the electrode potential

$$\phi = \phi^{o} - \frac{RT}{z_{-}F}\ln a_{\mathrm{A}^{z-}} \text{ . (9)}$$

Thus, the electrode potential of an electrode of the second kind depends on the activity of anions of a sparingly soluble compound, i.e. these electrodes are reversible with respect to anions. At the same time, the electrode can also be considered as an electrode of the first kind, reversible to metal cations. The electrode process can be represented as occurring in two stages:

MA LM $^{z+}$ + A $^{z-}$

M $^{z+}$ + $z$ eLM,

which gives the above electrode reaction. The electrode potential can then be represented by the equation:

$$\phi = \phi^{o}_{\mathrm{M}^{z+}/\mathrm{M}} + \frac{RT}{zF}\ln a_{\mathrm{M}^{z+}} \text{ . (10)}$$

But the activity of metal ions is related to the activity of anions through the solubility product of a sparingly soluble salt $L = a_{\mathrm{M}^{z+}}a_{\mathrm{A}^{z-}}$ . Then

$$\phi = \phi^{o}_{\mathrm{M}^{z+}/\mathrm{M}} + \frac{RT}{zF}\ln L - \frac{RT}{zF}\ln a_{\mathrm{A}^{z-}} \text{ . (eleven)}$$

Comparing this equation with equation (9), we see that the first two terms on the right correspond to the standard electrode potential of the second kind, reversible to anions, which differs from the standard potential of the metal electrode by an amount depending on the solubility product of the sparingly soluble compound.

$$\phi^{o}_{\mathrm{MA}/\mathrm{A}^{z-}} = \phi^{o}_{\mathrm{M}^{z+}/\mathrm{M}} + \frac{RT}{zF}\ln L \text{ . (12)}$$

The most practically important electrodes of the second type are silver chloride electrode, calomel electrode, mercury sulfate electrode, mercury oxide electrode. The potentials of such electrodes are well reproducible and stable, so these electrodes are often used as standard half-cells or reference electrodes.

*A silver chloride electrode* is a silver wire (or a platinum wire on which a layer of silver is electrolytically deposited), coated with a layer of silver chloride (you can also simply add silver chloride crystals to the solution), and immersed in a solution containing chlorine ions (KCl, HCl), t .e. system

$Cl^- | AgCl | Ag$

Silver chloride electrode potential

$$\phi = \phi^{o} - \frac{RT}{F} \ln a_{Cl^-} . \quad (13)$$

Other silver halide electrodes are also used - silver bromine $Br^- | AgBr | Ag$ and silver iodide $I^- | AgI | Ag$, the structure and functioning of which are similar to silver chloride.

*The calomel electrode* consists of mercury coated with a layer of paste made from a mixture of mercury and calomel, above which there is a solution of potassium chloride:

$Cl^- | Hg_2Cl_2 | hg$

Electrical contact is made using a platinum wire immersed in mercury. The electrode reaction occurring in a half-cell is expressed by the equation:

$Hg_2Cl_2 + 2e$ L$Hg + 2Cl^-$,

and the potential of the calomel electrode, like the silver-silver chloride electrode, is determined by the activity of chlorine ions:

$$\phi = \phi^{o} - \frac{RT}{F} \ln a_{Cl^-} . \quad (14)$$

The most commonly used calomel half-cells are saturated solutions of potassium chloride (saturated calomel electrode) or KCl solutions with concentrations of 1.0 mol/L (normal calomel electrode) or 0.1 mol/L (decimolar calomel electrode).

*The mercury sulfate electrode* $SO_4^{2-} | Hg_2SO_4 | Hg$ is similar to the calomel electrode with the difference that the mercury is coated with a layer of paste of mercury and mercury(I) sulfate, and sulfuric acid is usually used as a solution. The electrode potential depends on the activity of sulfate ions:

$$\phi = \phi^{o} - \frac{RT}{2F} \ln a_{SO_4^{2-}} . \quad (15)$$

*metal oxide electrodes* . Here, hydroxyl ions act as anions of the sparingly soluble compound of the electrode metal. Metal oxide electrodes include, for example, mercury oxide and antimony electrodes:

$OH^- | HgO | Hg$ and $OH^- | Sb_2O_3 | Sb$

The equations of electrode reactions and electrode potential are presented in the form:

$HgO + H_2O + 2e$ L$Hg + 2OH^-$

$Sb_2O_3 + 3H_2O + 6e$ L2Sb + $6OH^-$

$$\phi = \phi^{\circ} - \frac{RT}{F}\ln a_{OH^-} \ . \ (16)$$

Metal oxide electrodes, like metal salt electrodes of the second kind, can be considered as metal electrodes of the first kind; they are reversible not only with respect to hydroxyl ions, but also with respect to electrode metal ions. In addition, they are reversible with respect to hydrogen ions, since the ionic product of water $K_W = a_{H^+}a_{OH^-}$ at a given temperature is constant for any aqueous electrolyte solution.

## 37-Lecture.

## Topic: Electromotive force.

Classification of galvanic cells. Thermodynamics of galvanic cells. Equilibrium constant of a galvanic cell.

### ***Galvanic cell. EMF of a galvanic cell .***

Consider the simplest Daniel-Jacobi galvanic cell, consisting of two half-cells - zinc and copper plates, placed in solutions of zinc and copper sulfates, respectively, which are interconnected by means of an electrolytic key - for example, a strip of paper moistened with a solution of some electrolyte. Schematically, this element is depicted as follows:

$$Zn / Zn^{2+} // Cu^{2+} / Cu$$

On the surface of each electrode there is a dynamic equilibrium of the transition of metal ions from the electrode to the solution and back, characterized by the EDL potential (charge on the electrode q ). If you connect the copper and zinc electrodes externally with a metal conductor, a redistribution of charges will immediately occur - electrons will begin to move from the electrode with a more negative charge (in our case, zinc) to the electrode with a more positive charge (copper), i.e. an electric current will flow in the conductor. The change in the amount of charge of each electrodes disturbs the equilibrium - on the zinc electrode the process of transition of ions from the electrode to the solution (metal oxidation) will begin, on the copper electrode - from the solution to the electrode (metal reduction); in this case, the occurrence of a process on one electrode causes the simultaneous occurrence of the opposite process on the other:

$$Zn^0 \rightarrow Zn^{2+} + 2e^- \text{ (oxidation)}$$
$$Cu^{2+} + 2e^- \rightarrow Cu^0 \text{ (recovery)}$$

The electrode on which the process of oxidation (donation of electrons) occurs during the operation of a galvanic cell is called an anode, an electrode on in which the reduction process (acceptance of electrons) takes place - the cathode. When schematically depicting galvanic cells, write on the left anode, on the right - cathode (standard hydrogen electrode is always written left). The total redox process occurring in a galvanic cell is expressed by the following equation:

$$Cu^{2+} + Zn^0 \rightarrow Cu^0 + Zn^{2+}$$

Thus, a galvanic cell can be defined as a device for converting the chemical energy of a redox reaction into electrical energy due to the spatial separation of the oxidation and reduction processes. The work that an electric current generated by a galvanic cell can do is determined by the difference in electric potentials between the electrodes (usually called simply the potential difference) $\Delta\phi$ and the amount of electricity passed through the circuit q :

$$dA = \Delta\varphi \cdot dq.$$

The work done by the current of a galvanic cell (and, consequently, the potential difference) will be maximum during its reversible operation, when processes on the electrodes proceed infinitely slowly and the current strength in the circuit is infinitely small. The maximum potential difference that occurs during reversible operation of a galvanic cell is the electromotive force (EMF) of the galvanic cell.

## Electrode potential. Nernst equation .

the emf of a galvanic cell E as the difference some quantities characterizing each of the electrodes - electrode potentials; however, to accurately determine these values, a reference point is required - a precisely known electrode potential of any electrode. The electrode potential of an electrode $\varepsilon$ is the emf of an element composed of a given electrode and a standard hydrogen electrode (see below), the electrode potential of which is assumed to be zero. In this case, the sign of the electrode potential is considered positive if in such a galvanic cell the electrode under test is the cathode, and negative if the electrode under test is the anode. It should be noted that sometimes the electrode potential is defined as the potential difference at the electrode-solution interface, i.e. they consider it identical to the DES potential, which is not entirely correct (although these values are proportional).

The value of the electrode potential of a metal electrode depends on the temperature and activity (concentration) of the metal ion in the solution into which the electrode is immersed; mathematically, this dependence is expressed by the Nernst equation (here F is the Faraday constant, z is the ion charge):

$$\varepsilon = \varepsilon^0_M + \frac{RT}{zF}\ln a_{M^{z+}} \approx \varepsilon^0_M + \frac{RT}{zF}\ln[M^{z+}].$$

In the Nernst equation, $\varepsilon^{0}$ is the standard electrode potential, equal to the electrode potential at a metal ion activity equal to unity. The standard electrode potentials of electrodes in aqueous solutions are a series of voltages. The value of $\varepsilon$ 0 is a measure of the ability of the oxidized form of an element or ion to accept electrons, i.e. restore. Sometimes, at low ion concentrations, the difference between the concentration and activity of an ion in a solution is neglected, and the concentration of ions in the solution appears under the sign of the logarithm in the Nernst equation. The magnitude of the electrode potential determines the direction of the process occurring on the electrode during operation of the galvanic cell. At the electrode, the potential of which has a greater (sometimes said more positive) value, the reduction process will occur, i.e. this electrode will be the cathode.

***Let us apply the Nernst equation to describe the Daniel-Jacobi element*** . EMF is always a positive value, it is equal to the difference between the electrode potentials of the cathode and anode:

$$E = \varepsilon_{\mathrm{Cu}} - \varepsilon_{\mathrm{Zn}};$$

$$\varepsilon_{\mathrm{Cu}} = \varepsilon^{0}_{\mathrm{Cu}} + \frac{RT}{2F}\ln[\mathrm{Cu}^{2+}];$$

$$\varepsilon_{\mathrm{Zn}} = \varepsilon^{0}_{\mathrm{Zn}} + \frac{RT}{2F}\ln[\mathrm{Zn}^{2+}]; \quad E = \varepsilon^{0}_{\mathrm{Cu}} + \frac{RT}{2F}\ln[\mathrm{Cu}^{2+}] - \varepsilon^{0}_{\mathrm{Zn}} - \frac{RT}{2F}\ln[\mathrm{Zn}_{2+}],$$

or

$$E = \varepsilon^{0}_{\mathrm{Cu}} - \varepsilon^{0}_{\mathrm{Zn}} + \frac{RT}{2F}\ln\frac{[\mathrm{Cu}^{2+}]}{[\mathrm{Zn}^{2+}]}. \quad (69)$$

As can be seen from equation (69), the EMF of the Daniel-Jacobi element depends on the concentration (more precisely, activity) of copper and zinc ions; at their equal concentrations, the EMF of the element will be equal to the difference in standard electrode potentials:

$$E = \varepsilon^{0}_{\mathrm{Cu}} - \varepsilon^{0}_{\mathrm{Zn}}.$$

By analyzing equation (69), it is possible to determine the limit of irreversible operation of a galvanic cell. Since the zinc oxidation process occurs at the anode, the concentration of zinc ions during irreversible operation of the galvanic cell constantly increases; the concentration of copper ions, on the contrary, decreases. The ratio of the concentrations of copper and zinc ions is constantly decreasing, and the logarithm of this ratio at $[\mathrm{Cu}^{2+}] < [\mathrm{Zn}^{2+}]$ becomes negative. Thus, the potential difference during irreversible operation of the galvanic cell continuously decreases.

At $E = 0$ (when $\varepsilon_{\mathrm{Cu}} = \varepsilon_{\mathrm{Zn}}$) the galvanic cell cannot do work. The irreversible operation of the galvanic cell can also stop as a result of complete dissolution of the zinc anode.

Equation (69) also explains the performance of concentration circuits - galvanic cells consisting of two identical metal electrodes immersed in solutions of a salt of this metal with different activities $a_1 > a_2$. The cathode in this case will be the electrode with a higher concentration, because the standard electrode potentials of both electrodes are equal; for the EMF of a concentration galvanic element we obtain

$$E = \varepsilon_1 - \varepsilon_2 = \frac{RT}{zF}\ln\frac{a_1}{a_2}.$$

The only result of the concentration element is the transfer of metal ions from a more concentrated solution to a less concentrated one. Thus, the work of an electric current in a concentration galvanic cell is the work of a diffusion process of concentration equalization, which is carried out reversibly as a result of its spatial division into two opposite in direction reversible electrode processes.

## 38 Lecture.
## Topic: Kinetics of electrochemical processes.

Polarization of electrodes. Overvoltage. Tafel and Frumkin-Volmer equations .

***Polarization and overvoltage .*** Equilibrium electrode potentials can be determined in the absence of current in the circuit. When an electric current passes, the potentials of the electrodes change. *The deviation of the electrode potential from its equilibrium value during the passage of current* is called *electrochemical polarization* or simply *polarization* :

$\Delta E = E_i - E_r$, (4.27)

where $\Delta E$ – polarization; $E_i$ - electrode potential when current passes; $E_r$ – equilibrium potential.

The term “polarization” is used not only to denote the magnitude of the potential change, but also the very phenomenon of potential change during the passage of current. Since polarization can occur both at the cathode and at the anode, a distinction is made between *cathodic* and *anodic* polarizations $\Delta E_k$ and $\Delta E_a$. As a result of polarization, the anode potential shifts to the positive side, and the cathode potential shifts to the negative side.

From Faraday’s law it follows that the current is proportional to the amount of substance reacted at the electrode per unit time, i.e. speed of electrochemical reaction. Typically, the rate of electrode processes is calculated from the current density, i.e. current strength per unit electrode surface area:

$i = I/S$, (4.28)

where i is the current density, A/m $^2$; I – current value, A; S – electrode surface area, $^{m2}$.

Electrode polarization is a function of current density: the higher the current density, the greater the polarization value.

The graphical dependence of potential on current density is called *polarization curve* .

Polarization of electrodes occurs both during electrolysis and in chemical sources of electric current (galvanic cells, batteries). In both cases, it is a negative phenomenon: in chemical current sources it reduces their electrical characteristics, in electrolysis it contributes to an increase in the decomposition voltage of the electrolyte.

Let's consider the operation of a copper-zinc galvanic cell (Fig. 4.2). When the circuit is open, electrochemical equilibria are established on both the copper and zinc electrodes. When the circuit is closed, both electrodes have a polarizing effect on each other: electrons from the zinc electrode move to the copper electrode, while the potential of the copper electrode, under the influence of contact with zinc, shifts to the negative side, and the potential of the zinc electrode to the positive side. The copper electrode is cathodically polarized, and the zinc electrode is anodic. At the same time, electrochemical equilibria are disrupted on both electrodes and electrochemical processes begin to occur: the cathodic process on the copper electrode, and the anodic process on the zinc electrode.

To increase the terminal voltage in galvanic cells and reduce the decomposition voltage during electrolysis, the polarization of the anode and cathode is reduced.

The process of decreasing electrode polarization is called *depolarization.* It is carried out by changing the conditions for the electrode processes, for example, by introducing into the electrolyte or electrode material special substances - *depolarizers* capable of electrochemical oxidation or reduction, thereby changing the nature of the electrode processes. Depolarizers - oxidizers are $H_2Cr_2O_7$, $MnO_2$, air oxygen, depolarizers - reducers - $Na_2SO_3$, $Na_3PO_3$, etc.

Polarization of the electrode is a necessary condition for the electrode process to occur. In addition, the speed of the electrode process depends on its value: the more polarized the electrode, the faster the corresponding electrochemical reaction occurs on it.

The speed of electrochemical processes depends on various factors. A special feature of electrochemical reactions is the influence of potential on their speed. By its nature, any electrochemical process is complex, heterogeneous and consists of a number of stages, so its speed is determined by the speed of the slowest stage, which limits the speed of the entire process. The occurrence of polarization is due to the slowness of individual stages of the electrochemical process. The change in potential due to the slowness of the actual electrochemical stages of reactions is called electrochemical polarization. The amount of polarization required for a given electrode process to occur at a certain speed is called *the overvoltage* of a given electrode process.

The rate of electrochemical reactions, like chemical ones, can be increased by increasing the temperature and using a catalyst. As the temperature increases, the proportion of active molecules increases; in the case of using a catalyst, the activation energy decreases. The activation energy of an electrochemical reaction can also be reduced when the electrode potential changes compared to its equilibrium potential, i.e. with polarization. Since the reaction rate increases with a decrease in activation energy, an increase in polarization leads to an acceleration of the electrochemical reaction, i.e. to increase current density. And the greater the activation energy of the process, i.e. The slower the process proceeds in the forward and reverse directions at equilibrium, the greater the polarization required for a certain speed of the electrochemical process, expressed in terms of current density. The relationship between electrochemical overvoltage $\Delta E_{el.}$ and the current density is expressed *by the Tafel equation* :

$$\Delta E_{el.} = a + b \lg i \, . \quad (4.29)$$

The constant $b$ depends on the nature of the reaction and temperature and at 298 K usually has a value of 0.03 - 0.15 (most often 0.10 - 0.12). The constant $a$ depends on the nature of the reaction, the electrode material, the composition of the solution and the temperature. As can be seen from equation (4.29), $a = \Delta E_{el.}$ for $i = 1$. Constants $a$ and $b$ are determined from graphs of polarization versus the logarithm of current density. The table shows the values of $a$ and $b$ for the reaction of cathodic hydrogen evolution on various metals.

Constants in the Tafel equation for the reaction of cathodic hydrogen evolution on metals at 298 K and = 1 A/cm $^2$

| | Constants in solutions | | | | | Constants in solutions | | | |
|---|---|---|---|---|---|---|---|---|---|
| Metals | acidic | | alkaline | | Metals | acidic | | alkaline | |
| | *A* | *b* | *A* | *b* | | *A* | *b* | *A* | *b* |
| *Pt* | 0.10 | 0.03 | 0.31 | 0.10 | *Ag* | 0.95 | 0.10 | 0.73 | 0.12 |
| *Pd* | 0.24 | 0.03 | 0.53 | 0.13 | Zn | 1.24 | 0.12 | 1.20 | 0.12 |
| *Fe* | 0.70 | 0.12 | 0.76 | 0.11 | hg | 1.41 | 0.11 | 1.54 | 0.11 |
| Cu | 0.86 | 0.12 | 0.96 | 0.12 | Pb | 1.56 | 0.11 | 1.36 | 0.25 |

Different metals have different catalytic activities towards the reduction of hydrogen ions. The minimum hydrogen voltage in acidic solutions is observed on platinum and palladium, the maximum overvoltage is observed on lead and mercury. The overvoltage changes when replacing acidic solutions with alkaline ones.

**Chemical current sources**

Chemical current sources (CHS) are electrochemical devices, as a result of which the chemical energy of redox processes is converted into direct current electrical energy. These include galvanic cells, batteries, fuel cells. All types of chemical power sources use electrolytes - aqueous, non-aqueous, solid. The advantages of modern HITs include relatively high efficiency (up to 0.8) and high specific power (the amount of energy delivered per unit time by a unit of HIT mass), which allows them to compete with other current sources. Their main disadvantage is their limited service life.

Galvanic cells consist of two electrodes having different electrode potentials, an electrolyte, which allows ions to move from one electrode to another, and a metal conductor of electrons, as a result of the flow of which direct current electrical energy can be obtained.

Among the wide variety of galvanic cells, three main types can be distinguished.

*First type* . Plates of two different metals are placed in salt solutions containing their own ions. This type includes a copper-zinc galvanic cell (Daniel–Jacobi cell).

*Second type.* Plates of two different metals are in a solution of the same electrolyte. An example is the Volta cell, consisting of two plates (Zn and Cu) immersed in a sulfuric acid solution. During its operation the following processes occur:

(-) A: $Zn \leftrightarrow Zn^{2+} + 2\bar{e}$ - oxidation (anodic process)

(+) K: $2H^{+} + 2\bar{e} \leftrightarrow H_2\uparrow$ - reduction (cathode process)

The released hydrogen saturates the surface of the cathode (copper), resulting in an electrode of a different composition (not copper, but hydrogen).

Diagram of a Volta galvanic cell:

$$\mathbf{2\bar{e} \quad \rightarrow \qquad (-)\ Zn / Zn^{2+} |\ H2SO4\ \_\_\_\ |\ 2H^{+}\_ / H_2\ (Cu)\ (+)}$$

In parentheses on the right is indicated (Cu) - the place of hydrogen evolution.

*Third type* . Galvanic cells are composed of two electrodes of exactly the same nature (for example, copper), immersed in solutions of the same electrolyte, but of different concentrations. Such elements are called *concentration* .

Scheme of a copper concentration galvanic cell:

$$\mathbf{2\bar{e} \quad \rightarrow (-)\ Cu / CuSO4\ \_ ||\ CuSO4\ \_ / Cu\ (+),}$$

$$\mathbf{C_1 < C_2}$$

where $C_1$ and $C_2$ are the concentration of the electrolyte solution, mol/l.

The role of the anode is played by the electrode located in a more dilute solution, since its electrode potential has a lower value compared to the second electrode. The EMF of such a galvanic cell depends only on the ratio of the concentrations of potential-determining ions (in this case, on the concentration of $CuSO_4$ ).

Concentration galvanic cells have no practical significance as sources of electrical energy.

*Batteries* are galvanic cells that, based on reversible electrochemical reactions, can repeatedly accumulate chemical energy and release it for consumption in the form of direct current electrical energy.

Batteries are reusable devices that combine a galvanic cell and an electrolyzer. Under the influence of an external direct current, chemical energy accumulates (accumulates) in them, which is then converted into electrical energy as a result of a redox reaction. The process of accumulation of chemical energy is called *battery charge* , the process of its transformation into electrical *energy is called battery discharge* . In the first case, the battery works as an electrolyzer, in the second - as a galvanic cell.

The design and principle of operation of all batteries is the same. The main difference is the electrode material and the type of electrolyte. An oxidation process occurs at the anode, both during discharge and charge, and a reduction process occurs at the cathode.

The most common are acid and alkaline batteries.

*An acid battery* ( *lead battery* ) is a plate in the form of castings made of heartbley (solid lead with an admixture of antimony) of a cellular structure, assembled into batteries and placed in tanks made of ebonite or polypropylene with an electrolyte. A mixture of lead oxide (PbO) and glycerol is pre-pressed into the cells of the plates, which has the ability to harden in the form of lead glycerate. The electrolyte is a solution of sulfuric acid (35 - 40% solution of $H_2SO_4$). When lead oxide reacts with $H_2SO_4$, $PbSO_4$ is formed .

$PbO_{tv.} + H_2SO_{4(p-p)} \rightarrow PbSO_{4\,tv.} + H_2O$

During the initial and subsequent charges of the battery, when it operates as an electrochemical cell, $PbSO_4$ at the cathode turns into lead (Pb), and at the anode into lead dioxide ($PbO_2$), which are the electrodes:

**(-) K:** $\mathbf{PbSO_{4\,(tv)} + 2\bar{e} \rightarrow \underline{Pb}_{(tv)} + SO_4^{2-}}$ **(solution)**

**(+) A:** $\mathbf{PbSO_{4\,(tv)} + 2H_2O \rightarrow \underline{PbO}_{2\,(tv)} + 2\bar{e} + 4H^+ + SO_4^{2-}}$ **(solution)**

$\mathbf{2PbSO_{4\,(tv)} + 2H_2O \rightarrow Pb_{(tv)} + PbO_{2\,(tv)} + 2H_2SO_{4\,(solution)}}$

The EMF of a charged battery is approximately equal to 2 V (if 6 such batteries are connected in series, you get a regular car battery with EMF = 12 V).

