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Стисло викладено теоретичні відомості з традиційних розділів фізичної хімії: термодинаміка, хімічні та фазові рівноваги, електрохімія та кінетика. Особливу увагу приділено найбільш важким для розуміння питанням. Розгляд складних тем супроводжується розбором прикладів і завдань, наводяться контрольні завдання.

Для студентів хіміко-інженерних напрямків освіти.

R 83 Physical chemistry: Practical course for the self-study tutorial of the course of physical chemistry by students of chemical specialties and foreign students / S.I. Rudneva, N.D. Sakhnenko, A.V. Djenyuk – Kharkiv, 2018. –148 p.

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Brief summary of the traditional sections of physical chemistry, such as: thermodynamics, chemical and phase equilibrium, electrochemistry and kinetics are presented. The most difficult problems are studied in detail. The presentation of such complex topics is accompanied by the analysis of examples and problems, and the control tasks are given in the main sections of physical chemistry.

The manual is addressed to students of chemical engineering directions of education.

Figs. 25 . Tab. 23. Bibliogr. 7 denoms.

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Introduction

Modern physical chemistry is a powerful tool for the study of chemical processes, and therefore plays an important role in the training of engineer chemist-technologist. Given this and, on the other hand, given the limited number of hours devoted to physical chemistry in the curricula of the correspondence form of teaching, the author tried to present the material as briefly as possible, paying particular attention to the most difficult to understand questions. The presentation of such complex topics is accompanied by an analysis of examples and problems.

The main contents of the tutorial are traditional sections of physical chemistry: thermodynamics, chemical and phase equilibrium, electrochemistry and kinetics. In the section "Thermodynamics, chemical and phase equilibria", the main laws that determine chemical equilibria are considered. The flow of a chemical reaction is often accompanied by a change in the aggregate state of the reaction products in comparison with the initial substances. Obviously, mastering the laws of phase equilibria is extremely important. The purpose of studying "Electrochemistry" is the mastering of the basic laws related to the mutual transformations of the chemical and electrical forms of energy. The properties of solutions of electrolytes, the electrical conductivity of solutions, and the work of galvanic cells are examined in detail. The basic laws of velocity, rate constants and activation energies of chemical reactions are mastered in the study of "Kinetics".

The tasks are compiled in 25 variants. Calculation problems are very important for a better assimilation of the course of Physical Chemistry. Their implementation should teach the student the application of the theoretical provisions of the course to the solution of practical problems. The proposed teaching and methodological tutorial contains the main types of control tasks for the main sections of physical chemistry. The control tasks are designed in such a way that it is necessary to use reference literature when solving qualitative and quantitative problems. All the necessary reference data for calculations are represented at the end of the guidelines.

Chapter 1. CHEMICAL THERMODYNAMICS

1.1. The first law of thermodynamics.

A thermodynamic system is a body or group of bodies that are interacting, mentally or really separate from the environment. Systems can be homogeneous (uniform, consist of one phase) and heterogeneous (variegated, consist of two or more phases). If the system does not exchange material or energy with the environment, it is called isolated. A system that exchanges energy with the environment, but does not exchange matter, is closed. In case that there is an exchange between the system and the environment with matter and energy – we have an open system. The totality of all physical and chemical properties of the system characterizes its thermodynamic state. All quantities characterizing any macroscopic property of the system under consideration are the parameters of the state (temperature, volume, pressure, concentration, etc.). Any change in the thermodynamic state of the system (changing at least one level of state) is a thermodynamic process. The concept of reversible and equilibrium processes is extremely important in chemical thermodynamics. *Equilibrium processes* are processes that pass through a continuous series of equilibrium states. Nonequilibrium processes are processes after which the system can not be returned to its original state without any changes left in it. *Reversible processes* are processes in which the system returns to its original state without any changes in the environment. Otherwise, the processes will be irreversible. *Spontaneous processes* - processes that occur by themselves do not require the expenditure of energy from outside and bring the system to equilibrium. Some particular types of processes are: a) isothermal ($T = \text{const}$); b) isobaric ($p = \text{const}$); c) isochoric ($V = \text{const}$); d) adiabatic (there is no exchange of heat between the system and the environment). The measure of the system's ability to do work is energy. The energy of a system in

thermodynamics is its **internal energy (U)**. U is the problem of the **kinetic and potential energy of all the particles that make up the system**. When a system changes from one state to another, the quantitative change in the internal energy is:

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

The first law of thermodynamics is based on the self-actual law of nature – the law of conservation and transformation of energy. If the system absorbs some amount of heat (Q), then it is consumed by changing the internal energy of the system (ΔU) and completing work A . It should be noted that the work done by the system on the environment is considered positive; the change in internal energy is positive, if as a result of the process it has increased; heat is also positive if it is absorbed by the system. Thus, according to the first law of thermodynamics, ***the heat reported to the system is expended on increasing the internal energy of the system and on the work done by the system***: or for infinitesimally small quantities $\delta Q = dU + \delta A$. The work of expansion of gas is often only type of work in chemical systems.

To operate the gas expansion $\delta A = pdV$, and the first beginning becomes:

$$\delta Q = dU + pdV. \quad (1.1)$$

If the process proceeds at a constant volume ($V = \text{const}$), then:

$$pdV = 0 \quad \text{and} \quad \delta Q = dU, \quad \text{and} \quad Q_v = \int_1^2 dU = \Delta U.$$

For the isobaric process ($p = \text{const}$), we have:

$$Q_p = \int_1^2 dU + \int_1^2 pdV = (U_2 + pV_2) - (U_1 + pV_1) = H_2 - H_1 = \Delta H$$

Since the internal energy and the enthalpy are interrelated, it is easy to obtain a relationship between the heats of the corresponding processes.

$$Q_p = \Delta H = \Delta U + p\Delta V = \Delta U + \Delta vRT = Q_v + \Delta vRT \quad (1.2)$$

where Δv – is a change in the number of moles of gases due to the reaction: $\Delta v = (\sum v_i)^{prod} - (\sum v_i)^{init}$; v_i – is a stoichiometric coefficient in the chemical reaction equation.

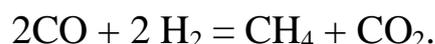
The thermal effect of a chemical reaction is called heat, which is released or absorbed as a result of a chemical reaction taking place at a constant pressure ($Q_p = \Delta H$) or volume ($\delta Q_v = \Delta U$).

This applies to conditions where the reaction products have the same temperature as the components. The first consequence of Hess's law is used to calculate the thermal effects of chemical reactions. It is most common. This method is used if reference data on the heat of formation of substances involved in the reaction are known. *The heat of formation is the thermal effect of the formation of one mole of a compound from simple substances. A simple substance is a substance that consists of atoms of one chemical element (for example, H₂).* In the reference literature, the heats of formation of ΔH_0 are given under standard conditions ($p=1,013 \cdot 10^5$ Pa, $T = 298$ K). According to the sign of the thermal effect of the reaction, there are exothermic (with the release of heat, $\Delta H < 0$) and endothermic (with absorption of heat, $\Delta H > 0$).

According to the corollary of the Hess law, the thermal effect of the reaction proceeding at constant pressure is equal to the difference between the problems of the heats of formation of the reaction products and the starting materials, taking into account their stoichiometric coefficients:

$$\Delta H_{298}^0 = \sum (v \Delta H_{298}^0)^{prod} - \sum (v \Delta H_{298}^0)^{init}. \quad (1.3)$$

Example. Determine at $T=298$ K and $p=1,013 \cdot 10^5$ Pa the thermal reaction effect:



How will this thermal effect change if the reaction is carried out in a closed vessel?

Solution. We determine the thermal effect of this reaction at $p = \text{const}$. According to the first consequence of Hess's law:

$$\begin{aligned}\Delta H^0_{\text{react}} &= \Delta H^0(\text{CH}_4) + \Delta H^0(\text{CO}_2) - 2\Delta H^0_{(\text{CO})} - 2\Delta H^0(\text{H}_2) = \\ &= -74,85 - 393,51 - (-2 \cdot 110,53) - (-2 \cdot 0) = -247,3 \text{ kJ/mol.}\end{aligned}$$

The thermal effect of this reaction under conditions of a closed vessel, i.e. at $V = \text{const}$ (ΔU) we calculate by the equation (1.2):

$$\Delta U = \Delta H + \Delta \nu RT = -247,3 \cdot 10^3 + (-2 \cdot 8,31 \cdot 298) = -62,93 \text{ kJ.}$$

Here $\Delta \nu = 2 - 4 = -2$. It is necessary to take into account only substances in the gas state when calculating the change in the number of moles of the reaction. When calculating the change in the number of moles of the reaction, only *substances in the gaseous state* must be taken into account.

Kirchhoff Law. Using Hess's law or its effect, it is possible to calculate the thermal effect of the reaction only under standard conditions. In practice, it is often necessary to calculate the thermal effect of the reaction at various temperatures. Therefore, it is necessary to be able to calculate the thermal effects for any given temperatures.

When calculating thermal effects at different temperatures, we come across a new value for us - the heat capacity (C). By heat capacity we mean the ratio of an infinitesimal amount of heat, which must be reduced to one mole of matter, to an infinitesimal increase in temperature, which is observed:

There are molar heat capacity at constant pressure $C_p = \left(\frac{\partial H}{\partial T} \right)_p$ and molar heat capacity at constant volume $C_v = \left(\frac{\partial U}{\partial T} \right)_p$. In general, the heat capacity depends on the temperature. In practice, the dependence of the heat capacity of complex substances on temperature is usually based on experimental data and approximated by equations of the form

$$C_p = a + bT + cT^2 + c' T^{-2}, \quad (1.4)$$

where a , b , c , c' – are empirical coefficients, individual for each case (in calculations are taken from the reference data). As a rule, for inorganic substances $c = 0$, and for organic $c' = 0$.

Example. Calculate the heat capacity CO_2 under $T=400\text{K}$. From the directory we take the values of the coefficients for CO_2 : $a = 44,14$; $b \cdot 10^3 = 9,04$; $c' \cdot 10^{-5} = -8,53$.

Solution.

$$C_{p,400} = 44,14 + 9,04 \cdot 10^{-3} \cdot 400 - 8,53 \cdot 10^5 \cdot 400^{-2} = 42,4 \text{ J/mol} \cdot \text{K}.$$

Let us find the dependence of the heat effect ΔH of the isobaric process on the temperature (for an isochoric process, the dependence of ΔU on T is analogous), in addition, knowing ΔH of the process, it is always possible to calculate ΔU from equation (1.2).

Since $\Delta H = H_2 - H_1$, then, by differentiating the equation with respect to temperature, we obtain $(d\Delta H/dT)_p = (dH_2/dT)_p - (dH_1/dT)_p$, but $(dH/dT)_p = C_p$, therefore,

$$d\left(\frac{\Delta H}{dT}\right)_p = C_{p,2} - C_{p,1} = \Delta C_p, \quad (1.5)$$

similarly

$$d\left(\frac{\Delta U}{dT}\right)_v = \Delta C_v, \quad (1.6)$$

where ΔC – is a change in heat capacity as a result of the process.

The obtained equations (1.5 and 1.6) are the differential form of the **Kirchhoff law: the temperature coefficient of the thermal effect of the chemical process (the change in the thermal effect of the reaction with a temperature change by one degree) is equal to the change in the heat capacity of the system as a result of this process.**

An analysis of the Kirchhoff law shows that **if $\Delta C_p > 0$, then the derivative is positive, that is, with increasing temperature, the thermal**

effect increases; if the heat capacity decreases as a result of the process, $\Delta C_p < 0$, then the derivative is negative, the thermal effect of the process decreases with increasing temperature. Since the sign of the change in the heat capacity as a result of the process is determined by the difference between the sum of the heat capacities of the reaction products and the initial substances, then the variants shown in Fig. 1.1 are possible.

Analyzing the data of the figure, we see that with a monotonic change in the heat capacity of the participants in the reaction, the thermal effect of the reaction increases monotonically if the total heat capacity of the reaction products over the entire temperature range is bigger than the total heat capacity of the initial substances (*a*); on the other hand, the thermal effect of the reaction decreases monotonically if the total heat capacity of the products over the entire temperature range is less than the total heat capacity of the starting materials (*b*).

In some cases, when the temperature of the heat capacity of the initial substances and reaction products changes, while remaining monotonous, the sum of nonmonotonic dependences is given. In such cases, the temperature dependence of the reaction's thermal effect passes through the extreme point (*c* and *d*). The points of the extremum on the dependence of the reaction's thermal effect correspond to the point at which the heat capacity of the initial substances is equal to the heat capacity of the reaction products.

We specify the effect of temperature on the reaction ΔH depending on the sign of the ΔC_p reaction.

When integrating the Kirchoff equation (1.4) in the range from T_1 to T_2 , we find

$$\Delta H_{T_2} = \Delta H_{T_1} + \int_{T_1}^{T_2} \Delta C_p dT. \quad (1.7)$$

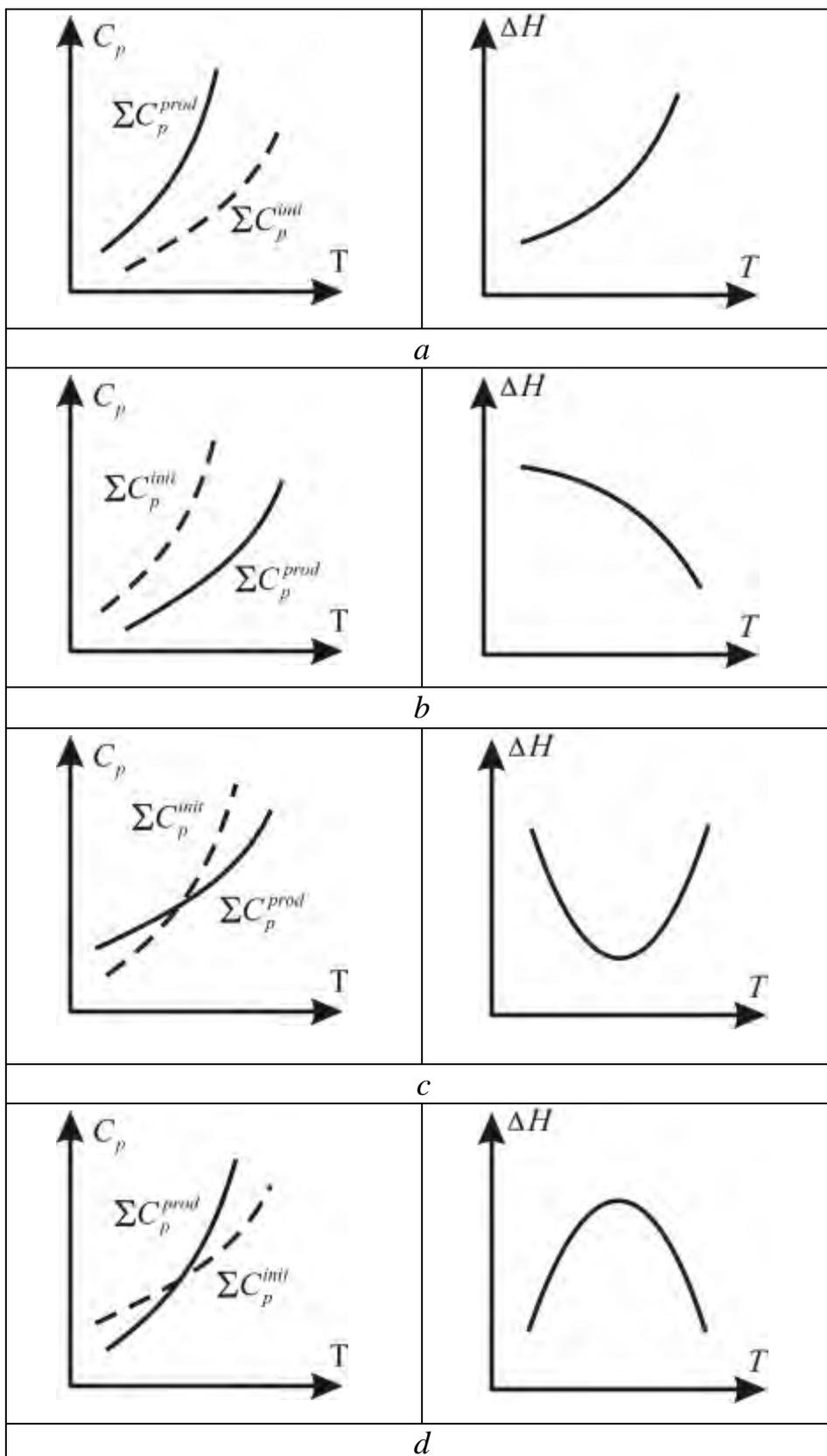


Fig. 1.1. The effect of temperature on the change in ΔH as a function of the sign of the ΔC_p of the chemical reaction

Equation (1.6) makes it possible to calculate the thermal effect of the reaction at a single temperature (T_2), if the heat effect at a different temperature (T_1) is known and the heat capacity as a result of the reaction (ΔC_p) is known.

While making calculations in a small temperature range (of the order of tens of degrees), we can assume that ΔC_p does not depend on temperature; then equation (1.7) takes the form

$$\Delta H_T^0 = \Delta H_{298}^0 + \Delta C_{p,298} \cdot (T - 298). \quad (1.8)$$

The change in the heat capacity during the course of the chemical reaction is calculated according to the generally accepted scheme:

$$\Delta C_p = \left(\sum v_i \cdot C_{p,i} \right)^{prod} - \left(\sum v_i \cdot C_{p,i} \right)^{init}. \quad (1.9)$$

ΔC_p – is the difference between the problems of the molar heat capacities of the reaction products and the starting materials.

The heat capacities of substances are taken with coefficients corresponding to the chemical reaction.

For more accurate calculations, accounting for the heat capacity versus temperature (equation 1.7) leads to the equation:

$$\Delta H_T^0 = \Delta H_{298}^0 + \int_{T_1}^{T_2} (\Delta a + \Delta bT + \Delta cT^2 + \Delta c'T^{-2}) dT, \quad (1.10)$$

where Δa , Δb etc. – is the difference of the algebraic problems of the coefficients in the equations for the specific heats for the products and components of the reaction, taken into account of the stoichiometric coefficients. So, for example, for a reaction in the general form:

$$\Delta c' = (ec'_E + fc'_F) - (ac'_A + bc'_B) = \Sigma(n_i c'_i)_{prod} - \Sigma(n_i c'_i)_{init}.$$

Integration of equation (1.8) leads to an expression that allows us to calculate the thermal effect of the reaction at any temperature:

$$\Delta H_{T_2}^0 = \Delta H_{T_1}^0 + \Delta a(T_2 - T_1) + \frac{\Delta b}{2}(T_2^2 - T_1^2) + \frac{\Delta c}{3}(T_2^3 - T_1^3) - \Delta c'(T_2^{-1} - T_1^{-1}). \quad (1.11)$$

As ΔH_T , it is advisable to choose ΔH_{298} , since this quantity can easily be calculated using tables of thermodynamic quantities.

When calculating the heat effect at one temperature, it is necessary to know the heat effect at the another temperature (for example at $T = 298\text{K}$, it can be found using reference data on the heats of formations and heat capacities of the participants in the reaction).

$$\Delta H_0 = \Delta H_{298} - \Delta a \cdot 298 - \frac{1}{2} \Delta b \cdot 10^{-3} \cdot 298^2 - \frac{1}{3} \Delta c \cdot 10^{-6} \cdot 298^3 + \Delta c' \cdot 10^5 \cdot 298^{-1}, \quad (1.12)$$

where ΔH_0 is the heat effect extrapolated to absolute zero temperature. So,

$$\Delta H_T = \Delta H_0 + \Delta a \cdot T + \frac{1}{2} \Delta b \cdot 10^{-3} \cdot T^2 + \frac{1}{3} \Delta c \cdot 10^{-6} \cdot T^3 - \Delta c' \cdot 10^5 \cdot T^{-1}. \quad (1.13)$$

This equation in the most general form expresses the dependence of the thermal effect of the reaction on temperature.

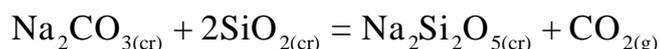
Example. Calculate the change in heat capacity during the reaction:



Solution.

$$\begin{aligned} \Delta C_p &= 2C_p(\text{Ag}) + 2C_p(\text{NO}_2) + C_p(\text{O}_2) - 2C_p(\text{AgNO}_3) = \\ &= 2 \cdot 25,48 + 2 \cdot 37,11 + 29,36 - 2 \cdot 93,05 = -31,56 \text{ J/mol.} \end{aligned}$$

Example. Calculate with a different degree of approximation the value of the thermal effect of the reaction under 700K.



Solution. For convenience of calculations we bring the data in the table 1.1.

Table 1.1 – Reference data and preliminary calculations

Substance	ΔH_{298}^0 J/mol·K	$c_{p,298}^0$ J/mol·K	The coefficients of equation		
			a	$b \cdot 10^3$	$c' \cdot 10^{-5}$
Na ₂ Si ₂ O ₅	–2398	156,6	185,69	70,54	–44,64
CO ₂	–393,5	37,1	44,14	9,04	–8,53
Na ₂ CO ₃	–1129	110,0	70,63	135,6	–
SiO ₂	–859,3	44,5	46,94	34,31	–11,3
2 SiO ₂	– 1718,6	89,0	93,88	68,62	–22,6
$\Delta_{\text{chem.s.}}$	+56,1	–5,3	65,32	–124,64	–30,57

The last line of the table shows the values calculated for the reaction ΔH_{298}^0 , $\Delta C_{p,298}^0$, Δa , $\Delta b \cdot 10^3$, $\Delta c' \cdot 10^{-5}$.

a) we calculate the approximate value ΔH_{700}^0 , assuming that ΔC_p doesn't depend on temperature, $\Delta H_{700}^0 = 56,1 \cdot 10^3 - 5,3 \cdot (700 - 298) = 53970$ J \approx 54,0 kJ (since the heat capacity is expressed in J, the heat effect in the calculation must also be expressed in J);

б) to calculate a more accurate value ΔH_{700} we write down the equation expressing the dependence of the thermal effect on temperature (see Equation 1.11), substituting into it the calculated coefficients Δa , Δb , $\Delta c'$ and temperatures $T_1 = 298$, $T_2 = 700$:

$$\Delta H_{700}^0 = 56,1 \cdot 10^3 + 65,32 \cdot (700 - 298) - \frac{124,64 \cdot 10^{-3}}{2} (700^2 - 298^2) + 30,57 \cdot 10^5 \left(\frac{1}{700} - \frac{1}{298} \right) = 51460 \text{ J} = 51,46 \text{ kJ}.$$

1.2. The second law of thermodynamics

In addition to the first law of thermodynamics we studied, there are two equally important laws. They are associated with the introduction of a new concept – **entropy**, *which characterizes the probability of*

spontaneous implementation of various states of the system, and as it was shown by L. E. Boltzman, is associated with the thermal processes occurring in the system. In this regard, we introduce the concept of spontaneous process. To spontaneous processes relate those processes that occur without any external influence and bring the system closer to an equilibrium state. An example of a mechanical spontaneous process can be the expansion of gas from a broken ampoule into an evacuated vessel; the thermal example of a spontaneous process is the transfer of heat from a warmer body to a less heated one.

All real processes in nature are spontaneous, that is, they go in a certain direction. So, for example, as a result of diffusion in the solution spontaneous leveling of the concentration throughout the volume occurs.

II beginning of thermodynamics just allows us to formulate the conditions for the flow of processes, their direction.

Entropy is the criterion by which one can judge the possible direction of the process. It turned out that spontaneously can only occur such processes, for which the following ratio is observed: $dS \geq \frac{\delta Q_{rev}}{T}$. In the case of finite changes in the system, the expression for the second law of thermodynamics takes the form: $\Delta S \geq \frac{Q_{rev}}{T}$. For a particular case of closed systems in which there is no energy exchange with the environment, we arrive at the general expression II of the beginning of thermodynamics—the Clausius inequality: $\Delta S \geq 0$. This means that any process that occurs without the intervention of external influences passes so that the entropy of the corresponding system only increases; if the balance is reached and the processes not, then the entropy of the system does not change, that is, $\Delta S = 0$. The statistical definition of entropy means that the system is moving toward a state that is most likely.

Unlike internal energy and enthalpy, the absolute values of entropy can be calculated. In accordance with *the Planck postulate, the entropy*

of an ideal atomic crystal at absolute zero temperature is zero. Planck's postulate is in strict agreement with the probabilistic interpretation of entropy according to Boltzmann. Indeed, in an ideal crystal, atoms can be placed uniquely, i.e.

$$S = k \cdot \ln 1 = 0. \quad (1.14)$$

With Planck's postulate, the entropy of one mole of a gaseous substance at a temperature T is equal to the problem of all entropy changes during the transition of a given substance from the state at absolute zero to the state at a given T:

$$S = 0 + \int_0^{T_{melt}} \frac{c_{p(cr)} \cdot dT}{T} + \frac{\Delta H_{melt}}{T_{melt}} + \int_{T_{melt}}^{T_{ev}} \frac{c_{p(liq)} \cdot dT}{T} + \frac{\Delta H_{ev}}{T_{ev}} + \int_{T_{ev}}^T \frac{c_{p(g)} \cdot dT}{T}, \quad (1.15)$$

where changes in entropy in the isothermal process: $\Delta S = \frac{\Delta H}{T}$ under $p = \text{const.}$

Phase transitions (melting, boiling ...) proceed at a constant temperature. For them, the entropy change:

$$\Delta S_{ph.t.} = \frac{\Delta H_{ph.t.}}{T_{ph.t.}}, \quad (1.16)$$

where $\Delta H_{ph.t.}$ the molar heat of the phase transition; the amount of heat necessary to transfer the mole of matter from one phase to another at a constant temperature $T_{ph.t.}$ (for example, the heat of fusion, the heat of evaporation).

Example. Calculate the change in entropy upon transition to mercury vapor at boiling point. Heat of evaporation at boiling point ($T_{boil} = 629,7\text{K}$) $\Delta H = 58,1 \text{ kJ/mol.}$

Solution. Since: $dS = \frac{dQ_{rev}}{T} = \frac{C_p dT}{T}$, then the change in entropy:

$$\Delta S_T = \Delta S_{298} + \int_{298}^T \frac{\Delta C_p dT}{T}. \quad (1.17)$$

When calculating in a small temperature range, it can be assumed that the heat capacity does not depend on temperature, then the integration of equation (1.15) gives:

$$S_{T_2} = S_{T_1} + c_p \cdot \ln \frac{T_2}{T_1} \quad \text{или} \quad \Delta S = c_p \cdot \ln \frac{T_2}{T_1}. \quad (1.18)$$

Example. Calculate the entropy of benzene at 328K.

Solution. By reference tables we find for liquid benzene: $S_{298}^0 = 173,2 \text{ J/mol}\cdot\text{K}$; $c_{p,298}^0 = 59,50 \text{ J/mol}\cdot\text{K}$.

By the equation (1.15a), we calculate the entropy of benzene at $T = 328 \text{ K}$: $S_{328} = 173,2 + 59,50 \cdot \ln(328/298) = 186,25 \text{ J/mol}\cdot\text{K}$.

When calculating over a wide temperature range, it is necessary to take into account the dependence of the heat capacity on temperature:

$$\begin{aligned} S_{T_2} &= S_{T_1} + \int_{T_1}^{T_2} (a + bT + cT^2 + c' \cdot T^{-2}) \frac{dT}{T} = \\ &= S_{T_1} + a \cdot \ln \frac{T_2}{T_1} + b(T_2 - T_1) + \frac{c}{2}(T_2^2 - T_1^2) - \frac{c'}{2}(T_2^{-2} - T_1^{-2}). \end{aligned} \quad (1.19)$$

Example. Calculate entropy of mole of zinc at 600K

Solution. According to the tables of thermodynamic quantities, we find for zinc:

$$S^0 = 41,59 \text{ J/mol}\cdot\text{K}; a = 22,38; b = 10,04 \cdot 10^{-3}; c' \cdot 10^5 = 0.$$

$$S_{600} = 41,59 + 22,38 \cdot \ln \frac{600}{298} + 10,04 \cdot 10^{-3} \cdot (600 - 298) = 60,29 \frac{\text{J}}{\text{mol}\cdot\text{K}}.$$

The change in entropy during the course of a chemical reaction under standard conditions can be calculated by the usual method, using the value of the standard entropies given in the handbook:

$$\Delta S_{298}^0 = \sum \nu_i \cdot S_{298}^0)^{prod} - \sum \nu_i \cdot S_{298}^0)^{init}. \quad (1.20)$$

Example. Calculate the change in entropy upon flow under standard reaction conditions $\text{CaO}_{(cr)} + \text{SO}_{3(g)} = \text{CaSO}_{4(cr)}$.

Solution. From the tables of thermodynamic quantities we find the entropy:

$$\Delta S_{\text{CaO}}^0 = 39,7 \text{ J/mol}\cdot\text{K}; \Delta S_{\text{SO}_3}^0 = 256,2 \text{ J/mol}\cdot\text{K}; \Delta S_{\text{CaSO}_4}^0 = 106,7 \text{ J/mol}\cdot\text{K}.$$

$$\Delta S_{\text{react}}^0 = 106,7 - (39,7 + 256,2) = -189,2 \text{ J/mol}\cdot\text{K}.$$

The entropy of a system is greater the smaller its ordering. Therefore, reactions that occur with the formation of gases or with the increase in the number of their moles are usually accompanied by an increase in entropy (the final state is less ordered than in the initial state) and vice versa. Thus, in the reaction from the example, the final state is more orderly than the initial state, and the entropy decreases ($\Delta S < 0$).

Calculating the change in entropy during the course of the chemical reaction with a change in temperature, it is necessary to take into account the dependence of the change in heat capacity on the temperature of this

reaction $\int_{298}^T \frac{\Delta C_p dT}{T}$.

Taking into account the above mentioned condition, the dependence of ΔS on T can be expressed by the equation

$$\Delta S_T = \Delta S^0 + \int_{298}^T \frac{\Delta C_p dT}{T}. \quad (1.21)$$

In a small temperature range, the heat capacities of the reagents can be considered constant, then

$$\Delta S_T = \Delta S^0 + \Delta c_p \cdot \ln T_2 / T_1. \quad (1.22)$$

If, however, an exact calculation of the entropy change is made with taking into account the heat capacity versus temperature, then the equation takes the form

$$\Delta S_T = \Delta S^0 + \frac{\Delta a \ln T}{298} + \Delta b(T - 298) + \frac{1}{2} \Delta c(T^2 - 298^2) - \frac{1}{2} \Delta c'(T^{-2} - 298^{-2}). \quad (1.23)$$

1.3. Thermodynamic potentials

To determine the state of equilibrium and the direction of the spontaneous process in a non-isolated system, D.U. Gibbs introduced a new state function (for isochoric processes, the Helmholtz function ΔF , and for the isobaric processes the Gibbs function ΔG) or the so-called normal affinity.

In accordance with the first law of thermodynamics, $dA = dQ - dU$; substituting into this equation the value $dQ = TdS$ according to the second law of thermodynamics, we obtain $dA = TdS - dU$.

Integrating this expression at constant volume and temperature, we obtain the value of the maximum work (for a reversible process):

$$A_{max} = A_V = T \cdot (S_2 - S_1) - (U_2 - U_1). \quad (1.24)$$

Transforming this equation, the work accomplished by the system as a result of the process can be represented as a difference of two functions:

$$A_{max} = - [(U_2 - TS_2) - (U_1 - TS_1)]. \quad (1.25)$$

We introduce the notation:

$$F = U - TS. \quad (1.26)$$

The function F is called isochorically isothermal (abbreviated – isochoric) potential. Then the work done by the system can be represented as a difference

$$A_{max} = - (F_2 - F_1) = - \Delta F. \quad (1.27)$$

If we consider the process taking place at a constant temperature and pressure, then its useful work will be less by the magnitude of the mechanical work of the expansion $p(V_2 - V_1)$:

$$A'_{max} = A'_p = A_V - p(V_2 - V_1) = (F_2 - pV_2) - (F_1 - pV_1) \quad (1.28)$$

We introduce the notation:

$$G = F + pV. \quad (1.29)$$

The function G is called the isobaric-isothermal potential (abbreviated to isobaric). It's obvious that

$$A'_{max} = G_2 - G_1 = - \Delta G, \quad (1.30)$$

that is, the maximum useful work of the isothermal process is equal to the reduction of the isobaric potential.

Substituting in the identity (1.29) the value $F = U - TS$, we obtain one more expression for the isobar potential:

$$G = F + pV = U - TS + pV = H - TS. \quad (1.31)$$

We write the relations (1.23) and (1.28) in the following form

$$U = F + TS \quad (1.32)$$

$$H = G + TS. \quad (1.33)$$

It follows from Eqs. (1.32) and (1.33) that neither the internal energy of the system (at $V = \text{const}$) nor the enthalpy (at $p = \text{const}$) can completely go into the work. In order to clarify the characteristics of the isochoric and isobaric potentials, we find the total differentials of these functions: $dF = dU - TdS - SdT$; $dG = (dU - TdS - SdT) + pdV + Vdp$. For the general case of reversible and irreversible processes it follows that $dU \leq TdS - pdV$. By substituting this value dU in the expression for the total differentials of the isochoric and isobaric potentials, we obtain:

$$dF \leq -SdT - pdV; dG \leq -SdT + Vdp.$$

From these relations follows:

–at a constant temperature and volume ($dT = 0, dv = 0$) $dF \leq 0$;

–at constant temperature and pressure ($dT = 0, dp = 0$) $dG \leq 0$.

The total differential of the Gibbs function has the form

$$dG \leq -SdT + Vdp, \quad (1.34)$$

therefore, when $p, T = \text{const}$, $dp = 0, dT = 0$ and $dG = 0$ for a reversible process; $dG < 0$ for an irreversible process. That is, the spontaneous flow of the isobaric process reduces the Gibbs function.

Thus, the criterion for the direction of the isothermal processes is the change in the corresponding potential: spontaneous isochoric-isothermal processes go in the direction of reducing the isochoric potential to an equilibrium state corresponding to the minimum value F for the given system (the equilibrium condition $dF = 0$), spontaneous

isobaric-isothermal processes go in the direction of reducing the isobaric potential to an equilibrium state corresponding to the minimum value of G (at equilibrium, $dG = 0$).

Characteristic functions are those functions of the state of the system by which all the thermodynamic characteristics of the system can be expressed in explicit form. The characteristic functions are the internal energy (U), the enthalpy (H), the entropy (S), the Helmholtz energy ($F = U - TS$), the Gibbs energy ($G = H - TS = F + pV$). The peculiarity of the characteristic functions is that they possess the characteristic property only for a certain choice of independent variables. For the Helmholtz energy, such variables are V, T , for the Gibbs energy – T, p . The Helmholtz energy and the Gibbs energy are thermodynamic potentials, i.e. such functions of a state whose loss in the reversible transition from state (1) to state (2) with two constant parameters (their natural variables) is equal to the useful work of the reversible process (maximum useful work, i.e. does not include the work of expansion).

The use of G and F as characteristic functions is explained by the fact that in chemical practice the reactions proceed either at constant pressure or at a constant volume, and, in turn, more often chemical reactions take place at constant pressure, rather than volume. Therefore, further reasoning will be carried out for isobaric processes, taking into account that this reasoning fully applies to isochoric processes.

The change in the free energy of Gibbs during the formation of a chemical compound from simple substances is called *the isobaric potential for the formation* of this compound;

Under standard conditions, the isobaric potential is denoted by ΔG_{298}^0 . Comparison of the ΔG^0 values of the formation of individual chemical compounds can provide extremely valuable information. From two identical compounds, the more stable is the one which has smaller

ΔG^0 . The stability of HCl is much higher than HI's; therefore, for HCl $\Delta G^0 = -95,5$ kJ/mol; and for HI $\Delta G^0 = -1,8$ kJ/mol.

Example. Calculate the standard isobaric potential of quartz formation.

Solution. We find the heat energy of quartz formation and entropy of all substances participating in the quartz formation reaction in the reference book ($\text{Si} + \text{O}_2 = \text{SiO}_2$), to calculate the ΔS of this reaction. Then, using equation (1.31)

$$\begin{aligned} \Delta G_{\text{SiO}_2}^0 &= \Delta H_{\text{SiO}_2}^0 - 298 \left[S_{\text{SiO}_2}^0 - (S_{\text{Si}}^0 + S_{\text{O}_2}^0) \right] = -859,3 \cdot 10^3 - 298 \cdot [42,1 - (18,7 + 205,0)] = \\ &= -805,2 \frac{\text{kJ}}{\text{mol}}. \end{aligned}$$

1.4. The Gibbs–Helmholtz equation

Using the equation $G = H - TS$, $F = U - TS$ and replacing S through partial derivatives of G or F with the temperature (1.29), (1.30), we obtain

$$F = U + T \left(\frac{\partial F}{\partial T} \right)_V, \quad G = H + T \left(\frac{\partial G}{\partial T} \right)_p. \quad (1.35)$$

Let the system transform from condition 1 to condition 2 for constant p and T . Then one can write:

$$\Delta G = \Delta H + T \left(\frac{\partial \Delta G}{\partial T} \right)_p. \quad (1.36)$$

Similarly, for a process with constant V and T , one can obtain:

$$\Delta F = \Delta U + T \left(\frac{\partial \Delta F}{\partial T} \right)_V. \quad (1.37)$$

The derived equations (1.36), and (1.37), which connect the isothermal potential with its temperature changing, are called the Gibbs–Helmholtz equations.

Analysis of the equation $\Delta G = \Delta H - T\Delta S$ leads to the following conclusions:

a) at very low temperatures, $T\Delta S \rightarrow 0$, and the direction of the process is determined by the sign ΔH ; only exothermic reactions ($\Delta H < 0$ and $\Delta G < 0$) will occur spontaneously;

b) as the temperature increases, the value of the $T\Delta S$ element increases; therefore, the growth of temperature especially facilitates which pass with entropy increasing; for example, when the $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ reaction proceeds, the entropy increases, since the final state is less orderly than the initial one, and the temperature increase the reaction ($T\Delta S$ increases and ΔG decreases);

c) but since the sign of ΔG is determined not only by the sign of the entropy change, but also by the sign of the thermal effect (ΔH), then the influence of both parameters must be taken into account when answering the question about the temperature effect on the reaction direction.

Let's consider various variants:

Variants	Sign ΔH	Sign ΔS	Sign ΔG
1	—	—	— +
2	—	+	—
3	+	+	+ —
4	+	—	+

An analysis of the data presented shows that the effect of T for different reactions is different. There are reactions (variants 1.3) for which an increase in temperature can even change the direction of the reaction. A schematic graphic interpretation of the data is presented in Fig.1.2 (a – d):

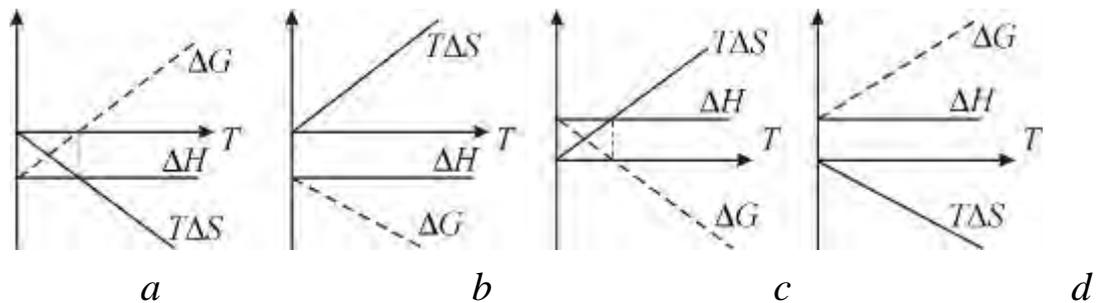


Fig.1.2. The sign ΔG dependence on the signs ΔH and ΔS

The change in the isobaric-isothermal potential in the chemical process is calculated by the same principles as the change in other thermodynamic characteristics.

$$\Delta G_{react}^0 = \sum (n_i \Delta G_i^0)^{prod} - \sum (n_i \Delta G_i^0)^{init}. \quad (1.38)$$

If there is no reference data on the isobaric potentials of the compounds formation, they can be calculated from the Gibbs-Helmholtz equation if the thermal effect of the reaction ΔH_{react}^0 and the entropy change ΔS_{react}^0 are known.

The calculation of ΔG_{react}^0 results in extremely valuable information for characterizing the chemical process. If the calculation leads to $\Delta G_{react}^0 < 0$, this means that there action goes in the forward direction; if $\Delta G_{react}^0 > 0$, then the direct process under the given conditions is unlikely, and the reverse process is probable; and finally, $\Delta G_{react}^0 = 0$ means that an equilibrium has been established between the initial components and reaction products.

Example. Calculate the variation of isobaric potential under standard conditions for the reaction $\text{MgO} + \text{CO}_2 = \text{MgCO}_3$.

Solution. We find the isobaric potentials of the formation for all the reaction participants in the reference book.

$$\Delta G_{\text{MgO}}^0 = -5669,4 \frac{\text{kJ}}{\text{mol}}; \Delta G_{\text{CO}_2}^0 = -394,4 \frac{\text{kJ}}{\text{mol}}; \Delta G_{\text{MgCO}_3}^0 = -1029,4 \frac{\text{kJ}}{\text{mol}}.$$

$$\Delta G_{react}^0 = -1029,4 - (-569,4 - 394,4) = -65,6 \frac{\text{kJ}}{\text{mol}}.$$

Example. Calculate ΔG^0 for the reaction $\text{CO} + \text{Cl}_2 = \text{COCl}_2 (g)$

Solution. The value of the isobar potential of COCl_2 is absent in the reference book, therefore we write out from the reference book the heats of formation and entropy of all participants in the reaction:

Table 1.2 – Reference data

Reactants	ΔH_{298}^0 kJ/mol	ΔS_{298}^0 J/mol·K
CO	-110,5	197,4
Cl ₂	0	223,0
COCl ₂	-223,0	289,2

Calculate:

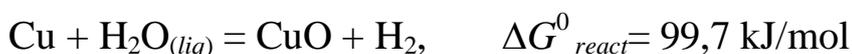
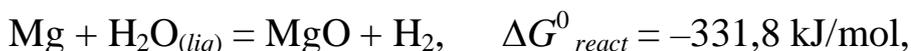
$$\Delta H_{react}^0 = -223,0 - (-110,5) = -112,5 \text{ kJ/mol};$$

$$\Delta S_{react}^0 = 289,2 - (197,4 + 223,0) = -131,2 \text{ J/mol}\cdot\text{K};$$

$$\Delta G_{react}^0 = -112,5 - 298 \cdot (-131,2) \cdot 10^{-3} = -73,4 \text{ kJ/mol}.$$

Calculation ΔG_{react}^0 enables a thermodynamic interpretation of chemical processes, the features of many of which had to be taken "on faith" in the courses of inorganic, organic and analytical chemistry.

Let us consider some examples.



Comparison of the values of ΔG^0 for the reactions shows that these reactions in the forward direction will go only in the case of magnesium and zinc, and the reaction with magnesium will go more intensively. Copper (as is well known) will not displace hydrogen from the water, and the reverse process is possible only for copper (ΔG_{react}^0 reverse process <0);

The change in normal affinity at temperature T (ΔG_T) is calculated by equation

$$\Delta G_T = \Delta H_T - T\Delta S_T. \quad (1.39)$$

Substituting the value of ΔH_T^0 from the equation of the dependence of the thermal effect on temperature (1.11) and the value of ΔS_T^0 from the equation of entropy dependence on temperature (1.8), we obtain expression

$$\Delta G_T^0 = \Delta H_{298}^0 - T\Delta S_{298}^0 + \int_{298}^T \Delta C_p dT - T \int_{298}^T \frac{\Delta C_p dT}{T}, \quad (1.40)$$

with the help of which, knowing $\Delta H_{298}^0, \Delta S_{298}^0$ and ΔC_p of the process (determined from the tables of thermodynamic quantities), it is possible to calculate ΔG_T^0 at any temperature. For approximate calculations, we can take ΔC as constant, then

$$\Delta G_T^0 = \Delta H_{298}^0 - T\Delta S_{298}^0 + \Delta C_p(T - 298) - T\Delta C_p \ln \frac{T}{298}. \quad (1.41)$$

During accurate calculations, the dependence on temperature must be taken into account; the solution of the integrals is given below

$$\begin{aligned} \Delta G_T^0 = & \Delta H_{298}^0 - T\Delta S_{298}^0 + \Delta a \cdot (T - 298) + \frac{\Delta b}{2} \cdot (T^2 - 298^2) + \\ & + \frac{\Delta c}{3} \cdot (T^3 - 298^3) - \Delta c' \cdot (T^{-1} - 298^{-1}) - T \cdot \Delta a \cdot \ln \frac{T}{298} - \\ & - T\Delta b (T - 298) - T \frac{\Delta c}{2} (T^2 - 298^2) + T \frac{\Delta c'}{2} (T^{-2} - 298^{-2}). \end{aligned} \quad (1.42)$$

Example. Calculate ΔG_T^0 at temperatures of 298, 500, 1000 and 1500K for the reaction $1/2 \text{ N}_2 + 1/2 \text{ O}_2 = \text{NO} (\text{g})$. Assume that ΔC_p is constant (independent of temperature).

Solution. We find the reference to the heat of formation ΔH_{298}^0 , the entropy S_{298}^0 and the heat capacity $C_{p,298}$ of all participants in the reaction:

Table 1.3 – Reference data

Reactants	ΔH_{298}^0 , kJ/mol	ΔS_{298}^0 , J/mol·K	$\Delta C_{p,298}$, J/mol·K
N ₂	0	191,5	29,10
O ₂	0	205,0	29,36
NO	90,37	210,6	29,83

We calculate for the reaction

$$\Delta H_{298}^0 = 90,37 \text{ kJ/mol};$$

$$\Delta S_{298}^0 = 210,6 - (0,5 \cdot 191,5 + 0,5205) = 12,3 \text{ J/mol}\cdot\text{K};$$

$$\Delta C_{p,298} = 29,83 - (0,5 \cdot 29,83 - 0,5 \cdot 29,36) = 0,60 \text{ J/mol}\cdot\text{K}.$$

Then, using equation (1.41)

$$\Delta G_T^0 = 90370 - T \cdot 12,3 + 0,6 \cdot (T - 298) + T \cdot 0,6 \cdot \ln \frac{T}{298} \text{ (J/mol)}.$$

Substituting the given temperatures into the expression obtained, we find:

Table 1.4 – Calculation results

T	298	500	1000	1500
ΔG_T^0 , kJ/mol	+86,7	+84,2	+77,8	+71,2

Example. Calculate ΔG_T^0 at the temperatures of 298, 500, 800, and 1000 K for the reaction $\text{Hg} (g) + 1/2 \text{O}_2 = \text{HgO} (cr)$.