When the battery is in operation - it is discharging, when it works as a chemical current source, electrode processes occur on the electrodes in the opposite direction.

As it is discharged, the materials of the cathode ($PbO_2$), anode (Pb) and electrolyte - sulfuric acid - are consumed. The voltage at the battery terminals drops and it needs to be charged. To charge the battery, the battery is connected to an external current source, the direction of the current is opposite to the discharge one.

Current-generating and electrode reactions in a lead-acid battery can be represented as:

$\mathbf{Pb_{(s)} + SO_4^{2-}{}_{(p-p)} \leftrightarrow PbSO_{4(tv)} + 2\bar{e}}$

$\mathbf{PbO_{2(sol)} + 2\bar{e} + 4H^+_{(solution)} + SO_4^{2-}{}_{(solution)} \leftrightarrow PbSO_{4(tv)} + 2H_2O}$

$\rightarrow$ **"discharge"**

$\mathbf{+\,Pb_{(sol)} + PbO_{2\,(sol)} + 2H_2SO_{4\,(sol)} \leftrightarrow 2PbSO_{4\,(sol)} + 2H_2O}$

$\leftarrow$ **"charger"**

**Acid battery diagram:**

$\mathbf{(-)\ Pb / Pb^{2+} \mid H_2SO_4 \mid Pb^{2+} / PbO_2\ (+)}$

The standard potential values for the electrodes of a lead battery have the following values: $E^o_{PbSO_4/Pb,SO_4^{2-}} = -0{,}356B$ , $E^o_{PbO_2,SO_4^{2-},4H^{+}/PbSO_4,2H_2O} = 1{,}685B$ .

The emf of a battery as a chemical current source is calculated by the equation:

$$E = E_K - E_A = E^0_{PbO_2,SO_4^{2-},4H^{+/}/PbSO_4,2H_2O} - E^o_{PbSO_4/Pb,SO_4^{2-}} + \frac{RT}{2F}\ln\frac{a^4_{H^+}\cdot a^2_{SO_4^{2-}}}{a^2_{H_2O}}$$

From this equation it is clear that the emf of the battery depends on the concentration (activity) of sulfuric acid, which increases when the battery is charged and decreases when it is discharged. The degree of battery discharge is judged by the electrolyte concentration, i.e. concentration of $H_2SO_4$. Using concentrated solutions of $H_2SO_4$, it would be possible to increase the emf of the battery, however, at a concentration of $H_2SO_4$ greater than 39%, the electrical conductivity of the solutions sharply decreases and the solubility of lead increases, therefore 32 - 39% solutions of $H_2SO_{4\text{ are optimal}}$.

While the battery is charging, the voltage at its poles increases. At the end, it reaches such a value that electrolysis of water begins, accompanied by the release of hydrogen at the cathode and oxygen at the anode:

**( -) K: $2H_2O + 2\bar{e} \leftrightarrow H_2\uparrow + 2OH^-$**

**(+) A: $4OH^- \leftrightarrow O_2\uparrow + 2H_2O + 4\bar{e}$**

**$2H_2O \leftrightarrow 2H_2\uparrow + O_2\uparrow$**

The so-called “boiling” of the electrolyte is a sign that the lead battery has finished charging. A charged battery can be immediately used for its intended purpose. During storage, the electrolyte is poured out of it and washed with water. It can remain in this form for up to 2 years and to use it you just need to fill in the electrolyte. When an uncharged battery is stored with a sulfuric acid solution, it “sulfates” - the formation of a large amount of $PSO_{4\text{ on the plates}}$. When a lead acid battery operates to produce current, $PSO_4$ is deposited in a very fine-grained form on the surface of the electrodes. When the battery is turned off, the fine-grained layer recrystallizes and larger crystals are formed, which can clog the pores of the electrode, reducing its surface area, or break off from the electrode and settle to the bottom of the battery. The sulfation process is the main cause of battery failure, so care must be taken to ensure that the battery is not left partially idle in a discharged state.

The advantages of a lead-acid battery are high efficiency (about 80%), high emf and its relatively small change during discharge, high electrical capacity, and stability in operation. Disadvantages - large mass and, therefore, low specific capacity, self-discharge of the battery during storage, short service life (2 - 5 years), as well as toxicity of lead and strong oxidizing properties of $H_2SO_4$.

+ *Alkaline batteries* differ in the material of the negatively charged electrode plates. The most common of them are cadmium - nickel (Cd - Ni) and iron - nickel (Fe - Ni) batteries. The active mass of the positive plates consists mainly of hydrated nickel (III) oxide, and also contains graphite, which is added to increase electrical conductivity. The electrolyte is a KOH solution (20%) containing a small amount of LiOH. The emf of a charged battery (Cd - Ni) is approximately 1.3 V.

### Questions for self-control.

What processes occur at the interface between a metal and an electrolyte solution?
Standard hydrogen electrode and standard metal electrode potential.
On what principle is the series of metal stresses constructed, what properties of a metal can be judged by its position in the series?

Calculation of electrode potentials of metals under non-standard conditions. Nernst equation.
The mechanism of current generation in a galvanic cell.
Scheme of operation of the Daniel-Jacobi galvanic cell (Zn/$ZnSO_4$ II $CuSO_4$/Cu).
Scheme of operation of the Volta galvanic cell Zn/$ZnSO_4$ $|$ $H_2SO_4$ $|$ $2H^+$/$H_2$ (Cu).
Concentration galvanic element (operating principle).
Polarization of the galvanic cell (cathode and anodic polarization). Ways to reduce polarization.
Redox processes occurring during operation of a lead (acid) battery .

## 39 -Lecture.

## Topic: Methods of electrochemical corrosion and corrosion protection.

Dependence of corrosion inhibitors and inhibitory properties on the structure of chemical compounds, anti-corrosion coatings, phosphating. Methods for studying metal corrosion: gravimetric, polarization curves, polar resistance and impedance methods.

### Methods of protection against electrochemical corrosion.

Corrosion is the process of spontaneous destruction of the surface of materials due to interaction with the environment. Its cause is the thermodynamic instability of chemical elements to certain substances.

Formally, polymers, wood, ceramics, and rubber are susceptible to corrosion, but the term “aging” is more often applied to them. The most serious damage is caused by rusting of metals, to protect which high-tech countermeasures are being developed. But we'll talk about this later. Scientists distinguish between chemical and electrochemical corrosion of metals.

### Chemical corrosion.

It usually occurs when the metal structure is exposed to dry gases, liquids or solutions that do not conduct electric current. The essence of this type of corrosion is the direct interaction of the metal with an aggressive environment.

Elements chemically corrode during heat treatment or as a result of prolonged use at sufficiently high temperatures. This applies to gas turbine blades, smelting furnace fittings, internal combustion engine parts, and so on.

As a result, certain compounds are formed on the surface: oxides, nitrides, sulfides.

### Electrochemical corrosion.

It is a consequence of contact of the metal with a liquid medium capable of conducting electric current. Due to oxidation, the material undergoes structural changes leading to the formation of rust (an insoluble product), or metal particles pass into ion solution.

Electrochemical corrosion: examples

It is divided into:

Atmospheric, which occurs when there is a liquid film on the metal surface in which gases contained in the atmosphere (for example, O2, CO2, SO2) are able to dissolve to form electrolyte systems.

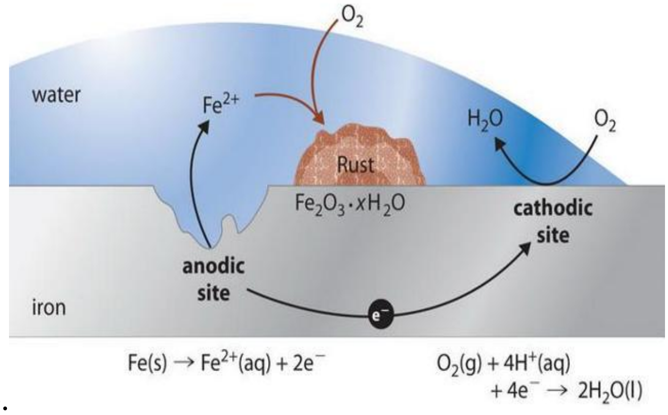
Liquid, which flows in a conductive liquid medium.

Ground water, which flows under the influence of groundwater.

Causes

Since usually any metal that is used for industrial needs is not ideally pure and contains inclusions of various types, electrochemical corrosion of metals occurs due to the formation of a large number of short-circuited local galvanic elements on the surface of the iron.

Their appearance can be associated not only with the presence of various (especially metal) impurities (contact corrosion), but also with surface heterogeneity, crystal lattice defects, mechanical damage, and the like.



## Interaction mechanism

The process of electrochemical corrosion depends on the chemical composition of materials and the characteristics of the external environment.

If the so-called technical metal is covered with a wet film, then two independent reactions occur in each of the indicated galvanic microelements that form on the surface.

The more active component of the corrosion pair gives up electrons (for example, zinc in a Zn-Fe pair) and passes into the liquid medium as hydrated ions (that is, it corrodes) according to the following reaction (anodic process):

M + nH2O = Mz+* nH2O + ze.

This part of the surface is the negative pole of the local microelement, where the metal is electrochemically dissolved.

On the less active area of the surface, which is the positive pole of the microelement (iron in the Zn-Fe pair), electrons are bonded due to the occurrence of a reduction reaction (cathode process) according to the following scheme:

Ox + ze = Red.

Thus, the presence of oxidizing agents in the water film, which are capable of binding electrons, provides the possibility of further progress of the anodic process. Accordingly, electrochemical corrosion can develop only if both anodic and cathodic processes occur simultaneously. Due to inhibition of one of them, the oxidation rate decreases.

## Polarization process

Both of the above processes cause polarization of the corresponding poles (electrodes) of the microelement. What are the features here? Typically, electrochemical corrosion of metals is more significantly slowed down by polarization of the cathode. Therefore, it will increase under the influence of factors that prevent this reaction and are accompanied by the so-called depolarization of the positive electrode.

In many corrosion processes, cathodic depolarization is carried out by the discharge of hydrogen ions or the reduction of water molecules and corresponds to the formulas:

In an acidic environment: $2H^{+} + 2e = H_2$.

In alkaline: $2H_2O + 2e = H_2 + 2OH^{-}$.

Potential range

The potential that corresponds to these processes, depending on the nature of the aggressive environment, can vary from -0.83 to 0 V. For a neutral aqueous solution at temperatures close to standard, it is approximately -0.41 V.

Consequently, hydrogen ions contained in water and in neutral aqueous systems can only oxidize metals with a potential less than -0.41 V (located in the voltage series up to cadmium).

Considering that some of the elements are protected by an oxide film, the number of metals susceptible to oxidation in neutral environments by hydrogen ions is insignificant.

If the wet film contains dissolved oxygen in the air, then it is capable, depending on the nature of the medium, of binding electrons through the effect of oxygen depolarization. In this case, the electrochemical corrosion scheme looks like this:

$O_2 + 4e + 2H_2O = 4OH^-$

$O_2 + 4e + 4H^+ = 2H_2O$.

The potentials of these electrode reactions at temperatures close to standard vary from 0.4 V (alkaline medium) to 1.23 V (acidic medium). In neutral environments, the potential of the oxygen reduction process under the specified conditions corresponds to a value of 0.8 V. This means that dissolved oxygen is capable of oxidizing metals with a potential of less than 0.8 V (located in the voltage series up to silver).

## The most important oxidizing agents .

Types of electrochemical corrosion are characterized by oxidizing elements, the most important of which are hydrogen ions and oxygen.

At the same time, a film containing dissolved oxygen is much more dangerous in terms of corrosion than moisture, where there is no oxygen, and which is capable of oxidizing metals exclusively with hydrogen ions, since in the latter case the number of types of materials capable of corroding is much smaller.

For example, steel and cast iron contain carbon impurities mainly in the form of iron carbide Fe3C. In this case, the mechanism of electrochemical corrosion with hydrogen depolarization for these metals is as follows:

(-) $Fe - 2e + nH_2O = Fe^{2+} nH_2O$ (rust may form);

(+) $2H^+ + 2e = H_2$ (in an acidified environment);

(+) $2H_2O + 2e = H_2 + 2OH^-$ (in a neutral and alkaline environment).

The mechanism of corrosion of iron, which contains copper impurities, in the case of oxygen depolarization of the cathode is described by the equations:

(-) $Fe - 2e + nH_2O = Fe^{2+} \cdot nH2O$;

(+) $0.5O_2 + H_2O + 2e = 2OH^-$ (in an acidified environment);

(+) $0.5O_2 + 2H+ + 2e = H_2O$ (in a neutral and alkaline environment).

Electrochemical corrosion occurs at different rates. This indicator depends on:

potential difference between the poles of a galvanic microcell;

composition and properties of the electrolyte medium (pH, presence of corrosion inhibitors and stimulators);

concentration (intensity of supply) of the oxidizing agent;

temperature.

## Protection methods .

Electrochemical protection of metals from corrosion is achieved in the following ways:

Creation of anti-corrosion alloys (alloying).

Increasing the purity of an individual metal.

Applying various protective coatings to the surface.

These coatings, in turn, are:

Non-metallic (paints, varnishes, lubricants, enamels).

Metal (anodic and cathodic coatings).

Formed by special surface treatment (passivation of iron in concentrated sulfuric or nitric acids; iron, nickel, cobalt, magnesium in alkali solutions; formation of an oxide film, for example, on aluminum).

Metal protective coating

The most interesting and promising is electrochemical protection against corrosion by another type of metal. Based on the nature of their protective effect, metallized coatings are divided into anodic and cathodic. Let's look at this point in more detail.

An anodic coating is a coating formed by a more active (less noble) metal than the one being protected. That is, protection is carried out with an element that is in the voltage range before the base material (for example, coating iron with zinc or cadmium).

With local destruction of the protective layer, the less noble metal coating will corrode. In the area of scratches and cracks, a local galvanic cell is formed, the cathode of which is the metal being protected, and the anode is the coating, which is oxidized. The integrity of such a protective film does not matter.

However, the thicker it is, the slower the electrochemical corrosion will develop, and the longer the beneficial effect will last.

Cathodic coating is a coating with a metal with a high potential, which in the series of voltages comes after the protected material (for example, spraying low-alloy steels with copper, tin, nickel, silver). The coating must be continuous, since when it is damaged, local galvanic cells are formed in which the base metal will be the anode and the protective layer will be the cathode.

How to protect metal from oxidation

Electrochemical protection against corrosion is divided into two types: sacrificial and cathodic. The protective coating is similar to the anodic coating. A large plate of a more active alloy is attached to the material to be protected.

A galvanic cell is formed, in which the base metal serves as the cathode, and the protector serves as the anode (it corrodes). Typically, zinc, aluminum or magnesium-based alloys are used for this type of protection.

The protector gradually dissolves, so it must be replaced periodically.

Electrochemical corrosion of pipelines causes a lot of trouble in public utilities and in industry in general. In the fight against it, the cathodic polarization method is most suitable.

To do this, a metal structure, which is protected from destructive oxidation processes, is connected to the negative pole of any external direct current source (it then becomes a cathode, and the rate of hydrogen evolution increases and the corrosion rate decreases), and a low-value metal is connected to the positive pole .

**Electrochemical protection methods** are effective in a conductive environment (a striking example is sea water). Therefore, protectors are often used to protect the underwater parts of marine vessels.

Treatment of aggressive environment

## 40 -Lecture.

## Topic: Concepts of chemical kinetics.

The rate of chemical reactions and its temperature dependence. Van't Hoff and Arrhenius equations.

Main characteristics of catalysts: activity, selectivity, selective action, productivity, regeneration ability, specific area. General approximations for controlling the selectivity of chemical reactions.

## General characteristics and classification of catalytic reactions.

The rate of many chemical reactions depends on the presence in the reaction mixture of substances (specially introduced or present in the form of impurities) that are not included in the stoichiometric equation of a chemical reaction and after the end of the reaction remain unchanged both in chemical composition and quantitatively. These substances that change the rate of a reaction, but are not stoichiometrically involved in the reaction, are called *catalysts* (Berzelius, 1836), and the very phenomenon of changing the rate in the presence of a catalyst is called *catalysis* . Catalytic reactions are very widespread both in chemical technology and in biological processes (enzymatic catalysis). Many reactions that do not appear to be catalytic are in fact accelerated by very small amounts of impurities (such as trace amounts of water or other substances) always present in the reaction mixture, and in some cases the catalyst may even be the reaction vessel itself.

The influence of a catalyst on the reaction rate is due to the fact that it is part of the active complex and changes the activation energy of the chemical reaction.

When the active complex decomposes, the catalyst is regenerated, i.e. theoretically, the catalyst is not consumed and remains chemically unchanged. Therefore, in principle, one small portion of the catalyst is sufficient to carry out a reaction with any amount of substrate (a substance that reacts with the catalyst). Of course, in real processes the catalyst is consumed due to side processes, poisoning, technological losses, changes in the state of the surface of solid catalysts, etc.

One of the most important properties of catalysts is their *selectivity* ( *selectivity* ) - each catalyst affects the rate of one reaction or any group of reactions. Different catalysts can form active complexes of the same type or of different composition and structure with the same starting materials. This can lead to a change in the direction of the process and to the formation of different products from the same starting substances.

The above does not mean that a catalyst can cause a process that is thermodynamically impossible under given conditions or affect the equilibrium position in reversible reactions. The point is that if, under given conditions, several parallel reactions are thermodynamically possible, then the catalyst, due to its selectivity, accelerates one of these reactions. The equilibrium position for it is achieved much faster than for other reactions, therefore the main products will be the substances formed in this reaction, and the products of other reactions will be present as impurities to the main ones.

In some cases, the reaction products themselves may be catalysts and the reaction will self-accelerate over time. Such reactions are called *autocatalytic.*

When a reaction occurs, the catalyst and reactants can be in the same phase (liquid or gaseous), and such reactions are *homogeneous catalytic reactions* . Most often, homogeneous catalysis is observed in solutions. In the case of *heterogeneous catalysis,* the catalyst and reactants are in different phases - in most cases, the catalyst is solid, and the reactants are in a gaseous phase or solution.

## Homogeneous catalytic reactions

Since the catalyst is not included in the stoichiometric equation of a chemical reaction, but affects its rate, it is logical to assume that the catalyst first forms some unstable intermediate compounds with the reacting substances, which, upon further transformations, give reaction products with regeneration of the catalyst. Sometimes intermediates are common but unstable chemical compounds that can be isolated and studied separately. However, in most cases, the extremely low stability of intermediate products does not allow their isolation, and the formation of an intermediate compound can sometimes be judged only indirectly by a change in some property of the solution. For example, during the reaction of metaphosphoric acid with potassium persulfate, the catalyst of which is hydroiodic acid, the appearance of a yellow color of the solution is observed, which disappears by the time the reaction is completed:

$$\mathrm{H_3PO_3 + K_2S_2O_8 + H_2O \xrightarrow{HI} H_3PO_4 + K_2SO_4 + H_2SO_4}$$

The intermediate product here is iodine and the reaction proceeds in two stages:

$$1)\ \mathrm{K_2S_2O_8 + 2HI \rightarrow I_2 + H_2SO_4 + K_2SO_4}$$

$$2)\ \mathrm{H_3PO_3 + I_2 + H_2O \rightarrow H3PO4 + 2HI}$$

The oxidation of thiosulfate ion by hydrogen peroxide is catalyzed by molybdic acid:

$$\mathrm{S_2O_3^{2-} + 4\,H_2O_2 \xrightarrow{MoO_4^{2-}} 2\,SO_4^{2-} + 2\,H^+ + 3\,H_2O}$$

It is assumed that the intermediate product is permolybdate ion and the reaction proceeds according to the following scheme:

$$1)\ \mathrm{4MoO_4^{2-} + 4H_2O_2 \rightarrow 4MoO_5^{2-} + 4H2O}$$

$$2)\ \mathrm{S_2O_3^{2-} + 4\,MoO_5^{2-} + H_2O \rightarrow 2\,SO_4^{2-} + 2\,H^+ + 4\,MoO_4^{2-}}$$

Based on the theory of the activated complex, the following scheme of catalytic action is assumed.

The non-catalytic reaction between substances A and B proceeds with the formation of the activated complex AB $^{\#}$:

$$A + B \rightarrow AB^{\#} \rightarrow C + D$$

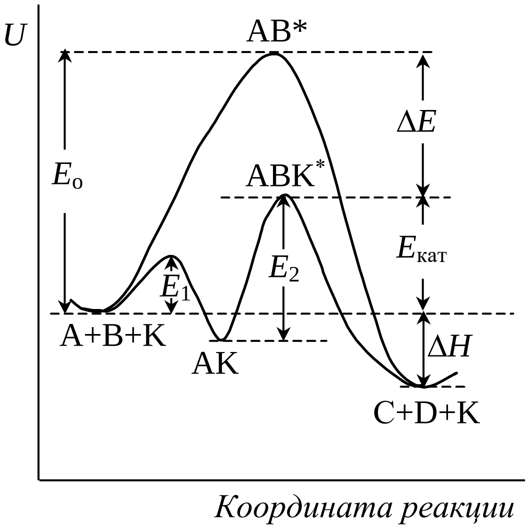
In the presence of catalyst K, the process occurs in several stages:

1) A reversible reaction of the formation of an intermediate product from a catalyst and any reactant:

$$A + K \underset{k_2}{\overset{k_1}{\rightleftarrows}} A\,K$$

2) The intermediate product forms an activated complex:

$$A\,K + B \xrightarrow{k_3} AB\,K^{\#}$$



Rice. 24.1. Non-catalytic and catalytic reaction pathway profiles .

3) The activated complex decomposes into reaction products and a catalyst:

$$AB\,K^{\#} \xrightarrow{k_4} C + D + K$$

In principle, it is possible to construct a potential energy surface and represent the profiles of the non-catalytic and catalytic reaction paths. An approximate diagram of them is shown in Figure 24.1.

As can be seen from the figure, during catalysis in this case it is assumed that the formation of the intermediate product is an exothermic process, and then the potential energy of the system increases due to the formation of the activated ABC # $^{\text{complex}}$ . The figure also shows a decrease in the activation energy of the catalytic reaction compared to the non-catalytic reaction $\Delta E = E_{\text{o}} - E_{\text{cat}}$ . If we assume that the pre-exponential factors in the Arrhenius equation are the same for both reactions, then the ratio of the rate constants of the catalytic and non-catalytic reactions is equal to

$$\frac{k_{\text{êàò}}}{k_{\text{íåêàò}}} = e^{\frac{\Delta E}{RT}} . \tag{24.1}$$

Since the value of $\Delta E$ is an exponent, even a small decrease in the activation energy leads to a significant increase in the reaction rate. For example, for the decomposition reaction of acetaldehyde

$$CH_3CHO \rightarrow CH_4 + CO,$$

proceeding at 800K in the gas phase, the activation energy is approximately 190 kJ/mol. The reaction is catalyzed by iodine vapor, and the activation energy is reduced to 135 kJ/mol, i.e. $\Delta E$ = 55 kJ/mol ( ≈28%). Applying formula (24.1), we obtain

$$\frac{k_{\text{кат}}}{k_{\text{некат}}} = e^{\frac{55000}{8{,}31 \cdot 800}} \approx 3500,$$

those. in the presence of a catalyst, the reaction proceeds 3500 times faster. The kinetics of a homogeneous catalytic reaction proceeding according to the scheme presented above depends on the properties of the AA intermediate product. To derive the kinetic equation for the reaction, we represent the rate of formation of the final product C as the rate of monomolecular decomposition of the activated complex:

$$v = \frac{d[\mathrm{C}]}{dt} = k_4\left[\mathrm{ABK}^{\#}\right]. \qquad (24.2)$$

Using the principle of stationary concentrations, we determine the concentration of the activated complex from the relation

$$k_3[\mathrm{A\,K}][\mathrm{B}] = k_4[\mathrm{AB\,K}^{\#}]. \qquad (24.3)$$

The principle of stationarity also applies to the intermediate product A K :

$$k_1[\mathrm{A}]\,[\mathrm{K}] - k_2[\mathrm{A\,K}] - k_3[\mathrm{A\,K}]\,[\mathrm{B}] = 0. \qquad (24.4)$$

The total catalyst concentration [ Ko ] can be represented as the sum of the current concentration of the free catalyst [ K ] and the concentration of the intermediate product [ $_{\mathrm{AK}}$ ] :

$$[\mathrm{K_o}] = [\mathrm{K}] + [\mathrm{A\,K}] = \mathrm{const}\,. \qquad (24.5)$$

Then equation (24.4) can be written as

$$k_1[\mathrm{A}]([\mathrm{K_o}] - [\mathrm{A\,K}]) - k_2[\mathrm{A\,K}] - k_3[\mathrm{A\,K}][\mathrm{B}] = 0, \quad (24.6)$$

where

$$[\mathrm{AK}] = \frac{k_1[\mathrm{A}][\mathrm{K_o}]}{k_1[\mathrm{A}] + k_2 + k_3[\mathrm{B}]}. \qquad (24.7)$$

$^{\#}$ ] using equations (24.3) and (24.7) and substituting it into equation (24.2), we obtain the equation for the reaction rate:

$$v = \frac{d[\mathrm{C}]}{dt} = \frac{k_1k_3[\mathrm{A}][\mathrm{B}]}{k_1[\mathrm{A}] + k_2 + k_3[\mathrm{B}]}[\mathrm{K_o}]. \qquad (24.8)$$

This equation underlies the description of the kinetics of homogeneous catalytic reactions. It establishes proportionality between the reaction rate and the catalyst concentration, which is confirmed by experience.

When analyzing this equation, we can consider some limiting cases. The intermediate product may be unstable, and the rate constant $k_2$ of the reverse decomposition A K may be very large, i.e. the intermediate product mainly decomposes into initial substances, its concentration is low, and therefore the rate of its transformation into the activated complex and further into the final products is very low ( $k_2 >> k_3$ [V]). In this case, the concentration of the intermediate product will be close to equilibrium, and in the denominator of equation (24.8) the values of $k_1$ [A] and $k_3$ $_{[B]}$ can be neglected compared to $k_2$. Then

$$v = \frac{d[\mathrm{C}]}{dt} = \frac{k_1 k_3}{k_2}[\mathrm{K}][\mathrm{A}][\mathrm{B}] = k[\mathrm{A}][\mathrm{B}][\mathrm{K_o}], \qquad (24.9)$$

those. in this case, the reaction proceeds in second order relative to the starting substances at a rate proportional to the concentration of the catalyst. An AK intermediate with these properties is called *an Arrhenius intermediate* . This name is due to the fact that the active form of the molecule, the existence of which was assumed in the derivation of the dependence of the reaction rate on temperature (see Section 22.7), belongs to compounds of this type.

In another extreme case, the formation of an intermediate product is possible, which, as it is formed, will immediately react further towards the formation of an activated complex and reaction products ( $k_1$ [ A ] $<<k_3$ [B] and $k_2 <<k_3$ [B]). In this case, the reaction rate

$$v = k_1 [\mathrm{A}][\mathrm{K_o}] \qquad (24.10)$$

and does not depend on the concentration of the second starting substance, since at any, even the smallest, concentrations it is sufficient for immediate consumption of AK . Intermediates of this type are called *Van't Hoff substances* , since since Van't Hoff the formation of such substances has been explained by a decrease in the overall order of the reaction compared to possible assumptions. We can say that in this case the reaction has zero order in substance B. The concentration of the van't Hoff substance, in contrast to the Arrhenius substance, is far from equilibrium.

Other schemes for the course of homogeneous catalytic reactions have also been proposed, but in all cases the reaction rate depends on the concentration of the intermediate product, and therefore on the concentration of the catalyst. If, for example, intermediate product P is obtained from starting material A and catalyst K according to the scheme

$$n + \mathrm{K\ L\ P},$$

then the equilibrium constant of this reaction is

$$K_c = \frac{[\mathrm{P}]}{[\mathrm{A}]^n([\mathrm{K_o}]-[\mathrm{P}])}, \qquad (24.11)$$

and the concentration of the intermediate product

$$[\mathrm{P}] = \frac{K_c[\mathrm{A}]^n[\mathrm{K_o}]}{1+K_c[\mathrm{A}]^n}. \qquad (24.12)$$

The overall rate of the reaction depends on the reaction rate of the decomposition of the intermediate

$$\mathrm{P} \xrightarrow{k} \text{reaction products} + \mathrm{K}$$

So the reaction speed

$$-\frac{d[\mathrm{A}]}{dt} = k[\mathrm{P}] = \frac{kK_c[\mathrm{A}]^n}{1+K_c[A]^n}[\mathrm{K_o}]. \qquad (24.13)$$

If the equilibrium is shifted o towards the formation of an intermediate product, that is, the value of $K_{with}$ [A] $^n$ >>1, then the reaction rate

$$-\frac{d[\mathrm{A}]}{dt} = k[\mathrm{K_o}] \qquad (24.14)$$

If the equilibrium is shifted towards the starting substances ( $K_c$ [A] $^n$ <<1), then

$$-\frac{d[\mathrm{A}]}{dt} = kK_c[\mathrm{A}]^n[\mathrm{K_o}]. \qquad (24.15)$$

The equilibrium constant $K_c$ depends on temperature, therefore, with a change in temperature, it is possible to change the order of the reaction in terms of reactants and m. Such a change was found , for example, for the decomposition reaction of hydrogen peroxide, which is catalyzed by ions $\mathrm{Cr_2O_7^{2-}}$. In the temperature range from 0 to 56 °C, the order of this reaction in $H_2O_2$ changes from zero to the second.

## 41-Lecture.

## Topic: Order of reactions and methods of determination.

Differential and integral kinetic equations of chemical reactions. Kinetic curves.

**Kinetic equation of a chemical reaction. Order of reaction.**

One of the tasks facing chemical kinetics is determining the composition of the reaction mixture (i.e., the concentrations of all reagents) at any time, for which it is necessary to know the dependence of the reaction rate on concentrations. In general, the greater the concentration of reactants, the greater the rate of the chemical reaction. Chemical kinetics is based on the so-called. *basic postulate of chemical kinetics* :

*The rate of a chemical reaction is directly proportional to the product of the concentrations of the reacting substances, taken to certain powers.*

That is, for the reaction

aA + bB + dD + ... —> eE + ...

can be written:

$$V = k \cdot C_A^{\,x} C_B^{\,y} C_D^{\,z} \ldots \quad \text{(II.4)}$$

The proportionality coefficient k is *the rate constant of a chemical reaction* . The rate constant is numerically equal to the reaction rate at concentrations of all reactants equal to 1 mol/l.

The dependence of the reaction rate on the concentrations of reactants is determined experimentally and is called *the kinetic equation* of a chemical reaction. Obviously, in order to write the kinetic equation, it is necessary to experimentally determine the rate constant and exponents at the concentrations of the reactants. The exponent at the concentration of each of the reacting substances in the kinetic equation of a chemical reaction (in equation (II.4) respectively x, y and z) is a *particular order of the reaction* for this component. The sum of the exponents in the kinetic equation for a chemical reaction (x + y + z) is the *overall reaction order* . It should be emphasized that the reaction order is determined only from experimental data and is not related to the stoichiometric coefficients of the reactants in the reaction equation. The stoichiometric reaction equation is a material balance equation and in no way can determine the nature of the course of this reaction in time.

In chemical kinetics, it is customary to classify reactions according to the magnitude of the overall reaction order. Let us consider the dependence of the concentration of reactants on time for irreversible (one-sided) reactions of zero, first and second orders.

### 2.1.2 Zero order reactions

For zero-order reactions, the kinetic equation has the following form:

$$V = k_0 \quad \text{(II.5)}$$

The rate of a zero-order reaction is constant over time and does not depend on the concentrations of the reactants; This is typical for many heterogeneous reactions (taking place at the phase interface) in the case when the rate of diffusion of reagents to the surface is less than the rate of their chemical transformation.

### 2.1.3 First order reactions

Let us consider the time dependence of the concentration of the starting substance A for the case of a first-order reaction A —> B. First-order reactions are characterized by a kinetic equation of the form (II.6). Let us substitute expression (II.2) into it:

$$V = k_1 C_A \quad \text{(II.6)}$$

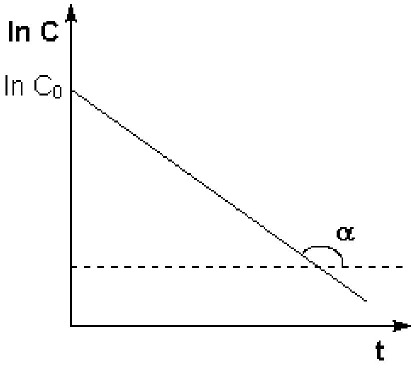
$$V = k_1 C_A = -\frac{dC}{dt} \quad \text{(II.7)}$$

After integrating expression (II.7) we obtain:

$ln C = -kt + g$ (II.8)

We determine the integration constant g from the initial conditions: at time t = 0, the concentration of C is equal to the initial concentration of $C_o$. It follows that g = ln $C_o$. We get:

$ln C = ln C_o - k_1 t$ (II.9)



Rice. 2.3 Dependence of the logarithm of concentration from time for reactions first order.

Thus, the logarithm of concentration for a first-order reaction depends linearly on time (Fig. 2.3) and the rate constant is numerically equal to the tangent of the angle of inclination of the straight line to the time axis.

$k_1 = -tg\,\alpha$ (II.10)

From equation (II.9) it is easy to obtain an expression for the rate constant of a one-way first-order reaction:

$k_1 = \frac{1}{t} ln \frac{C_o}{C}$ (II.11)

Another kinetic characteristic of the reaction is ***the half-life*** $t_{1/2}$ - the time during which the concentration of the starting substance is halved compared to the original. Let us express $t_{1/2}$ for a first-order reaction, taking into account that C = ½$C_o$:

$ln(\frac{1}{2}C_o) = ln C_o - k_1 t$ (II.12)

From here

$t_{1/2} = \frac{\ln 2}{k_1}$ (II.13)

As can be seen from the resulting expression, the half-life of the first-order reaction does not depend on the initial concentration of the starting substance.

2.1.4 Second order reactions

For second-order reactions, the kinetic equation has the following form:

$V = k_2 C_A^2$ (II.14)

or

$V = k_2 C_A C_B$ (II.15)

Let us consider the simplest case, when the kinetic equation has the form (II.14) or, what is the same, in the equation of the form (II.15) the concentrations of the initial substances are the same; equation (II.14) in this case can be rewritten as follows:

$V = k_2 C^2 = -\frac{dC}{dt}$ (II.16)

After separation of variables and integration we get:

$\frac{1}{C} = k_2 t + g$ (II.17)

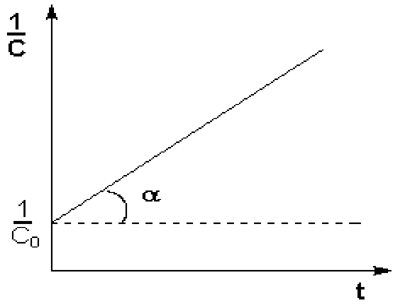
The integration constant g, as in the previous case, is determined from the initial conditions. We get:

$\frac{1}{C} = k_2 t + \frac{1}{C_o}$ (II.18)

Thus, for second-order reactions with a kinetic equation of the form (II.14), a linear dependence of the inverse concentration on time is characteristic (Fig. 2.4) and the rate constant is equal to the tangent of the angle of inclination of the straight line to the time axis:

$k_2 = tg\,\alpha$ (II.19)

$k_2 = \frac{1}{t}\left(\frac{1}{C} - \frac{1}{C_o}\right)$ (II.20)



Rice. 2.4 Dependence of inverse concentration on time for reactions second order

If the initial concentrations of the reactants $C_{o, A}$ and $C_{o, B}$ are different, then the reaction rate constant is found by integrating equation (II.21), in which $C_A$ and $C_B$ are the concentrations of the reactants at time t from the beginning of the reaction:

$V = -\frac{dC}{dt} = k_2 C_A C_B$ (II.21)

In this case, for the rate constant we obtain the expression

$$k_2 = \frac{1}{t\,(C_{0,A} - C_{0,B})} \ln \frac{C_{0,B}C_A}{C_{0,A}C_B} \quad (II.22)$$

The order of a chemical reaction is a formal kinetic concept, ***the physical meaning*** of which for elementary (single-stage) reactions is as follows: the order of the reaction is equal to the number of simultaneously changing concentrations. In the case of elementary reactions, the reaction order may be equal to the sum of the coefficients in the stoichiometric reaction equation; however, in the general case, the reaction order is determined only from experimental data and depends on the reaction conditions. Let us consider, as an example, the elementary reaction of hydrolysis of ethyl ester of acetic acid (ethyl acetate), the kinetics of which is studied in a laboratory workshop in physical chemistry:

$CH_3COOS_2H_5 + H_2O$ —> $CH_3COOH + C_2H_5OH$

If this reaction is carried out at close concentrations of ethyl acetate and water, then the overall order of the reaction is two and the kinetic equation has the following form:

$$V = k[CH_3COOC_2H_5][H_2O] \quad (II.23)$$

When carrying out the same reaction under conditions of a large excess of one of the reagents (water or ethyl acetate), the concentration of the substance in excess remains practically unchanged and can be included in the rate constant; the kinetic equation for two possible cases takes the following form:

1) Excess water:

$$V = k'[CH_3COOC_2H_5] \quad (II.24)$$

$$k' = k[H_2O] \quad (II.25)$$

2) Excess ethyl acetate:

$$V = k''[H_2O] \quad (II.26)$$

$$k'' = k[CH_3COOC_2H_5] \quad (II.27)$$

In these cases we are dealing with the so-called. ***pseudo-first order reaction*** . Carrying out the reaction with a large excess of one of the starting substances is used to determine the partial orders of the reaction.

## Methods for determining reaction order

Carrying out a reaction under conditions where the concentration of one of the reagents is much lower than the concentration of the other (others) and the reaction rate depends on the concentration of only this reagent is used to determine particular reaction orders - this is the so-called. excess concentration method or Ostwald isolation method . The reaction order for a given substance is determined by one of the methods listed below.

***The graphical method*** consists in plotting the dependence of the reagent concentration on time in various coordinates. For various particular orders, these dependencies have the following form:

| Reaction order | Dependence of concentration on time |
|---|---|
| 1 | $\ln C = \ln C_o - k\tau$ |
| 2 | $\frac{1}{C} = k\tau + \frac{1}{C_o}$ |
| 3 | $\frac{1}{C^2} = k\tau + \frac{1}{C_o^{\ 2}}$ |

If you plot these dependencies based on experimental data, then only one of them will be a straight line. If, for example, a graph constructed from experimental data turns out to be rectilinear to the coordinates *ln* C = f(t), then the partial order of the reaction for a given substance is equal to one.

***The method for selecting a kinetic equation*** consists of substituting experimental data from studying the dependence of the concentration of a substance on time into kinetic equations of various orders. By substituting the values of the reagent concentration at different times into the equations given in the table, the values of the rate constant are calculated. The partial order of a reaction for a given substance is equal to the order of the kinetic equation for which the value of the rate constant remains constant over time.

| Reaction order | Expression for the rate constant |
|---|---|
| 1 | $k = \frac{1}{\tau} \ln \frac{C_0}{C}$ |
| 2 | $k = \frac{1}{\tau}\left(\frac{1}{C_o} - \frac{1}{C}\right) = \frac{1}{\tau}\frac{C_o - C}{C_o C}$ |
| 3 | $k = \frac{1}{\tau}\frac{C_o^{\ 2} - C^2}{2C_o^{\ 2}C^2}$ |

***The method for determining the half-conversion time*** is to determine $t_{1/2}$ for several initial concentrations. As can be seen from the equations given in the table, for a first-order reaction the half-conversion time does not depend on $C_o$, for a second-order reaction it is inversely proportional to $C_o$, and for a third-order reaction it is inversely proportional to the square of the initial concentration.

| Reaction order | Expression for half-life |
|---|---|
| 1 | $\tau_{1/2} = \frac{ln 2}{k}$ |
| 2 | $\tau_{1/2} = \frac{1}{k} \cdot \frac{1}{C_o}$ |
| 3 | $\tau_{1/2} = \frac{1}{k} \cdot \frac{3}{2C_o^2}$ |

Based on the nature of the dependence of t $_{1/2}$ on C $_o$ , it is easy to draw a conclusion about the order of the reaction for a given substance. This method, unlike those described above, is also applicable for determining fractional orders.

### 2.1.6 Molecularity of elementary reactions

Elementary (simple) reactions are reactions that occur in one stage. They are usually classified according to ***molecularity* :**

***The molecularity of an elementary reaction is the number of particles that, according to the experimentally established reaction mechanism, participate in an elementary act of chemical interaction.***

***Monomolecular*** - reactions in which a chemical transformation of one molecule occurs (isomerization, dissociation, etc.):

$I_2 \longrightarrow I\bullet + I\bullet$

***Bimolecular*** – reactions, the elementary act of which occurs when two particles (identical or different) collide:

$CH_3Br + KOH \longrightarrow CH_3OH + KBr$

***Trimolecular*** – reactions, the elementary act of which occurs during the collision of three particles:

$O_2 + NO + NO \longrightarrow 2NO_2$

Reactions with molecularities greater than three are unknown.

For elementary reactions carried out at close concentrations of the starting substances, the values of molecularity and order of the reaction are the same. However, there is no clearly defined relationship between the concepts of molecularity and reaction order, since the reaction order characterizes the kinetic equation of the reaction, and molecularity characterizes the reaction mechanism.

## 42-Lecture.

## Topic: Theories of chemical kinetics.

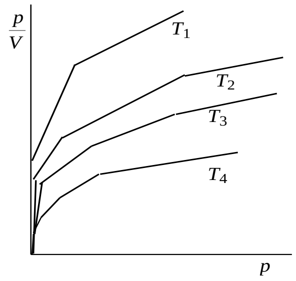
Theories of chemical kinetics: active collisions and activated complex or transition state theories.

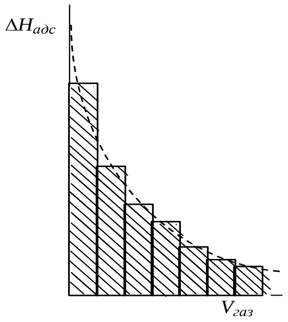
## Active sites of heterogeneous catalysts

Numerous experimental data on heterogeneous catalytic reactions have led to the conclusion that not the entire catalyst surface is catalytically active, but only a small part of it. This is evidenced by facts obtained in the study of adsorption, poisoning of catalysts, the influence of the nature of the surface on catalytic activity, etc.

If we follow Langmuir's theory of adsorption, according to which the surface is homogeneous, then the adsorption isotherm can be represented as a linear equation

$$\frac{p}{V} = \frac{p}{V_m} + \frac{1}{KV_m}. \quad (25.1)$$





Rice. 25.1. Gas adsorption isotherms Fig. 25.2. Heat of gas adsorption
on a solid adsorbent at different conditions on the catalyst surface
temperatures: ( $T_1 > T_2 > T_3 > T_4$ )

If this equation is valid, then there should be a linear dependence in the coordinates $p / V$ - $p$ , by which it is possible to determine the parameters $V_m$ and $K$. However, in many cases there is no such linear dependence, but in small pressure intervals, separate linear sections can be distinguished (Fig. 25.1). This dependence can be explained if we assume that different parts of the surface have different adsorption potentials.

The adsorption inhomogeneity of the surface is also confirmed by the data on the heats of adsorption . With successive adsorption of identical portions of a gas on the catalyst surface, the heat of adsorption naturally decreases, i.e. less and less active areas of the surface are filled with adsorbate (Fig. 25.2).

Data on the action of poisons also show that the activity of different areas of the catalyst surface is not the same. The catalytic activity of many catalysts is almost completely lost when the fraction of adsorbed poison is only 0.5 - 1% of the maximum adsorption. It follows that the surface consists of a set of adsorption centers, but only a small part of them are catalytically active, i.e. The concepts of adsorption and catalytically active centers cannot be identified.

Back in the 20s of the twentieth century, Taylor proposed a theory according to which the active centers of the catalyst are surface atoms of the crystal lattice, located above the average surface level. Such "peaks" have free valences and are capable of forming reactive intermediates.

Since the adsorption of reacting molecules is usually activated, it should be assumed that the interaction of the adsorption center with the substrate molecule forms a surface compound of the chemisorption type. From this follows the conclusion that only those adsorption centers or their combination that are capable of forming an active intermediate surface compound with the adsorbed substance will be catalytically active. An essential factor determining the possibility of the formation of such a compound is the nature of the surface.

If we consider an ideal crystal at a temperature of absolute zero, then all its particles occupy strictly defined positions, forming a regular crystal lattice. As the temperature rises, this order is disrupted. Some particles leave their places at lattice sites and occupy positions in interstices ("Fresnel defects") or emerge from them to the surface ("Schottky defects"). The formation of defects in the volume also leads to the formation of defects on the surface, the appearance of vacant places on it and particles on the faces in places that do not correspond to the correct crystalline order.

In real crystals, there are always various violations of the crystal lattice. These disturbances include *dislocations* - various distortions of the lattice planes in comparison with their geometrically correct arrangement in an ideal crystal. Stoichiometric violations, as well as foreign impurities, also cause local distortions of the geometric order in the crystal. These distortions can lead to the fact that the crystal will be divided by "cracks" into separate microscopic blocks fastened together. Such a block structure is characteristic of many crystalline solids (silica gels, alumogels, activated carbon, etc.) widely used in heterogeneous catalysis. In a real crystal, the number of defects is much greater than in a hypothetical ideal crystal. Various surface disturbances sharply increase the adsorption surface and the number of adsorption and catalytically active centers, and the surface can become energetically inhomogeneous.

Theories of heterogeneous catalysis consider various models of surface structure.

*A homogeneous surface* is represented as a surface on all adsorption centers of which the heat of adsorption is the same, and the catalytic transformation occurs with the same activation energy. In reality, such surfaces are rare and are most likely for purely metal catalysts.

*The inhomogeneity of the surface* can be expressed in *the energy nonequivalence* of the active centers. Then the reacting substance falling on the surface will be distributed over the adsorption centers in accordance with the energy of these centers and react with the corresponding activation energy.