Solution. Similarly to the previous one, we find:

$$\Delta H_{298}^0 = -151,2 \text{ kJ/mol}; \Delta S_{298}^0 = -204,2 \text{ J/mol}\cdot\text{K};$$

$$c_{p,298, 298} = 10,3 \text{ J/mol}\cdot\text{K}.$$

$$\text{Hence, } \Delta G_T^0 = -151200 + 204,2T + 10,3 (T-298) - 10,3T \ln (T/298).$$

From this equation we obtain the values of ΔG_T^0 for the given temperatures:

Table 1.5 – Calculation results

T	298	500	800
ΔG_T^0 , kJ/mol	-90,4	-49,7	+9,2

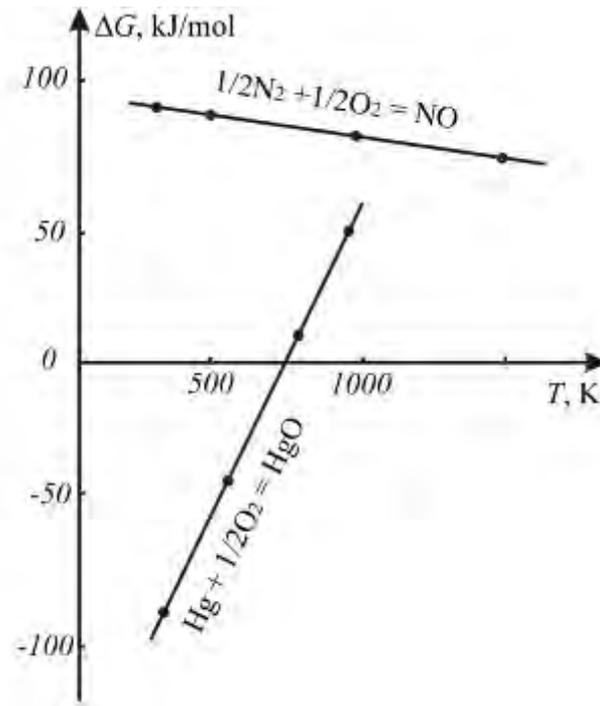


Fig.1.3. Temperature dependence on the ΔG_T^0 reaction.

The construction of the temperature dependence of the ΔG_T chemical reaction allows us to establish the optimum conditions for carrying out the process. In the picture, these dependences are plotted for the reactions of nitrogen and mercury oxidation. Their analysis shows that the formation of NO in the entire investigated temperature range is impossible; the formation of mercury oxide occurs better at low temperatures and at $T > 770K$ the reverse process of mercury oxide decomposition into mercury and oxygen occurs.

1.5. Chemical potentials

In processes in which the number of substances constituting the system is constant, the change in the internal energy of the system is a consequence of the transfer of heat and the performance of work.

For chemistry, the most interesting cases are when the amount of substances changes. The chemical reaction can be considered as the addition of reaction products to the system and removal of the initial

substances expressed in moles (n_i). Therefore, you must enter a parameter that takes into account the change in the composition of the system. Such a parameter is a quantity called the **chemical potential (μ)** and takes into account the change in the Gibbs function (G) with the addition of 1 mole of the i component to the system 1, with constant T, p and the number of moles of all other components:

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{P, T, n_1, n_2, \dots, n_{i-1}} \quad (1.43)$$

On the basis of what has been said, the combined equation of the first and second principles of thermodynamics for equilibrium processes must be supplemented by the term $\sum \mu_i dn_i$:

$$dG = -SdT + Vdp + \sum \mu_i dn_i \quad (1.44)$$

Analyzing the equation, we can see that μ_i is like a potential for chemical energy, just as pressure is in these equations the potential of mechanical energy, and temperature is the potential of thermal energy. It is known that when two systems are brought into contact, their potentials are equalized. So, the pressure is equalized by changing the volumes the temperature is due to a change in the entropies.

By analogy, one can say that the μ_i for each component should be equated by changing the amount of this component in the systems.

Thus, the chemical potential of the i component of the system is equal to the derivative of the Gibbs energy of the system with respect to the number of moles of the i component with constant P, T , the number of remaining components. For $p, T = \text{const}$

$$dG = \sum \mu_i dn_i \quad (1.45)$$

Integrating this equation by mass with a constant composition, we obtain

$$G = \sum \mu_i n_i \quad (1.46)$$

The integration constant is zero, since if all n are zero, the Gibbs energy is also zero. The expression (1.42) for an individual substance passes into

$$\mu = G/n, \quad (1.47)$$

so, the chemical potential of the individual substance is equal to the Gibbs molar energy.

The chemical potential of an ideal gas

It follows from (1.43) that for a constant temperature $dG = Vdp$, therefore, $d\mu = Vdp$ and for an ideal gas

$$d\mu = \frac{RT}{p} dp = RT d \ln p, \quad (1.48)$$

from which it follows that

$$\mu_i = \mu_i^*(T) + RT \ln p_i, \quad (1.49)$$

where μ^* is the integration constant. In the tables, all standard thermodynamic quantities were calculated at $T = 298\text{K}$ and $p^0 = 1 \text{ atm}$. Substituting $p^0 = 1 \text{ atm}$ into equation (1.49), we obtain, that is, in this system of units is the standard chemical potential.

In the system of SI units, $p^0 = 1,013 \cdot 10^5 \text{ Pa}$ and

$$\mu_i^0 = \mu_i^*(T) + RT \ln p_i^0. \quad (1.50)$$

Subtracting equation (1.46) from equation (1.45), we find

$$\mu_i - \mu_i^0 = \mu_i^* - \mu_i^* + RT \ln p_i / p^0 = RT \ln \tilde{p}_i, \quad (1.51)$$

where $\tilde{p}_i = \frac{p_i}{p^0}$ is the relative partial pressure. If the system pressure is expressed in atm, then $\tilde{p}_i = p_i$, if p is expressed in Pa, then $\tilde{p}_i = p/1,013 \cdot 10^5$, that is \tilde{p}_i – a dimensionless quantity. Thus, in the general case

$$\mu_i = \mu_i^0(T) + RT \ln \tilde{p}_i \quad (1.52)$$

If the partial pressure is expressed in atmospheres, then the equation takes the form

$$\mu_i = \mu_i^0(T) + RT \ln p_i \quad (1.53)$$

This formula relates the chemical potential in mixture with the chemical potential of the pure component and the partial pressure of this component in the mixture.

Since $p_i = p_{tot} \cdot N_i$, where p_{tot} is the total pressure in the mixture, N_i is the mole fraction of the component ($N_i = n_i / \sum n_i$), then

$$\mu_i = \mu_i^0(T) + RT \ln p_{tot} + RT \ln N_i = \mu_i^0(p, T) + RT \ln N_i \quad (1.54)$$

In Eq. (1.54), the standard chemical potential is a function not only of temperature but also of pressure.

To describe the processes taking place in real gases, we use the method proposed by Lewis. He proposed to keep for the real systems the same kind of thermodynamic equations as for the ideal ones, replacing in them some variables (pressure, concentration) with other variables. Instead of the partial pressure p_i in thermodynamic equations for real systems, he introduces a new variable f_i – fugacity, which has the dimension of pressure. At low pressures, when the properties of a real gas system approach the properties of ideal gases, the fugacity becomes equal to the partial pressure p_i of the component. The coefficient of fugacity

$\gamma_i = \frac{f_i}{p_i}$ is a dimensionless quantity. At low pressures $(f_i/p_i) = 1$, and hence

$$(\gamma_i)_{p \rightarrow 0} = 1.$$

According to Lewis equation for the chemical potential of the real gas of the i -th component for a real gas mixture is written in the form

$$\mu_i = \mu_i^0 + RT \ln p_i + RT \ln \gamma_i = \mu_i^0 + RT \ln f_i \quad (1.55)$$

When describing the properties of real solutions instead of concentration, expressed in molar fractions, a new variable, activity, is substituted. Then equation (1.55) takes the form

$$\mu_i = \mu_i^0 + RT \ln c_i + RT \ln \gamma_i = \mu_i^0 + RT \ln a_i. \quad (1.56)$$

In this case, the more diluted the solution, the more the system is closer to the ideal in its properties, that is, with $c \rightarrow 0$ $\gamma \rightarrow 1$, and the activity becomes equal to the concentration.

If the system is in a state of equilibrium, then the equilibrium condition, taking into account a possible change in the composition of the system, is

$$dG = -SdT + Vdp + \sum \mu_i dn_i = 0.$$

At constant temperature and pressure this condition is expressed as

$$\sum \mu_i dn_i = 0. \quad (1.57)$$

We derive an important correlation between the chemical potentials of a component that forms part of several phases of a heterogeneous system. Consider a two-phase system with p , $T = \text{const}$, in which one component passes from one phase to another. The transition of the dn_i moles of the component from phase (1) to phase (2) at equilibrium and constant pressure and temperature causes a change in the isobaric potential dG of the system, which consists of changes in the isobaric potentials dG' and dG'' of both phases:

$$dG = dG' + dG'' = \mu'_i dn'_i + \mu''_i dn''_i, \text{ because } dn''_i = -dn'_i$$

(how much matter has left from one phase, as much has come to another phase), and under the condition of equilibrium $dG = 0$, then

$$\mu'_i dn'_i + \mu''_i dn''_i = dn''_i (\mu'_i - \mu''_i) = 0$$

$$(\mu'_i - \mu''_i) = 0; \text{ whence } \mu'_i = \mu''_i.$$

Obviously, this conclusion can be extended to all other phases. Thus, the chemical potentials of a given component in all phases of a system in equilibrium are equal to each other.

In the absence of equilibrium, we have $dG = (\mu'_i - \mu''_i) dn'_i < 0$. It follows that if $\mu'_i - \mu''_i > 0$ ($\mu'_i > \mu''_i$), then $dn'_i < 0$, if $\mu'_i - \mu''_i < 0$ ($\mu''_i > \mu'_i$), then $dn'_i > 0$, that is, the component passes from the second phase to the

first if its chemical potential in this phase is greater than in first; if the chemical potential of the component in the second phase is less than in the first phase, the component will pass from the first phase to the second phase. Thus, the component spontaneously passes from a phase in which its chemical potential is greater, to a phase in which its chemical potential is less. The transition will continue until the chemical potentials of this component in both phases are equal.

Chapter 2. CHEMICAL EQUILIBRIUM

For chemistry in general and for chemical technology, in particular, it is extremely important to determine the conditions for the system to reach equilibrium and, most importantly, to determine the conditions under which equilibrium is shifted in such a way that the yield of the reaction product of interest to us is maximized. That is why the section of chemical thermodynamics dealing with the study of chemical equilibrium, sometimes called chemical static, refers to the most important sections of physical chemistry. In this section, we will become acquainted with general provisions relating to chemical equilibrium.

2.1. The law of mass action

Kinetic derivation of the law of acting masses (LAM). According to LAM, the reaction rate is proportional to the concentrations of the components in degrees equal to their stoichiometric coefficients. If there is a reversible process in the system: $aA + bB \leftrightarrow eE + fF$, then the rate of the direct reaction at the moment of equilibrium becomes equal to the rate of the reverse reaction. The rate of the direct reaction in accordance with the LAM:

$$w_1 = k_1 c_A^a c_B^b, \quad (2.1)$$

In turn, the rate of the reverse reaction can be expressed by the following expression:

$$w_2 = k_2 c_E^e c_F^f, \quad (2.2)$$

where k_1 and k_2 are the coefficients of proportionality, called the rate constants of reactions).

The state of equilibrium does not mean the termination of direct and reverse reactions, but only the equalization of their velocities, i.e. $w_1 = w_2$ or $k_1 c_A^a c_B^b = k_2 c_E^e c_F^f$, whence

$$\frac{c_E^e c_F^f}{c_A^a c_B^b} = \frac{k_1}{k_2} = K_c. \quad (2.3)$$

As follows from (2.3), K_c is a constant, called the equilibrium constant of the process, the index "c" for a constant means that the content of the components in the reaction mixture at the moment of equilibrium is expressed in terms of the concentration of the participants in the reactions. Equations (2.1 – 2.3) express the law of mass action. **Since the equilibrium constant expresses the ratio of the product of the equilibrium concentrations of the reaction products to the product of the equilibrium concentrations of the initial substances, the magnitude of the equilibrium constant itself characterizes the ratio of the reaction products to the starting materials, that is, characterizes the degree of reaction to the formation of the products.** Consequently, the equilibrium constant is one of the most important characteristics of the reaction. **To increase the yield of reaction products, it is necessary to increase the equilibrium constant of this reaction.**

The law of mass action can also be derived thermodynamically. Let in the chemical system where the reaction takes place, all participants of which are gases, in equilibrium conditions from a mole A and b moles B e moles E and f of moles F. Then, in accordance with equation (1.41), we obtain

$$dG = \sum \mu_i dn_i = e\mu_E + f\mu_F - a\mu_A - b\mu_B = 0. \quad (2.4)$$

Substituting in (1.48a) the values of μ from (1.39) and grouping the homogeneous terms, we find

$$(e\mu_E^0 + f\mu_F^0 - a\mu_A^0 - b\mu_B^0) + RT(e \ln p_E^0 + f \ln p_F^0 - a \ln p_A^0 - b \ln p_B^0) = 0 \quad (2.5)$$

or

$$\ln \frac{p_E^e p_F^f}{p_A^a p_B^b} = -\frac{1}{RT} (e\mu_E^0 + f\mu_F^0 - a\mu_A^0 - b\mu_B^0). \quad (2.6)$$

If we assume that the chemical reaction passes at a constant temperature, then the right-hand side of the equation is a constant value and, consequently, the left-hand side is also constant:

$$\frac{p_E^e p_F^f}{p_A^a p_B^b} = K_p, \quad (2.7)$$

where K_p is the equilibrium constant. This value does not depend on the pressure in the system, since ΔG_i^0 and μ_i^0 depend only on the temperature.

We give various expressions for the chemical potential considered in the previous section. Each of them corresponds to the "own" expression for the equilibrium constant:

$$\mu_i = \mu_i^0(T) + RT \ln p \quad K_p = \frac{p_E^e p_F^f}{p_A^a p_B^b}; \quad (2.8)$$

$$\mu_i = \mu_i^0(T) + RT \ln \tilde{p}_i; \quad K^0 = \frac{\tilde{p}_E^e \tilde{p}_F^f}{\tilde{p}_A^a \tilde{p}_B^b}; \quad (2.9)$$

$$\mu_i = \mu_i^0(T) + RT \ln c_i; \quad K_c = \frac{c_E^e \cdot c_F^f}{c_A^a \cdot c_B^b}; \quad (2.10)$$

$$\mu_i = \mu_i^0(P, T) + RT \ln N_i; \quad K_N = \frac{N_E^e \cdot N_F^f}{N_A^a \cdot N_B^b}. \quad (2.11)$$

The constants are related by simple correlations. Let us determine how the K_p and K_c constants are related. It follows from the Mendeleev-Clapeyron equation that $p = n/V \cdot RT = c \cdot RT$, where $n/V = c$ is the molar concentration. Let us express the equilibrium constant K_p of the of the equilibrium constant K_c , with allowance for the relation found:

$$K_p = \frac{c_E^e (RT)^e c_F^f (RT)^f}{c_A^a (RT)^a c_B^b (RT)^b} = K_c (RT)^{e+f-a-b}$$

or

$$K_p = K_c(RT)^{\Delta n}, \quad (2.12)$$

where Δn is the change in the number of moles of gaseous substances in the reaction.

The correlation between K_p and K_N is easily obtained by expressing the partial pressures of the participants in the reaction (p_i) through their mole fractions (N_i). Since, according to Dalton's law, $p_i = p_{gen} \cdot N_i$,

$$K_p = K_N p^{-\Delta n}. \quad (2.13)$$

The connection between K^0 is derived from the relation, from which

$$K^0 = K_p \cdot (p^0)^{-\Delta n}. \quad (2.14)$$

Obviously, if the number of moles as a result of the reaction does not change, then $K_p = K_c = K_N = K^0$.

The dimension of K_p is $(\text{atm})^{\Delta n}$ or $(\text{N/m}^2)^{\Delta n}$; dimensionality of K_c is $(\text{mol/l})^{\Delta n}$ or $(\text{mol/m}^3)^{\Delta n}$, K_N and K^0 are dimensionless quantities. If $\Delta n = 0$, then, obviously, any equilibrium constant is dimensionless. It should be specially emphasized that if the equilibrium constant has a dimension, then its numerical value also depends on the stoichiometric coefficients of the chemical equation it relates to. Thus, for the process of synthesis of ammonia from elements written as

$$3\text{H}_2 + \text{N}_2 = 2\text{NH}_3, \quad K_p = \frac{p_{\text{NH}_3}^2}{p_{\text{H}_2}^3 p_{\text{N}_2}}, \text{ but for the same process written as}$$

$$3/2\text{H}_2 + 1/2\text{N}_2 = \text{NH}_3, \quad K'_p = \frac{p_{\text{NH}_3}}{p_{\text{H}_2}^{3/2} p_{\text{N}_2}^{1/2}}, \text{ and it is not difficult to see that}$$

$$K'_p = \sqrt{K_p}$$

Therefore, giving the value of the equilibrium constant, it is necessary to indicate to which form the chemical reaction records it refers.

Example. At 298 K, the reaction equilibrium constant

$$\text{C}_2\text{H}_4(\text{r.}) + \text{H}_2\text{O}(\text{r.}) = \text{C}_2\text{H}_5\text{OH}(\text{r.}), \quad K_p = 2,66 \cdot 10^{-4} (\text{atm})^{-1}. \text{ Calculate } K.$$

Solution. By the equation (2.11), $K_c = K_p(RT)^{-\Delta n}$; $\Delta n = 1 - 2 = -1$. If the calculation is carried out in the SI system, then $R = 8,31 \text{ J/mol}\cdot\text{K}$;

$$K_c = 2,66 \cdot 10^{-4} \cdot (8,31 \cdot 298)^1 = 658,72 \cdot 10^{-3} (\text{mol/m}^3) = 658,72 (\text{mol/l}).$$

To describe non-ideal systems, we use the activity method, which we mentioned above when deriving an expression for the chemical potential of real systems. According to this method, for real gases the expression for the chemical potential of the component takes the form $\mu_i = \mu_i^0(T) +$

$RT \ln f_i$, and consequently, the equilibrium constant $K_f = \frac{f_E^e f_F^f}{f_A^a f_B^b}$; a for real

solutions

$$\mu_i = \mu_i^0(T) + RT \ln a_i \text{ и } K_a = \frac{a_E^e a_F^f}{a_A^a a_B^b}.$$

In deriving the above correlations, it was assumed that all participants in the chemical reaction are gases. If the substances participate in the reaction in condensed (i.e., liquid or solid) aggregate states, then at a constant temperature the partial vapor pressures of such participants in the process do not change. In fact, if the element of the process in the steam reacted and its partial pressure decreased at some point in time, the condensed phase would again send its molecules to the vapor. Therefore, if any heterogeneous system, for example, $\text{ZnO}_{(\text{cr.})} + \text{CO}_{(\text{g})} \leftrightarrow \text{Zn}_{(\text{liq.})} + \text{CO}_2$ is in a state of equilibrium, i.e.

$K'_p = \frac{p_{\text{Zn}} \cdot p_{\text{CO}_2}}{p_{\text{ZnO}} \cdot p_{\text{CO}}}$ then, taking into account that $p_{\text{Zn}}/p_{\text{ZnO}} = 1$, The

equilibrium constant of this process should be expressed as $K_p = \frac{p_{\text{CO}_2}}{p_{\text{CO}}}$.

Thus, the expression K_p for a heterogeneous process contains the partial pressures of only the gaseous reaction participants.

2.2. The chemical isotherm equation

Let the reaction take place in a system at a constant temperature, therefore, the system is not in an equilibrium state. We denote the nonequilibrium partial pressures of the process participants through, then their chemical potentials, according to equation (1.52), will be written as $\mu_i = \mu_i^0 + RT \ln p'_i$, but ΔG will not be zero.

In accordance with (1.41)

$$\Delta G = (e\mu_E + f\mu_F - a\mu_A - b\mu_B) = (e\mu_E^0 + f\mu_F^0 - a\mu_A^0 - b\mu_B^0) + RT(e \ln p'_E + f \ln p'_F - a \ln p'_A - b \ln p'_B). \quad (2.15)$$

But according to (2.5a)

$$(e\mu_E^0 + f\mu_F^0 - a\mu_A^0 - b\mu_B^0) = -RT \ln \frac{p_E^e p_F^f}{p_A^a p_B^b} = -RT \ln K_p. \quad (2.16)$$

Consequently,

$$\Delta G = RT \left[\ln \frac{p_E^e p_F^f}{p_A^a p_B^b} - \ln K_p \right]; \quad (2.17)$$

$$\Delta F = RT \left[\ln \frac{c_E^e c_F^f}{c_A^a c_B^b} - \ln K_c \right]. \quad (2.18)$$

Denoting $\frac{p_E^e p_F^f}{p_A^a p_B^b} = \Pi(p_i^{n_i})$ и $\frac{c_E^e c_F^f}{c_A^a c_B^b} = \Pi(c_i^{n_i})$

we obtain a more compact form of the equations (2.17) and (2.18):

$$\Delta G = RT \left[\ln \Pi(p_i^{n_i}) - \ln K_p \right]; \quad (2.19)$$

$$\Delta F = RT \left[\ln \Pi(c_i^{n_i}) - \ln K_c \right]. \quad (2.20)$$

Equations (2.17 – 2.20) are called the chemical reaction isotherm equations. It is obvious that if the term including nonequilibrium pressures $\Pi(p_i^{n_i}) < K_p$, then $\Delta G < 0$, and the reaction proceeds in the direct direction; if $\Pi(p_i^{n_i}) > K_p$, then $\Delta G > 0$, the reaction proceeds in the

opposite direction; Finally, if $\Pi(p_i'^{n_i}) = K_p$, that is, $\Delta G = 0$, then the reaction does not go, because the system is in a state of equilibrium.

Thus, the equation of the chemical reaction isotherm makes it possible, by knowing the nonequilibrium partial pressures (concentrations) of participants in the chemical reaction and knowing the value of the equilibrium constant, to determine in which direction the process will go.

It is also obvious that using the isotherm equation, it is possible to select non-equilibrium pressures (or concentrations) in such a way that the system approaches the equilibrium state as much as possible or to achieve the maximum yield of reaction products.

If we take atm or mol / n in equations (2.17) or (2.18) $p'_A = p'_B = p'_E = p'_F = 1$ atm or $c'_A = c'_B = c'_E = c'_F = 1$ mol/l, we arrive at the following expressions for the standard isobaric and isochoric potentials of the chemical reaction:

$$\Delta G^0 = -RT \ln K_p, \quad (2.21)$$

$$\Delta F^0 = -RT \ln K_c. \quad (2.22)$$

Using these equations, *knowing the standard reaction potential, one can find the equilibrium constant of the reaction.*

2.3. Environmental effects on the equilibrium state

The pressure does not affect the value of the equilibrium constants K_p and K_c . Pressure can only affect the equilibrium position, and the direction of the equilibrium shift is uniquely determined by the Le Chatelier principle:

If the system, which is in equilibrium, exerts an external influence, then in the system processes occur that oppose this action.

Thus, for example, the reaction $4\text{HCl} + \text{O}_2 \leftrightarrow 2\text{H}_2\text{O}_{(\text{r.})} + 2\text{Cl}_2$ in the forward direction proceeds with a decrease in the number of moles of gas, which leads to a decrease in the pressure in the reaction vessel; so increasing the pressure will facilitate the flow of direct reaction, and a decrease in pressure will shift the equilibrium to the left. Naturally, the change in pressure will not affect the equilibrium of the reaction, the course of which is not accompanied by a change in the number of moles (for example, $\text{CO} + \text{H}_2\text{O}_{(\text{r.})} \leftrightarrow \text{CO}_2 + \text{H}_2$). Thus, **determining the influence of pressure on the equilibrium of heterogeneous processes, it is necessary to take into account only the change in the number of moles of gaseous reaction participants.**

The change in temperature affects the value of the equilibrium constant and the equilibrium position. And this influence is also determined by the Le Chatelier principle. Suppose that the direct reaction is exothermic, and the reverse reaction is endothermic. If heat is applied to the system, the system will tend to neutralize the heating: the equilibrium shifts to the left, towards the endothermic reaction, as heat is absorbed.