Heterogeneity The surface can also be *geometric* ; it is determined by the block separation of the catalyst surface. The reactant, falling on a particular block, will be adsorbed, and if this center is also catalytically active, it will react on the centers inside the block, regardless of the presence of more energetically active centers on other blocks. In this case, it is not the energy distribution that is decisive, but the distribution of centers among geometric blocks.

All modern theories of heterogeneous catalysis are based on the idea of the existence of catalytically active centers, but the specific structure of such centers is assumed to be different in different theories.

## Multiplet theory of catalysis

The accumulated experimental material made it possible to concretize the concept of *an active center* and compare its structure and composition with the structure of the molecules that undergo transformation. This was first done in *the multiplet theory* of A. A. Balandin (1929), which considers the active center of a heterogeneous catalyst.

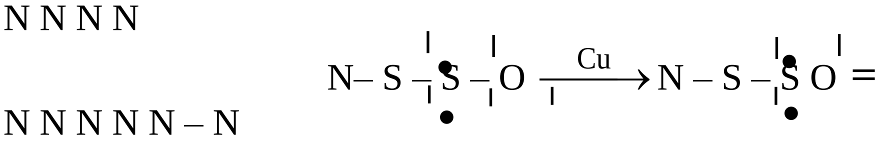
The main provisions of this theory are as follows:

1. A catalytically active center is a set of a certain number of adsorption centers located on the surface in geometric accordance with the structure of the molecule that is undergoing transformation. This position is called *the principle of geometric* ( *structural* ) *correspondence* .

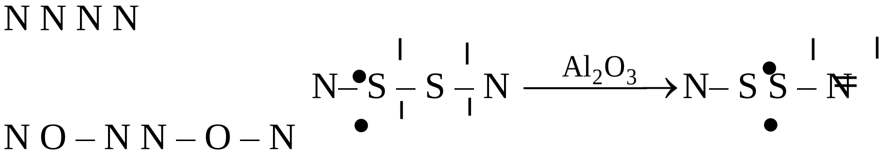
*a multiplet complex* is formed , resulting in a redistribution of bonds, which, as a result, leads to the formation of reaction products.

Thus, in theory, the catalytic action is associated with the relationship between the geometric arrangement of adsorption centers and the geometry of the reacting molecule. For various reactions, the number of adsorption centers (each of which is identified with one metal atom) in the active center can be equal to 2, 3, 4, 6, etc. These active centers are called *doublets, triplets, quadruplets, sextets* , and in general, *multiplets.*

For example, the dehydrogenation of ethyl alcohol, according to the theory of multiplets, occurs on a doublet, while hydrogen atoms of the $CH_2$ and OH groups are attracted to one atom of the doublet, and the oxygen atom and carbon atom of the $CH_2$ group are attracted to the other . As a result, C–H and O–H bonds are broken and H–H and C=O bonds are formed with the formation of acetaldehyde and hydrogen molecules:



At other distances between the catalyst atoms in the doublet, another process is possible: the hydrogen atom of the $CH_3$ group and the oxygen atom are attracted to one catalyst atom, and both carbon atoms to the other:



As a result of the reaction, ethylene and water are formed.

In the reactions of dehydrogenation of cycloparaffins, the catalysts are metals with face-centered or hexagonal crystal lattices, but only those in which the distance between the centers of atoms in the lattice lies in the range from 24.8 to 27.7 nm ( Ni , Cu, Rh, Ir, Pd, Pt ). Metals with similar crystal lattices, but with other interatomic distances (Th, Pb, Au, Ag) do not show catalytic activity during the dehydrogenation of six-membered rings.

This is explained by the fact that the geometric correspondence between the active center and the molecule must be observed. The fact that metals with slightly different interatomic distances are catalytically active indicates that some deformation of bond angles is possible during the formation of a multiplet complex.

The arrangement of particles in a multiplet complex during the dehydrogenation of cyclohexane on a sextet is shown schematically in Fig. 25.3.

During the redistribution of bonds on the active center, carbon atoms 1 and 6 are attracted to the catalyst atom *b* , 5 and 4 - to the atom *g* , and 3 and 2 - to the atom *e* , and the hydrogen atoms of $CH_2$ groups are attracted to the catalyst atoms *a* , *c* and *e* . As a result, six C–H bonds are broken, three C=C bonds and three H–H bonds are formed, i.e. the products are a benzene molecule and three hydrogen molecules.

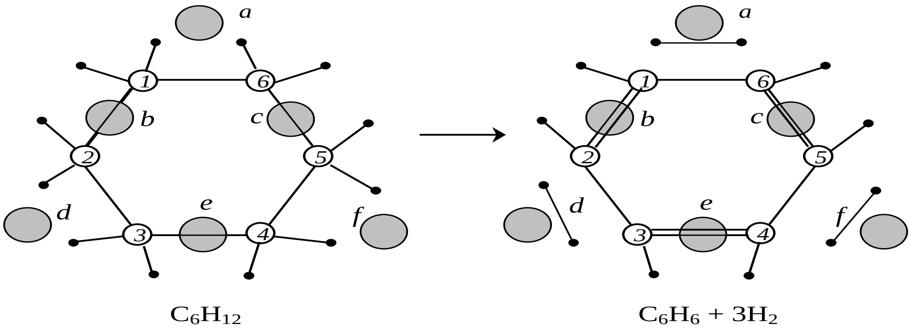


Fig.25.3. Cyclohexane dehydrogenation scheme

Thus, the multiplet theory makes it possible to qualitatively explain the empirical regularities established in the study of the catalytic transformations of many organic substances. However, later works also revealed deviations from the simple scheme of geometric correspondence. For example, it turned out that the active center of the dehydrogenation of cyclohexane on $Cr_2O_3$ does not consist of six, but of two atoms, and five-membered cycles can also be dehydrogenated on the same catalyst under certain conditions. All this shows that the true mechanism of the catalytic action is more complicated than the simple scheme of the multiplet theory.

In addition to the principle of geometric correspondence, another provision was later introduced into the theory - *the principle of energy correspondence* . In accordance with this principle, the activation energy of a heterogeneous catalytic reaction is a complex quantity that can, to a first approximation, be represented as depending on two components. The first of them is determined by the binding energy between atoms in the reacting molecule, and the other is determined by the energy of interaction of the reacting molecule with the catalyst atoms during the formation of a multiplet complex. This implies the dependence of the catalytic activity of a catalyst on its affinity for the reacting parts of the molecule. Let us imagine a heterogeneous catalytic reaction with the following scheme:

Starting materials + Catalyst →Multiplet complex→

Catalyst + Reaction Products

For the first stage (formation of a multiplet complex) to occur, the reacting molecule must receive the energy necessary to break the bonds. On the other hand, the energy of formation of a multiplet complex is released. To a first approximation, the difference between these energies is the activation energy. With a very low affinity of the catalyst for the substrate, the decrease in activation energy will be insignificant, and the catalytic activity will be low. As the affinity of the catalyst for the substrate increases, the activation energy decreases more and more and the catalytic activity increases. But the reaction products are formed at the second stage - the decomposition of the multiplet complex. To carry out this stage, the multiplet complex must receive the energy necessary to break the bonds in it, and at the same time the energy for the formation of the final products is released. The speed of the second stage is determined by the difference between these energies. Therefore, an increase in the affinity of the catalyst for the substrate leads to an acceleration of the catalytic process only to a certain limit, while the reaction rate is determined by the first stage. With a significant increase in bond strength in a multiplet complex, the overall reaction rate will be determined by the second stage, the activation energy of which will increase, which will lead to inhibition of the process.

## Active Ensemble Theory

As already noted, the theory of multiplets is primarily applicable to explain the catalytic action of metal catalysts with a relatively uniform surface. In industrial production, supported catalysts are very often used, i.e. those in which the catalytically active substance is applied to the surface of a solid with a well-developed surface (silica gel, aluminum gel, asbestos, activated carbon, etc.). The carrier itself does not exhibit a catalytic effect, but it increases the specific activity of the catalyst, can change the catalytic activity and sometimes selectivity within small limits, and increases thermal stability and resistance to poisons.

These effects can be associated with the block structure of the carrier surface. The presence of various microcracks and other defects leads to the fact that the carrier surface consists of a large number of individual microsections (blocks) separated by geometric and energy barriers. Catalyst atoms, falling on individual blocks, can move along the surface only within the block, since moving to a neighboring block requires excess energy to overcome the barrier (Fig. 25. 4 ) . N.I. Kobozev called these blocks “ *areas of free migration”* ”, or simply “areas of migration”.

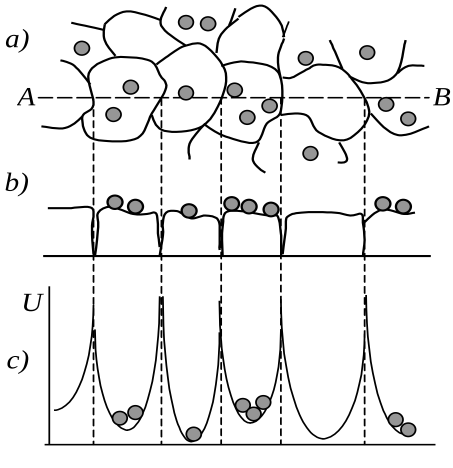


Fig.25. 4 . Distribution of catalyst atoms over regions of free migration of the catalyst: geometric barriers on the support surface ( *a,b* ); energy barriers on the surface of the carrier ( *c* )

Thus, the supported catalyst atoms are located on the surface in the form of separate aggregates, “assemblies”, consisting of a certain number of atoms localized in migration regions.

Let us define *the total catalytic activity A* of the catalyst as the number of substrate molecules reacting in 1 *s* on all catalyst atoms located on the surface of 1 *g* of the sample. If any combination of catalyst atoms located on the surface of the support in migration regions are catalytically active, then the total catalytic activity should be directly proportional to the number of supported catalyst atoms *N* , and *the specific activity* (activity per catalyst atom) $a = A/N$ should be constant. If only certain combinations of atoms ( *p*- atomic ensembles) are catalytically active , the catalytic activity will be proportional to the probability of formation of *a p* -atomic ensemble.

have a maximum, and specific activity also has a maximum or decreases exponentially with increasing *N.* Thus, the experiment confirmed the selectivity of the catalytic action of various ensembles. Based on these data, N.I. Kobozev developed a theory in 1939, which was called the *theory of active ensembles* .

The main position of the theory can be formulated as follows: the carrier of catalytic activity is the atomic (precrystalline) phase of the catalyst located on the surface, relative to which the surface of the carrier (or the crystalline phase of the catalyst itself) is an inert support. For each process, the catalytically active center is an ensemble of a certain number *n* of catalyst atoms.

Let us consider the distribution of atoms on the surface of a catalyst consisting of individual migration regions. If the specific surface area of the carrier *is S* and the average area of one region is Δ, then the number of migration regions on the surface of 1 *g* of the carrier is equal to

$$Z_o = \frac{S}{\Delta}. \qquad (25.2)$$

*N catalyst atoms are deposited* on the surface of 1 *g* of support , then on average there are

$$\nu = \frac{N}{Z_o} \qquad (25.3)$$

atoms. In reality, different numbers of atoms can fall into different migration regions. The probability of one atom from their total number *N falling* into one of $Z_o$ areas is equal to $1/Z_o$ , and the probability of hitting *n* atoms is $(1/Z_o)^n$ . Others ( *N–n* ) atoms will fall into any of the remaining ( $Z_o - 1$) regions. Then the probability $W_o$ the formation of *an n* -atomic ensemble of catalyst atoms will be

$$W_o = \left(\frac{1}{Z_o}\right)^n \left(\frac{Z_o - 1}{Z_o}\right)^{N-n}. \qquad (25.4)$$

Since all atoms are identical and can be rearranged without changing the distribution, to obtain the total probability of the formation of an *n* -atomic ensemble, the probability must be multiplied by the number of combinations from *N* to *n* :

$$W = \frac{N!}{n!(N-n)!}\left(\frac{1}{Z_o}\right)^n \left(1 - \frac{1}{Z_o}\right)^{N-n} = \frac{N!}{n!(N-n)!}\left(\frac{\nu}{N}\right)^n \left(1 - \frac{\nu}{N}\right)^{N-n}. \qquad (25.5)$$

Since the total number of catalyst atoms $N$ ($10^{20} - 10^{23}$) is significantly greater than the number of atoms $n$ in the ensemble (1 – 10), the passage to the limit can be used:

$$W_n = \lim W_{N\to\infty} . \tag{25.6}$$

For individual factors of equation (25.5) we have:

$$\lim_{N\to\infty} \frac{\nu^n}{n!} = \frac{\nu^n}{n!} ; \tag{25.7}$$

$$\lim_{N\to\infty} \frac{N!}{N^n(N-n)!} = \lim_{N\to\infty} \frac{N(N-1)...(N-n+1)}{N^n} = \lim_{N\to\infty} 1\cdot\left(1-\frac{1}{N}\right)...\left(1-\frac{n-1}{N}\right) = 1; \tag{25.8}$$

$$\lim_{N\to\infty}\left(1-\frac{\nu}{N}\right)^{N-n} \approx \lim_{N\to\infty}\left[\left(1-\frac{\nu}{N}\right)^{-N/\nu}\right]^{-\nu} = e^{-\nu} . \tag{25.9}$$

Finally, for the probability of formation we obtain

$$W_n = \frac{\nu^n}{n!} e^{-\nu} . \tag{25.10}$$

Thus, it is clear that the distribution of catalyst atoms on the block surface of the support obeys Poisson’s law. As can be seen from Fig. 25.5 , all curves pass through a maximum, i.e. Depending on the concentration on the surface of the carrier, mainly ensembles of a certain number of atoms are formed.

*n -atomic ensemble* is catalytically active , then the number of such ensembles on the surface of 1 $g$ of support is equal to

$$Z_n = Z_o W_n = Z_o \frac{\left(\frac{N}{Z_o}\right)^n}{n!} e^{-N/Z_o} . \tag{25.11}$$

Let us denote by $r_n$ activity of one $n$ -atomic ensemble, then the total $A$ and specific *activity* of the catalyst will be equal, respectively:

$$A_n = r_n Z_n = r_n Z_o \frac{1}{n!}\left(\frac{N}{Z_o}\right)^n e^{-N/Z_o}\ ; \quad (25.12)$$

$$a_n = \frac{A}{N} = r_n \frac{1}{n!}\left(\frac{N}{Z_o}\right)^{n-1} e^{-N/Z_o}\ . \quad (25.13)$$

of these dependences give a maximum in $N$. Let's differentiate them by $N$ :

$$\frac{dA_n}{dn} = r_n \frac{1}{n!}\left(\frac{N}{Z_o}\right)^{n-1} e^{-N/Z_o}\left(n - \frac{n}{Z_o}\right) ;(25.14)$$

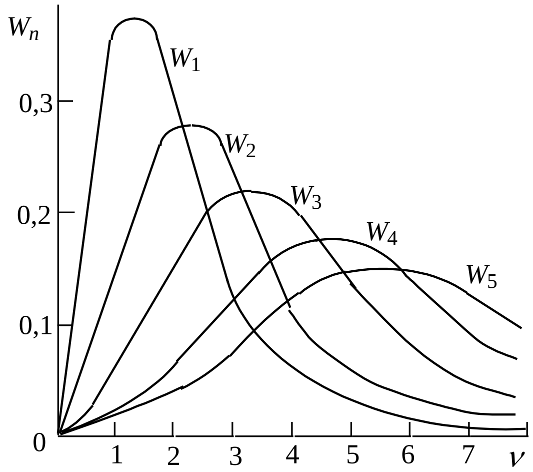


Fig.25. 5 . Probability of formation of *an n* -atomic ensemble depending on the average number of atoms in the free migration region

$$\frac{da_n}{dn} = r_n Z_o \frac{1}{n!}\frac{N^{n-2}}{Z_o^{n-1}} e^{-N/Z_o}\left(n - 1 - \frac{n}{Z_o}\right). \qquad (25.15)$$

So at the maximum point the derivatives are equal to zero, then from the equations it follows:

$$n = \frac{N^{A}_{\text{макс}}}{Z_o} \text{ and } n - 1 = \frac{N^{a}_{\text{макс}}}{Z_o}\ . \qquad (25.16)$$

Solving this system of two equations, we obtain conditions that allow us to determine from experimental data the number of atoms in the active ensemble and the number of migration regions on the surface of the carrier:

$$n = \frac{N^{A}_{\text{макс}}}{N^{A}_{\text{макс}} - N^{a}_{\text{макс}}}\ ; \qquad (25.17)$$

$$Z_o = N^{A}_{\text{макс}} - N^{a}_{\text{макс}}\ . \qquad (25.18)$$

If $n = 1$, then equation (25.9) takes the form:

$$a_1 = r_1 e^{-N/Z_o}\ , \qquad (25.19)$$

those. if the experimental specific activity curve does not have a maximum and decreases exponentially with increasing catalyst concentration, then the active center is a monatomic ensemble.

# 43-Lecture.
# Topic: Chain and photochemical reactions.

Stages of chain reactions. Bouguer-Lambert-Beer equations.

### Photochemical reactions . Basic laws of photochemistry

Photochemical reactions are usually understood as reactions the occurrence of which is caused by the action of light - radiation with frequencies of the visible spectrum or close to them.

At the beginning of the 19th century, it was established that *only those rays that are absorbed by reacting substances are chemically active* (Grotthuss-Dreper law , which is sometimes called the I law of photochemistry). This statement is obvious and always true. However, the converse statement that the rays that are absorbed are chemically active is generally incorrect, since the absorption of light does not necessarily lead to a chemical reaction.

Absorption of monochromatic light of wavelength $\lambda$is described *by the Lambert–Beer law* : the attenuation *dI of* light intensity passing through a layer of thickness *dx* is directly proportional to the thickness of the layer, the intensity of the incident light *I* and the number of absorbing particles *n* (or their concentration in the layer):

$$-dI = kI\,dx \tag{23.1}$$

where the proportionality coefficient *k* is the molecular absorption coefficient, which is a measure of the absorption capacity of a molecule for a given wavelength and, to a first approximation, does not depend on concentration. After integrating over *x* from 0 to *l* ( *l* is the total thickness of the absorbing layer) and *I* from $I_0$ (intensity of incident light) to *I* (intensity of emerging light), we obtain the expression for the Lambert–Beer law:

$$I = I_0 e^{-knl} . \tag{23.2}$$

If the concentration is expressed by the number of moles of a substance per liter of solution ( *c* ), then

$$I = I_0 e^{-\varepsilon nl} , \tag{23.3}$$

where $\varepsilon$is the molar absorption coefficient related to *k* by the relation $kn = \varepsilon c$ .
Bunsen and Roscoe (1855) established that the chemical effect of light is directly proportional to the product of the light intensity and the duration of its action. This dependence is approximate, as noted above, not all absorbed light energy is always completely spent on the chemical process.

A generalization of all the laws was made by Van't Hoff (1904), who formulated a quantitative law underlying the kinetics of photochemical reactions: *the amount of photochemically changed substance is proportional to the absorbed light energy* . The mathematical expression of this formulation can be obtained as follows. The amount of light energy $A$ absorbed per unit time by a photochemical system is equal, according to the Lambert–Beer law

$$A = I_0(1 - e^{-\varepsilon cl}), \qquad (23.4)$$

and the amount of photochemically changed substance $dc$ per unit time, i.e. reaction rate is proportional to $A$ :

$$-\frac{dc}{dt} = kAdt = kI_0(1 - e^{-\varepsilon cl})dt. \qquad (23.5)$$

If the concentration is very low or the absorbing layer is very thin ( $l = dx$ , the value of $cl$ is small), then after expanding the exponential into a series we obtain

$$-\frac{dc}{dt} = kI_0\varepsilon cdx = k_I c, \qquad (23.6)$$

those. a photochemical reaction proceeds in first order, its rate is proportional to the concentration of the reactant.

At high concentrations or a thick absorbing layer ( $cl$ is large, $e^{-\varepsilon cl}$ << 1), the entire light flux is absorbed and

$$-\frac{dc}{dt} = kI_0, \qquad (23.7)$$

those. the reaction rate is constant and does not depend on the concentration of the reactant (zero order).

The most important for explaining the kinetics of photochemical reactions is the Stark–Einstein *law of quantum equivalence* (1912), which states that *for each absorbed quantum of radiation h* $\nu$ *there corresponds one changed molecule* (the second law of photochemistry). A change here means both a chemical transformation and a change in the energy state of the molecule.

The number of light quanta absorbed per unit time is $n_{h\nu} = A / h\nu$, therefore, during this time $n_p = A / h\nu$ molecules must undergo a change. But, as experience shows, very often the number of photochemically reacted molecules is not equal to the number of absorbed quanta. In this regard, the concept of *quantum yield was introduced to characterize photochemical processes* $\gamma$. The quantum yield is the ratio of the number of chemically reacted molecules to the number of absorbed quanta:

$$\gamma = \frac{n_p}{n_{h\nu}} = \frac{n_p}{A/h\nu}. \qquad (23.8)$$

Then the rate of the chemical reaction

$$-\frac{dn}{dt} = \frac{dn_p}{dt} = \gamma\frac{dn_{h\nu}}{dt} = \gamma\frac{A}{h\nu}, \tag{23.9}$$

or taking into account equation (23.4)

$$-\frac{dc}{dt} = \gamma\frac{I_0}{h\nu}(1-e^{-\varepsilon cl}). \tag{23.10}$$

This equation combines all the laws of photochemistry and represents a general expression for the rate of a photochemical reaction.

## 44-Lecture.

## Topic: General concepts about catalysis.

### Homogeneous and heterogeneous catalysis. Types of heterogeneous catalysis. Catalysts and their properties.

The rate of a chemical reaction at a given temperature is determined by the rate of formation of the activated complex, which, in turn, depends on the value of the activation energy. In many chemical reactions, the structure of the activated complex may include substances that are not stoichiometrically reagents; It is obvious that in this case the activation energy of the process also changes. In the case of the presence of several transition states, the reaction will proceed mainly along the path with the lowest activation barrier.

***Catalysis is the phenomenon of changing the rate of a chemical reaction in the presence of substances whose state and quantity remain unchanged after the reaction.***

Distinguish between *positive* and *negative* catalysis (respectively, an increase and decrease in the reaction rate), although often the term "catalysis" means only positive catalysis; negative catalysis is called *inhibition* .

A substance that is part of the structure of the activated complex, but is not stoichiometrically a reagent, is called a catalyst. All catalysts are characterized by such common properties as specificity and selectivity of action.

***Specificity*** A catalyst lies in its ability to accelerate only one reaction or a group of similar reactions and not affect the rate of other reactions. For example, many transition metals (platinum, copper, nickel, iron, etc.) are catalysts for hydrogenation processes; aluminum oxide catalyzes hydration reactions, etc.

***Selectivity*** catalyst - the ability to accelerate one of the parallel reactions possible under given conditions. Thanks to this, it is possible, using different catalysts, to obtain different products from the same starting materials:

[Cu]: $CO + H_2 \longrightarrow CH_3OH$

[Ni]: $CO + H_2 \longrightarrow CH_4 + H_2O$

[$Al_2O_3$]: $C_2H_5OH \longrightarrow C_2H_4 + H_2O$

[Cu]: $C_2H_5OH \longrightarrow CH_3CHO + H_2$

The reason for the increase in the reaction rate with positive catalysis is the decrease in activation energy when the reaction proceeds through an activated complex with the participation of a catalyst (Fig. 2.8).