The Planck equation. Thus, for reactions whose participants behave like ideal gases, K_p and K_c does not depend on the pressure. However, the composition of the equilibrium mixture may depend on the pressure. When the total pressure in the equilibrium mixture changes, the partial pressures of all participants in the reaction change by an equal number of times. If the number of moles does not change in the reaction, the composition of the mixture will remain in equilibrium. If $\Delta n \neq 0$, then the composition of the mixture as a result of the change in pressure becomes non-equilibrium and a chemical reaction will take place, that is, the equilibrium will shift. An analogous result is the addition of an inert gas while maintaining a constant total pressure. In this case, the volume of the

system increases and the partial pressures of all the participants in the reaction decrease; the addition of an inert gas is equivalent to expanding the system. If the inert gas is added at a constant volume, then the total pressure does not change to a shift in equilibrium, since p_i remains unchanged.

The yield of reaction products at equilibrium is conveniently characterized by the quantity K_N : $K_N = \frac{N_E^e N_F^f}{N_A^a N_B^b}$, where N_i are the mole fractions of the reaction participants. The correlation between K_p and K_N , according to (2.12), is expressed as follows: $K_p = K_N p^{-\Delta n}$, where p is the total pressure of the gas mixture. If we take the logarithm from both sides of this expression and differentiate it by the total pressure at a constant temperature, we obtain Planck's equation expressing the dependence of the equilibrium constant (K_N) on the pressure:

$$(\partial \ln K_N / \partial p)_T = -\Delta n / p = -\Delta v / RT, \quad (2.23)$$

where Δv – change in volume as a result of the reaction.

An analysis of the Planck equation shows that the effect of pressure on the equilibrium constant is determined by the sign of the change in the number of moles of gaseous reaction participants (Δv). If $\Delta v < 0$, that is, the reaction proceeds with a decrease in the number of moles of gases, then an increase in pressure will increase the yield of reaction products, and vice versa, if $\Delta v > 0$, an increase in pressure will shift the reaction in the opposite direction. Thus, at $\Delta n > 0$, an increase in pressure leads to a decrease in K_N , that is, as the pressure increases, the equilibrium shifts toward a decrease in volume. This is another illustration of the Le Chatelier principle.

Equations of isobar and isochore of chemical reaction

We derive equations that allow us to calculate the dependence of K_p and K_c on the temperature. To this end, we differentiate (2.20) with respect to T :

$$\frac{d\Delta G}{dT} = -R\ln K_p - RT \frac{d\ln K_p}{dT}. \quad (2.24)$$

We substitute from (2.23) the expression u into the Gibbs-Helmholtz equation (1.32):

$$-RT\ln K_p = \Delta H - RT\ln K_p - RT^2 \frac{d\ln K_p}{dT},$$

whence

$$\frac{d\ln K_p}{dT} = \frac{\Delta H}{RT^2}. \quad (2.25)$$

Integrating (2.24) from T_1 to T_2 and assuming that ΔH is a constant, which is permissible in a small temperature range or with approximate calculations, we find:

$$\ln K_{p,T_2} = \ln K_{p,T_1} + \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right). \quad (2.26)$$

Equations (2.24) and (2.25) are called the isobar equations of the chemical reaction (respectively, in differential and integral form). Using equation (2.25), knowing the equilibrium constant at one temperature and the magnitude of the reaction's thermal effect, it is possible to calculate the equilibrium constant at any other temperature.

In exact calculations, we start with Eq. (2.25), substituting for it the expression (1.11) instead of ΔH , which takes into account the dependence of ΔH on the temperature, and integrating, we obtain the equation for calculating K_p :

$$\ln K_p = -\frac{\Delta H_0}{RT} \Delta H + \frac{\Delta a}{R} \ln T + \frac{\Delta b}{2R} T + \frac{\Delta c}{6R} T^2 + \frac{\Delta c'}{2R} T^{-2} + D \quad (2.27)$$

Here D is the integration constant, which is calculated from the known equilibrium constant at 298 K.

The analysis of equation (2.24) leads to the following conclusions:

- if the reaction is exothermic ($\Delta H < 0$), then $d\ln K_p/dT < 0$, i.e. with increasing temperature K_p scattering decreases and the equilibrium shifts to the left;

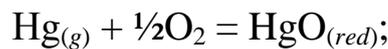
- for the endothermic reaction ($\Delta H > 0$) $d\ln K_p/dT > 0$, i.e. increasing the temperature increases K_p , and consequently, shifts the equilibrium to the right. The Le-Chatelier principle leads to the same conclusion.

For isochoric processes, it is possible to obtain analogous isochore equations for the chemical reaction.

$$\frac{d\ln K_c}{dT} = \frac{\Delta U}{RT^2}, \quad (2.28)$$

$$\ln K_{c,T_2} = \ln K_{c,T_1} + \frac{\Delta U}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right). \quad (2.29)$$

Example. Calculate K_p at 800 K for the exothermic reaction:



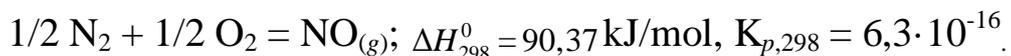
$\Delta H_{298}^0 = -151,2 \text{ kJ/mol}$; $K_{p,298} = 2,4 \cdot 10^8 \text{ (atm)}^{-1,5}$. ΔH is considered constant.

Solution. According to the equation (2.25):

$$\begin{aligned} \ln K_{p,800} &= \ln K_{p,298} + \frac{\Delta H}{R} \left(\frac{1}{298} - \frac{1}{800} \right) = 19,29 - \frac{151200(800 - 298)}{8,31 \cdot 298 \cdot 800} = \\ &= 19,29 - 38,31 = -19,02; \end{aligned}$$

$$K_{p,800} = 5,25 \cdot 10^{-9} \text{ (N/M}^2\text{)}^{-1,5}; \text{ (} K_{800} < K_{298}\text{)}.$$

Example. Calculate K_p at 800K for the endothermic reaction:



Solution.

$$\ln K_{p,800} = \ln K_{p,298} + \left(\frac{1}{298} - \frac{1}{800} \right) = -35,0 + \frac{90370(800 - 298)}{8,31 \cdot 298 \cdot 800} =$$
$$= -35,0 + 22,9 = -12,1;$$

$$K_{p,800} = 5.5 \cdot 10^{-6}; (K_{800} > K_{298}).$$

The equations (2.26) and (2.28) may be used to determine the thermal effect of a chemical reaction if the equilibrium constants at two temperatures are known. They also imply that $\ln K$ is a linear function $1/T$ (fig.2.1). It is obvious that $\text{tg}\alpha = -\Delta H / R$, and the thermal effect of the reaction may be calculated by the slope angle of the line $\ln K = f(1/T)$.

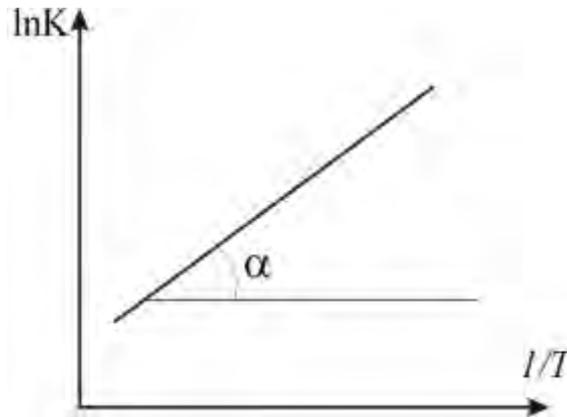


Fig. 2.1. Temperature dependence of the equilibrium constant

Example. K_p are given for the reaction $1/2N_2 + 1/2O_2 = NO(g)$:

Table 2.1 – Reference data

T	298	500	1000
K_p	$6.3 \cdot 10^{-16}$	$1.6 \cdot 10^{-9}$	$8.5 \cdot 10^{-5}$

Calculate the thermal effect of the reaction within this temperature interval.

Solution. Calculate $\ln K_p$ and $1/T$:

$$\ln K_{298} = -35,00; 1/298 = 3,35 \cdot 10^{-3}; \ln K_{500} = -20,25; 1/500 = 2 \cdot 10^{-3};$$

$$\ln K_{1000} = -9,37; 1/1000 = 1 \cdot 10^{-3}$$

Place $\ln K = f(1/T)$ on a graph (fig. 2.2). Points lie on the line:

$$\operatorname{tg}\alpha = -\frac{35,00 - 9,37}{(3,35) \cdot 10^{-3}} = 10906 \text{ (by extreme points).}$$

$$\Delta H = -R \operatorname{tg}\alpha = 8,31 \cdot 10906 = 90600 \text{ J/mol} = 90,6 \text{ kJ/mol.}$$

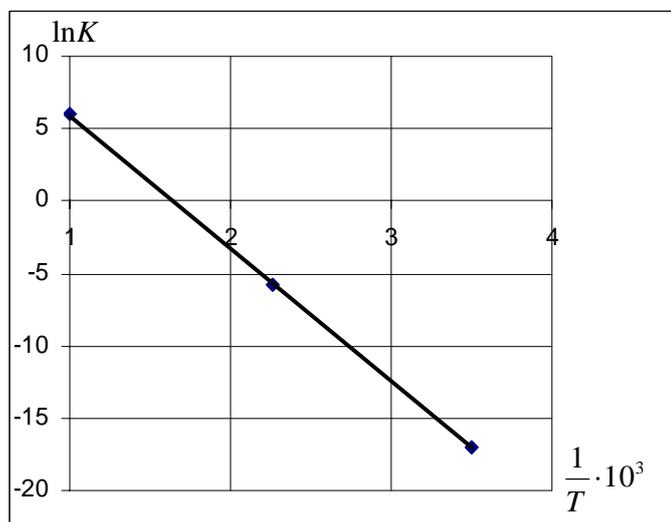


Fig.2.2. The dependence of $\ln K$ on $1/T \cdot 10^3$ for the above reaction

2.4 Determination of equilibrium constants

Calculating equilibrium constants of reactions at any temperatures without equilibrium experiments is one of the most important practical applications of chemical thermodynamics. In these calculations, total entropies are used. Calculating equilibrium constants of reactions at any temperatures is based on the two initial equations (1.39) and (2.21) for the standard Gibbs energy:

$$\Delta G_T^0 = \Delta H_T^0 - T \Delta S_T^0 \quad \text{and} \quad \Delta G_T^0 = -RT \ln K_{p,T}.$$

In order to pass from ΔG_{298}^0 to ΔG_T^0 , it is necessary to recalculate ΔH_{298}^0 to ΔH_T^0 and ΔS_{298}^0 to ΔS_T^0 for the given temperature. For this purpose, we use the Kirchhoff equation (1.7)

$$\Delta H_T^0 = \Delta H_{298}^0 + \int_{298}^T \Delta C_p \cdot dT$$

and the equation (1.15)

$$\Delta S_T^0 = \Delta S_{298}^0 + \int_{298}^T \frac{\Delta C_p dT}{T}.$$

If we substitute the expressions for ΔH_T^0 and ΔS_T^0 into the equation (1.41), the resultant equations for calculating ΔG_T^0 will be as follows:

$$\Delta G_T^0 = \Delta H_{298}^0 - T\Delta S_{298}^0 + \int_{298}^T \Delta C_p \cdot dT - T \int_{298}^T \frac{\Delta C_p}{T} dT. \quad (2.30)$$

We use the equation (2.21) to find the K_p value for the given temperature:

$$\ln K_{p,T} = -\frac{\Delta G_T^0}{RT} = -\frac{\Delta H_{298}^0}{RT} + \frac{\Delta S_{298}^0}{R} - \frac{\int_{298}^T \Delta C_p dT}{RT} + \frac{\int_{298}^T \frac{\Delta C_p dT}{T}}{R}. \quad (2.31)$$

If we neglect the influence of the heat capacity change on the ΔG_T^0 value, that is, if we assume that $\Delta C_p = 0$, the equations (2.30) and (2.31) will be roughly approximate and will give:

$$\Delta G_{298}^0 = \Delta H_{298}^0 - T\Delta S_{298}^0 \quad \text{or} \quad \ln K_{p,298} = -\frac{\Delta H_{298}^0}{R \cdot 298} + \frac{\Delta S_{298}^0}{R} \quad (2.32)$$

The given approximate solution (the so-called first approximation of Ulich) is necessary for rapid assessment of the possibility of a reaction at temperature T and at the equilibrium position.

When a particularly precise determination of the equilibrium position is not required, ΔC_p may be considered not equal to zero but constant (the second approximation of Ulich). Provided that $\Delta C_p = \text{const}$, integrating the equation (2.29) we get:

$$\ln K_{p,T} = -\frac{\Delta H_{298}^0}{RT} + \frac{\Delta S_{298}^0}{R} - \frac{\Delta C_p (T - 298)}{RT} + \frac{\Delta C_p}{R} \ln \frac{T}{298}. \quad (2.33)$$

For precise calculation, empirical power series for $\Delta C_p = \Delta a + \Delta bT + \Delta cT^2 + \Delta c'T^2$ is substituted into (2.31). In this case, we get:

$$\ln K_{p,T} = -\frac{\Delta H_{298}^0}{RT} + \frac{\Delta S_{298}^0}{R} - \frac{1}{RT} \left[\Delta a(T-298) + \frac{\Delta b}{2}(T^2-298^2) + \frac{\Delta c}{3}(T^3-298^3) - \Delta c'(T^{-1}-298^{-1}) \right] + \frac{1}{R} \left[\Delta a \left(\ln \frac{T}{298} \right) + \Delta b(T-298) + \frac{\Delta c}{2}(T^2-298^2) - \frac{\Delta c'}{2}(T^{-2}-298^{-2}) \right]. \quad (2.34)$$

When calculating ΔG and equilibrium constants, it is necessary to take into account that for the forward reaction these values amount to K_p and ΔG correspondingly while for the reverse reaction they are equal to $1/K_p$ and $-\Delta G$.

Example. Calculate the approximate and exact $\ln K_p$ values at 700K for the reaction $\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}_{(g)}$.

Solution. For ease of calculation, we tabulate the given data:

Table 2.2 – Reference data and preliminary calculations

Reactants	H_{298}^0 kJ/mol	S_{298}^0 J/mol·K	$C_{p,298}$ J/mol·K	a	$b \cdot 10^3$	$c \cdot 10^6$	$c' \cdot 10^{-5}$
CH ₄	-74.9	186.2	35.79	17.45	60.46	-1.12	
H ₂ O	241.8	188.7	33.56	30.00	10.71		0.33
CO	-100.5	197.4	29.15	28.41	4.10		-0.46
H ₂	0	130.6	28.83	27.28	3.26		0.50
3H ₂	0	391.8	86.49	81.84	9.78		1.50
Δ	-206.2	-214.3	-46.29	-62.80	57.29	-1.12	-0.71

a) the first approximation by the equation (2.32):

$$\ln K_p = \frac{206200}{8,31 \cdot 700} - \frac{214,3}{8,31} = 35,45 - 28,79 = 9,66;$$

б) the second approximation by the equation (2.33). Since the first two terms of the equation from the previous example amount to 4.20,

$$\ln K_p = 9,66 + \frac{46,29 \cdot (700 - 298)}{8,31 \cdot 700} - \frac{46,29}{8,31} \ln \frac{700}{298} = 9,66 + 3,20 - 4,76 = 8,10.$$

b) the third approximation by the equation (2.32):

$$\begin{aligned} \ln K_p = 9,66 - \frac{1}{8,31 \cdot 700} \cdot \left[-62,8 \cdot (700 - 298) + \frac{57,29 \cdot 10^{-3}}{2} \cdot (700^2 - 298^2) - \right. \\ \left. - \frac{1,12 \cdot 10^{-6}}{3} \times (700^3 - 298^3) + 0,71 \cdot 10^5 \left(\frac{1}{700} - \frac{1}{298} \right) \right] + \frac{1}{8,31} \left[-628 \cdot \ln \frac{700}{298} + \right. \\ \left. + 57,29 \cdot 10^{-3} \cdot (700 - 298) - 1,12 \cdot 10^{-6} \cdot (700^2 - 298^2) + \frac{0,71 \cdot 10^5}{2} \times \right. \\ \left. \times \left(\frac{1}{700^2} - \frac{1}{298^2} \right) \right] = 9,66 + \frac{14430}{8,31 \cdot 700} - \frac{31,85}{8,31} = 9,66 + 2,48 - 3,84 = 8,30. \end{aligned}$$

2.5 Determination of the composition of the equilibrium mixture

The final objective of any practical calculation of equilibrium constants is to calculate the ratio between initial and forming substances in an equilibrium mixture. In order to determine the system composition at the stable equilibrium and consequently the reaction yield, it is necessary to know the equilibrium constant and the composition of the initial mixture. Depending on the type of reaction and the ratio in which the reactants are mixed, we get equations of varying complexity from which the equilibrium composition of the system is calculated.

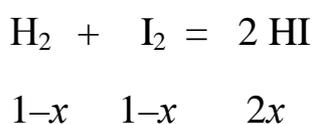
1. Reactions without a change in the number of molecules

The simplest equations for calculating equilibrium composition are obtained when the sum of stoichiometric coefficients on the left-hand and right-hand sides of a chemical equation is equal, that is at $\Delta v = 0$. For such reactions, according to (2.11) – (2.13):

$$K_p = K_c = K_N = K^0. \quad (2.35)$$

It follows that in the expression of the law of mass action instead of partial pressures or concentrations the values proportional to them, for instance, amount of substance in moles, may be substituted.

Let us consider calculation of equilibrium composition and product yield using the example of the hydrogen iodide synthesis. Assume that the initial mixture contains one mole of each initial substance, that is I_2 and H_2 are mixed in the equivalent ratios. We designate the amount of the hydrogen iodide formed by the moment of the equilibrium establishment as $2x$ mol. The equilibrium mixture will then contain



The general amount of substance in the system will be: $1-x+1-x+2x = 2$ (mol), that is it remains unchanged through the reaction.

Instead of the relative partial pressures we will substitute into the equation of equilibrium constant K^0 corresponding amounts of substances in moles for each component in the system

$$K^0 = (2x)^2 / (1-x)^2. \quad (2.36)$$

Extracting the square root of both terms of the equation (2.34) we get the first-degree equation $\sqrt{K^0} = 2x/(1-x)$, which is easily solved. At $T = 718K$ the constant $K^0 = 45,7$. From this we find $x = 0,772$.

2. Reactions with a change in the number of molecules.

Now let us consider equilibrium of the reactions that proceed with a change in the number of molecules. The simplest of such reactions are those in which one molecule dissociates into two similar or different molecules. Such reactions include, for instance, dissociation of molecular

iodine, bromine, chlorine, nitrogen and others into atoms, and also the reactions $\text{N}_2\text{O}_4 = 2 \text{NO}_2$, $\text{PCl}_5 = \text{PCl}_3 + \text{Cl}_2$ etc.

Let us consider the dissociation reaction $\text{N}_2\text{O}_4 = 2\text{NO}_2$. We express the equilibrium constant of the reaction through the degree of N_2O_4 dissociation indicated by α .

As a result of partial dissociation $(1 - \alpha) \cdot n_0$ moles of n_0 moles of N_2O_4 remains and we get $2\alpha \cdot n_0$ moles of NO_2 . The general number of molecules in the equilibrium mixture will amount to $\sum v = (1 + \alpha) \cdot n_0$. In this connection, the partial pressures will be equal to:

$$p_{\text{NO}_2} = pN_{\text{NO}_2} = p \frac{n_{\text{NO}_2}}{\sum n} = p \frac{2\alpha}{1 + \alpha} p_{\text{N}_2\text{O}_4} = pN_{\text{N}_2\text{O}_4} = p \frac{n_{\text{N}_2\text{O}_4}}{\sum n} = p \frac{1 - \alpha}{1 + \alpha}.$$

If we substitute these expressions into the equation for K_p , we will have:

$$K_p \frac{4\alpha^2 p^2 (1 - \alpha)}{(1 + \alpha)^2 (1 - \alpha) p} = \frac{4\alpha^2 p}{1 - \alpha^2}. \quad (2.37)$$

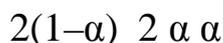
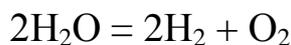
Since K_p is independent of pressure, the equation shows that the degree of N_2O_4 dissociation decreases with increasing pressure (in accordance with the equilibrium law).

This is the difference between the reactions proceeding with a change in the number of molecules and the reactions considered previously.

For the reactions proceeding with a change in the number of molecules, it is necessary to distinguish equilibrium constants expressed in different ways (through p or c etc.) as far as their numerical values are not identical.

Let us consider briefly one more type of reactions for which $\sum v = 1$. This type includes the reactions: $2\text{CO}_2 = 2\text{CO} + \text{O}_2$; $2\text{SO}_3 = 2\text{SO}_2 + \text{O}_2$ etc.

For instance, we express the equilibrium constant of the water vapour dissociation through the dissociation degree α :



The number of moles ν of reactants are written under the dissociation equation (the number of moles before dissociation is $\nu_0 = 2$).

Let us make up expression for p_i :

$$p_{\text{H}_2\text{O}} = \frac{2(1-\alpha)}{2+\alpha} \cdot p; \quad p_{\text{H}_2} = \frac{2\alpha}{2+\alpha} \cdot p; \quad p_{\text{O}_2} = \frac{\alpha}{2+\alpha} \cdot p.$$

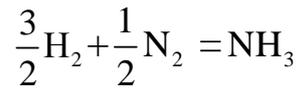
If we substitute these expressions into the equation for K_p , we will have:

$$K_p = \frac{p_{\text{H}_2}^2 p_{\text{O}_2}}{p_{\text{H}_2\text{O}}^2} = \frac{\alpha^2 \cdot p}{(1-\alpha)^2 \cdot (2+\alpha)}. \quad (2.38)$$

With respect to α , this equation is cubic. It becomes linear when dissociation degree is very low (for the water vapour it takes place at $T \leq 1700\text{K}$). In this case, α value may be omitted in parentheses in the denominator of the equation (2.36). As a result, we would have:

$$K_p = \frac{\alpha^2 p}{2}. \quad (2.39)$$

Another stoichiometric type includes one of the most important reactions of inorganic synthesis, which is producing ammonia from nitrogen and hydrogen. In this case, it is convenient to follow the course of the reaction measuring the mole fraction of ammonia in the equilibrium mixture. If the stoichiometric mixture of nitrogen and hydrogen is taken during ammonia synthesis, the mole fractions of H_2 and N_2 will have the values written under the reaction equation:



$$\frac{3}{4}(1-x) \frac{1}{4}(1-x)x$$

The equilibrium constant expressed through mole fractions will take on the form:

$$K_p = \frac{P_{\text{NH}_3}}{P_{\text{H}_2}^{3/2} P_{\text{N}_2}^{1/2}} = \frac{x}{\left(\frac{3}{4}\right)^{3/2} (1-x)^{3/2} \left(\frac{1}{4}\right)^{1/2} (1-x)^{1/2} P} = \frac{16}{\sqrt{27}} \cdot \frac{x}{(1-x)^2 P} \quad (2.40)$$

These several specific examples of gas equilibria show that the form of the equilibrium constant may change depending on the stoichiometric type of the reaction and the value chosen as characteristics of the process (dissociation degree, fractional conversion, mole fraction etc.).

Examples of problem sets

Assignment 1

For the following reaction:

Table 2.3 – Problem set

№	Reaction	№	Reaction
1	$C_2H_5Cl = C_2H_4 + HCl$	14	$CO_2 + H_2 = CO + H_2O (g)$
2	$S_2(g) + 2 H_2 = 2 H_2S$	15	$CH_4 + I_2 (g) = CH_3I (g) + HI$
3	$MgO + CO_2 = MgCO_3$	16	$2CO + 2 H_2 = CH_4 + CO_2$
4	$2H_2 + CO = CH_3OH (g)$	17	$C_2H_6 = C_2H_4 + H_2$
5	$4HCl + O_2 = 2 H_2O (g) + 2 Cl_2$	18	$C_6H_6 (g) + 3 H_2 = C_6H_{12} (g)$
6	$2 NO_2 = 2 NO + O_2$	19	$CO + 0,5 O_2 = CO_2$
7	$N_2O_4 = 2 NO_2$	20	$PCl_3 + Cl_2 = PCl_5$
8	$CaCO_3 = CaO + CO_2$	21	$Mg(OH)_2 = MgO + H_2O (g)$
9	$SO_2 + 0,5 O_2 = SO_3$	22	$NO + 0.5 O_2 = NO_2$
10	$CO + 3 H_2 = CH_4 + H_2O (g)$	23	$Ca(OH)_2 = CaO + H_2O (g)$
11	$SO_2 + Cl_2 = SO_2Cl_2 (g)$	24	$H_2 + C_2H_4 = C_2H_6$
12	$COCl_2 = CO + Cl_2$	25	$CO + H_2O (g) = HCOOH (g)$
13	$CO_2 + 4 H_2 = CH_4 + 2 H_2O (g)$		

- 1) calculate the thermal effect of ΔH and ΔU at $T = 298K$;
- 2) calculate the approximate value of ΔH at $T = 323K$ assuming that ΔC_p does not depend on temperature;

3) express by equation the temperature dependence of the thermal effect of the reaction; considering the temperature dependence of heat capacity, calculate the value of the thermal effect at the temperatures of 400, 500 and 600K and plot the graph of the temperature dependence of thermal effect;

4) calculate the entropy change ΔS_0 and determine the normal affinity ΔG_0 under the standard conditions;

5) determine the normal affinity ΔG_0 at $T = 500\text{K}$;

a) approximately, neglecting the influence of the heat capacity change in the course of the reaction;

б) precisely.

The thermodynamic values necessary for the problem solving are given in Appendix 1 at the end of the textbook.

Assignment 2

For the reaction from the *assignment 1*:

1) calculate K_p and K_c at $T = 298\text{K}$ (express the value of K_p in atmospheres and in SI units);

2) derive the temperature dependence of the equilibrium constant in equation $\ln K_p = f(T)$;

3) calculate the values of K_p at the temperatures of 400, 500 and 600K using this equation and plot the graph of the temperature dependence of $\ln K_p$;

4) determine the direction of the reaction at 500K if the partial pressure of all the gaseous reactants in the reaction mixture is $p = 1 \cdot 10^4$ Pa;

5) determine the influence of external factors (p and T) on the equilibrium yield of the reaction products.

Assignment 3

Gaseous substances A and B react according to the given equation of a reaction with the production of a gaseous substance C.

1) Express K_p and K_c through the equilibrium amount of substance C equal to x if the initial substances A and B are taken in stoichiometric ratio at equilibrium pressure in system p (Pa), and at temperature T (K).

2) Calculate the values of K^0 , K_p and K_c at $T = 500\text{K}$ if $p = 9740000$ Pa, and $x = 0,45$.

Table 2.4 – Problem set

№	Equation of reaction	№	Equation of reaction
1	$2A + 0.5B = 2C$	14	$2A + 2B = 3C$
2	$0.5A + 0.5B = C$	15	$2A + 2B = C$
3	$0.5A + B = 0.5C$	16	$A + 2B = 2C$
4	$A + 3B = 3C$	17	$2A + B = 2C$
5	$2A + 0.5B = 3C$	18	$0.5A + B = 3C$
6	$3A + 0.5B = 2C$	19	$A + B = 3C$
7	$2A + 3B = 2C$	20	$0.5A + B = 2C$
8	$0.5A + 0.5B = 3C$	21	$3A + 0.5B = C$
9	$A + 2B = C$	22	$A + B = 1.5C$
10	$2A + 3B = 3C$	23	$2A + 2B = 1.5C$
11	$A + B = 0.5C$	24	$1.5A + 0.5B = C$
12	$0.5A + B = 2C$	25	$1.5A + B = 1.5C$
13	$3A + B = 3C$		

Chapter 3. PHASE EQUILIBRIA

3.1. Basic concepts. The phase rule

The flow of a chemical reaction is often accompanied by a change in the state of matter of the reaction products in comparison with the initial substances. Obviously, the calculation of the process energy should include consideration of the energy characteristics of the phase transition processes accompanying the chemical reaction.

The study of the phase transition processes also makes it possible to establish the fact and stoichiometry of chemical interaction in the system, to determine the molecular state of compounds in a solution, and solve a range of similar problems using methods of physical and chemical analysis.

Physicochemical analysis is a research technique based on studying the dependence of equilibrium system properties on composition. These dependences are usually expressed in the form of composition-property diagrams, the analysis of which determines the nature and thermodynamic characteristics of the phase transitions and chemical interactions occurring in the system, the composition and stability of the resulting chemical compounds. The basis for physicochemical analysis is the phase rule and the principles of continuity and correspondence formulated by Nikolai Semenovich Kurnakov.

According to the continuity principle, with a continuous change in the composition of a system, its properties change continuously if the number of phases in the system remains constant. The curves that show these properties are also continuous. According to the correspondence principle, each geometric image in the diagram (a point, a line of a certain shape, a part of a plane bounded by several lines) corresponds to a certain

phase (chemical compound or solution) or a complex of phases. When chemical compounds form in the system, so-called singular points appear in the diagram. The singular points are the points of intersection of the two branches of the curve that correspond to the chemical compound composition. Thus, physicochemical analysis determines compositions of a chemical compound, composition and boundaries of various phases using the diagram, without separation of these phases and without their chemical analysis. Therefore, it is one of the main techniques for studying metal alloys, minerals, solutions and melts of salts, and the theoretical basis of many technological processes.

The major task of the section is to impart to students strong skills in calculating phase equilibria and phase transition processes, in reading the composition-property diagrams of two-component systems of various types.

Before proceeding to studying phase equilibria, it is necessary to master the basic concepts: *phase, component, degree of freedom*. We should learn to apply the phase rule to determination of the system variability or the number of equilibrium phases. Particular attention should be paid to the correct determination of the number of components in the system.

A *phase (P)* is a set of homogeneous parts of a system that have identical chemical composition and thermodynamic properties and are separated from other homogeneous parts by interfaces. According to the number of phases "*P*", single-phase systems (a mixture of gases, a solution in water), two-phase systems (water in equilibrium with vapour, a saturated solution in the presence of crystals, a mixture of crystals) and others are distinguished.

Each substance that may be extracted from the system and can exist separately is called a constituent part of the system. Thus, the aqueous

solution containing ions K^+ , Na^+ , Cl^- , NO_3^- includes five constituents: KCl , $NaCl$, KNO_3 , $NaNO_3$ and H_2O .

Components (C) are *independent* constituent parts of a system, that is, their concentrations do not depend on one another and may be changed arbitrarily. The example given above demonstrates a three-component system. Concentrations of constituent parts may be connected either by the condition of chemical equilibrium (if chemical interaction is possible between them) or by the conditions of stoichiometric correlation. Thus, the number of components " C " of a system is equal to the number of its constituent parts minus the number of coupling equations. It is not essential what substances are components, since the system properties are determined not by the nature but by the number of components. According to another definition, the number of components is equal to the smallest number of substances sufficient to form each phase of the given system.

Example. Determine the number of components of the system that consists of crystalline ammonium chloride, and gaseous ammonia and hydrogen chloride.

Solution. The system consists of three components between which the chemical interaction $NH_4Cl \rightleftharpoons NH_3 + HCl$ is possible and, therefore, we have the coupling equation $p_{NH_3} \cdot p_{HCl} = K_p$ between them. In this case, the system becomes two-component. If we specify one more condition, for instance, $p_{NH_3} = p_{HCl}$, the system will become single-component, that is, one ammonium chloride will be sufficient for the formation of both new phases.

The number of degrees of freedom (F) is the number of the system parameters that can be changed arbitrarily and independently of one another within certain limits without causing a change in the number of phases of the system. Usually such parameters are temperature, pressure

and concentration of components. According to the number of degrees of freedom, systems fall into non-variant ($F = 0$), monovariant ($F = 1$), bivariant ($F = 2$) etc. Thus, a system of liquid in equilibrium with vapour is monovariant. It is possible to change the temperature arbitrarily, but a certain vapour pressure should correspond to each temperature, so that the equilibrium remains and one of the phases does not disappear, namely so that the liquid does not evaporate or the vapour does not condense. According to the general laws of thermodynamics, at equilibrium, the change in the Gibbs free energy $dG = -SdT + VdP + \sum \mu_i dn_i = 0$. For the phase transitions characterized by a constant temperature and pressure, this condition has the following form:

$$\sum \mu_i dn_i = 0 \text{ and } \mu_i(\alpha) = \mu_i(\beta), \quad (3.1)$$

where α and β are equilibrium phases, that is, the chemical potential of each component in equilibrium phases is identical. For a multiphase multicomponent system, the equality of chemical potentials of each component in all phases of the equilibrium system is a sign of equilibrium.

Let us work out equations for a more general case, when a heterogeneous system consists of " P " phases, each of which includes all the " C " components without exception. If the components of the system are indicated by a subscript, and the phases are marked by a superscript, the following equations may be written for the equilibrium in the presence of " C " components and " P " phases:

$$\begin{aligned} \mu_1^1 &= \mu_1^2 = \mu_1^3 = \dots = \mu_1^P \\ \mu_2^1 &= \mu_2^2 = \mu_2^3 = \dots = \mu_2^P \\ &\dots\dots\dots = \\ \mu_c^1 &= \mu_c^2 = \mu_c^3 = \dots = \mu_c^P. \end{aligned} \quad (3.2)$$

Each line in the system of equations makes it possible to compose ($P - 1$) of independent equations. The number of lines in the system of equations

amounts to " C ", therefore the total number of independent equations is equal to: $C \cdot (P-1)$. Independent variables included in this system of equations are temperature, pressure and concentration of components. We have " C " components in each phase. However, if arbitrary values of temperature and pressure are set, it is no longer possible to choose arbitrarily the concentrations of all the components without exception. The concentration of one of the components should be accurately determined. Thus, the number of independent concentrations in each phase is $(C-1)$, and the total number of independent concentrations in each phase is $P \cdot (C-1)$. Besides the number of concentrations found, temperature and pressure are also independent variables, therefore the total number of independent variables for the above system of equations is $P(C-1)+2$.

If the number of independent variables is equal to the number of equations that connect them, that is: $C \cdot (P-1) - P \cdot (C-1) + 2$, each independent variable takes on a certain value, and the entire system can exist in this only possible combination of temperature, pressure and concentration of the components in all the phases.

If the number of equations is less than the number of independent variables, the variance indicated by the letter " F " will be equal to $F = P(C-1) + 2 - C(P-1)$. Here V is the number of variables that can take arbitrary values for a given number of equations, that is, the number of degrees of freedom.

The corollary of this general statement is the equation relating the number of degrees of freedom to the number of components and the number of phases of an equilibrium system under the condition of constant pressure and temperature:

$$F = C - P + 2. \quad (3.3)$$

This equation is a mathematical expression of the **Gibbs phase rule**: *the number of degrees of freedom in the equilibrium system on which, of external factors, only pressure and temperature have influence, is equal to the number of components minus the number of phases plus two.*

Sometimes systems are considered at a certain constant parameter, for instance, at constant pressure. Then the number of degrees of freedom is correspondingly reduced:

$$F = C - P + 1. \quad (3.4)$$

Example. Determine the variance of the system formed as a result of the thermal decomposition of CaCO_3 .

Solution. The reaction equation is $\text{CaCO}_3 = \text{CaO} + \text{CO}_2$. The system is heterogeneous, $P = 3$ (two solid and one gaseous phases). There are three constituent parts and one coupling equation, hence $C = 3 - 1 = 2$. The number of degrees of freedom $F = 2 - 3 + 2 = 1$, the system is univariant. Only one parameter may be changed arbitrarily: either temperature or concentration.

3.2. One-component systems

For a single-component system, the phase rule is expressed by the formula:

$F = 1 - P + 2 = 3 - P$. Therefore, the maximum number of degrees of freedom is two (with the minimum number of phases $P = 1$). It means that two coordinate axes are required to display the state of the system in a diagram. The parameters of the system are pressure, temperature and molar volume. They are mutually related (equation of state for gases). Therefore, any two parameters may be chosen as independent. Phase diagram is usually plotted in the coordinates $P - T$ (fig. 3.1).

The fields of the diagram correspond to single-phase systems – crystalline, liquid and gaseous (the number of degrees of freedom $F = 2$). Within the field, both parameters may be arbitrarily changed. The lines correspond to the equilibrium conditions between two phases ($P = 2$, $F = 1$): the line OA corresponds to the equilibrium between the liquid and gaseous phases (vapour); OC – solid and liquid; OB – solid and gaseous phases.

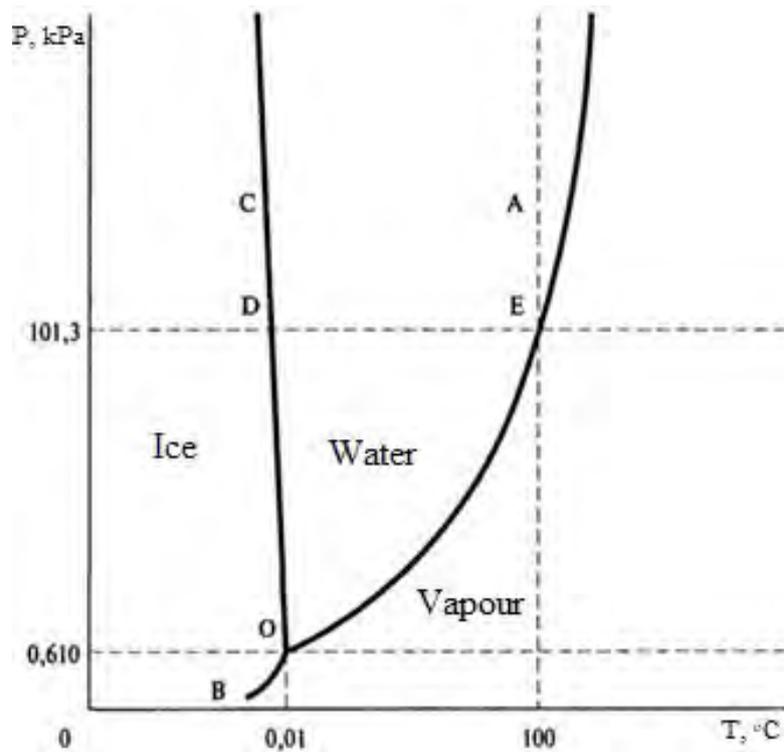


Fig. 3.1. Phase diagram for water (scheme)

The fields of the diagram correspond to single-phase systems – crystalline, liquid and gaseous (the number of degrees of freedom $F = 2$). Within the field, both parameters may be arbitrarily changed. The lines correspond to the equilibrium conditions between two phases ($P = 2$, $F = 1$): the line OA corresponds to the equilibrium between the liquid and gaseous phases (vapour); OC – solid and liquid; OB – solid and gaseous phases.

For two-phase equilibrium systems, only one parameter may be set, and in this connection, it may only have a well-defined value. For instance, the line OA (vapourization curve) expresses the temperature dependence of the saturated vapour pressure, or the pressure dependence of the boiling point. The line OC (melting curve) shows the pressure dependence of the melting temperature. OB (sublimation line) is the pressure dependence of the sublimation temperature, or the temperature dependence of the saturated vapour pressure over the solid phase. At the point O of the intersection of all the three curves, the three phases are in equilibrium, $F = 0$, that is, such a system may exist only at well-defined temperature and pressure. The point O is called a “triple point”. Its coordinates for water are $p = 610\text{Pa}$, $T = 0.01^\circ\text{C}$.

Phase diagrams are usually constructed on the basis of experimental data, however the equilibrium lines of phases may be calculated from the Clausius-Clapeyron equation. If two phases (1) and (2) are in equilibrium at constant temperature and pressure, then $\mu_1 = \mu_2$. Alternatively, for an individual substance $G_1 - G_2$. If pressure and temperature are changed by infinitesimals without disturbing the equilibrium, the new equilibrium condition will be written as $G_1 + dG_1 = G_2 + dG_2$, hence $dG_1 = dG_2$. A change in Gibbs energy with a change in temperature and pressure, according to (1.34), $dG \leq -SdT + Vdp$, then $-S_1dT + V_1dp = -S_2dT + V_2dp$, or $\Delta S dT = \Delta V dp$, or $dp/dT = \Delta S/\Delta V$. However, for phase transitions, the entropy change $\Delta S = \Delta H / T$, therefore,

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V}, \quad (3.5)$$

This equation is called the ***Clausius-Clapeyron equation***. It relates the enthalpy change (thermal effect) of the phase transition to the derivative dP/dT , which characterizes the change in the equilibrium pressure with a change in temperature or the pressure dependence of the

phase transition temperature. In the phase diagram, the value dp/dT determines the slope of the dependence curves $p = p(T)$. The derivative will be positive if $\Delta V > 0$, that is, if at the phase transition the volume increases (vapourization, sublimation, melting of the vast majority of substances), and negative if $\Delta V < 0$ (melting of ice). Therefore, the vapourization and sublimation temperatures always increase with increasing pressure, the melting point of various substances may both increase and decrease (melting of the ice) as the pressure increases.

For vapourization and sublimation processes, it is convenient to represent the equation (1.30a) in a different form. The volume of the condensed phase may be neglected in comparison with the vapour volume and the specific volume may be considered as $\Delta V \approx V_{vap} = RT/p$, then $\Delta H = Tdp/dT$; $RT/p = RT^2 d \ln p / dT$ or

$$\frac{d \ln p}{dT} = \frac{\Delta H}{RT^2}. \quad (3.6)$$

Assuming the heat of phase transition to be constant and integrating this equation, we obtain

$$\ln p = -\frac{\Delta H}{RT} + \text{const}, \quad \text{or} \quad \ln \frac{p_2}{p_1} = \frac{\Delta H \cdot \Delta T}{R \cdot T_1 \cdot T_2}. \quad (3.7)$$

The first expression shows that the saturated vapour pressure is a linear function $1/T$; the second one connects the saturated vapour pressure at two temperatures (or the boiling point of the liquid at two pressures).

Example. At atmospheric pressure $p_1 = 1,013 \cdot 10^5 \text{Pa}$, water boils at temperature $T = 373 \text{K}$. Calculate the boiling point of water at pressure $p_2 = 2,026 \cdot 10^5 \text{Pa}$.

Solution. In order to solve the problem, we must know the heat of water vapourization at $T = 373 \text{K}$, $\Delta H = 40,6 \text{kJ/mol}$. We determine T_2 by transforming the Clausius-Clapeyron equation:

$$T_2 = \frac{T_1 \cdot \Delta H}{\Delta H - RT_1 \ln \left(\frac{p_2}{p_1} \right)} = \frac{373 \cdot 40600}{40600 \cdot 8,31 \cdot \ln 2} = 394\text{K}.$$

Pay attention to the dimensions of the values: heat of vapourization is J/mol, temperature is K, and pressure may be expressed in different units, since the equation includes the ratio of pressures.

3.3. Two-component systems. Common properties of solutions

Let us consider some features of formation of various solutions. The gaseous state of matter is characterized by weak interaction between particles and large distances between them. Therefore, gases are mixed in virtually any ratio (at very high pressures, when the density of gases approximates to the density of liquids, limited solubility may be observed). For gas mixtures, Dalton's law is valid: the total pressure of a gas mixture is equal to the sum of the partial pressures of the gases comprised. Liquid substances, depending on their nature, may be mixed in any ratio (unlimited mutual solubility); be virtually insoluble in one another; have limited solubility.

The temperature dependence of the solutions concentration is usually represented graphically in a diagram of mutual solubility.

One of the most important features of a solution is its quantitative composition, which is the concentration of the solution. The concentration may be expressed in different ways: mole fraction (N_A) is the amount of moles of a constituent divided by the total amount of moles of both constituents in the system; molarity (c_A) is the amount of moles of solute per litre of solution; molality (m_A) is the amount of moles of solute in 1000 g of solvent; mass fraction is the amount of grams of solute in 100 ml of solution (expressed as a percentage).

Graphically, the composition of a two-component system is represented on a segment of a straight line, the length of which is taken as

unity, if the composition is expressed in molar fractions, or for one hundred units, if the composition is expressed in percents. The extreme points of a segment correspond to pure components, all intermediate points to mixtures. So in the Fig.3.2a the point A corresponds to the pure component A ($N_A = 1$), and the point (x) is the mixture containing ($N_A = 0,75; N_B = 0,25$). Similarly, in Fig.3.2b, the point (x) corresponds to the composition: 40% A, 60% B.

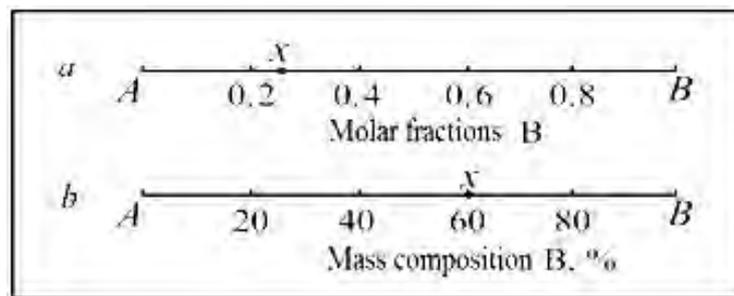


Fig. 3.2. Graphic representation of the composition of a two-component system

For representing the phase diagram of a two-component system, such coordinates are required: pressure-temperature-composition, that is, the diagram must be three-dimensional. To simplify the diagrams, one usually considers either the pressure-composition relationship $p=f(N)$ (at $T = \text{const}$), or the temperature-composition relationship $T=f(N)$ (at $p = \text{const}$). At the ends of the composition axis, perpendiculars (ordinates) are disposed, on which the parameter which is under the investigation – pressure or temperature – is located.

Solution is a single-phase system of a variable composition consisting of two or more components. Solutions can be not only liquid, but also gaseous (mixture of gases), and solid (for example, an alloy of gold with copper). There are distinguished ideal, extremely dilute and real solutions. The ideal solution is a solution which formation is not accompanied by a thermal effect and a change in the total volume, and the change in entropy is the same as by mixing the ideal gases, that is,

$\Delta H_{mix} = 0$, $\Delta V_{mix} = 0$, $\Delta S_{mix} = \Delta S_{id. gases}$. Ideal solutions form substances with similar physical and chemical properties. Extremely dilute solutions are solutions with an infinitesimal concentration; they can be regarded as ideal. Real solutions are those that do not obey the thermodynamic laws of ideal and extremely dilute solutions.

One of the main problems of the theory of solutions is the establishment of the dependence of the solution's properties on its composition and the properties of the pure components. The formation of a solution from the components is a spontaneous process, that is why, at constant temperature and pressure solution formation is accompanied by the reduction of the isobaric potential G (Gibbs energy) of the system.

Real gases do not obey the equation of state of ideal gases, and the deviation is greater the higher the pressure. To maintain the same kind of thermodynamic equations for real gases as for ideal gases, the pressure is replaced in them by another variable, the so-called fugacity f (or volatility). Fugacity is a quantity, that is also connected with the thermodynamic properties of a given gas, as pressure is associated with these properties in an ideal gas; Fugacity has the dimension of pressure and is connected with pressure by the relation $f = p \cdot \gamma$, where γ is the coefficient of fugacity (dimensionless quantity). Chemical potential of real gas

$$\mu_i = \mu^0 + RT \ln f = \mu^0 + RT \cdot \ln(p \cdot \gamma).$$

At low pressures, γ is usually somewhat less than a unit, and for $\gamma \rightarrow 0$, $p \rightarrow 0$. At high pressure and low temperature, close to critical, γ can reach high values; for example, for methane at $p = 1,107 \text{ Pa}$ and $t = 70^\circ\text{C}$ $\gamma = 47$. Fugacity coefficients are determined on the basis of experimental data.