Since, according to the Arrhenius equation , the rate constant of a chemical reaction is exponentially dependent on the activation energy, a decrease in the latter causes a significant increase in the rate constant. Indeed, if we assume that the pre-exponential factors in the

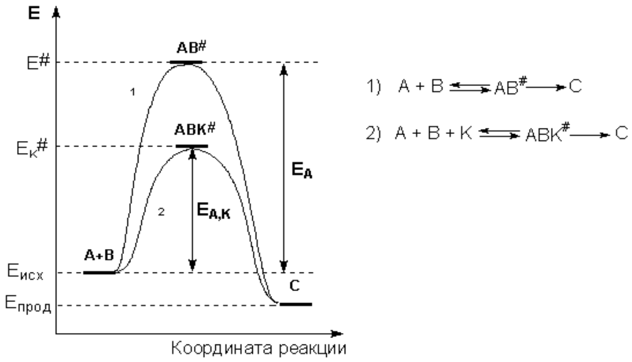
Arrhenius equation (II.32) for catalytic and non-catalytic reactions are close, then for the ratio of rate constants we can write:

$$\frac{k_К}{k} = \frac{A_К}{A}\exp\left(\frac{E_А - E_{А,К}}{RT}\right) \approx \exp\left(\frac{-\Delta E_А}{RT}\right) \qquad (II.44)$$

If $\Delta E_A = -50$ kJ/mol, then the ratio of the rate constants will be $2.7\ 10^{6}$ times (indeed, in practice such a decrease in $E_A$ increases the reaction rate by approximately $10^{5}$ times).

It should be noted that the presence of a catalyst does not affect the magnitude of the change in the thermodynamic potential as a result of the process and, therefore, ***no catalyst can make it possible for a thermodynamically impossible process to spontaneously proceed*** (a process whose $\Delta G$ ($\Delta F$) is greater than zero). The catalyst does not change the value of the equilibrium constant for reversible reactions; the effect of the catalyst in this case consists only in accelerating the achievement of an equilibrium state.

Depending on the phase state of the reactants and the catalyst, homogeneous and heterogeneous catalysis are distinguished.



**Rice. 2.8** Energy diagram of a chemical reaction without a catalyst (1) and in the presence of a catalyst (2).

### Homogeneous catalysis.

Homogeneous catalysis - catalytic reactions in which the reactants and catalyst are in the same phase. In the case of homogeneous catalytic processes, the catalyst forms intermediate reactive products with the reagents. Let's consider some reaction

$A + B \longrightarrow C$

In the presence of a catalyst, two fast steps are carried out, resulting in the formation of particles of the intermediate compound AA and then (via the activated complex $AVK^{\#}$) the final reaction product with catalyst regeneration:

$A + K \longrightarrow AK$

$AK + B \longrightarrow C + K$

An example of such a process is the decomposition of acetaldehyde, the activation energy of which is $E_A = 190$ kJ/mol:

$\mathbf{CH_3CHO \longrightarrow CH_4 + CO}$

In the presence of iodine vapor, this process occurs in two stages:

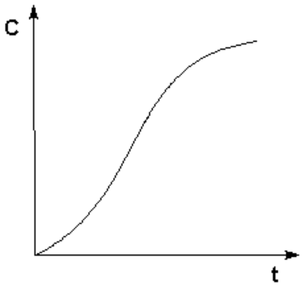
$\mathbf{CH_3CHO + I_2 \longrightarrow CH_3I + HI + CO}$

$\mathbf{CH_3I + HI \longrightarrow CH_4 + I_2}$

The decrease in the activation energy of this reaction in the presence of a catalyst is 54 kJ/mol; the reaction rate constant increases approximately 105 times. The most common type of homogeneous catalysis is acid catalysis, in which hydrogen ions $H^+$ act as a catalyst .

### Autocatalysis.

***Autocatalysis*** – the process of catalytic acceleration of a chemical reaction by one of its products. An example is the hydrolysis of esters catalyzed by hydrogen ions. The acid formed during hydrolysis dissociates to form protons, which accelerate the hydrolysis reaction. The peculiarity of an autocatalytic reaction is that this reaction proceeds with a constant increase in the concentration of the catalyst. Therefore, in the initial period of the reaction, its speed increases, and at subsequent stages, as a result of a decrease in the concentration of reagents, the speed begins to decrease; the kinetic curve of the product of an autocatalytic reaction has a characteristic S-shaped appearance (Fig. 2.9).



**Rice. 2.9** Kinetic curve of the product of an autocatalytic reaction

**heterogeneous catalysis.**

***Heterogeneous catalysis*** – catalytic reactions occurring at the interface between the phases formed by the catalyst and reactants. The mechanism of heterogeneous catalytic processes is much more complex than in the case of homogeneous catalysis. In each heterogeneous catalytic reaction, at least six stages can be distinguished:

1. Diffusion of starting substances to the catalyst surface.
2. Adsorption of starting materials on the surface with the formation of some intermediate compound:

A + B + К —> АВК

3. Activation of the adsorbed state (the energy required for this is the true activation energy of the process):

AVK —> AVK $^{\#}$

4. Decomposition of the activated complex with the formation of adsorbed reaction products:

АВК $^{\#}$ —> СДК

5. Desorption of reaction products from the catalyst surface.

CDК —> C + D + К

6. Diffusion of reaction products from the catalyst surface.

A specific feature of heterocatalytic processes is the ability of the catalyst to promote and poison.

***Promotion*** is an increase in the activity of a catalyst in the presence of substances that are not themselves catalysts for a given process (promoters). For example, for the nickel metal catalyzed reaction

**$CO + H_2 \longrightarrow CH_4 + H_2O$**

the introduction of a small cerium impurity into a nickel catalyst leads to a sharp increase in the activity of the catalyst.

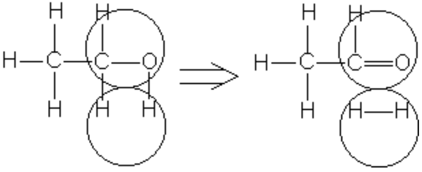
***Poisoning*** **is** a sharp decrease in the activity of the catalyst in the presence of certain substances (so-called catalytic poisons). For example, for the reaction of ammonia synthesis (the catalyst is sponge iron), the presence of oxygen or sulfur compounds in the reaction mixture causes a sharp decrease in the activity of the iron catalyst; at the same time, the ability of the catalyst to adsorb starting materials decreases very slightly.

To explain these features of heterogeneous catalytic processes, G. Taylor made the following assumption: not the entire surface of the catalyst is catalytically active, but only some of its areas - the so-called. ***active centers*** **,** which can be various defects in the crystal structure of the catalyst (for example, protrusions or depressions on the surface of the catalyst). Currently, there is no unified theory of heterogeneous catalysis. ***Multiplet theory*** was developed for metal catalysts . The main provisions of the multiplet theory are as follows:

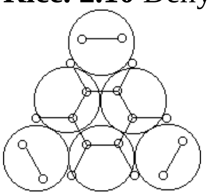
1. The active center of a catalyst is a set of a certain number of adsorption centers located on the surface of the catalyst in geometrical accordance with the structure of the molecule undergoing the transformation.
2. During the adsorption of reacting molecules on the active center, a multiplet complex is formed, resulting in a redistribution of bonds, leading to the formation of reaction products.

The theory of multiplets is sometimes called the theory of geometric similarity of the active center and reacting molecules. For different reactions, the number of adsorption centers (each of which is identified with a metal atom) in the active center is different - 2, 3, 4, etc. Such active centers are called doublet, triplet, quadruplet, etc., respectively. (in the general case, a multiplet, which is what the theory owes its name to).

For example, according to the theory of multiplets, the dehydrogenation of saturated monohydric alcohols occurs on a doublet, and the dehydrogenation of cyclohexane occurs on a sextet (Fig. 2.10 - 2.11); The theory of multiplets made it possible to relate the catalytic activity of metals to the value of their atomic radius.



**Rice. 2.10** Dehydrogenation of alcohols on a doublet



**Rice. 2.11** Dehydrogenation of cyclohexane on a sextet

*Weak connection Strong donor connection  Strong acceptor bond*

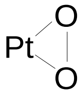
## 45-Lecture.

## Topic: Heterogeneous catalysis.

Physical and chemical adsorption. Theories of heterogeneous catalysis: adsorption and intermediate compounds, multiplet, active ensembles, electronic and chain theories.

### General characteristics of heterogeneous catalytic processes

In heterogeneous processes, the reacting components and the catalyst are in different phases and the reaction occurs in the boundary layer - at the phase interface. In practice, most often the catalyst is in the solid phase, and the reactants are in the liquid or gaseous phase. Therefore, for heterogeneous catalytic reactions, the transport of reactants from the bulk of the liquid or gaseous phase to the surface of the catalyst and their adsorption are of particular importance. The whole process can be divided into several stages: 1) transport of reactants to the catalyst surface (diffusion); 2) adsorption of the reactant on the surface of the catalyst; 3) reaction on the surface of the catalyst; 4) desorption of products with release of the catalyst surface; 5) removal of products into the gas or liquid phase. Depending on the conditions of the process and its features, any of these stages can be the slowest, and, consequently, the speed of the catalytic process can be limited by one of them. Therefore, in cases where the activity of a catalyst is determined, the process must be carried out in such a way that its rate is determined by the third stage.

To explain the catalytic action, the idea was put forward (Mendeleev, Sabatier, Zelinsky) about the formation of intermediate products. According to this idea, the catalyst forms an intermediate compound with one of the reactants, activating this reagent and facilitating the reaction. Typical intermediate compounds are sorption compounds such as  Ni–H, Pd–H, etc.

This implies one of the basic principles of heterogeneous catalysis: the catalyst has an affinity for one or more reagents. The affinity of the catalyst for the reacting substances ensures the formation of an intermediate compound, which in many cases is unstable and decomposes in further transformations into final products with regeneration of the catalyst.

As in the case of homogeneous catalysis, the catalyst in heterogeneous reactions has the property of selectivity. For the same substances, different catalysts accelerate one of the thermodynamically possible reactions under given conditions, which leads to the formation of different final products as the main substance (other substances may be present as impurities). For example, from a mixture of carbon monoxide with hydrogen (water gas), depending on the catalyst and experimental conditions, various products can be formed. If the reaction is carried out over metallic nickel at 510 – 530 K, then methane is obtained:

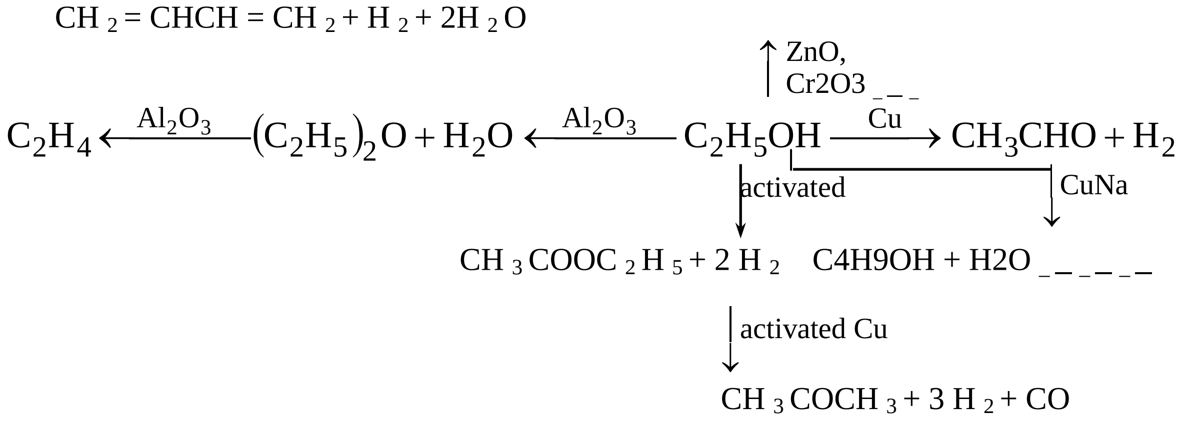
$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

Methyl alcohol is formed on copper under elevated pressure:

$$CO + 2H_2 \rightarrow CH_3OH$$

and on metal cobalt a mixture of higher olefins and paraffins is obtained.

Various products can be obtained from ethyl alcohol during its catalytic transformations, depending on the choice of catalyst and flow conditions (temperature, pressure):



The reasons for the selective action of catalysts in each case may be different. According to the theory of intermediate products, this action is associated with the formation of intermediate compounds of different chemical natures on different catalysts.

Often, to give the catalyst greater selectivity, increase its thermal stability and mechanical strength, and also increase activity, catalysts are used not in the form of pure substances, but in the form of complex multicomponent systems. *Mixed catalysts* are usually a mixture of two or more oxides, for example, $Al_2O_3 + ThO_2$; $Al_2O_3 + Cr_2O_3$; CoO + MgO. The activity of such catalysts is usually a function of composition and at a certain content of components maximum activity is achieved.

The activity of a catalyst can be increased by adding a substance to it that does not itself have catalytic properties. Such substances are called *promoters* , and the phenomenon itself is called *promotion* . There are two types of promoting action - *structure-forming promotion* and *modification* . Structure-forming promoters stabilize the active phase of the catalyst with respect to temperature or some other factors. Apparently, they increase the lifetime of the microcrystalline phase of the catalyst, which is unstable due to the thermodynamically spontaneous thermal enlargement of the catalyst crystals. An example would be the promotion of an iron catalyst for ammonia synthesis with aluminum oxide. The addition of small amounts of $Al_2O_3$ doubles the initial activity of the catalyst and maintains its stability over a long period of time. Modifying promoters change the structure and chemical composition of the active phase. Their action probably boils down to the synthesis of active centers of a new chemical nature on the surface of the catalyst, and sometimes a change in the selectivity of the catalyst is observed.

The presence of certain substances in the reaction system, often in extremely small quantities, can significantly reduce or completely suppress the activity of the catalyst. Such substances are called *catalytic poisons* , and the phenomenon itself is called catalyst *poisoning* . Typical catalytic poisons are sulfur compounds, hydrocyanic acid and some of its derivatives, carbon monoxide, free halogens, mercury and some of its salts, compounds of phosphorus, arsenic, lead, etc., and even water vapor. Catalyst poisoning mainly occurs as a result of adsorption of the poison on the surface and blocking of the active sites of the catalyst. Since adsorption can be reversible and irreversible, poisoning of the catalyst can be reversible and irreversible. In case of reversible poisoning, the activity of the catalyst is restored after removal of the poison, but in case of irreversible poisoning, it is not possible to restore the activity of the catalyst. The greatest toxic effect is exerted by the first portions of the poison, which sharply, by 70–80%, reduce the activity of the catalyst, after which the toxicity of the poison decreases. Poisoning isotherms usually satisfy an exponential relationship:

$$\frac{A_{\text{отр}}}{A_{\text{о}}} = e^{-\alpha c}, \tag{24.16}$$

where $A_{\text{neg}}$ is the activity of the poisoned catalyst; *Oh* _ – initial activity; *c* is the amount of poison adsorbed by the catalyst; $\alpha$– poisoning coefficient, depending on the nature of the poison, as well as the nature and properties of the catalyst and some process parameters. For small amounts of poison, the linear approximation is valid:

$$\frac{A_{\text{отр}}}{A_{\text{о}}} = 1 - \alpha c\,. \tag{24.17}$$

Research into poisoning processes played a significant role in the development of the theory of catalysis. The practical consequence was the development of requirements for the purity of starting materials and equipment for carrying out catalytic reactions.

## 18-Lecture.

## Topic: Exponential equation Boltzmann , representing the energy distribution of molecules.

### Expression of thermodynamic functions of states by sum.

Statistical thermodynamics establishes a connection between the macroscopic properties of a system and the properties of the particles that form the system, based on the laws of mechanics and probability theory. Statistical thermodynamics deals with the mechanics of large numbers of particles. Mechanical variables act as random variables with certain probabilities of occurrence. Thermodynamic quantities are considered either as average values of random variables (for example, the internal energy of a system in thermal contact with the environment) or as characteristics of a probability distribution (temperature, entropy, chemical potential). Statistical thermodynamics explains all the provisions of classical thermodynamics, and also makes it possible to develop methods for calculating thermodynamic functions and equilibrium constants based on experimentally obtained molecular characteristics.

All molecules that make up any system differ from each other in their position in space, i.e. coordinate values, as well as movement speeds and energies. If we assume that these quantities can change continuously, then any macrostate will correspond to an infinitely large number of microstates.

As already noted in section 3.8, to describe the position of a particle, the concept of phase space is used - an imaginary multidimensional space, the coordinates of which are the Cartesian coordinates of atoms and projections of momentum ( $p = mv$ ) onto three-dimensional coordinate axes. For a monatomic molecule, phase space has six coordinates - *three* position coordinates $x$ , $y$ , $z$ and three projections of momentum onto the coordinate *axes* $p_x$ , $p_y$ , $p_z$ . For *an* $n$ -atomic molecule, 6 $n$ quantities are required, and the phase space in this case will be 6 $n$ -dimensional.

Each molecule of the system is represented by a point in phase space, and the microstate of the system is characterized by a set of such points.

The phase space is divided into separate cells - areas so small that a change in coordinates within one area cannot change a given microstate. Counting the number of microstates, i.e.

thermodynamic probability of a state, in this case comes down to finding the number of possible ways of placing all molecules in different cells of phase space.

The specific calculation of thermodynamic probability depends on further assumptions about the regions and particles. According to classical Boltzmann statistics, the size of the regions is indefinite, the particles are distinguishable (they can be numbered), and their energy spectrum is continuous. Quantum statistics take into account that the possible states of a system can only be discrete, and the distribution methods are influenced by the spin number of particles. For identical particles with half-integer spin ( *fermions* ), the Pauli exclusion is satisfied: in a given quantum single-particle state there can be no more than one particle. For particles with zero or integer spin ( *bosons* ), there are no restrictions on how states can be filled. The differences between fermions and bosons lead to the fact that ensembles of these particles obey different statistics: Fermi–Dirac (for fermions) and Bose–Einstein (for bosons). However, far from absolute zero, *molecular systems* behave almost identically, regardless of whether they are composed of bosons or fermions, and their features do not appear in the distribution. In such cases, when calculating quantum states, it is formally permissible to describe the system as formed by numbered particles, to consider the methods of distributing particles among the cells of phase space as for classical particles according to Boltzmann statistics, but to introduce a correction for the indistinguishability of identical particles using the factor 1/ N *!* . Then the thermodynamic probability of the state of a system consisting of *N* particles is equal to

$$W = \frac{N!}{\prod_i N_i!}, \tag{14.1}$$

where P $N_i$ ! – the product of factorials of the number of particles located in each cell of the phase space.

According to the Stirling formula, valid for large *N* ,

$$\ln N! \approx N \ln N - N \tag{14.2}$$

or

$$N! \approx N^N e^{-N}. \tag{14.3}$$

Substituting this value into equation (14.1), we obtain:

$$W = \frac{N^N e^{-N}}{\prod N_i^{N_i} e^{-N_i}} = \frac{N^N e^{-N}}{\prod N_i^{N_i} \prod e^{-N_i}}. \tag{14.4}$$

Since $\Sigma N_i = N$ , then $\prod e^{-N_i} = e^{-N}$ and

$$W = \frac{N^N}{\prod N_i^{N_i}}. \tag{14.5}$$

If we substitute this expression into the Boltzmann formula (3.40), we obtain for entropy:

$$S = k \ln W = k ( N \ln N - \Sigma N_i \ln N_i ).$$

## Laboratory exercises

# Introduction

Laboratory (practical) classes are one of the most important parts of the educational and pedagogical process. Here students gain experimental work skills, the ability to handle instruments, independently draw conclusions from the experimental data obtained, and thereby more deeply and fully assimilate the theoretical material of the discipline being studied.

This publication draws attention to the dimensions of units that are given in the system of international units of measurement (SI).

Laboratory work is aimed at practical mastery by students of the scientific and theoretical principles of physical and colloidal chemistry, mastering the techniques of experimental research and analysis of the results obtained, instilling skills in working with laboratory equipment, instrumentation and computer technology.

When performing laboratory work, students must learn safe handling of chemical reagents, instruments and utensils, acquire skills in studying chemical processes and using reference and scientific literature.

The laboratory workshop provides safety rules when working in an inorganic chemistry laboratory, provides the conditions and analytical effects of qualitative reactions for the most important classes of compounds, and also lists the required minimum of laboratory equipment and chemical glassware.

For a more in-depth study of the course of physical and colloidal chemistry, the workshop includes tables, diagrams, drawings that deepen knowledge of the fundamentals of physical chemistry. Test questions and tests given after each topic help reinforce the learning material.

The theory and skills acquired during the study of physical and colloidal chemistry will allow students to better understand the processes occurring in nature and during the production of chemicals.

To complete each laboratory work you must:

1) familiarize yourself with the recommended textbook with the section of physical and colloid chemistry to which this work relates;
2) carefully read and understand the content of the theoretical introduction to the laboratory work being performed, which examines the basic laws of the physical and chemical processes being studied, the physical meaning of the dimension of quantities that are used in solving a practical problem, and also formulates the purpose of the work, which must be clearly represented in order to fully consciously perform experimental work; 3) familiarize yourself with the diagram and description of the device, the list of necessary glassware and reagents and the procedure for drawing up a report;

4) perform the experiment;
5) draw up a report on the work;
6) answer security questions.

## Compilation of a report

At the end of each laboratory work, a report is compiled. In the report, indicate the work number, its name and completion date. Then write down the basic equations and formulas using which the corresponding calculations were performed. Enter the obtained experimental data into a table, calculate the average values and make calculations indicating the dimensions of the obtained values.

If one of the obtained experimental values is much different from the others, it is discarded and not taken into account when calculating the average value.

Some jobs require drawing up a graph or making calculations based on graphs. Therefore, the correctness and accuracy of the answer largely depends on the correct construction of graphs and the choice of scales along the coordinate axes. For graphs, as a rule, you should choose the largest possible scales.

When constructing them, you should indicate the units of measurement along the coordinate axes. Usually, it is not the numerical values of experimental data that are plotted on the coordinate axes, but certain scale numbers of the obtained values of quantities. For example, in the experiment it was obtained: 0.02; 0.03; 0.05; in this case, scale values are plotted: 2, 3, 5, etc., and when integers with some fractional part are obtained in the experiment, only integers should be plotted on the corresponding coordinate axis.

In some experiments, the functional dependence of two quantities is linear, that is, described by a straight line, but the experimental data do not fit on a straight line, but have a scatter, which is explained by some experimental errors. In this case, the straight line is drawn so that all the obtained points (experimental data) lie evenly on both sides of the straight line. Using the constructed curves, you can find values that are between the experimental points (data obtained experimentally). For example, using a graph of the dependence of the solubility of substances on temperature, using the solubility curve, you can find solubility at any temperature, and not just at the measured one.

When plotting a graph, it is recommended to use graph paper.

# GENERAL RULES FOR PERFORMANCE AND LABORATORY WORK TECHNIQUE

Laboratory work is one of the most important components of a chemistry course. To complete them, the student needs to become familiar with laboratory equipment, measuring instruments, as well as the technique of conducting basic laboratory operations.

Since the chemical laboratory contains electrical appliances, gas, toxic and flammable substances, students must strictly adhere to internal regulations and safety regulations.