3.4 Vapor-liquid equilibrium

If the ideal solution is in balance with the gaseous phase (saturated vapor), then the balance condition for such a system will be the equality of the chemical potentials of each component in the vapor and in the solution, i.e.: $\mu_{vapor} = \mu_{sol-n}$ or $d\mu_{vapor} = d\mu_{sol-n}$. For each component, the chemical potential in the gas phase is $\mu_p = \mu_{vapor}^0 + RT \ln p$, and in the solution $\mu_{vapor} = \mu_{vapor}^0 + RT \ln N$; differentiating these expressions, for balance conditions, we get $RT = \ln p = RT \ln N$ or $d \ln p = d \ln N$. During the formation of the solution from the components, the vapor pressure of each of them varies from p_0 to p and the mole fraction from 1 to N . Integrating the last equation within these limits, we get $\ln p / p^0 = \ln N / 1$, wherefrom $p = p^0 \cdot N$. In general

$$p_i = p_i^0 \cdot N_i \quad (3.8)$$

The equation expresses ***Raoult law: the partial pressure of the saturated vapor of the component above the solution is proportional to the molar fraction of this component in the solution.*** Graphically, the dependence of the vapor pressure of the component vapor on the composition for an ideal solution has a linear dependence (Fig. 3.3).

In real solutions, both positive (b) and negative (c) deviations from Raoult law are observed (Fig.3.8). The reason for the deviations is the change in the particle size during the formation of the solution (due to dissociation, association or formation of compounds between the components) or the difference in the interaction energy between homogeneous and heterogeneous molecules. If heterogeneous molecules (A–B) in the solution interact with less force than homogeneous molecules (A–A or B–B), this facilitates the transition of molecules from the liquid to vapor (in comparison with a pure liquid). In this case, we will have positive deviations from Raoult law, that is, the vapor pressure will be greater. Conversely, the increase of the interaction of

heterogeneous molecules in solution (solvation, formation of a hydrogen linkage, formation of chemical compounds) adds additional difficulties for the transition of molecules to the gaseous phase, which leads to negative deviations from Raoult law.

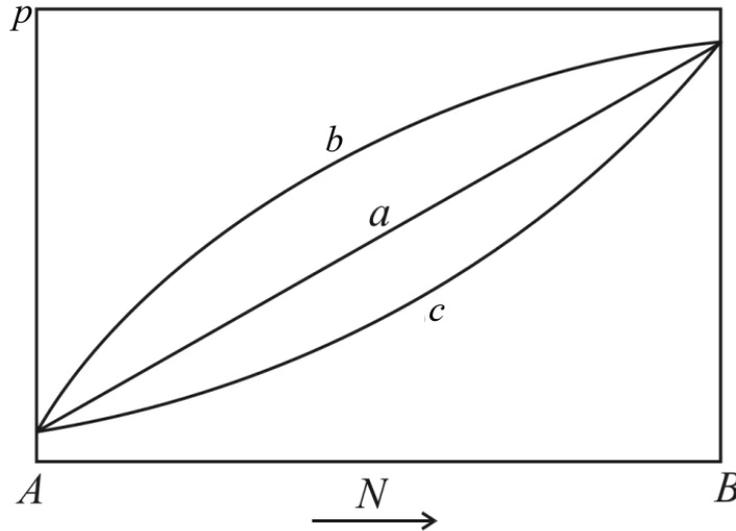


Fig.3.3. The pressure of the saturated vapor component over the ideal (curve "a") and non-ideal solutions (curves "b" and "c")

When forming a solution, homogeneous molecules are mutually removed, this process is accompanied by the absorption of heat. In the first case, the heat of mixing will be positive, since the mutual removal of homogeneous molecules with a sufficiently "strong intermolecular interaction" requires the expenditure of energy, that is, the process passes with the absorption of heat. When the interaction of heterogeneous molecules is stronger than homogeneous, the heat of mixing will be released. Thus, the sign of the deviation from Raoult law and the sign of the heat of mixing must in general coincide.

The deviation of the properties of non-ideal solutions from the ideal ones is taken into account quantitatively, using in the thermodynamic equations instead of the molar fraction N , the activity $a = \gamma \cdot N$, where γ is the activity coefficient. For a non-ideal solution, Raul's law $p_i = p_i^0 \cdot a_i$, the

activity and activity coefficient of the component can be calculated according to Raoult law if the partial pressure of saturated vapor is known.

Example. Calculate the activity and activity coefficients of acetone in aqueous solutions, put the results in the table (3 and 4 graphs).

Table 3.1 – Calculation results

N_2	$p \cdot 10^4, \text{Pa}$	α	γ
0	0	0	–
0,2	1,88	0,614	3,07
0,4	2,25	0,735	1,84
0,6	2,48	0,910	1,35
0,8	2,71	0,886	1,11
1,0	3,06	1,0	1,0

Solution. In the first and second columns of the table, the mole fractions of acetone in a mixture with water and the partial pressures of saturated acetone vapor over the mixture at 298K are given. For pure acetone, the saturated vapor pressure $p^0 = 3,06 \cdot 10^5 \text{ Pa}$, for $N = 0,2$, the activity of acetone $a = 1,88 \cdot 10^4 / 3,06 \cdot 10^4$, and the activity coefficient $\gamma = a / N = 0,614 / 0,2 = 3,07$. A similar calculation is made for all concentrations. We put the results in the table and build a diagram of the dependence of $p \rightarrow N$ and $\gamma \rightarrow N$.

If the dissolved substance is not volatile, then it has no gas phase, and there are only solvent vapors above the solution. The vapor pressure above the solution is always lower than that over the pure solvent. If we denote the solvent by the index A, and the solute by the index B, in this case Raoult law can be represented in the following form: $p_A = p_A^0 \cdot N_A$. If

instead of N_A make $1 - N_B$, then as a result of simple transformations we get the following expression:

$$p_A / p_A^0 = N_A = 1 - N_B$$

or

$$\frac{p_A^0 - p_A}{p_A^0} = N_B. \quad (3.8)$$

That is, the relative decrease in the vapor pressure of the solvent over the solution is equal to the molar fraction of the dissolved substance (the second formulation of the Raoult law). In deriving the Raoult law, equations for the chemical potentials of ideal systems were used, so the law is valid for dilute solutions and the more accurate the lower the concentration of the dissolved substance.

The reduction in vapor pressure over the solution depends on the molar concentration, that is, on the number of particles in the solution volume, and not on their nature (such properties are called colligative ones). Therefore, significant deviations from the law are observed in solutions of electrolytes and in the association of a dissolved substance. Measurement of any colligability property allows to determine the molecular mass of the dissolved substance.

The saturated vapor pressure increases with increasing temperature. When it reaches an external pressure, the liquid boils. In Fig.3.4, the dependence of saturated vapor pressure on temperature is represented by the curves: p^0 – for a pure solvent, p_1 – for a solution with a lower concentration, p_2 – for a solution of higher concentration; p_{ex} - external pressure; T_{boil0} – the boiling point of the solvent, T_{boil1} – the boiling point of the first solution, T_{boil2} – the boiling point of the second (more concentrated) solution.

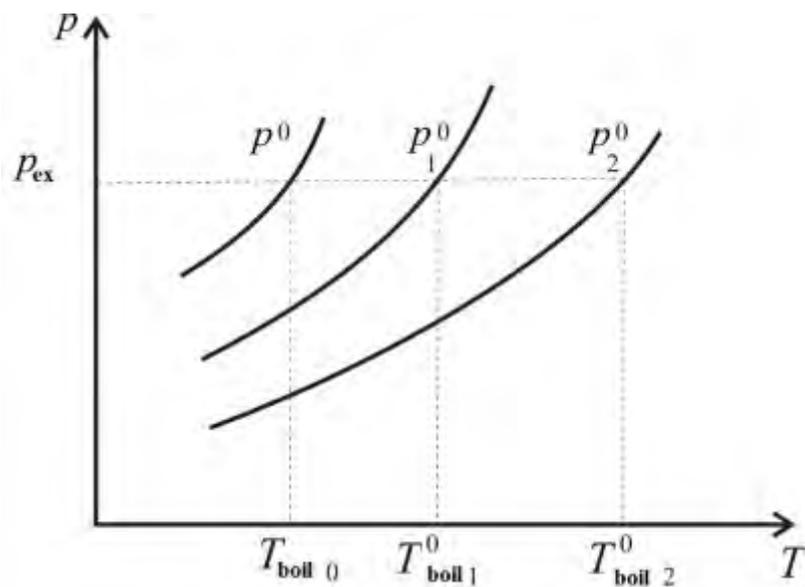


Fig.3.4. Graphical interpretation of the second consequence of Raoult law

It can be seen from the graph that a decrease in the saturated vapor pressure above the solution leads to an increase in the boiling point of the solution in comparison to the pure solvent. It can be shown that for dilute solutions, an increase in the boiling point is proportional to the molar concentration of the solution: $\Delta T_{boil} = E \cdot m$. The coefficient of proportionality is equal to the ebullioscopic constant (E); it is equal to the calculated increase in the boiling point of a single-molar solution and does not depend on the nature of the solute. The ebullioscopic constant is typical for a given solvent and can be calculated theoretically by the equation:

$$E = \frac{RT_0^2 \cdot M}{1000 \cdot \Delta H_{ev}} \quad (3.9)$$

where T_0 is the boiling point of the solvent, M is the molecular weight of the solvent, and ΔH_{ev} is the molar heat of evaporation of the solvent.

An increase in the boiling point of the solution is a colligative property, therefore, by measuring the increase in the boiling point of the

solution with a known mass concentration, it is possible to determine the molecular mass of the solute; the method is called ebullioscopic.

Example. 10g of solid are dissolved in 100g of benzene; The boiling point then rose from 80,1 to 80,9°C. Find the molecular mass of the solute.

Solution. If g grams of substance with a molecular mass M are dissolved in G grams of the solvent, then the molality of the solution is $m = 1000 \cdot g / (M \cdot G)$, then $\Delta T = E \cdot 1000 \cdot g / (M \cdot G)$, whence $M = 1000 \cdot g \cdot E / (\Delta T \cdot G)$. Using the tabulated value of the ebullioscopic benzene constant $E = 2,63$, we find the molecular mass:

$$M = \frac{E \cdot g \cdot 1000}{G \cdot \Delta T} = \frac{1000 \cdot 2,63 \cdot 10}{100 \cdot (80,9 - 80,1)} = 329.$$

Similarly, the ebullioscopic constant can be determined experimentally if the molecular mass of the solute is known.

If two volatile liquids form an ideal solution, that is, both obey Raoult law, then the vapor pressure over the solution will be equal to the sum of the partial pressures: $p = p_A + p_B = p_A^0 \cdot N_A + p_B^0 \cdot N_B$. Since the partial pressures change linearly due to the composition change than the total pressure also changes linearly (Fig.3.5).

It follows from the **Mendeleev-Clapeyron** equation that the partial pressures of the components in the vapor are proportional to their molar fractions in the vapor: $p_A/p_B = N'_A / N'_B$ (the upper index refers to the gaseous phase - vapor). And on the basis of the Raoult law $p_A = p_A^0 \cdot N_A$ and $p_B = p_B^0 \cdot N_B$, then $p_A/p_B = (p_A^0 \cdot N_A) / (p_B^0 \cdot N_B)$. And, obviously

$$\frac{N'_A}{N'_B} = \frac{N_A}{N_B} \cdot \frac{p_A^0}{p_B^0} \quad (3.10)$$

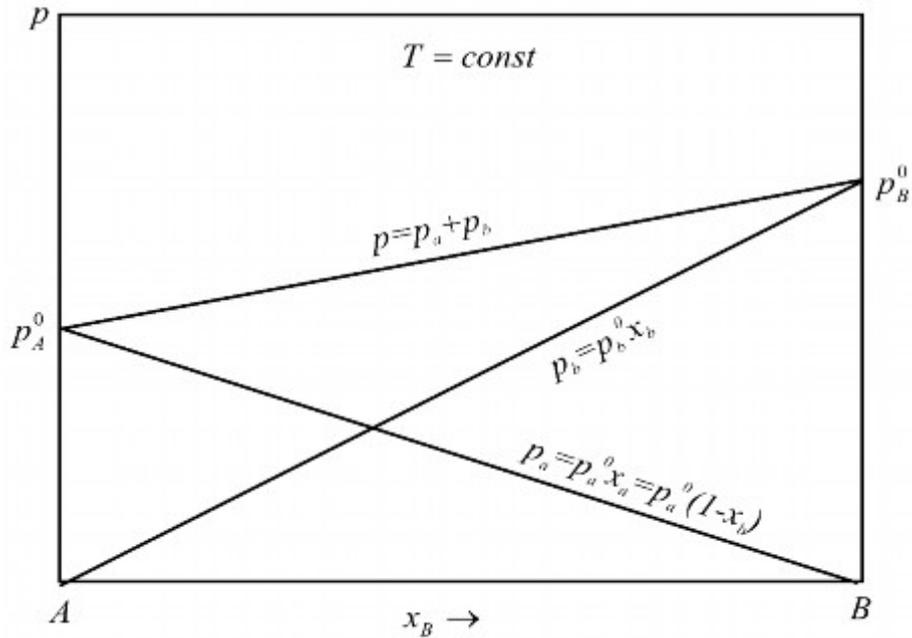


Fig. 3.5. The dependence of the vapor pressure of an ideal solution on the composition

The resulting equation connects the composition of the vapor with the composition of the liquid. Its analysis leads to the following conclusions: firstly, the composition of the vapor does not coincide with the composition of the liquid (except the case when $(p_A^0 = p_B^0)$); secondly, if $p_A^0 > p_B^0$, then $N'_A / N'_B > N_A / N_B$, that is, in vapors in comparison with the liquid there will be more component A, which is characterized by a higher vapor pressure and, consequently, a lower boiling point. These conclusions are combined in *the first law of Konovalov: in a binary system, vapor, in comparison with the liquid that is in equilibrium with it, is enriched with that component which addition to the system increases the total vapor pressure or reduces the boiling point of the mixture.* The relationship between the boiling point of the solution and the equilibrium compositions of the liquid and the vapor is represented in the form of diagrams (Fig.3.6).

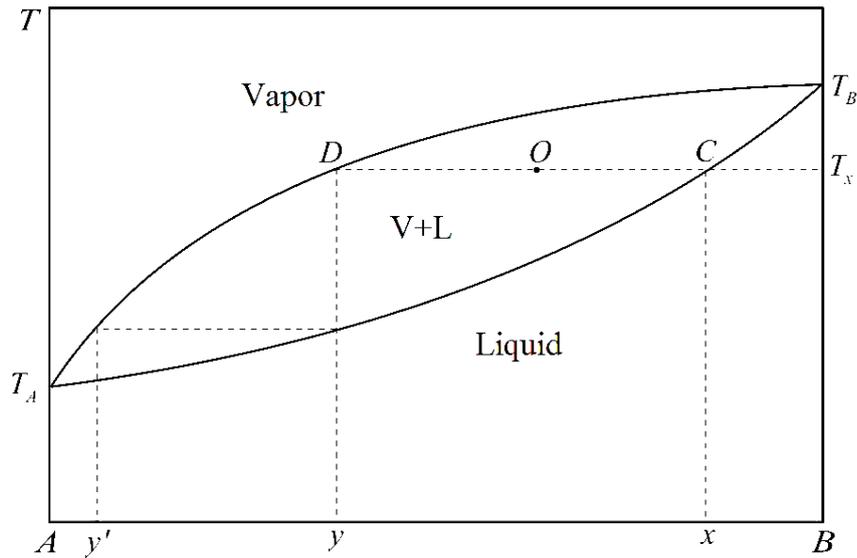


Fig. 3.6. Diagram of boiling temperature – composition for an ideal solution

Since the composition of the liquid is not identical with the composition of the vapor, the phase diagram contains two curves: the lower (boiling curve) shows the dependence of the boiling point on the composition of the liquid phase, and the upper (condensation curve) is the dependence of the boiling point on the composition that is in equilibrium with the vapor liquid. Thus, from the given liquid compositions, using the diagram, it is possible to determine the boiling point of this liquid and the composition of the vapor formed during boiling. The area between the curves corresponds to a two-phase system (liquid + vapor). Assume that the initial mixture has composition (x) (Fig.3.6). It boils at T_x , forming vapor of composition (y) enriched with a more volatile component of A. If we select and condense this vapor, we get a liquid of composition (y) which, when boiled, will give vapor of composition (y') containing even more component A. The relative quantities of vapor and liquid in a two-phase system can be determined by the rule of the lever: the point corresponding to the composition of the double heterogeneous system divides the straight line connecting the figured points of the equilibrium phases into segments, inversely proportional to the amounts of these phases; that is, if the composition of the system is specified by point O,

then the ratio of the vapor and liquid quantity $g_{vap}/g_{liq} = [OC]/[OD]$. According to the phase rule, the ratios of masses or numbers of moles are determined depending on the units in which the composition is expressed in the diagram. As a result of a series of successive distillations, practically pure component A can be driven away, and the solution remaining for each subsequent distillation will be enriched with component B and, as a result, will turn in almost pure B. This separation process is called fractional distillation.

If there are significant deviations from Raoult law, a maximum or minimum pressure may appear on the curve of the vapor pressure - composition, and on the corresponding diagram the boiling point-composition may appear minimum or maximum (Fig.3.7). For such solutions, Konovalov second law is correct: the points of maximum and minimum on the curve of total vapor pressure correspond to solutions having the same composition of liquid and vapor. Such mixtures are called azeotropic or inseparably boiling; their composition varies with boiling. For example, ethanol with water forms an azeotrope with a minimum boiling point and a mass ethanol content of 96%.

Azeotropic mixtures are mixtures with a limiting deviation from ideality, which still have complete mutual solubility. A further small additional deviation from ideality leads to the appearance of an area of mutual insolubility, that is, to a stratification of the system. The appearance of an extremum is possible not only in systems which components differ significantly in properties, but also in systems with substances having almost the same vapor pressure. In this case, a small deviation from the linear dependence leads to the appearance of an extremum, and this extremum is in the middle part of the diagram. In the case of a big difference between pA_0 and pB_0 , the extremum is shifted to the edge of the diagram. In fractional distillation of a solution containing an azeotropic mixture, not pure components A and B are produced, but

one of the components and an azeotropic mixture. In the pure form, that component is distinguished, the content of which is greater in the separated mixture than in the composition of the azeotrope.

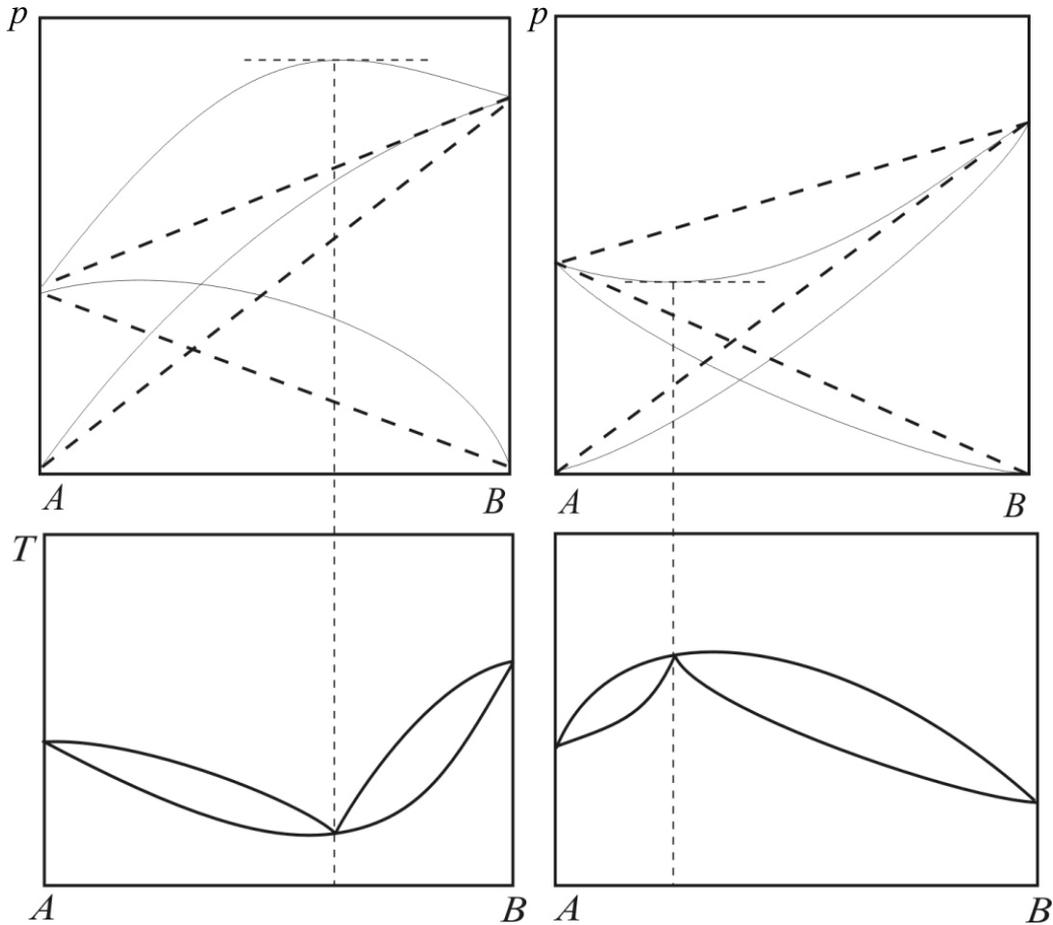


Fig. 3.7. Diagrams vapor pressure–composition and boiling point - composition for non-ideal solutions

The main regularities of the effect of temperature on the composition of the vapor equilibrium with the liquid mixture follow from thermodynamic relationships, called the **rules of Vrevsky**: *when increases the temperature of the vapor, which is in equilibrium with the volatile mixture of the specified composition, it is enriched by the component whose partial molar evaporation heat is greater.* If component B has a lower saturated vapor pressure than component A (Fig.3.8 and 3.9), then it has a higher boiling point and a greater molar

heat of evaporation. For liquid mixtures in vapors, the mole fraction of component B increases with increasing temperature.

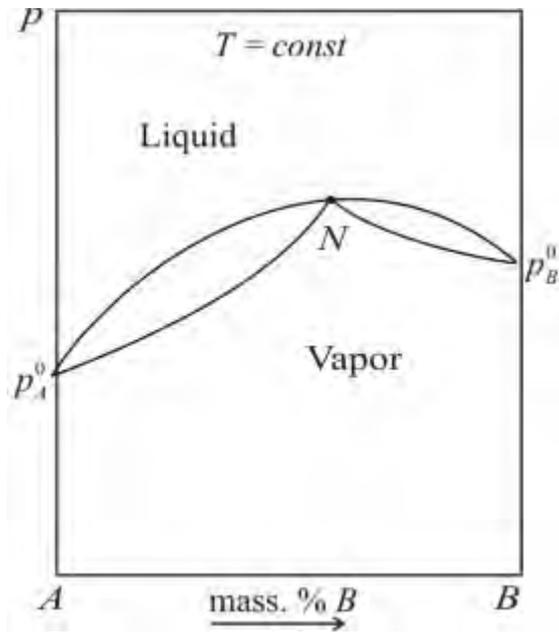


Fig. 3.8. The dependence of the vapor-liquid composition on the temperature for solutions with a positive deviation from the Raoult law

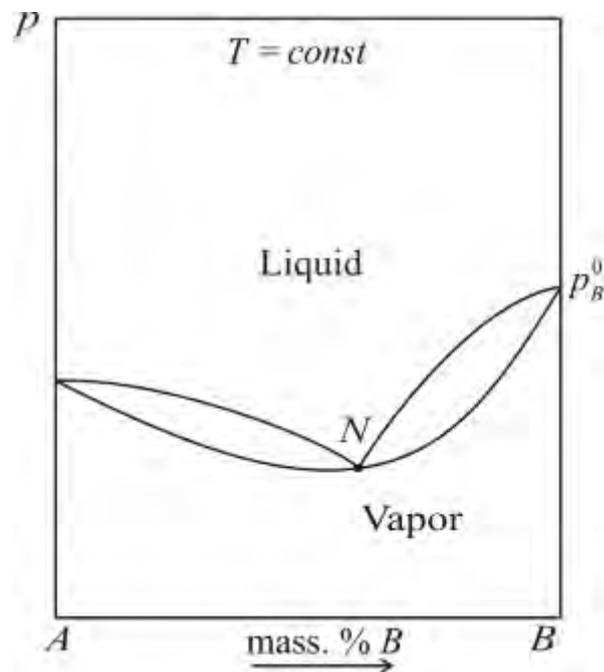


Fig. 3.9. The dependence of the vapor-liquid composition on the temperature for solutions with a negative deviation from Raoult law.

Example. Determine which fractions and in what quantities can be obtained by distillation of 1 kg of an aqueous solution of formic acid with a mass content of 50%, if an azeotrope with a maximum boiling point and a mass water content of 25,5% is formed in this system.

Solution. Since the stock solution contains more water than the azeotrope, it can be dispersed into an azeotrope and water. Water will be distilled, since its boiling point is lower than that of an azeotrope. All formic acid (500g) will enter the composition of the azeotrope, where its content is 74,5%, that is, the mass of the azeotrope will be $500 / 0,745 = 671g$ the mass of water will be $1000 - 671 = 329g$.

Practically important is the process of distilling liquids that do not mix. If two liquids do not dissolve into each other, then each of them evaporates independently of the other. In this case, the total vapor pressure over the mixture will be equal to the sum of the saturated vapor pressures of the pure components. The mixture will boil when the total vapor pressure becomes equal to the external pressure, that is, at a lower temperature than each component separately. Since the partial and total vapor pressure for immiscible liquids does not depend on the quantitative composition of the mixture, both the boiling point of the mixture and the composition of the vapor will be constant for any composition of the liquid phase. Many organic substances decompose when heated at a temperature lower than the boiling point. For their purification, vacuum distillation is used (to reduce the boiling point) or distillation together with another liquid with which they do not mix. If organic substances do not mix with water, then such distillation is called "steam distillation". In the receiver, the compound that is purified is condensed together with water and the condensate is stratified into two liquids that are mechanically separated. The method requires additional heat input, but is structurally much simpler than distillation under vacuum.

3.5. Fluid-liquid equilibrium

The limited solubility of liquids is observed in systems with a significant deviation from the ideal when the energy of interaction of dissimilar molecules is much less than that of homogeneous ones. The solubility depends on the temperature and when the temperature changes it can shift to a limitless (full blending). The dependence of mutual solubility on temperature at constant pressure is depicted on the diagrams of the bundle curve (Fig.3.10 and 3.11).

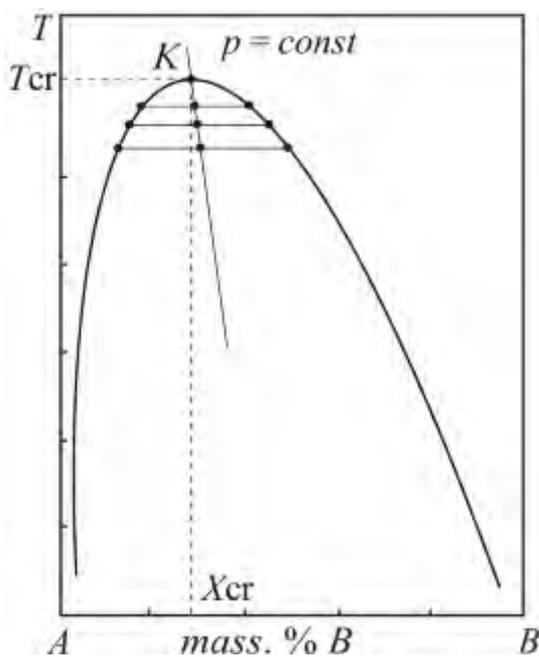


Fig. 3.10. The state diagram of the water (A) – phenol (B) with the upper critical dissolution temperature

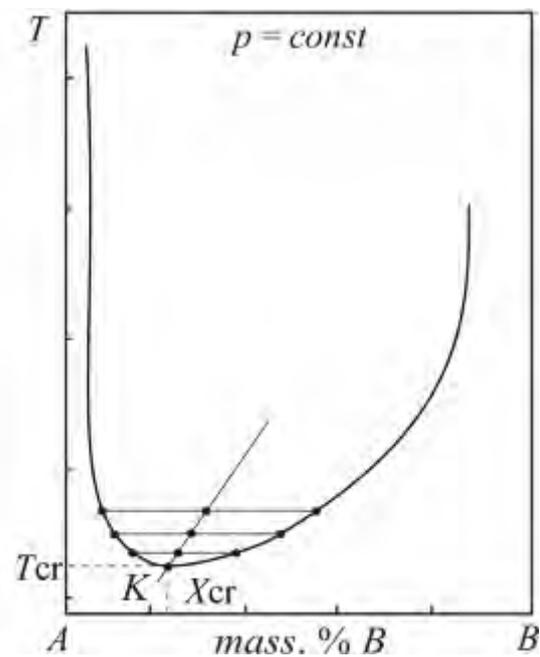


Fig. 3.11. The state diagram of the triethylamine (A) – water (B) system with a lower critical dissolution temperature.

The bundle curve divides the diagram into a homogeneous (above the curve) and heterogeneous (below the curve) region. If the state of the system is expressed by a point inside the separation curve, then the system consists of two liquid phases whose compositions are determined by the points of the bundle curve and parallel lines. The maximum point of the curve (K) is called the critical dissolution temperature. The straight

lines connecting the points of equilibrium layers (parallel lines inside curve of a bundle) are called nodes or conods. According to Alekseev's rule, the midpoints of the nodes lie on one straight line passing through the critical point K.

Example. A mixture of 60g of carbon disulfide and 40 g of methanol is at 20°C. Determine the phase composition of the mixture from the diagram (Fig.3.12).

Solution. From the given composition (40%) and 20°C, we find the figurative point of the system. The system is heterogeneous, consists of two solutions: 1) methanol in carbon disulfide, the concentration of which is determined by the point a_1 (2% CH_3OH); 2) carbon disulfide in methanol (point b_1 , 48% CH_3OH). The number of solutions can be determined graphically according to the rule of the lever: Therefore, the amount of the second solution = $100 \times 4,7 / 5,7 = 82,5$ g, and the amount of the first = $100 - 82,5 = 17,5$ g. The mixture becomes homogeneous with heating up to 30°C (point b_2).

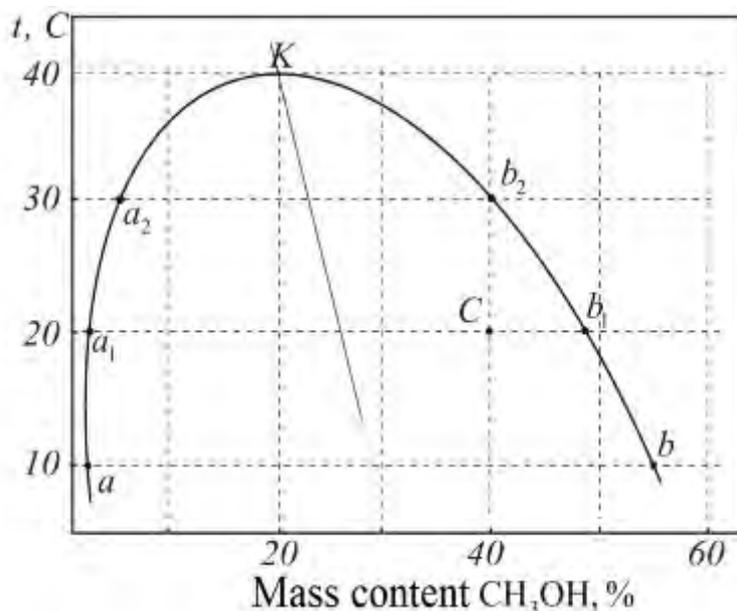


Fig. 3.12. The system state diagram: carbon disulfide (A) – methanol (B)

If a third component is added to two mutually insoluble or boundedly soluble liquids, which is capable of dissolving in them, then at equilibrium the chemical potential of this component in both liquid phases will be the same.

$$\mu_{\alpha} = \mu_{\beta}; \mu_{\alpha}^0 + RT \ln \cdot a_{\alpha} = \mu_{\beta}^0 + RT \ln \cdot a_{\beta}; \ln \frac{a_{\alpha}}{a_{\beta}} = \frac{(\mu_{\beta}^0 - \mu_{\alpha}^0)}{RT} = \text{const}$$

or for a two-phase equilibrium system

$$a_1 / a_2 = k, \quad (3.11)$$

where a is the activity of the component, k is the distribution coefficient.

Equation (3.11) was called *the distribution law: the ratio of the activities (concentrations) of a substance distributed between two liquid phases that do not mix is constant at a given temperature*. At low concentrations, instead of activities in the calculations, one can use concentrations, then (3.11) will be written as

$$c_1 / c_2 = k \quad (3.12)$$

If the dissolved substance, as a result of association or dissociation in one of the solvents, has a different particle size in both liquids, then the distribution law takes the form, where $n > 1$, if in the first solvent the particle size is smaller than in the second one.

An extraction process is based on the using of the distribution law - extraction of a substance from a solution by another solvent that does not mix with the former. Extraction is widely used in industry, for example, for obtaining substances of high purity, separation from ores of rare and dispersed elements, and the like.

Example. The coefficient of iodine distribution between water (1) and chloroform (2). In a liter of aqueous solution is 0,2g of iodine. How much iodine can be extracted from this solution with 50ml of chloroform by five consecutive extractions?

Solution. We introduce the following notation: V_1 is the volume of the aqueous solution, V_2 is the volume of chloroform used for one extraction, g_0 is the amount of dissolved iodine in the initial solution, g_1 is the amount of iodine that remained in the aqueous solution after the first extraction. Then the amount of iodine got during the first extraction will be $(g_0 - g_1)$, and the concentration of iodine in water and in chloroform at equilibrium, accordingly: $c_1 = g_1 / V_1$, $c_2 = (g_0 - g_1) / V_2$.

The coefficient of distribution $k = \frac{c_1}{c_2} = \frac{g_1 V_1}{V_1 (g_0 - g_1)}$, then taking into account this ratio, it is possible to calculate the amount of iodine that remained in the aqueous solution after the first extraction:

$g_1 = g_0 \frac{k \cdot V_1}{k \cdot V_1 + V_2}$. In the case of a second extraction with the same volume,

we similarly obtain $g_2 = g_1 \frac{k \cdot V_1}{k \cdot V_1 + V_2} = g_0 \left(\frac{k \cdot V_1}{k \cdot V_1 + V_2} \right)^2$. In the case of a

series of successive extractions: $g_n = g_0 \left(\frac{k \cdot V_1}{k \cdot V_1 + V_2} \right)^n$. For five consecutive

extractions of 10 ml of chloroform we get:

$$g_5 = 0,2 \left(\frac{0,0077 \cdot 1000}{0,0077 \cdot 1000 + 10} \right)^5 = 0,003.$$

So, it is extracted $0,2 - 0,003 = 0,197$ g or $0,197 \cdot 100 / 0,2 = 98,5\%$ of iodine.

If the extraction is carried out at once with the entire volume of chloroform

$$g_1 = 0,2 \frac{0,0077 \cdot 1000}{0,0077 \cdot 1000 + 50} = 0,027,$$

that is, it is extracted $0,2 - 0,027 = 0,173$ g of iodine or $0,173 \cdot 100 / 0,2 = 86,5\%$ (less than with multiple extraction). Conclusion: to get rid of the

soap solution when washing clothes, it is better to rinse it several times in a small basin than once in a huge bath.

3.6 Solid-liquid equilibrium

Reduction of vapor pressure over a solution of a non-volatile substance results in a decrease in its freezing point (the onset of crystallization). In Fig.3.14 is showed the dependence of the vapor pressure on the temperature of the solvent p^0 , solution p and solid solvent P . At the freezing point, the aqueous and solid phases are in equilibrium, and the vapor pressure over them should be the same. Thus, the freezing point of the solution T is determined by the intersection of the curves p and P and always below the freezing point of the pure solvent T_0 (if the solvent crystallizes out of the solution). A decrease in the freezing point is a colligative property, that is, it is proportional to the concentration of the solution, where K is the cryoscopic constant, m is the molality of the solution.

$$K = \frac{RT_0^2 \cdot M}{1000 \cdot \Delta H_{melt}}, \quad (3.13)$$

where M is the molecular weight of the solvent, ΔH_{melt} is the molar heat of solvent melting. The cryoscopic constant of the solvent is a constant equal to the calculated decrease in the freezing point of a single-molar solution. Having determined the decrease in the freezing point of a solution of a known mass concentration, it is possible to determine the molecular mass of the dissolved substance according to the formula $M = 1000 \cdot K \cdot g / \Delta T \cdot a$, where g is the mass of the solute, and a is the mass of the solvent.

The solubility of solids in liquids depends on the nature of the substance and the solvent, the temperature and the presence of permanent substances, especially electrolytes, in the solution. Solids dissolve better

in solvents similar in chemical composition, to their nature (polar substances dissolve better in polar solvents, non-polar substances dissolve in non-polar solvents).

If the solid is in equilibrium with the solution, $A_{cr} \leftrightarrow A_{sol-n}$, then this solution is called saturated, and its concentration (N_A) is the solubility of the solid. Considering this equilibrium in the same way as the equilibrium of a heterogeneous chemical reaction and applying the chemical reaction isobar equation, we can write: $d \ln N / dT = \Delta H / (RT^2)$, where ΔH is the heat of dissolution of a mole of substance in a saturated solution.

The process of dissolution can be represented in the form of two coherent processes: melting of solid and mix of two liquids. If the solution is ideal, then the second process is not accompanied by a heating effect. In this case ΔH_m represents fusion heat of solid:

$$\frac{d \ln N}{dT} = \frac{\Delta H_m}{RT^2}, \quad (3.14)$$

where ΔH_m – molecular heat of melting of dissolved solid, N – solubility of solid in the solution, T – crystallizing temperature of fusion (of freezing of the solution).

This is the **Shreder** Equation *that shows dependence of ideal solubility of solid (expressed in terms of the molecular heat) on the temperature or if this equation is used to a solvent, then it shows connection of temperature of freezing of the solution with solvent concentration.*

Dependence of temperature of mixture melting on composition is graphically shown in so-called fusibility diagrams (under constant pressure). The way how the diagram is built depends on mutual solubility of elements in liquid and solid phase and on presence of chemical interaction between them.

Systems with complete solubility of the components in liquid phase and with mutual insolubility in solid phase.

If the components of such system don't interact then when it comes to cooling of the fusion with any compound one of the pure components (solvent) crystallizes until the solution becomes saturated, after this both components crystallize simultaneously. Fields of diagram correspond to the following conditions (figure 3.13): I – liquid fusion, II – crystals A and B, III – liquid fusion and crystals A, IV – liquid fusion and crystals B. The line T_AET_B , above which the system is in liquid phase is called liquidus; the line FEG , below which the system is in solid phase, – solidus. Point of intersection of these lines (E) matches with balance of three phases (fusion, A_{cr} , B_{cr}), is called eutectic, and conforming compound – eutectic mixture.

It is possible to calculate theoretically the eutectic diagram of fusibility due to Shreder Equation, as a line T_AE represents dependence of solubility A and a line ET_B – solubility B from the temperature.

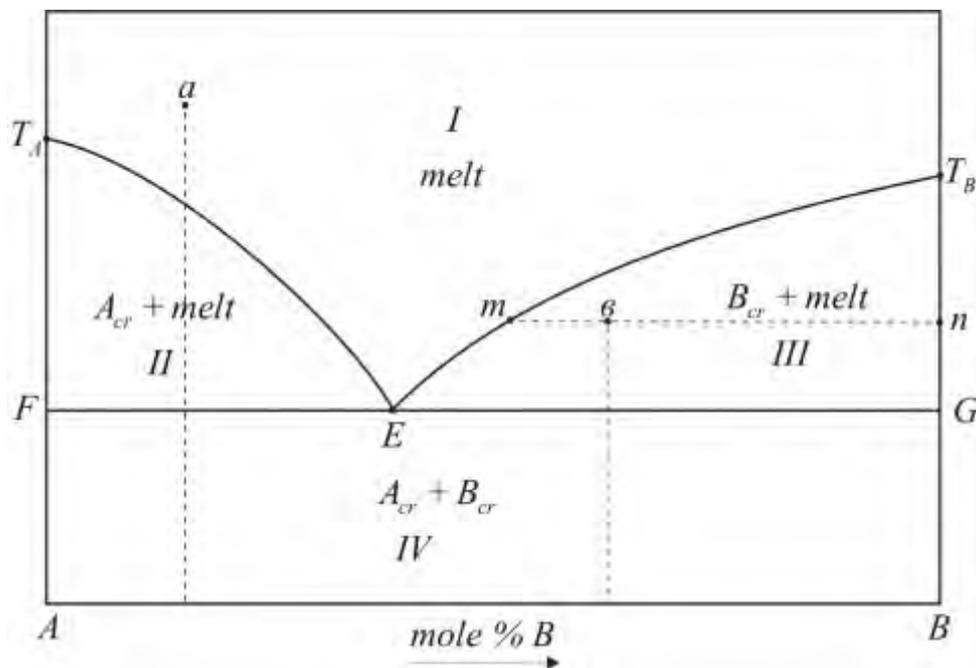


Fig. 3.13. Diagram of fusibility of two-component system with eutectic

Method of thermal analysis is used in construction of diagram of fusibility and it is based on temperature measuring in the process of crystallization of mixtures with different compound. If to fuse a liquid mixture of required compound and to cool after, writing down change of temperature and time, then the temperature and time curve (cooling curve) will be smooth without phase changes and connected with them heating effects and while changing the phase condition on the curve there are some indicative thresholds and fissures to appear, according to which one can find out temperatures of the beginning and end of the crystallization and there are built liquidus and solidus curves. Cooling shapes depend on the type of a diagram.

Let us consider in more detail solution of practical problems for phase equilibriums. Equilibrium of the system liquid – vapour in binary systems when $p = \text{const}$ is depicted with a help of a diagram in coordinates temperature – compound. Two curves are built on the diagram, the lower one identifies liquid content, boiling at required temperature and the upper one – the composition of equilibria with its vapour. The area between curves is in charge for binary phase system (liquid – vapour). The relative quantity of vapour and liquid can be defined with a "lever rule": point that meets the composition of a binary system, splits a line, which unites figurative points of equilibrium phases on line segments which are inversely related to the number of these phases. When heterogeneous system consists of " C " components and " P " phases and each of these phases includes all the components, then this system is complied with the Gibbs's phase rule: the number of degrees of freedom of the system in equilibrium, which is influenced from external factors only by pressure and temperature, is equal to the number of components minus the number of phases plus the constant two:

$$F = C - P + 2.$$

Sometimes as it happens in our case, the systems are considered with a constant parameter. For example, at a constant temperature or under constant pressure. Then the number of degrees of freedom decreases:

$$F = C - P + 1.$$

Total vapour pressure, which is in balance with a liquid mixture of two volatile components *A* and *B* is equal to the sum of partial pressure of the components:

$$p = p_A + p_B.$$

For ideal mixtures of liquids according to the Raoult law partial pressure is

$$p_A = p_A^0 \cdot N_A; \quad p_B = p_B^0 \cdot N_B,$$

where p_A^0 – is the vapor pressure over the pure component *A*, a *N* – is the mole fraction of this component in the solution. Weight quantity of one of the components in pair can be calculated for the ideal mixture from the following ratio:

$$\text{wt.\% } A = \frac{p_A M_A}{p_A M_A + p_B M_B} \cdot 100 \%,$$

where *M* – molecular mass.

Task 4

In the table below you can find equilibrium compositions of liquid (*x*) and vapour (*y*) phases of binary mixture *A-B* depending on the temperature under constant pressure. The compositions “*x*” and “*y*” are represented in mole percent of *A*. Based on these data:

- 1) to build an equilibrium diagram liquid –vapour;
- 2) to build a dependency graph of vapour composition (*y*) on liquid composition (*x*);
- 3) to define boiling temperature of mixture, which contains *a* (mol) % of component *A*, composition of first vapour bubble and at which

temperature the last drop of liquid disappears and what is its composition?