Before each laboratory lesson, the student must study the appropriate section of the textbook, lecture notes and description of the laboratory work. When performing laboratory work, the student makes notes in the laboratory journal, and upon completion of the work, draws up a written report on the work done.

## General rules for working in the laboratory

1. Work in the laboratory must be carried out in accordance with safety requirements.

2. It is prohibited to wear outerwear, talk loudly, eat food, or smoke in the laboratory. It is prohibited to turn on and off switches, gas taps, and appliances without the permission of the teacher.

3. You should prepare for the experiment in advance using the job description, textbook and lecture notes.

4. The workplace should not be cluttered with unnecessary items. The desktop can contain only what is required to complete the current job. You should work in a robe.

5. The experiment is always carried out in clean dishes.

6. Reagents intended for general use must be kept in places specially designated for them (in a fume hood or on special tables); they cannot be moved from there.

7. After removing the required amount of reagent from the jar or flask, the stoppers or pipettes from them are immediately returned to their place. If a special pipette is not included with the solution bottle, you must use a clean pipette. Solid reagents are removed with a spatula or porcelain spoon.

8. If the reagent is taken in excess and is not completely consumed, it should not be returned to the bottle or jar.

9. Upon completion of work, you should clean your workplace, close the taps and turn off the appliances.

10. During laboratory work, it is prohibited to conduct unrelated experiments without the permission of the teacher.

11. If an unusual situation arises in the laboratory, immediately notify the teacher and leave the room.

## Safety and Precautions

1. Conduct experiments involving the use or formation of toxic substances only in a fume hood, the doors of which should be lowered by a third.

2. If the operation of ventilation units is stopped, all experiments carried out in fume hoods must be stopped.

3. It is prohibited to conduct any experiments with explosive and flammable substances and mixtures.

4. When heating substances in a test tube, use a holder. Do not direct the opening of the test tube towards the workers.

5. Do not lean over a vessel that is heating or boiling liquid to avoid splashing your face.

6. If you need to determine the smell of the gas being released, then with a slight movement of your palm, direct a stream of gas from the neck of the vessel towards you and sniff carefully.

7. When diluting concentrated acids and alkalis, pour them in small portions into water (not vice versa!), continuously stirring the resulting solution.

8. If a bottle with a flammable liquid tips over or breaks, immediately turn off all sources of open flame in the vicinity, cover the spilled liquid with sand, collect it and transfer it to an iron box intended for waste.

9. If a concentrated acid solution gets on your skin, rinse the burn area with a stream of cold water for several minutes. After this, the burned area can either be washed with a 2-3% soda solution or washed with soap.

10. In case of a burn with concentrated alkali solutions, rinse the burned area with a stream of cold water until the skin no longer seems slippery, then rinse with a 1% solution of acetic acid and again with water.

11. In case of a thermal burn, cool the affected area by placing it under running cold water. After sufficient cooling, apply burn ointment.

12. In case of severe burns, after first aid, consult a doctor.

13. If a solution of any reagent gets into your eye, immediately rinse it with plenty of water (or tap water), and then immediately consult a doctor.

14. In case of poisoning with gaseous substances (hydrogen sulfide, chlorine, carbon monoxide , bromine vapor), go out (take the victim) into fresh air, and then consult a doctor.

15. If injured by glass, you must make sure that there is no glass in the wound, wipe the skin around the wound with cotton wool moistened with alcohol, lubricate it with iodine and bandage the wounded area.

# Molecular solutions.

## Questions for the colloquium.

General characteristics of solutions. Ideal solutions. Osmotic pressure. Diffusion and osmosis. Van't Hoff equation. The practical importance of osmosis. Plasmolis. Vapor pressure over solutions. Raoult's law. Ebullioscopy and cryoscopy.

Solutions of gases in liquids. The influence of pressure and temperature on the solubility of gases in liquids. Henry's Law.

Solutions liquid – liquid. Limited mutual solubility of liquids. Effect of temperature on solubility. Vapor pressure over ideal solutions.

## Theoretical part .

Dilute solutions of nonelectrolytes have a number of properties (colligative properties), the quantitative expression of which depends on the number of particles of the dissolved substance present in the solution.

The dependence of these properties on concentrations is expressed by the equations:

1. Decrease in vapor pressure of the solvent above the solution, Δp (Raoult's law):

$$\Delta p = p_0 \frac{n_2}{n_1 + n_2} \qquad (1)$$

where p $_0$ is the saturated vapor pressure over a pure solvent; n $_1$ – amount of solvent; n $_2$ – amount of dissolved substance.

2. Decrease in the crystallization temperature of the solution, $\Delta t_{\text{crystal}}$ :

$$\Delta t_{crist} = K\, m\,, (2)$$

where K is the cryoscopic constant of the solvent, m is the molal concentration of the solute.

3. Increase in the boiling point of the solution, $\Delta t_{\text{kip}}$ :

$$\Delta t_{kip} = E\, m\,, (3)$$

where E is the ebullioscopic constant of the solvent.

4. Osmotic pressure R.kPa:

$$P = C_M RT\,, (4)$$

where C $_M$ – molar concentration; R – gas constant (8.314 J/mol*K), T – temperature (K).

Table 4 – Constant values

| Substances | Constant values | |
|---|---|---|
| | Cryoscopic, K | Ebullioscopic, E |
| Water | 1.86 | 0.52 |
| Benzene | 5.1 | 2.57 |
| Ethanol | - | 1.16 |
| diethyl ether | 1.73 | 2.02 |

## Examples of problem solving

*Example 1* . Calculate at what temperature a solution containing 54 g of glucose $C_6H_{12}O_6$ in 250 g of water should crystallize .

Solution. When calculated per 1000 g of H2O , the glucose content in the solution is 216 g. Since the molar mass of glucose is 180 g/mol, the molality of the solution is m = 216/180 = 1.20 mol per 1000 g of H2O .

Using the formula $\Delta t_{crist} = K\ m$ we find: $\Delta t_{crist} = 1.86 * 1.20 = 2.23$ K. therefore, the solution will crystallize at – 2.23 $^0$ .

*Example 2.* At 25 $^0$C, the saturated vapor pressure of water is 3.166 kPa (23.75 mm Hg). find at the same temperature the saturated vapor pressure over a 5% solution of carbamide (urea) $CO(NH2)_2$ .

Let's use the formula $\Delta p = p_0 \frac{n_2}{n_1 + n_2}$. To do this, we calculate the number of moles of water ( $n_1$ ) and the number of moles of urea ( $n_2$ ) using the formula

n = m / M . $M(H_2O)$ = 18 g/mol, $M(CO(NH_2)_2)$ = 60.05 g/mol. A 5% solution contains water 95 g urea 5 g, then

$n_1 = 95 / 18 = 5.272$ mol; $n_2 = 5/60.05 = 0.083$ mol

$$\Delta p = 3{,}166 \frac{5{,}272}{5{,}272 + 0{,}083} = 3{,}119 \text{ кПа или } 23{,}31 \text{ мм рт.ст.}$$

## Tasks for independent solution

1 . What is the osmotic pressure of a 0.5 M glucose solution $C_6H_{12}O_6$ at 25 $^0$C?

2. Calculate the osmotic pressure of a solution containing 16 g of sucrose $C_{12}H_{22}O_{11}$ in 350 g of $H_2O$ at 293 K. Consider the density of the solution equal to unity.

3. At 25 $^0$ C, the osmotic pressure of a certain solution is 1.24 MPa. Calculate the osmotic pressure at 0 $^0$C.

4. A solution containing 2.30 g of substance in 100 ml has an osmotic pressure of 618.5 kPa at 298 K. Determine molecular weight.

5. What is the osmotic pressure of saturated vapor over a 10% solution of urea $CO(NH2)_2$ at 100 $^0$C ?

6. By how many degrees will the boiling point of water increase if 9 g of glucose $C_6H_{12}O_6$ are dissolved in 100 g of water ?

7. At what approximately temperature will a 50% sucrose solution $C_{12}H_{22}O_{11}$ boil ?

8. At what approximately temperature will a 40% solution of ethyl alcohol $C_2H_5OH$ boil?

9. How many grams of sucrose $C_{12}H_{22}O_{11}$ must be dissolved in 100 g of water in order to: a) lower the crystallization temperature by 1 degree? b) increase the boiling point by 1 degree?

10. When 5.0 g of a substance is dissolved in 200 g of water, a non-conducting solution is obtained that crystallizes at -1.45 $^{0}$C. Determine the molecular weight of the dissolved substance.

11. At 315 K, the saturated vapor pressure above water is 8.2 kPa (61.5 mmHg). How much will the vapor pressure decrease at the indicated temperature if 36 g of glucose $C_6H_{12}O_6$ are dissolved in 540 g of water ?

12. At 25 $^{0}$C, the osmotic pressure of a solution containing 2.80 g of a high-molecular compound in 200 ml of solution is 0.70 kPa. Find the molecular mass of the solute.

13. How many moles of non-electrolyte must 1 liter of solution contain so that its osmotic pressure at 25 $^{0}$C is equal to 2.47 kPa?

14. When 13.0 g of non-electrolyte was dissolved in 400 g of diethyl ether $(C_2H_5)_2O$, the boiling point increased by 0.453 K. Determine the molecular weight of the dissolved substance.

15. 100 g of $H_2O$ contains 4.75 g of sucrose $C_{12}H_{22}O_{11}$. Find: a) the crystallization temperature of the solution, b) the boiling point of the solution. The density of the solution is considered equal to unity.

16. What is the molarity of a nonelectrolyte solution if its osmotic pressure at 0 $^{0}$C is 2.27 kPa?

17. 200 g of water: 1 ) 31 g of urea $CO(NH2)_2$; 2) 90 g of glucose $C_6H_{12}O_6$. Will the boiling points of these solutions be the same? Justify your answer with calculations.

18. A certain aqueous solution of a nonelectrolyte boils at 373.52 K. What is the molal concentration of this solution?

19. Find at 65 $^{0}$C the vapor pressure above a solution containing 13.68 g of sucrose $C_{12}H_{22}O_{11}$ in 90 g of water, if the saturated vapor pressure above water at the same temperature is 25.0 kPa (187.5 mm Hg .)

20. The boiling point of an aqueous solution of sucrose $C_{12}H_{22}O_{11}$ is 101.4 $^{0}$C. Calculate the molal concentration and mass fraction of sucrose in the solution. At what temperature does this solution freeze?

## DETERMINATION OF THE MOLECULAR MASS OF A SOLVED SUBSTANCE USING THE CRYOSCOPIC METHOD

### Tasks for work

1. Set the Beckmann thermometer to the temperature range being used.

2. Determine the freezing point of a pure solvent and the temperature at which the non-electrolyte solution begins to crystallize.

3. Calculate the molal concentration of the solution and the molecular weight of the solute.

4. Calculate the relative error in determining the molecular weight and the maximum error of the method; compare the obtained values.

## Description of work

A diagram of the setup used for cryoscopic measurements is shown in Fig. 1. The experiment uses a Beckman differential thermometer, which must first be adjusted to the temperature range used. It should be taken into account that if you handle the Beckmann thermometer carelessly, a drop of mercury may fall into the upper reservoir of the thermometer, and it will have to be adjusted again. For accurate measurements, it is necessary that the cooling of the liquid under study occurs as slowly as possible. For this purpose, there is an air gap between the outer and inner tubes. When conducting an experiment, the liquid under study must be constantly stirred to ensure uniform cooling.

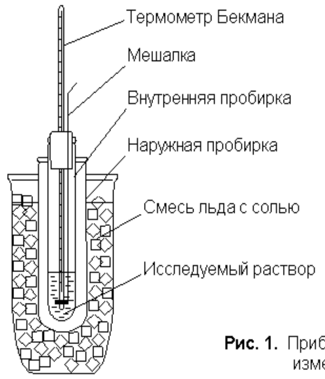


**Рис. 1.** Прибор для криометрических измерений.

## 1. Calibration of the Beckmann thermometer

To determine the decrease in the crystallization temperature of the solution, the Beckman thermometer must be calibrated. To do this, in the first experiment, distilled water is frozen.

50 ml of distilled water is poured into the inner test tube, thoroughly washed with distilled water and dried. The Beckmann thermometer is placed in a test tube so that the lower reservoir of the thermometer is completely immersed in water. The inner tube with a thermometer and a stirrer is placed in the outer one and the latter is immersed in the cooling mixture. Continuously stirring the water, observe the movement of the mercury column in the capillary of the thermometer. During the experiment, supercooling of the water usually

occurs (by about 1 °C). In this case, following a slow decrease in the level of mercury in the capillary, its rapid increase and stabilization is observed at a value that corresponds to the crystallization temperature of water. The resulting t $_o$ value on the scale of the Beckmann thermometer, corresponding to 0 °C, is recorded.

The inner tube is removed from the outer tube and carefully heated by hand to melt the formed ice crystals (if the experiment is carried out correctly, the crystals should form in the volume of liquid and not on the walls of the test tube). After all the crystals have melted and the water temperature has increased by 1-2 °C above to $_,$ the experiment is repeated. If the difference between the first and second obtained t $_{\text{o values}}$ exceeds 0.1 °C, the experiment is carried out again.

Based on the results of the experiments, the average value $\bar{t}_o$ on the scale of the Beckmann thermometer corresponding to 0 °C is calculated, which is subsequently used to calculate the decrease in the crystallization temperature of the solution.

## 2. Determination of the decrease in the crystallization temperature of the solution

A certain amount of a soluble substance - a non-electrolyte - is weighed out on an analytical balance (as directed by the teacher or laboratory assistant). Having removed the thermometer and stirrer from the inner test tube, the sample is completely transferred into the test tube and stirred with a stirrer until the substance is completely dissolved. Care should be taken to ensure that no crystals remain stuck to the walls of the test tube.

The inner tube is placed in the outer one and the solution is cooled in the same manner as described above, fixing the temperature at which the solution begins to crystallize $_{tcr}$ .

Since the concentration of the solution increases as solvent crystals precipitate, the highest temperature value reached after supercooling is taken as the temperature at which crystallization of the solution begins, $_{tcr}$ . The experiment is repeated three times and the average value is taken as the temperature at which the solution begins to crystallize $\bar{t}_{кр}$ .

Calculate the decrease in the crystallization temperature of the solution:

$$\Delta t_{кр} = \bar{t}_o - \bar{t}_{кр} \quad (1)$$

## 3. Calculation of the molecular weight of a dissolved non-electrolyte

Based on the obtained value of the decrease in the crystallization temperature of the solution, the molecular mass of the dissolved substance is calculated:

$$M = K\frac{1000 \cdot g_2}{g_1 \cdot \Delta t_{\text{кр}}} \quad (2)$$

Here K is the cryoscopic constant of water (K = 1.86);
$g_1$ – mass of solvent;
$g_2$ is the mass of the dissolved substance.

Using the obtained and true values of molecular weight, the relative error in determining the molecular weight is calculated and compared with the maximum error of the method.

## Laboratory work on the topic: “Galvanic cells”

Purpose of the work: to study the possibility of converting chemical energy into electrical energy during the operation of a galvanic cell. Investigate the influence of various factors on the magnitude of the EMF of elements.

### Theoretical introduction

To perform this work you need knowledge of the following issues:

1. Electrode potential of the metal. The mechanism of its occurrence.
2. Factors influencing the value of the electrode potential. Nernst equation.
3. A range of metal stresses. The reducing ability of metal atoms and the oxidizing ability of their ions.
4. The principle of operation of galvanic cells. Processes occurring on the electrodes. Determination of the EMF of an element.

When a metal is immersed in an electrolyte solution, an electrical double layer is formed at the interface. The positively charged layer is created by the cores of atoms located at the nodes of the crystal lattice and forming the interface. The negatively charged layer is formed by conduction electrons located in the interstices of the crystal lattice. At the phase interface (metal - electrolyte) a potential jump occurs, called ***the electrode potential of the metal*** . It is impossible to measure it directly, so it is measured relative to some electrode, which is called ***reference electrode*** . Most often, the reference electrode is a normal hydrogen electrode.

***The electrode potential of a metal immersed in a solution of its salt with a concentration of 1 mol/l, measured relative to a normal hydrogen electrode at a temperature of 25 $0^{C}$, is called the normal or standard electrode potential of the metal $E_0$.***

The electrode potentials of metals measured in this way are arranged in increasing order of their values in the so-called ***a series of metal voltages ,*** or a series of standard electrode potentials. A number of voltages and numerical values of electrode potentials are given in Table 1.

Table 1.

| Electrode | $E_0$, B | Electrode | $E_0$, B | Electrode | $E_0$, B |
|---|---|---|---|---|---|
| $Li^+/Li$ | – 3.02 | $Mn^{2+}/Mn$ | – 1.180 | $2H^+/_{H2}$ | 0.000 |
| $Rb^+/Rb$ | – 2.99 | $Zn^{2+}/Zn$ | – 0.763 | $Sb^{3+}/Sb$ | 0.20 |
| $K^+/K$ | – 2.925 | $Cr^{3+}/Cr$ | – 0.740 | $Bi^{3+}/Bi$ | 0.23 |
| $Ba^{2+}/Ba$ | – 2.900 | $Fe^{2+}/Fe$ | – 0.440 | $Cu^{2+}/Cu$ | 0.337 |
| $Sr^{2+}/Sr$ | – 2.890 | $Cd^{2+}/Cd$ | – 0.400 | $Cu^+/Cu$ | 0.52 |
| $Ca^{2+}/Ca$ | – 2.870 | $Co2^+/Co$ | – 0.403 | $Hg_2^{2+}/2Hg$ | 0.790 |
| $Na^+/Na$ | – 2.714 | $Ni^{2+}/Ni$ | – 0.250 | $Ag^+/Ag$ | 0.799 |
| $La^+/La$ | – 2.370 | $Sn^{2+}/Sn$ | – 0.166 | $Pd^{2+}/Pd$ | 0.830 |
| $Mg^{2+}/Mg$ | – 2.370 | $Pb^{2+}/Pb$ | – 0.126 | $Hg^{2+}/Hg$ | 0.854 |
| $Al^{3+}/Al$ | – 1.700 | $Fe^{3+}/Fe$ | – 0.036 | $Pt^{2+}/Pt$ | 1.20 |
|  |  |  |  | $Au^{3+}/Au$ | 1.500 |

$_{E0}$ ***values, the oxidizing ability of ions increases, and the reducing ability of atoms decreases.*** In other words, metals are good reducing agents, and their ions are oxidizing agents.

The magnitude of the electrode potential is the main characteristic of a metal, with the help of which its chemical properties can be assessed. So, the lower the value of the electrode potential of a metal, the easier the metal gives up electrons, the more chemically active it is, its reducing ability is greater, it is easier to oxidize and more difficult to reduce: M – n e – = M n+ ( $^{\text{oxidation}}$ process $^{)}$ . The greater the value of the electrode potential of the metal, the easier the metal ion is reduced (accepts electrons) to a free atom, the higher its oxidizing ability: $M^{n+} + n e^- = M$ (reduction process).

The magnitude of the electrode potential of a metal depends on the nature of the metal, the concentration of electrolyte ions, and temperature. Mathematically, this dependence is expressed by the Nernst equation:

$$\mathbf{E = E_0 + ( RT / nF ) \ln C}$$

Here E is the metal potential at a given ion concentration, V; $E_0$ – standard electrode potential of the metal, V; R – universal gas constant (8.316 J/degree mol); T – absolute temperature, K; n is the charge of the metal ion; F – Faraday number (96500 C/mol); C – concentration (or activity) of metal ions in solution, M.

Taking the temperature equal to 25 $^0$C and substituting all the constants into the Nernst equation, including the coefficient for converting the natural logarithm into the decimal one (equal to 2.3), we obtain:

$$\mathbf{E = E_0 + (0.059/ n ) \log C \ (*)}$$

Example 1. Determine the electrode potential of a copper electrode immersed in a centimolar solution of copper sulfate.

According to the table 1, we find the standard electrode potential of copper: $E_0(Cu^{2+} / Cu) = 0.34$ V. The concentration of copper ions in a centimolar solution is C = 0.01 M = $10^{-2}$ M. Substituting these data into the Nernst equation, we obtain: $E = 0.34+(0.059/2) \log 10^{-2} =0.34+(0.059/2)(-2)=0.28$ V. The metal in this case is charged positively, therefore, the solution in the layer adjacent to the metal is charged negative.

Example 2. Determine the value of the electrode potential of a zinc electrode immersed in a decimolar solution of zinc sulfate.

According to the table 1, we find the standard electrode potential of zinc: $E_0(Zn^{2+} / Zn) = -0.76$ V. The concentration of zinc ions in a decimolar solution is C = 0.1 M = $10^{-1}$ M. Substituting these data into the Nernst equation, we obtain: $E = -0.76 + (0.059/2) \log 10^{-1} = -0.76-0.028 = -0.788$ V. In this case, the metal is negatively charged, therefore, the electrolyte in the near-electrode layer is charged positively.

Thus, depending on the activity of the metal, the nature of the double electrical layer that occurs when metals are immersed in a solution of their salts changes.

***A galvanic cell is a device that converts chemical energy into electrical energy*** . Structurally, a galvanic cell consists of two different metals (electrodes) immersed in an electrolyte solution and connected to each other by a conductor. The electrolyte can be a solution of acid, alkali or salt. The occurrence of electric current in this element is due to the potential difference between the metals used and the redox reactions occurring at the electrodes.

***Let us pay attention to the name of the electrodes in the galvanic cell*** . The metal having the lower electrode potential will be the electrode supplying electrons to the resulting circuit. It is the negative pole and is called ***anode*** **_** At the anode there is always a process of oxidation - the release of electrons: $M - n e^- = M^{n+}$.

The metal having a higher electrode potential will be the positive pole and is called ***cathode*** _ At the cathode, the process of reduction of the positively charged ion (cation) of the electrolyte always occurs; for example: $M^{n+} + n e^- = M$.

Let us consider the occurrence of electric current in a copper-zinc galvanic cell. First of all, you need to decide which metal (copper or zinc) will be the cathode and which will be the anode. According to the table 1 we find the standard electrode potentials of these metals: $E_0(Zn^{2+}/Zn) = -0.76$ V, $E_0(Cu^{2+}/Cu) = 0.34$ V. Since $E_0(Zn^{2+}/Zn) < E_0(Cu^{2+}/Cu)$, which means that zinc will function as an anode (–), and copper will function as a cathode (+). Therefore, an oxidation process will occur on the zinc electrode: $Zn - 2e^- = Zn^{2+}$, and reduction on the copper electrode: $Cu^{2+} + 2e^- = Cu$. In this case, electrons are received not by the metal, but by the cations of the electrolyte in which the cathode is immersed; metals serve as conductors of electrons.

Ionic form of the ongoing process: $Zn + Cu^{2+} = Zn^{2+} + Cu$.

Molecular form of the ongoing process (provided that the electrolyte consists of solutions of sulfates of these metals):

$Zn + CuSO_4 = ZnSO_4 + Cu$.

Typically, a galvanic cell is depicted with a brief electrochemical diagram, where one line indicates the boundary between the electrode and the solution (sometimes indicating their concentration), two lines indicate the boundary between solutions, and the signs of the electrodes (poles) are shown in brackets: $(-)\ Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu\ (+)$.

***Electromotive force (EMF)*** calculated as the difference between the electrode potentials of the cathode and anode. The EMF of a “working” galvanic cell must be positive; otherwise, the electrode processes go in the opposite direction (the polarity of the electrodes is reversed).

Example 3. Calculate the EMF of an element formed by a nickel electrode immersed in a 0.01 M solution of nickel sulfate and a copper electrode immersed in a 0.1 M solution of copper sulfate. What processes take place at the electrodes?

First of all, you should write down the circuit of the galvanic cell: since

$E^0 ( Ni / Ni^{2+} ) = =–0.25 V < E^o ( Cu / Cu^{2+} ) = 0.34 V$ , then the anode will be nickel, the cathode will be copper:

A (–) Ni | $NiSO_4$ || CuSO4 | Cu(+)K

Process at the anode: Ni –2 e = $Ni^{2+}$ (oxidation); process at the cathode: $Cu^{2+}$ +2 e = Cu (reduction). EMF = E ( Cu / Cu2 $^+$ ) – E ( Ni / Ni2 $^+$ ). Since the given solution concentrations are different from 1 M, it is necessary to calculate the electrode potentials of nickel and zinc using the Nernst equation

$E (Ni/Ni^{2+}) = E^0(Ni/Ni^{2+}) + (0.059/2)\log 0.01 = – 0.25 – 0.059 = – 0.309$ B.

$E (Cu/Cu^{2+}) = E^o(Cu/Cu^{2+}) + (0.059/2)\log 0.1 = 0.34 – 0.029 = 0.311$ B.

From here EMF = 0.311 – (–0.309) = 0.620 V.

***One type of galvanic cell is a concentration galvanic cell. The principle of its operation is based on the difference in concentrations of electrolyte solutions with identical electrodes*** . Let's consider the operation diagram of such an element.

Example 4. Determine the emf of the processes occurring on the electrodes of a galvanic cell consisting of silver plates immersed in solutions of silver nitrate with a concentration of 1 M and 0.01 M.

Using the Nernst equation and Table 1, we calculate the electrode potentials of the electrodes and determine the polarity.

$E_1 = E^o (Ag/Ag^+) +0.059 \log 1=0.80$ V; $E_2 = E^o (Ag/Ag^+) +0.059 \log 0.01=0.80–0.118=0.682$B.

Thus, the element diagram is:

(–) Ag | AgNO3 $_($0.01)|| AgNO3 $_($1)| Ag (+).

EMF of the element: EMF = 0.8 – 0.682 = 0.118 V. That is, here the anode will be an electrode immersed in a solution with a lower electrolyte concentration, the cathode will be an electrode immersed in a solution with a higher concentration.

In a real galvanic cell, the measured EMF is always slightly less than the theoretically calculated one:

$$\mathbf{E = E_o – IR – E_{polar} – \Sigma E_{contact}}$$

Here E is the real potential difference, $E_o$ is the EMF of the element, calculated theoretically, I is the current strength, R is the system resistance, $E_{polar}$ is the polarization potential difference that prevents the passage of current, $\Sigma E_{cont}$ is the sum of the contact potentials.

Polarization processes are the result of a change in the electrode potentials of the cathode and anode under the action of a passing current (for more details, see the textbook). For many reasons, the anode and cathode processes are inhibited, as a result of which metal ions accumulate at the anode, it becomes large, an excess of electrons accumulates at the cathode, and it becomes more negative:

$E_A = E_o + \eta$(anodic polarization); $E_K = E_o – \eta$(cathode polarization).

Here **η, is** ***the overvoltage*** (potential change compared to the standard value under equilibrium conditions).

## Practical part

### Experience 1. The state of galvanic cells and the study of the influence of the electrode material on the EMF of a galvanic cell

Fill specially prepared vessels to the top with a 1 M solution of zinc sulfate and a 1 M solution of copper sulfate. Place a zinc electrode in a solution of zinc sulfate, and a copper electrode in a solution of copper sulfate. Connect with a conductor, measure the EMF of this element, draw up its diagram, write down the processes occurring on the electrodes. Calculate the EMF and compare with the measured value.

Replace sequentially first the copper and then the zinc electrodes with steel and aluminum electrodes (possible in any combination). Measure the EMF of the resulting elements. Compare the theoretical and practical values of EMF and draw conclusions. Enter the results of the experiment in Table 2.

table 2

| Electrode | Electro- | $E^o$, V | Electrode | EMF | Element |
|---|---|---|---|---|---|

| material, its polarity | lit | | process | Theoretical | Practical | diagram |
|---|---|---|---|---|---|---|
| Cu<br>Zn | | | | | | |
| Cu<br>Fe | | | | | | |
| Zn<br>Fe | | | | | | |

## Experiment 2. Measuring the EMF of a redox galvanic cell.

Pour a 1 N solution of potassium permanganate into one vessel, add 10 drops of 3 N sulfuric acid, 2-3 drops of 1 N solution of manganese sulfate ( II ). Pour a 1 N solution of manganese ( II ) sulfate and 2-3 drops of potassium sulfate into another vessel. Place graphite electrodes in both vessels so that they are 2/3 immersed in the liquid. Connect the vessels with an electrolytic key containing saturated potassium chloride. Connect the electrodes to the terminals of the millivoltmeter and measure the EMF.

Draw up a diagram of the redox reaction underlying the operation of this element. What half-elements does this galvanic cell consist of? Write electron-ion equations.

### Experiment 3. Study of the dependence of the emf of a galvanic cell on the electrolyte concentration.

Construct a galvanic cell consisting of copper and zinc electrodes immersed in one-molar solutions of their salts (copper and zinc sulfates, respectively). Measure the EMF of this element. Dilute salt solutions 100 times. To do this, use a graduated pipette to take 1 ml of 1 M salt, transfer it to a clean vessel and add 100 ml of water. The result is a 0.01 M solution. Measure the EMF of an element composed of a 0.01 M solution of zinc sulfate and a 1 M solution of copper sulfate; from 0.01 M solution of copper sulfate and 1 M solution of zinc sulfate; from 0.01 M salt solutions. Enter the measurement results in Table 3.

Table 3

| Electrodes | Electrolyte | Concentration, M | EMF of the element | |
|---|---|---|---|---|
| | | | calculated | measured |
| Zn<br>Cu | $ZnSO_4$<br>$CuSO_4$ | 1<br>1 | | |
| Zn<br>Cu | $ZnSO_4$<br>$CuSO_4$ | 0.01<br>1 | | |
| Zn<br>Cu | $ZnSO_4$<br>$CuSO_4$ | 1<br>0.01 | | |
| Zn<br>Cu | $ZnSO_4$<br>$CuSO_4$ | 0.01<br>0.01 | | |

Draw a conclusion: at what concentration ratio is the greatest EMF value obtained? Compare measured and calculated EMF.

### Test questions and assignments

1. How is the electrode potential of a metal determined?

2. A range of metal stresses. Changes in the oxidative and reduction abilities of atoms depending on the value of the electrode potential.

3. Given ions: copper, silver, aluminum, iron. Which ion has the greatest oxidizing power? Arrange the ions in order of increasing reducing power.

4. Determine in which pair of elements: Cr – Zn or Al – Fe we should expect a higher emf and why? Indicate the signs of the electrodes.

5. Draw a diagram of two galvanic cells, in one of which copper would be the anode, and in the other - the cathode. Write electrode processes.

6. Calculate the EMF and indicate in which direction the process will go in a galvanic lead-zinc cell at the concentrations of zinc and lead ions, respectively: 0.0001 M and 1 M; 1 M and 0.0001 M. Write electrode processes.

## 10- laboratory work
## Calculation of thermodynamic parameters of liquids.

**Purpose of the work:** determination of the surface tension of a liquid at various temperatures using the Rebinder method; calculate the change in entropy and enthalpy per unit area.

**Tasks:**
- build a graph σ= f ( T );
- Determine T $_{\text{critical}}$ critical temperature;
- Calculate bribes in practice and theoretically;
- Calculate the entropy and enthalpy changes using the Gibbs molar energy of the surface, the generalized equations of the 1st and 2nd laws of thermodynamics, and the relation σ=f(T).
-

**Computational equations:** $\sigma_x = \sigma_{\text{эт}} \cdot \dfrac{\Delta h_x}{\Delta h_{\text{эт}}}$ (1); $K = \dfrac{\sigma_{\text{эт}}}{\Delta h_{\text{эт}}}$ (2) ; $\sigma_x = K\Delta h_x$ (3);

$$P_{\text{таж.}} = c^{\frac{1}{4}} \cdot M = \frac{\sigma^{\frac{1}{4}} \cdot M}{\rho_x} \quad (4); \qquad P_{\text{наз.}} = \Sigma mP_{\text{атом}} + \Sigma mP_{\text{бог}} + \Sigma mP_{\text{халка}} \quad (5);$$

$$\left[\frac{\partial(\Delta G)}{\partial \mathrm{T}}\right]_p = -\Delta S \quad \text{or} - \left(\frac{\partial \sigma}{\partial \mathrm{T}}\right)_p = \Delta S \ (6); \ \Delta N = \Delta G + T\,\Delta S = \sigma - T\left(\frac{\partial \sigma}{\partial \mathrm{T}}\right)_p \ (7).$$

**Execution of work:** Surface tension is determined by dynamic and static methods. In dynamic methods, it is determined at the moment of formation of the boundary between surfaces; in static methods, the equilibrium at the boundary between surfaces is determined. Because dynamic methods are more complex, they are used only to solve specific problems. The most commonly used static methods are: drop counting and weighing; capillary rise; break the ring; fall of silence; methods for creating maximum pressure in the bubble. Determining the maximum pressure in a gas bubble, that is, the Rebinder method, can give more accurate results, which is why this method is used in our practice.

A glass tube with a capillary tip is lowered into the vessel under study and connected to the surface of the liquid. Initially, the liquid level is slightly above the tip of the capillary, and after the thermostat sets the desired temperature, excess liquid is removed with a pipette if necessary. Air is then sucked out of the container or, conversely, the surface of the liquid is compressed by a compressor. In the first case, the maximum difference Δh is determined, which is formed in the pressure gauge when an air bubble passes through the outer layer. In the second case, pressure is created directly through the capillary tube inside the bubble, and the maximum difference between the levels $h_1$ and $h_2$ observed on the pressure gauge is determined when the air inside the bubble passes through the surface layer.

As with other methods, in the Rehbinder method the constant of the surface tension measuring device is calculated as $K = \sigma_{fl} / \Delta h_{fl}$ for a reference liquid with a known surface tension. To do this, the maximum pressure gauge difference required to pass a bubble through the surface layer of the reference liquid is determined experimentally. The maximum difference in the pressure gauge readings is measured 15-20 times at different temperatures etet for the reference liquid and $\Delta h_{standard}$ for the test liquid, and the arithmetic average values are obtained.

The Baczynski equation, which is considered valid for the case far from critical temperatures, is used in the experimental determination of parachor:

$$\sigma = c\rho_x^4,$$ where ***c* is the proportionality coefficient** .

Density at a given temperature is determined pycnometrically: $\rho_x = \frac{g_2 - g_0}{g_1 - g_0} \cdot \rho_{H_2O}$

From the values $\sigma_x$ and $\rho_x$ found in the experiment, the parachor $P_{theorite}$ is calculated using equation (4). The theoretical parahor $P_{theor}$ value is calculated using equation (5), using its additive (determining) property.

The results obtained are entered into the table:σ = f(T) is found on the graph of $T_{crit}$ ¬ and thermodynamic parameters from equations (4) and (5).

*13- table*

***Results of determination of surface tension, parachor and thermodynamic parameters.***

| T, K | Pressure gauge readings | | | | | | | | $T_{crit}$, T,K | R experience | R theory | ΔG, J /mol | ΔS, J /mol deg | ΔH, J /mol |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Reference liquid | | | | Test liquid | | | | | | | | | |
| | $h_1$ | $h_2$ | $\Delta h_{floor}$ | $\sigma_{this}$, Dina/cm | $h_1$ | $h_2$ | $\Delta h_x$ | $\sigma_x$, Dina/cm | | | | | | |
| 293.2 | | | | | | | | | | | | | | |
| 303.2 | | | | | | | | | | | | | | |
| 313.2 | | | | | | | | | | | | | | |
| 323.2 | | | | | | | | | | | | | | |

When calculating thermodynamic quantities, the unit of measurement must be taken into account. In reference books, the unit of measure is given in dyne / cm, which is $10^{-7}$ J / $cm^2$ or $10^{-3}$ J / $m^2$ . At the end of the experiment, measurement errors are evaluated.

## Practical exercises No. 1.

### Basic concepts of physical chemistry

Chemical thermodynamics is a science that studies the conditions for the stability of systems and laws.

Thermodynamics is the science of macrosystems. It allows a priori to determine the fundamental impossibility of a particular process. Physical and chemical phenomena in thermodynamics are studied using the basic laws of thermodynamics. The state of the objects under consideration in thermodynamics is determined by directly measured quantities characterizing the substances; the mechanism of the process and the structure of the substance itself are not considered.

Chemical thermodynamics studies the application of the laws of thermodynamics to chemical and physicochemical phenomena.

It mainly covers:

1) heat balances of processes, including thermal effects of physical and chemical processes;

2) phase equilibria for individual substances and mixtures;

3) chemical equilibrium.

Heat balances are based on the first law of thermodynamics. Based on the second and third laws, an analysis of phase and chemical equilibria is carried out.

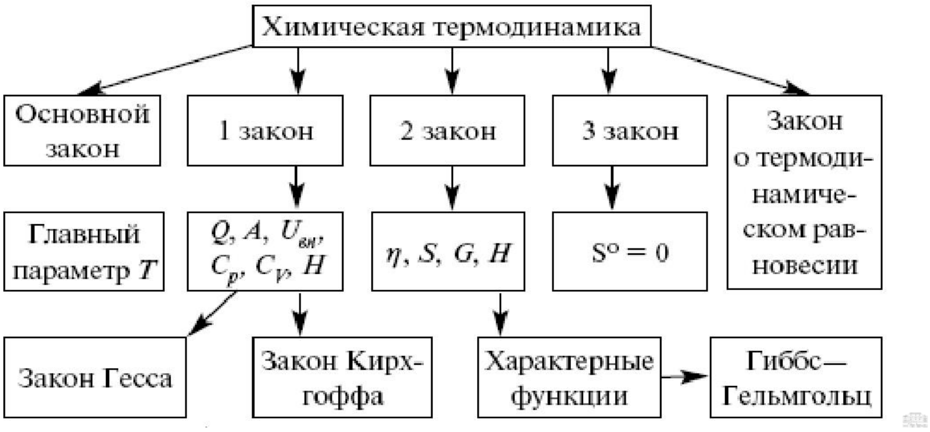
The study of the laws that describe chemical and physical equilibrium is of great importance in chemical thermodynamics. Their value allows solving problems for production and research work. Consider the main tasks:

1) determination of the conditions under which this process becomes possible;

2) finding the limits of stability of the studied substances under certain conditions;

3) elimination of adverse reactions;

4) selection of the optimal process mode (pressure, concentration of reagents, etc.).



*Basic concepts and definitions*

### 1. Systems and their classification

A system is a body or several bodies interacting with each other (diffusion, heat transfer, chemical reaction) and separated from the environment.

The state of a system in thermodynamics is determined using a set of variables called state parameters that characterize the thermodynamic state at equilibrium. Any change that occurs in a system and is associated with a change in at least one of the state parameters is called a thermodynamic process.

Systems have certain boundaries separating them from the external environment, and can be homogeneous or heterogeneous.

A homogeneous system is a system in which all macroscopic properties in any of its parts have the same value or continuously change from point to point. Examples: unsaturated solutions, steam, gas mixtures. The constituent parts of a homogeneous system cannot be separated from it using simple mechanical techniques (filtration, selection, etc.).

A heterogeneous system is a system whose constituent parts are separated from each other by visible interfaces on which sharp abrupt changes in any property occur. Examples: a saturated solution of a salt in equilibrium with crystals of this salt, two immiscible liquids, etc.). The components of such systems can be separated from each other using mechanical operations.

A set of bodies that energetically interact with each other and with other bodies, exchanging matter with them, is called a thermodynamic system.

Systems are divided into isolated (those systems that do not exchange energy and matter with other systems), open (those systems that exchange both matter and energy with the environment), closed (systems in which there is only an exchange of energy).

2. Thermodynamic parameters. Thermodynamic indicators. Voltage balance

Any TDS is characterized by the following parameters: temperature, pressure, density, concentration, molar volume. In any TDS, processes necessarily occur, and they can be equilibrium, nonequilibrium, reversible and irreversible. If in a tight dynamic system a certain property of the system does not change over time, i.e. it will be the same at all points of the volume, then such processes are equilibrium. In nonequilibrium processes, the property of the system will change over time without the influence of the environment.

Reversible processes are processes in which the system returns to its original state.

Irreversible - when the system does not return to its original state. Functions may depend on the process path. Functions that depend on the initial and final states of the system and do not depend on the process path are state functions; internal energy, enthalpy, entropy and others are complete differentials. Functions that depend on the initial and final states of the system and depend on the process path are not state functions and are not total differentials Q , A. Functions can be divided into two groups: extensive and intensive.

the system and is additivity (can be added): V , H , U ext, S , G , F.

the mass of the system and does not have the property of additivity: Q , A , T , P.

Pressure is a state parameter determined by the force acting in a body per unit surface area normal to it. It characterizes the interaction of the system with the external environment.

Temperature determines the measure of the intensity of thermal movement of molecules. The value of the temperature degree and the beginning of its counting are arbitrary. It would be possible to choose not water as a standard, but any other substance (as long as its properties clearly change with temperature, are reproducible and easy to measure). Such arbitrariness disappears if we use the thermodynamic (absolute) temperature scale, based on the second law of thermodynamics. The starting point of this universal scale is the value of the extremely low temperature - absolute zero, equal to 273.15 o C.

Equation of state. The equation relating the thermodynamic parameters of a system in an equilibrium state is the equation of state.

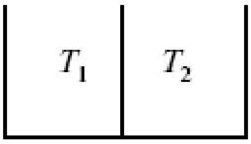
Due to the relationship between the properties of the system, to determine its state, it is enough to indicate only a certain number of properties. Thus, the state of a gas can be considered given if two parameters are specified, for example, temperature and volume, and the value of the third parameter - pressure - can be determined from the equation of state

P = f ( V , T ), ? ( P , V , T ) = 0.

Graphically, this equation is the equation of a surface constructed on three mutually perpendicular axes, each of which corresponds to one thermodynamic parameter. Thus, the thermodynamic surface is the geometric locus of points depicting the equilibrium states of the system as functions of thermodynamic parameters.

Heat concept

Let us be given an isolated vessel, which is separated by a semi-permeable partition (Fig. 1). In the first part of the vessel the temperature is T1 , in the second - the temperature $T_2$ ; $T_1 > T_2$ .



$$\frac{mv_1^2}{2} > \frac{mv_2^2}{2}$$

Rice. 1

Molecules, hitting a semi-permeable partition, will give off part of the energy, and others will receive it, without mechanical movement.

The form of energy transfer from one part of the system to another is called heat Q.

The measure of energy transferred from one system to another is the amount of heat. Q is not a state function and is not a total differential? Q. _

Work concept

The work of a process is the energy transferred from one body to another during their interaction, which does not depend on the temperature of these bodies and is not associated with the transfer of matter from one body to another.

The exchange of energy between the system and the external environment is determined by the work performed by this system:

$A = PdV$ .

Work (A) is determined by the sum of the products of forces acting on a system of forces (pressure and volume changes).

The work is not a total differential, ?A.

If equilibrium processes occur, then the work of the equilibrium process will be the maximum value compared to the nonequilibrium process

? $A_{\text{is equal}}$ > ? $A_{\text{unequal}}$ _

If a certain amount of heat is imparted to a body, this means that the body needs to be heated, and to cool the system - to produce the opposite effect of heating, i.e., to remove energy.

Work and heat are quantitative characteristics of two forms of energy exchange between the system and the environment.

### The concept of internal energy

Internal energy of the system $U_{\text{in}}$ consists of the energy of translational and rotational motion of molecules, the energy of intramolecular vibrational motion of atoms and atomic groups, the energy contained in the nuclei of atoms, and the energy of intermolecular interaction.

$U_{\text{int}}$ is a complete differential, it does not depend on the path of the process, but depends on the initial and final states of the system, it is uniquely continuous and finite. The absolute value of U cannot be determined; only its changes can be determined.

Q and A qualitatively and quantitatively characterize the form of energy transfer; the relationship between Q , A , U establishes the first law of thermodynamics.

### Thermodynamic indicators

Thermodynamic indicators include those that can be calculated using the laws of thermodynamics, based on the conditions that the system is in equilibrium. Decomposition voltage:

$$U_p = \frac{\Delta G}{nF} = E_A - E_K ,$$

where ΔG is the change in thermodynamic potential; n – number of electrons participating in a chemical reaction; F – Faraday number.

$$U_p = \frac{A}{nF},$$

where A is the maximum work that the system is capable of performing in an equilibrium state.

$$U_p = \frac{Q}{nF} \pm T\frac{dG}{dt},$$

where Q is the thermal effect of reactions;

$U_p$ is a thermodynamic characteristic of an electrochemical system, which depends little on the electrolysis conditions.

System deviation is polarization. An electrochemical reaction is a heterogeneous process, and its rate can be limited by one of the stages:

1) supply of the reactant to the phase boundary;

2) discharge and ionization;

3) removal of reaction products.

The polarization determined by the slow stage of mass transfer is concentration. If the slow stage is the ionization discharge stage, then the polarization is called overvoltage. The nature and significance of polarization depend on many factors: the nature of the reactant, the electrode material, the state of the electrode surface, the current density, the composition of the solution and the electrolysis mode. Kinetic parameter is a parameter determined under real conditions of an electrochemical system: ? current, $E_{ACTIVE}$ , diffusion coefficient, transfer coefficient? (to the cathode), ? (per anode) – share of consumption for the process:

1) current strength in the electrochemical apparatus $J = {}_{iK} S_{units}$ loading, A , Z , $_{iK}$ – depending on the electrolyte;

2) the rate of electrolysis - the formation of a mass of substance per unit time

$$V = \frac{\Delta m}{\Delta t} = \frac{Jtq}{t} = Jq,$$

where q is the electrochemical equivalent, v electrolysis is J current, if in 1 cm $^2$ – v – i current.

Energy balance - establishes the relationship between the type of energy entering the electrolyzer and the energy leaving it, demonstrating the equality of income and expense items. Electric energy const current supplied to the electrolyzer is:

**$W_{EL} = UJt$ .**

The general energy balance equation has the following form:

**$W_e + \Delta Q_{arrival} = W_{el.chemical\ r\text{-}ii} + W_{current} + Q_{flow},$**

where $\Delta Q_{arrival}$ – thermal energy entering the electrolyzer with electrolyte and electrodes due to secondary processes;

$W_{el.chemical\ r\text{-}ii}$ – – current energy expended on the electrochemical reaction;

$W_{current}$ – current energy converted into thermal energy;

Q consumption – thermal energy carried away by the electrolyte, electrodes, gases during the evaporation of $H_2O$, radiation and convection.

## Practical lesson No. 3. The first law of thermodynamics

The first law of thermodynamics is the law of conservation of energy isolated system. It is not derived from any simpler provisions, but is a generalization of numerous observations that do not contradict it. It should be considered as a postulate that is valid for any isolated system. When applying the first law to closed systems, it is implied that after heat transfer, all processes in a closed system proceed as in isolated. (Energy exchange with the environment can be considered instantaneous: time is excluded in thermodynamic processes.)

The first law of thermodynamics states that heat [ Math Error ] $\delta Q$ communicated to the system goes to increase its internal energy $dU$ and to perform work against external pressure [ Math Error ] $\delta A = pdV$ :

[Math Error] $\delta Q = dU +$ [Math Error] $\delta A$ (II. 1)

Internal energy consists of kinetic and potential energy of particles entering the system. In thermodynamics it is enough limit ourselves to the fact that internal energy depends on the nature of the particles and temperature. However, to explain the properties of the internal energy can be indicated that it includes immeasurable absolute values depending on intraparticle energy states, i.e.

$U_{\text{full}} = U_T + \text{const}$ . Here we can take the “zero” energy $U_0$ as a constant at $T = 0$ with the condition that zero-point energy does not depend on temperature. Since the differential is of constant value

is equal to zero, then $dU_{\text{full}} = dU_T$ .

The internal energy depends only on the state parameters, therefore, its change in the process flowing through any intermediate states is completely determined by the initial and final

states. Therefore, internal energy is a function state, the differential of such a function is a complete differential:

$$\int_{\text{нач}}^{\text{кон}} dU = U_{\text{кон}} - U_{\text{нач}} = \Delta U$$

On the contrary, the work of transition from the same initial to the same final state depends on the nature of the process (cf. isothermal and isobaric expansion of a gas). Mathematically this means that the integral $\int_{\text{нач}}^{\text{кон}} \delta A = \int_{\text{нач}}^{\text{кон}} p\,dV$ maybe be solved if the dependence p = f ( V , T) is known. So it's equal In theory ( II . 1) the right and therefore the left side depend on the path process, i.e. heat and work are functions of the process. To distinguish between state and process functions, elementary heat and work are designated in equation ( II . 1) by the letter [ Math Error ] $\delta$ .

**Thermal effects**

Let us consider special cases of application of equation ( II . 1):

V = const, then [Math Error] $\delta Q_v = dU$

$\mathbf{Q}_V = \Delta \mathbf{U}$ (II.2)

p = const, then [Math Error] $\delta Q_p = dU + pdV = d(U + pV)$

$Qp_{\_} = \Delta(U + pV)$

By entering the designation $H = U + pV$ , where $H$ — state function, called enthalpy, we can write:

$\mathbf{Q}_p = \Delta \mathbf{H}$ ( II .3)

Since heat is released due to a decrease in internal energy (or enthalpy) and is absorbed with an increase in internal energy, then in exothermic reactions Δ**U** < 0 or Δ H < 0, and in endothermic conditions Δ U > 0 or Δ H > 0. In what follows, the values Δ**U** and _ Δ N are called thermal effects. Thermal effect is heat process performed either at constant pressure ( Δ N), at provided that the only possible work is work against external pressure, or at a constant volume ( Δ**U )** . In most cases, chemical processes occur at constant pressure, so in what follows we consider only isobaric thermal effects Δ N.

**Examples of problem solving**

**Task-3.** Calculate the change in internal energy upon evaporation of 50 g of toluene at 30 ° C . Note that toluene vapor obeys the ideal gas laws and that the volume of the liquid is very small compared to the volume of the vapor. The latent heat of vaporization of toluene is 347.8 J/mol.

**Solution: Internal energy and enthalpy are related as follows:**

$H=U+PV$ yoki $\Delta U=\Delta HP\Delta V$

$P\Delta V=nRT$ Given the spot

$\Delta U=\Delta H-nRT$ can be written as

Molecular mass of toluene - 92 g, number of moles n = m / M = 50/92 = 0.54

The total mass of toluene is taken into account when calculating the change in internal energy.

$T=273+30=303K$

$\Delta U=347.8\cdot 50-0.54\cdot 8.31\cdot 303=16029J=16.03$ kJ.

When 50 g of toluene is evaporated at 30 ° C , the internal energy of the system changes by 16.03 kJ.

**Task-2** . Calculate the change in internal energy when 72 g of water evaporates at boiling point. The latent heat of vaporization of water at normal pressure is 44041 J/mol, the specific volume of water vapor is 1.699 l/g. Ignore the volume of the liquid.

Solution: According to the first law of thermodynamics, Q = A + Δ U , the pressure of water vapor is equal to atmospheric pressure (boiling point). P = 101325 Pa

The process occurs at constant pressure (isobaric process). $A_p = P(V_{bug'} - V_{suyuq}) = P\,V_{bug'}$ $V_{bug'} >> V_{suv}$ what is this for

$A=101.325\cdot 1.699\cdot 10^{-3}\cdot 18=3098.72$ J

$\Delta U=QA=72/18(44041-3098.78)=163.8$ kJ

ΔI is positive, so the heat absorbed during evaporation is used to increase internal energy.

$\Delta U=U_2-U_1$ $U_2>U_1$

Problem- 3. Calculate the work done in evaporating 10 g of toluene, the amount of heat, internal energy and enthalpy. The boiling point of toluene is 383 K, the specific heat of evaporation is 336 kJ / mol. Ignore the volume of liquid when considering steam to be an ideal gas.

Solution: Toluene evaporates at constant pressure, so the enthalpy change is equal to the heat of evaporation.

$$Q_p = \Delta H = n\, l_{bug'} = \frac{m}{M}\, l_{bug'}$$

$L_{bug'}$ specific heat of vaporization, n - number of moles, m - mass, M - molecular weight - 92 g.

$\Delta H$ = (10/92) 33.6 = 3.65 kJ = 3.65 $10^{-3}$ j

Work done in an isobaric process

$A_p = P(V_{bug'} - V_{suyuq}) = P V_{bug'}$ $V_{bug'} >> V_{sub}$ since

$A_p = PV_{bug'} = nRT$ = (10/92) 8.31 383 = 346 J

Enthalpy change $\Delta H$

$\Delta H = \Delta U + P\Delta V = \Delta U + PV_{bug'}$ since

$\Delta U = \Delta H - PV_{bug'} = \Delta H - nRT$ = 3650-346 = 3304 J

4 - Task. Pressure 0.8 $m^3$ hydrogen at 20 ° C is 84800 Pa. When heated, the gas occupied a volume of $^{3.6}$ m3 . How much work has been done so far?

Solution: work is done in an isobaric process

$A_p = P(V_2 - V_1)$ = 84800 (3.6-0.8) = 237440 J = 237.44 kJ

5 - 30 L outlet Ideal gas 96460 Pa, isothermally compressed at 24 ° C . How much heat is released when the volume of gas decreases by a factor of 5?

Solution: Work is done in an isothermal process

$$A_t = Q_t = nRT\ln\frac{V_2}{V_1} = 2{,}303\cdot nRT\ \lg\frac{V_2}{V_1};$$

The number of moles is determined from the equation of state of an ideal gas:

$$PV = nRT \qquad n = \frac{PV}{RT} = \frac{96460\cdot 30\cdot 10^{-3}}{8{,}31\cdot 297} = 1{,}17\ \text{mol}$$

From this $Q_t$ = 2.303 1.17 8.31 297 lg (6/30) = 6653.44 lg0.2 = -4650.75J = -4.65 kJ

**self-resolved issues**

1. Determine the change in internal energy upon evaporation of 50 g of alcohol at boiling point. The specific heat of vaporization is 857.7 J/g and the specific volume of steam at 100 ° C is 607 10-3 L/g. Calculate the volume of the liquid.

2. The volume of an ideal gas is increased from 1.5 liters to 10 liters at a constant temperature of 298K. It consumes 9.66 × 105 J of heat. How many moles of gas were involved in this process?

3. When 90 g of water evaporates at 100 ° C , the change in internal energy is 188.1 kJ. The specific volume of water vapor is 1.699 l / g, pressure is 1.0133 105 Pa. Calculate the heat of formation of water vapor.

4. Calculate the work done when the volume of 110 g of carbon monoxide at 290 K expands from 50 to 175 liters.

5. 5000 J of work was performed by heating 2 moles of an ideal gas at constant pressure. Calculate the change in internal energy and enthalpy during this process. Sv = 2.5 R
6. Calculate the amount of heat released when 100 g of carbon monoxide CO is compressed from 50 to 10 L at 0 ° C.

7. How much heat is required to heat a mixture of 100 kmol of gases with a volume fraction of 20% carbon monoxide CO and 80% carbon monoxide CO 2 at a temperature of 100 ° C to 700 ° C at normal pressure?

## Practical lesson No. 4. Second law of thermodynamics

The second law of thermodynamics considers questions about the direction and limits of processes. Like the first beginning, it justified only by experience.

Of the numerous formulations of the second principle, one of the most general belongs to Clausius: heat cannot pass by itself from a colder body to a hotter one.

Reversible and irreversible processes

There are processes that occur spontaneously only in one direction, ending with the onset of equilibrium. Besides spontaneous transfer of heat from a hot body to a cold one; such processes include expansion of gas into emptiness, free fall of a body, diffusion, and chemical reactions. Leakage them in the opposite direction by itself, without external influence, is impossible. Thus, it is known that the reaction $H_2 + Cl_2 = 2HC1$ (g) is accompanied by the release of heat, which can be “transferred” at system temperature into a vessel with water (thermostat). If water quite a lot, then its temperature will hardly change.

According to the law of conservation of energy, the reverse reaction will require the same amount of heat. However, to return the system to the initial state, it is necessary to impart heat to the reaction products, which can only be taken from a thermostat that is at a higher temperature than the system. To create such a thermostat heat should be obtained from the environment, and the reaction system will return to its original state, but in the environment there will inevitably be changes associated with the transfer of heat to heat the thermostat.

Processes, the occurrence of which in forward and reverse directions are accompanied by changes in the environment, are thermodynamically irreversible. Such processes include all natural test spontaneous (spontaneous) processes.

However, under certain conditions the reaction can be carried out with the same or some other degree of reversibility. For example, an irreversible reaction substitution

$Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$

can be carried out in a galvanic cell, in half-elements of which reactions take place

$Cu^{2+} + 2e \rightarrow Cu$ and $Zn - 2e \rightarrow Zn^{2+}$. When the element is short-circuited, an irreversible process will occur with a change in enthalpy ΔH. No useful work except work against external pressure (this is included in the amount of ΔH) does not occur.

To obtain electrical work in an element, you need to connect some device to it (motor, lighting lamp), in other words, resistance $R$. _ As the resistance increases, the voltage drop between the poles of the element and at $R \rightarrow$ *[ Math Error ]*$\infty$ it becomes greatest and equal to the electromotive force (e.m. c.) element. If you turn on the source current, e. d.s. which differs by an infinitesimal amount from e. d.s. element, then the process can be carried out in the forward and reverse directions with infinitesimal chemical transformations corresponding to a state of dynamic equilibrium. It is not important that the forward and reverse processes are separated in time. Such a process is called quasi-static, which emphasizes the independence of equilibrium states from time. Quasi-static the process does not create residual changes in either the system or the environment and, by definition, is thermodynamically reversible (quasi-reversible).

Likewise, reversible heat transfer is possible with a vanishingly small temperature difference between the thermostat and the system.

It is often argued that a quasi-static process is infinitely slow. This is visual, but not strict. Rather, we should talk about a change in equilibrium states, regardless of the duration of the process. A completely reversible process is idealized. In such a process, proceeding in one direction, the work produced by a chemical reaction could have the greatest value. It is a measure of system performance and is called maximum.

In an isobaric process; $A_{max} = A_{max\,,\,chem} + A_{max\text{-}mech}$ .

Where $A_{max\text{-}chem}$ also called maximum useful work $A_{max\text{-}fur}$ is working against external pressure.

The concepts chemical and thermodynamic should not be confused reversible process. In the first case we are talking about the direction of the process, in the second - about the way it is carried out. Chemically reversible the process can go in the forward and reverse directions, but is thermodynamically irreversible (see above about the reaction $H_2 + Cl_2$ ). A thermodynamically reversible process occurs only through states of dynamic equilibrium.

**Work, heat and entropy**

The second law of thermodynamics states that even with a reversible process, only part of the heat of the process can go into work, the other part in the form of heat is transferred from more heated to cooler parts of the system. This phenomenon is called energy dissipation. Recall that the process is reversible if the temperature difference is infinitesimal, i.e., in the limit, heat is transferred at a constant temperature.

The relationship between the total heat of the process and that part of it that can go into work in an isobaric-isothermal process, expressed by the equation:

$\Delta H = \Delta G\_ + T\Delta S$ (11.10)

where $\Delta H$ is the entire heat of the process, equal to the thermal effect of the irreversible reaction; L G is that part of the total energy that can be converted into useful work in a reversible process; it is called isobaric work capacity, isobaric free energy or free enthalpy; the current accepted term for G is Gibbs energy.

Since the system performs work $A_{max\text{- chemical}}$ due to the decrease in Gibbs energy, there is a relationship between them: $-\Delta G = A_{max\text{-}chem}$ . Part of the total heat TAS , which even at quite in a reversible process is not converted into work, but is given away in the form heat ( $T\Delta S = Q_{arr}$ ) is called bound energy.

Here $S$ is entropy, and $\Delta S$ is the change in entropy of the system at reversible heat transfer. It is equal to the transferred heat divided by the temperature at which the heat is transferred:

$\Delta S = Q_{arr}/T$ (I. 1)

Like energy and enthalpy, entropy S is a function of state. Like energy, entropy can be represented as amounts $S_T + S_0$ however, with the exception of certain cases, $S_0 = 0$, therefore, the absolute values of entropy are known.

Spontaneous ( essential ) processes always occur in the direction of reducing the performance of the system, i.e. spontaneous process $\Delta G < 0$. Thus, by the sign of $\Delta G$ you can determine the direction of the process, and by its absolute value evaluate its “driving force” or, as is often said, “chemical affinity”.

Gibbs energy $G$ is also a function of the state, i.e. its the change does not depend on the process path and can be calculated by a law similar to Hess's law. Changes in Gibbs energy at formation of compounds from simple substances $\Delta G^\circ_{f\,,\,298}$ and absolute entropy of substances $S^\circ_{298}$ included in the previously mentioned thermodynamic tables. $\Delta G^\circ_{298}$_ and $\Delta S^\circ_{298}$ during the reaction can be calculated in the same way as the thermal effect $\Delta H^\circ_{298}$ .

Examples of problem solving.

Issue 1. Calculate the efficiency of an ideal Carnot machine that uses steam at 140° C and produces steam at 105° C .

Solution:

$$\eta = \frac{T_1 - T_2}{T_1}$$

$T_1$ =140+273=413 K $T_2$ =105+273=378K

$$\eta = \frac{413-378}{413} = 0{,}085$$

or 8.5%

Issue 2. When 42 g of nitrogen is cooled from 150 ° C to 20 ° C , the pressure increases from 5 105 to 2.5 106 Pa. Calculate the change in entropy if the heat capacity Cp = 1.039 J/g deg.

Solution: Calculate the change in entropy

$\Delta S = nR\ln\cdot(P_1/P_2) + nC_p\ln\cdot(P_2/P_1)$ we use the formula.

$T_1$ =273+150=423 K $T_2$ =273+20=293 K

Molar heat $_{capacity}$ $C_p$ = M C p =28·1.039=29.09 J/g · deg.

We count the number of goods

n=m/M=42/28=1.5 mol

$$\Delta S = 1{,}5\cdot 2{,}3\ (8{,}314\lg\frac{5\cdot 10^5}{2{,}5\cdot 10^6} + 29{,}09\lg\frac{293}{423}) = -20{,}63\ J/grad$$

The (-) sign indicates a decrease in entropy as the gas cools. ($S_1 > S_2$ ).

Issue 3. Calculate the change in the isobaric-isothermal potential of oxygen formation in air at 298 K. The partial pressure of oxygen in air is 0.21 atm.

Solution: We use the equation $\Delta G_T = \Delta G^{\circ}_T + RT\ln P$ . Because the $\Delta G^{\circ}_{273} = 0$ for oxygen

$\Delta G_T = RT\ln P = 8.31\cdot 298\cdot 2.3\cdot\log 0.21 = -3866.6$ J/mol

Thus, any reaction producing oxygen occurs at atmospheric pressure, and not at 1 atm.

**Questions for independent solution.**

1. Calculate the change in Gibbs energy Δ G ° for the $C_{\text{graphite process}} + 2H_{2(g)} = CH_{4(g)}$ at 250° C . Use the ΔH ° and ΔC ° values of the substances in the table and the standard calorific value of methane.

2. An ideal Carnot machine uses steam at 250° C and releases steam at 40° C . Calculate the efficiency of the machine.

3. A Carnot machine operating at 350 to 50 ° C operates at 33.52 J per cycle. How much heat should the car be given at this time and how much heat is generated?

4. In the reverse carnot cycle, 419 kJ of heat is taken from the heater at 0° C and transferred to the refrigerator at 77° C . How much work is required for this cycle to occur?

5. The Carnot machine operates in the range of 200-300K and converts 85.8 kJ of heat into work. How much heat is lost to the refrigerator at 200 K?

## Practical lesson No. 5. The third law of thermodynamics

### NERNST EQUATION

Nernst derived using the thermodynamic electrochemical cycle expression of the electrode potential in the form (Ox and Red are the oxidized and reduced forms of the substance)

$$E = E^\circ + \frac{RT}{zF}\ln\left(c_{\mathrm{Ox}}/c_{\mathrm{Red}}\right)$$

Using average ionic activities instead of concentrations, we give this equation the form

$$E(\mathrm{A}^{z+},\ \mathrm{D}) = E^\circ + \frac{RT}{zF}\ln\left(a_{\mathrm{A}^{z+}}/a_{\mathrm{D}}\right) = E^\circ + \frac{2{,}3RT}{zF}\lg\left(a_{\mathrm{A}^{z+}}/a_{\mathrm{D}}\right)$$

where is meant .

For all $a_i = 1$ $E(A^{z+}, D) = E^\circ$ (E° is the standard potential). In brackets at E, the acceptor-donor transformation at this electrode is written without taking into account stoichiometry. Standard potential E° corresponds to the same transformation, and therefore the expression in parentheses can be omitted. By r we mean not the charge of the acceptor or donor, but the number of electrons participating in recovery. If recovery is not complete, you can write:

$$\mathrm{A}^{z+} + ne \rightleftarrows \mathrm{D}^{(z-n)+}$$

$$E(\mathrm{A}^{z+},\ \mathrm{D}) = E^\circ + \frac{RT}{nF}\ln\left(a_{\mathrm{A}^{z+}}/a_{\mathrm{D}^{(z-n)+}}\right)$$

(for an example, see the Redox Electrodes section).

Multiplier 2.3 *RT* / *zF* (Appendix V ) in the Nernst equation

equal to 2.3·8.31477965002= $1.98\cdot10^{-4}$ T/ *z* , so at 298 K:

$$E(\mathrm{A}^{z+},\ \mathrm{D}) = E^\circ + \frac{0{,}0591}{z}\lg\left(a_{\mathrm{A}^{z+}}/a_{\mathrm{D}}\right)$$

### Activated complex and rate constant elementary reaction

At the top of the potential barrier, a certain configuration (activated complex) of reacting particles is formed. This complex is considered as a molecule in a state of transition to final substances. For example, in the reaction of bromine with hydrogen; In r +. $H_2$ -> HB r + H, an activated complex is initially formed: B r ••• H ••• H, which turns into reaction products. Thus:

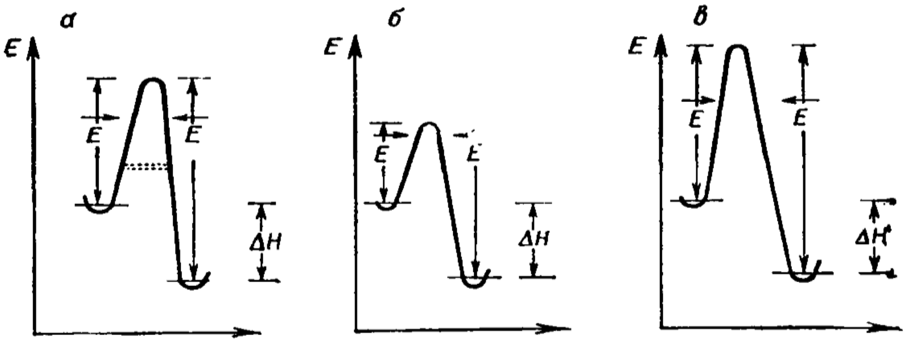
B r + $H_2$ —► B r -H-H —► HB r + H

Atoms in a complex vibrate in different directions, but, as said, vibrations along the line of valence bonds are significant (this direction of vibration is called the reaction coordinate). You can consider the relative displacement of atoms by imagining that the first and third atom are motionless, and the second is approaching the first, then the third. At the end of one vibration, when the Br and H atoms approach each other, the complex disintegrates. The “lifetime” of the complex is inversely proportional to the oscillation frequency v. During this time, the complex is in quasi-stationary equilibrium with the original particles. Let's consider this equilibrium in general form: $A + B \leftrightarrow X^{\neq}$ where A and B are the initial particles; $X^{\neq}$—activated complex.

This equilibrium corresponds to the product of concentrations $\Pi_c^{\neq} = [X^{\neq}]/[A][B]$ , which is not a thermodynamic—dimensionless—equilibrium constant. To move on to this last one, all concentrations should be assigned to the corresponding standard values; To do this, we express the product of concentrations in the form:

$$\Pi_c^{\neq} = \left\{ \frac{[X^{\neq}]/[X^{\neq}]^{\text{ст}}}{[A]/[A]^{\text{ст}}\,[B]/[B]^{\text{ст}}} \right\} \frac{[X^{\neq}]^{\text{ст}}}{[A]^{\text{ст}}\,[B]^{\text{ст}}}$$

The indices (st) denote arbitrarily chosen standard concentrations, and the product in curly brackets is the thermodynamic equilibrium constant between the activated complex and starting materials. Means:



Rice. 1. Activation energy of the same reaction:

*( a —in the absence of a catalyst; b—in the presence of a catalyst; c—in the presence of an inhibitor. The dotted line shows a possible decrease in the activation energy due to the tunneling effect.* $\vec{E}$ и $\overleftarrow{E}$ *— Arrhenius activation energies of forward and reverse reactions; ΔH —thermal affect reaction. The abscissa axes show the reaction coordinates.)*

$$\Pi_c^{\neq} = K_{\text{тд}}^{\neq}\,\Pi_c^{\neq\text{ст}}$$

The rate of decomposition of the complex (reaction rate) v is proportional to its concentration and the frequency of decomposition

$$v = \chi\,[X^{\neq}]\,\nu$$

Proportionality coefficient % - called transmission; it is usually equal to one. From the reaction equation it follows that its rate, equal to the rate of decay of the activated complex, equal to

$$[X^{\ddagger}] = \Pi_c^{\ddagger}[A][B] = K_{тд}^{\ddagger}\Pi_c^{\ddagger\,ст}[A][B],$$ where .

Therefore, the reaction rate constant is: $\kappa = K_{тд}^{\ddagger}\Pi_c^{\ddagger\,ст}\nu$ . The reaction rate constant has the same dimensional expression as And $\Pi_c^{\ddagger\,ст}\nu$ ,T. i.e. in first order reactions time $^{-1}$ , and in second order reactions - concentration $^{-1}$ -time $^{-1}$ .

As usual, single values are taken as standard concentrations.