Table 3.2 – Variants of task

№	System	T , K	Composition A , mol.% $x y$	T , K	Composition A , mol.% $x y$	a , %	T_1
1	$A - \text{HNO}_3$	391	0 0	400	40 51	55	395
	$B - \text{C}_2\text{H}_4\text{O}_2$	395	10 2	390	53 84		
		399	20 8	378	65 96		
	$p = 1,01 \cdot 10^5 \text{ Pa}$	402	34 34	358	100		
2	$A - \text{H}_2\text{O}$	435	0 0	372	30 90,5	10	371
	$B - \text{C}_5\text{H}_4\text{O}_2$	432	110	371	50 90,6		
		419	236	370,9	90,890,8		
	$p = 1,01 \cdot 10^5 \text{ Pa}$	396	6 68	372	99 95		
		383	10 81	373	100100		
3	$A - \text{HF}$	373	0 0	382	4463	65	370
	$B - \text{H}_2\text{O}$	376	10 2	372	5286		
		380	19 7	360	5896		
	$p = 1,01 \cdot 10^5 \text{ Pa}$	383	2818	335	7098		
		385	3636	318	80 99		
		384	4048	292	100100		
4	$A - \text{HNO}_3$	373	00	394	40 60	55	385
	$B - \text{H}_2\text{O}$	380	71	391	46 76		
		385	122	385	53 89		
	$p = 1,01 \cdot 10^5 \text{ Pa}$	391	207	372	62 95		
		394	28 14	357	100100		
		395	38 18				
5	$A - \text{H}_2\text{O}$	384	4 28	365,7	75 75	20	370
	$B - n\text{-C}_4\text{H}_{10}\text{O}$	382	7 34	367	98 80		
		376	16 48	370	99 89		
	$p = 1,01 \cdot 10^5 \text{ Pa}$	369	30 66	373	100 100		
		366	50 74				
6	$A - \text{H}_2\text{O}$	371	14 40	362	67 67	35	364
	$B - \text{iso-C}_4\text{H}_{10}\text{O}$	369	17 45	365	98 72		
		366	26 54	366	99 76		
	$p = 1,01 \cdot 10^5 \text{ Pa}$	363	40 63	373	100 100		

Continuation of Table 3.2

№.	System	T, K	Composition		T, K	Composition		a, %	T ₁
			A, mol.%	x y		A, mol.%	x y		
7	A – H ₂ O	378	0	0	365	93	71	25	370
	B – C ₅ H ₁₂ O	372	10	23	367	98	78		
		368	18	43	369	99	86		
	<i>p</i> = 1,02·10 ⁵ Pa	365	38	58	373	100	100		
		364	66	66					
8	A – CS ₂	329	0	0	312	66	66	25	315
	B – CH ₃ COCH ₃	323	6	23	313	84	73		
		317	19	41	314	89	77		
	<i>p</i> = 1,01·10 ⁵ Pa	314	32	53	316	95	86		
		313	45	60	319	100	100		
9	A – CH ₃ OH	350	0	0	329	74	59	25	330
	B – CCl ₄	340	2	26	331	88	70		
		335	3	38	336	98	91		
	<i>p</i> = 1,01·10 ⁵ Pa	330	17	50	338	100	100		
		328	55	55					
10	A – CH ₃ OH	352	0	0	329	65	65	80	330
	B – C ₆ H ₆	341	2	19	331	87	74		
		337	3	30	333	95	85		
	<i>p</i> = 9,67·10 ⁴ Pa	332	5	47	336	100	100		
		330	8	55					
11	A – CH ₃ OH	353	0	0	331	61	61	5	333
	B – C ₆ H ₆	342	3	31	332	87	74		
		338	6	40	333	93	82		
	<i>p</i> = 1,0·10 ⁵ Pa	332	23	56	336	98	92		
12	A – C ₂ H ₆ O	353	0	0	341	59	47	75	345
	B – C ₆ H ₆	348	4	15	342	72	55		
		343	16	31	345	87	69		
	<i>p</i> = 1,01·10 ⁵ Pa	341	30	40	347	92	79		
		340,7	42	42	351	100	100		
13	A – C ₃ H ₆ O	334	0	0	335	58	67	55	335
	B – CHCl ₃	336	19	10	333	74	77		
		336,8	38	38	331	89	94		
	<i>p</i> = 1,0·10 ⁵ Pa	336,4	47	53	329	100	100		

Continuation of Table 3.2

№	System	T, K	Composition		T, K	Composition		a, %	T ₁
			A, mol.%	x y		A, mol.%	x y		
14	A – C ₃ H ₆ O	338	0	0	329	56	64	10	330
	B – CH ₃ OH	336	5	14	328,6	80	80		
		333	18	32	329	98	93		
	<i>p</i> = 1,01·10 ⁵ Pa	331	28	43	330	100	100		
		330	38	51					
15	A – C ₃ H ₆ O	333	0	0	333	62	72	55	331
	B – CHCl ₃	334	7	4	332	69	80		
		335	22	18	330	82	90		
	<i>p</i> = 9,76·10 ⁴ Pa	335,4	40	40	328	100	100		
		335	46	53					
16	A – C ₄ H ₁₀ O	326	0	0				65	325
	B – C ₆ H ₁₂ O ₂	325	9	13	325	72	60		
		324	28	32	326	83	71		
	<i>p</i> = 6,7·10 ³ Pa	323,7	37	37	327	89	81		
		324	52	47	329	100	100		
17	A – CCl ₄	351	0	0	337	52	59	25	345
	B – C ₂ H ₆ O	348	3	14	336,6	63	63		
		345	8	48	338	76	71		
	<i>p</i> = 0,99·10 ⁵ Pa	342	15	40	341	85	79		
		340	21	47	344	92	86		
		338	33	54	349	100	100		
18	A – C ₄ H ₁₀ O	353,5	0	0	350	74	67	25	350
	B – C ₆ H ₁₂ O ₂	352	10	14	351	85	79		
		351	17	23	352	92	88		
	<i>p</i> = 0,2·10 ⁵ Pa	350	30	36	353,3	100	100		
		349,4	49	49					
19	A – <i>cis</i> -C ₂ H ₂ Cl	337,6	0	0	326	65	65	30	331
	B – CH ₃ OH	335	4	13	326	92	75		
		332	10	26	328	97	84		
	<i>p</i> = 1,01·10 ⁵ Pa	330	16	36	330	99	90		
		328	23	43	333,8	100	100		
		326	37	54					

Continuation of Table 3.2

№.	System	T , K	Composition		T , K	Composition		a , %	T_1
			A , mol.%	$x y$		A , mol.%	$x y$		
20	$A - C_4H_{10}O$	399	0	0	390	78	78	30	391
	$B - C_6H_{12}O_2$	394	23	34	390,5	90	93		
	$p = 1,01 \cdot 10^5$ Pa	392	36	48	391	100	100		
		391	47	57					
21	$A - CHCl_3$	338	0	0	326	63	63	75	330
	$B - CH_3OH$	335	7	17	327	73	70		
		332	15	33	329	81	78		
	$p = 0,9 \cdot 10^5$ Pa	329	28	47	332	93	90		
		327	47	57	334	100	100		
22	$A - C_3H_8O$	373	0	0	360,8	42	42	80	365
	$B - H_2O$	368	1	11	362	68	54		
		365	2	22	363	77	62		
	$p = 1,01 \cdot 10^5$ Pa	362	7	35	366	92	82		
		361	20	40	370	100	100		
23	$A - C_7H_8$	381	0	0	373,5	55	55	15	376
	$B - C_4H_{10}O$	379	5	9	375	76	65		
		377	10	19	376	82	70		
	$p = 1,01 \cdot 10^5$ Pa	375	21	32	379	93	83		
		374	35	44	383	100	100		
24	$A - trans-$ C_2H_2Cl	338	0	0	316	44	73	25	320
		334	1	11	315	77	77		
	$B - CH_3OH$	328	8	29	316	96	86		
		322	17	50	318	99	93		
	$p = 1,01 \cdot 10^5$ Pa	318	29	64	321	100	100		
25	$A - CCl_4$	347	0	0	345	78	73	25	345
	$B - C_4H_8O_2$	346	12	16	346	97	93		
		345	32	36	346,4	100	100		
	$p = 0,91 \cdot 10^5$ Pa	344,6	59	59		97			

4) to define the mole composition of vapour, which is in balance with liquid binary system that boils at T_1 .

Chapter 4. ELECTROCHEMISTRY

4.1 Electrolyte solutions. Electrolytic dissociation

Electrolytes are substances that produces an electrically conducting solution when dissolved in a polar solvent. To explain the processes that take place in these solutions let us use the Arrhenius theory of electrolytic dissociation which is based on particular points:

1. Some substances, called electrolytes, when dissolved in suitable solvents, are able to split into oppositely charged particles – ions. This is an electrolytic dissociation.

2. Electrolytes do not split on dissolving in full. The fraction of the total number of molecules present in solution as ions is known as degree of dissociation ($\alpha = \frac{n_{diss}}{n_{diss} + n_{nondiss}}$). Another quantitative characteristic is dissociation constant. The degree of dissociation depends on substance nature, temperature and concentration: degree of dissociation α increases on solution diluting. Electrolytic dissociation constant depends only on substance nature and temperature.

3. Interface forces between ions are absent and they act as ideal gases in the solution, i. e. the theory of electrolytic dissociation relates only very dilute solutions.

All electrolytes according to the number of generated ions at dissociation divide into binary, ternary etc. Besides, electrolytes are divided according their ability of dissociation on weak and strong. A strong electrolyte is a solute that completely, or almost completely, ionizes or dissociates in a solution, a weak electrolyte – only partly. The terms –degree of dissociation and dissociation constant – are used only for weak electrolytes and both of them are connected between them in an equation. For example, let us look at binary electrolyte dissociation:



In accordance with the law of mass action, $K_D = \frac{c_{M^+} \cdot c_{A^-}}{c_{MA}}$, if c – electrolyte concentration, and α – degree of dissociation, then equilibrium concentrations of particular ions and non-dissociative electrolyte molecules will be

$$c_M^+ = \alpha \cdot c, \quad c_A^- = c \cdot \alpha, \quad c_{MA} = c \cdot (1 - \alpha). \quad (4.2)$$

Substituting these ratios in expression for dissociation constant, on the example of weak binary electrolyte it is observed *Wilhelm Ostwald's dilution law, according to which in dilute solutions the dissociation constant of a weak electrolyte does not depend on concentration of solution and is defined:*

$$K_D = \frac{c \cdot \alpha^2}{1 - \alpha} \quad (4.3)$$

Despite some disadvantages of the Arrhenius theory, some its statements allow to solve majority of problems, especially the theory explains conditions of equilibrium in solutions of electrolytes.

In this theory much attention is paid to studying of distribution character of ions in the solution that is defined with correlation between energy of electrostatic cooperation and energy of chaotic ion movement. As these energies are comparable in degree, the real distribution of ions in an electrolyte is intermediate between chaos and balance. This explains singularity and peculiarity of electrolyte solution, the difficulties which take place while building the theory of electrolyte solution, because in the first place it is necessary to observe the character of ion distribution.

Electrostatic forces aim to create such distribution, when every ion is surrounded only with ion of opposite charge but this process is resisted with chaos ion motion leading to random distribution. These opposite sets

cause that some ionic atmosphere is formed close to every ion and there is predominance of ions of opposite charge (in comparison with a central one).

The Arrhenius theory did not consider these circumstances and a lot of conclusions of this theory failed to go through the experience. For example, dissociation constant of electrolyte changes in a wide range of concentrations. Instability of dissociation constants which has been observed in many weak electrolytes under conditions of moderate concentration, is also connected with demonstration of this interaction and in particular, with force of interionic cooperation, which is not accounted and foreseen by the theory of electrolytic dissociation. With increase of electrolyte dissociation incomplete dissociation of molecules, interionic attraction, their hydration reaction and other effects in a greater degree influence on different solution characteristics. Their combined impact on any of thermodynamic properties can be expressed in a formal way **through an activity coefficient** of electrolyte in the particular solution. The point of the activity method is that in thermodynamic calculations the analytic concentration of a component in the solution is not used, but "corrected concentration" (activity) is, i.e. the one the component would have if the system (dissolved solid – solvent) were ideal.

The activity is connected with the concentration of ratio $c = \gamma \cdot a$, where γ – activity coefficient, a magnitude, thanks to which real system deviations from ideal one are quantitatively considered. In highly diluted solutions while ionic interaction becomes minor, the solution activity approaches to its concentration and the magnitude of activity coefficient to one, i.e. while diluting the solution $m \rightarrow 0$, $a \rightarrow m$ u $\gamma \rightarrow 1$. Observed changes of activity coefficient with raising of concentration reproduce

combined impact on characteristics of solution, effects of interionic attraction, their hydration, incomplete dissociation (if it takes place) etc.

Consequently, the activity coefficient describes an action of moving of a mol of substance from the real environment to the ideal one. This process can be explained like this. Chemical potential of the real system:

$$\mu = \mu^0 + RT \ln a. \quad (4.4)$$

Then $\mu = \mu^0 + RT \ln a = \mu^0 + RT \ln \gamma \cdot c = \mu^0 + RT \ln c + RT \ln \gamma = \mu_{id} + RT \ln \gamma$, and $\ln \gamma = (\mu - \mu_{id}) / RT = A / RT$, where A – an action of transport from real system to the ideal. Therewith for the standard condition of an electrolyte solution the condition of imagined solution is taken, where in the same time activity, concentration and activity coefficient equal one.

Taking into consideration the information above, the concentration constant of weak electrolyte dissociation (4.3) should be replaced on a thermodynamic constant of dissociation K^0 , expressed through the activity of participants of the process. Total activity (a) characterizes an electrolyte at large, without splitting it on cations and anions. Because of impossibility of identifying of activity of separate ions the notion "mean activity" (a_{\pm}) was introduced and it depends on activity of cations and anions (a_+) and (a_-). In order to find ratios that connect all mentioned magnitudes, let us consider the simplest process of electrolytic dissociation of a binary strong electrolyte. According to (4.1)



On electrolyte solution in the water the balance between its dissociated and not dissociated forms is set, so their chemical potentials become equal:

$$\mu = \mu_+ + \mu_- \quad (4.5)$$

Let us express the chemical potentials of the participants of electrolytic dissociation through their activity:

$$\mu = \mu^0 + RT \ln a, \mu_+ = \mu_+^0 + RT \ln a_+, \mu_- = \mu_-^0 + RT \ln a_- \quad (4.6)$$

Let us insert (4.6) in (4.5):

$$\mu = \mu_+ + \mu_- = \mu^0 + RT \ln a = \mu_+^0 + RT \ln a_+ + \mu_-^0 + RT \ln a_- \quad (4.7)$$

In the standard condition $\mu^0 = \mu_+^0 + \mu_-^0$, therefore, $RT \cdot \ln a = RT \cdot \ln a_+ + RT \cdot \ln a_- = RT \cdot \ln(a_+ \cdot a_-)$, where $a = a_+ \cdot a_- = a_{\pm}^2$. So, mean activity a_{\pm} – is geometric mean magnitude of activity of cation a_+ and anion a_- ,

$$a_{\pm} = \sqrt{a_+ \cdot a_-} \quad (4.8)$$

As activity is multiplication of concentration and activity coefficient, then all ratio above demands introduction of mean activity coefficient and mean concentration: $\gamma_{\pm} = \sqrt{\gamma_+ \cdot \gamma_-}$ and $c_{\pm} = \sqrt{c_+ \cdot c_-}$, so $a_{\pm} = \sqrt{a_+ \cdot a_-}$,

$$a_{\pm} = \gamma_{\pm} \cdot c_{\pm} \quad (4.9)$$

Let us transform all previous arguments for the common electrolytic dissociation of the strong electrolyte $K_{v+}A_{v-}$



Total number of ions that is formed on electrolyte dissociation,

$$v = v_+ + v_- \quad (4.11)$$

Chemical potential of electrolyte μ is connected with chemical potentials of ions μ_+ and μ_- in the following ratio

$$\mu = v_+ \cdot \mu_+ + v_- \cdot \mu_- \quad (4.12)$$

Let us express the chemical potentials of the participants of electrolytic dissociation through their activity:

$$\mu = \mu^0 + RT \ln a, \mu_+ = \mu_+^0 + RT \ln a_+, \mu_- = \mu_-^0 + RT \ln a_- \quad (4.13)$$

Let us insert (4.12) in (4.13)

$$\mu^0 + RT \ln a = \nu_+ \mu^0_+ + \nu_+ RT \ln a_+ + \nu_- \mu^0_- + \nu_- RT \ln a_-, \quad (4.14)$$

as in the standard condition

$$\mu^0 = \nu_+ \mu^0_+ + \nu_- \mu^0_-, \quad (4.15)$$

if to reduce both parts of the equality to RT , then there is a ratio:

$$\ln a = \nu_+ \ln a_+ + \nu_- \ln a_- = \ln (a_+)^{\nu_+} + \ln (a_-)^{\nu_-} = \ln (a_+)^{\nu_+} (a_-)^{\nu_-},$$

or

$$a = a_+^{\nu_+} \cdot a_-^{\nu_-} \quad (4.16)$$

Instead of multiplication of activities, as it was mentioned before (4.8), the mean is put in, that is defined as a geometric mean of cation and anion activities:

$$a = \sqrt[\nu]{a_+ \cdot a_-} \quad (4.17)$$

$$\text{Then} \quad a = a_{\pm}^{\nu} \quad (4.18)$$

Molality of the cation m_+ and anion m_- in the electrolyte solution

$$m_+ = m \cdot \nu_+ \quad \text{and} \quad m_- = m \cdot \nu_-, \quad (4.19)$$

their activity coefficients γ_+ and γ_- , then ion activities:

$$a_+ = \gamma_+ \cdot m_+ \quad \text{and} \quad a_- = \gamma_- \cdot m_-. \quad (4.20)$$

For the coefficients of activity the notion of mean activity coefficient of γ_{\pm} electrolyte is also inserted

$$\gamma_{\pm} = \sqrt[\nu]{\gamma_+^{\nu_+} \cdot \gamma_-^{\nu_-}} \quad (4.21)$$

also for mean ionic molarity of m_{\pm} electrolyte

$$m_{\pm} = \sqrt[\nu]{m_+^{\nu_+} \cdot m_-^{\nu_-}} = \sqrt[(\nu_+ + \nu_-)]{(m \cdot \nu_+)^{\nu_+} \cdot (m \cdot \nu_-)^{\nu_-}} = m \cdot \sqrt[\nu]{\nu_+^{\nu_+} \cdot \nu_-^{\nu_-}}. \quad (4.22)$$

Let us denote L as multiplicand with m – molality in the expression (4.22)

$$L = v_{\pm} = \sqrt[3]{v_+^{v_+} \cdot v_-^{v_-}} \quad (4.23)$$

Then the calculation of mean electrolyte molality is done with a formula:

$$m_{\pm} = m \cdot v_{\pm} = Lm. \quad (4.24)$$

The mean activity is expressed with mean molality of electrolyte:

$$a_{\pm} = \gamma_{\pm} \cdot m_{\pm} = \gamma_{\pm} \cdot m \cdot L \quad (4.25)$$

Example. One should determine the mean ionic activity of 0.1 molal water solution BaCl_2 , if $\gamma_{\pm} = 0,5$. (using different methods of calculation).

Solution.

1) In this case $v_+ = 1, v_- = 2$, so, $v = 3$.

The mean ionic activity $a_{\pm} = \sqrt[3]{a_+^{v_+} \cdot a_-^{v_-}}$. Activity of a cation $a_+ = \gamma_{\pm} \cdot m_+$, of anion $a_- = \gamma_{\pm} \cdot m_-$, in its turn, concentration of a cation $m_+ = m \cdot v_+ = 0,1 \cdot 1 = 0,5$, of an anion $m_- = m \cdot v_- = 0,1 \cdot 2 = 0,2$; then:

$$a_+ = \gamma_{\pm} \cdot m_+ = 0,5 \cdot 0,1 = 0,05 \text{ and } a_- = \gamma_{\pm} \cdot m_- = 0,5 \cdot 0,2 = 0,1.$$

$$\text{In such a way, } a_{\pm} = \sqrt[3]{a_+^{v_+} \cdot a_-^{v_-}} = \sqrt[3]{0,05^1 \cdot 0,1^2} = 0,079.$$

$$2) a_{\pm} = \gamma_{\pm} \cdot m_{\pm}, m_{\pm} = \sqrt[3]{m_+^{v_+} \cdot m_-^{v_-}} = \sqrt[3]{0,1 \cdot (0,2)^2} = 0,158,$$

$$m_+ = m v_+ = 0,1 \cdot 1 = 0,1, m_- = m v_- = 0,1 \cdot 2 = 0,2;$$

$$a_{\pm} = \gamma_{\pm} \cdot m_{\pm} = 0,5 \cdot 0,158 = 0,079.$$

$$3) a_{\pm} = \gamma_{\pm} \cdot m_{\pm} = \gamma_{\pm} \cdot m \cdot L, L = v_{\pm} = \sqrt[3]{v_+^{v_+} \cdot v_-^{v_-}} = \sqrt[3]{1^1 \cdot 2^2} = 1,58;$$

$$a_{\pm} = 0,5 \cdot 0,1 \cdot 1,58 = 0,079.$$

Comparison of different methods of calculation leads to the same result. In our opinion, the third method is the most rational one. So, for calculation of the mean ionic activity of electrolyte solution its necessary to know its analytic concentration, to confirm its mean activity coefficient

for this concentration in the manual and calculate L . L does not depend on a type of an electrolyte, it depends only on the quantity of cations (v_+) and anions (v_-) in the formula of the electrolyte.

In the table 4.1 there are ratios between molality m , mean ionic molality m_{\pm} , mean activity coefficient γ_{\pm} and mean ionic activity a_{\pm} for some types of electrolytes.

Table 4.1 – Mean ionic activities of different types of electrolytes

Type of electrolyte	Example	γ_{\pm}	$m_{\pm} = m \cdot v_{\pm} = m \cdot L$	$a_{\pm} = \gamma_{\pm} \cdot m_{\pm}$
1-1; 2-2; 3-3	KCl; CuSO ₄ ; AlPO ₄	$\sqrt{\gamma_+ \cdot \gamma_-}$	M	$m\gamma_{\pm}$
1-2, 2-1	MgCl ₂ , K ₂ SO ₄	$\sqrt[3]{\gamma_+ \cdot \gamma_-^2}$	$4^{1/3} m$	$1,58 m\gamma_{\pm}$
1-3, 3-1	AlCl ₃ , Na ₃ PO ₄	$\sqrt[4]{\gamma_+ \cdot \gamma_-^3}$	$27^{1/4} m$	$2,28 m\gamma_{\pm}$
2-3, 3-2	[Ca ₃ (PO ₄) ₂] [Al ₂ (SO ₄) ₃]	$\sqrt[5]{\gamma_+ \cdot \gamma_-^4}$	$108^{1/5} m$	$2,55 m\gamma_{\pm}$

Ionic strength of solution

As a result of experimental studies it has been observed that occurring while electrolytic dissociation ions have more influence on ionic activity coefficients, moreover, the more ionic valence is, the more powerful this influence is. Taking into account this influence, Gilbert N. Lewis suggested the concept of ionic strength: the mean activity coefficient of the compound " γ_{\pm} " that dissociates into ions is a function of ionic strength of I solution; i.e. for all solutions with the same ionic strength, regardless of the electrolyte nature, the activity coefficients for all ions of the same type (with the same valence) will be equal. Then

ionic strength I , which is for the solution of the strong electrolyte, that contains i -type ions with m_i (or c_i) concentrations and charges z_i , can be defined as

$$I = \frac{1}{2} \sum_i m_i z_i^2, \text{ or } I = \frac{1}{2} \sum_i c_i z_i^2, \quad (4.26)$$

Example. To calculate the ionic strength of a molar solution 0,2 in CaCl_2 .

Solution: Ionic concentration of the cation is $m_+ = m \cdot \nu_+ = 0,2 \text{ mol/kg}$, its charge is 2^+ ; and ionic concentration of the anion is $m_- = m \cdot \nu_- = 0,2 \cdot 2 = 0,4 \text{ mol/kg}$, and its charge is 1^- . Then $I = \frac{1}{2} (0,2 \cdot 2^2 + 0,4 \cdot 1^2) = 0,6$.

Example. To calculate the ionic strength of a solution containing 0,01 mol/kg in H_2SO_4 and 0,02 mol/kg in CuSO_4 .

Solution: While calculating the ionic strength of the solution containing the mix of electrolytes, the concentrations of all ions presented in the solution with their charge must be considered. The concentrations of all presented ions:

$$[\text{H}^+] = 0,01 \cdot 2 = 0,02; [\text{Cu}^{2+}] = 0,02; [\text{SO}_4^{2-}] = 0,01 + 0,02 = 0,03.$$

$$\text{Then } I = \frac{1}{2} \cdot (0,02 \cdot 1^2 + 0,02 \cdot 2^2 + 0,03 \cdot 2^2) = 0,11.$$

As the ionic strength of the solution does not depend on the nature of an electrolyte, but is defined only with its concentration and the charge of the ions, let us conclude the simple ratios that connect the ionic strength of the solution with its concentration for different types of the electrolytes.

For 1–1 valent electrolyte $m_+ = m_- = m$, the charge of the anion and the cation = 1. $I = \frac{1}{2} \cdot (m \cdot 1 + m \cdot 1) = m$. The results of similar calculations for other types of electrolytes are represented in the following table:

Table 4.2 – Calculation results

Type of electrolyte	Ionic strength (I)
1:1 (NaNO ₃)	$I = m$
1:2 (Li ₂ CO ₃ , CaF ₂)	$I = 1/2 (2 \cdot m \cdot 1 + m \cdot 4) = 3 m$
1:3 (AlF ₃ , K ₃ (PO ₄))	$I = 1/2 (3 \cdot m \cdot 1 + m \cdot 9) = 6 m$
2:2 CuSO ₄	$I = 1/2 (m \cdot 4 + m \cdot 4) = 4 m.$
2:3 Al ₂ (SO ₄) ₃ , Mg ₃ (PO ₄) ₂	$I = 1/2 (2 \cdot m \cdot 9 + 3 m \cdot 4) = 15 m.$

Dependence of γ on the ionic strength of the solution is kept with concentration of the solution less than 0,02 mol/kg, while on concentration up to 0,2 mol/kg this rule is followed approximately. In the solutions with mean and high concentrations the character of ionic interaction is being complicated by strong concentration of ions and the peculiarities of electrolytes appear.

Debye–Hückel theory

In solutions of strong electrolytes in addition to electrostatic forces of attraction and repulsive forces between charged particles, there are also the Van der Waals forces, ion-dipole interaction forces and other short-range forces. In the expression for the chemical potential of an ion

$$\mu_i = \mu_i^0 + RT \ln \cdot m_i + RT \cdot \ln \gamma_i$$

the first two components give partial free energy of one mol of an ideal solution of i -ions and third component characterizes excess free energy in comparison with free energy in the solution, which is taken for the ideal one. The calculation of this free energy is the main task of the theory of the electrolytic solution. In general, the task is very difficult. That is why some simplifying approximations are used. The backbone of modern

theories of the electrolytic solutions is the Debye–Hückel theory. This theory gives an opportunity to calculate the energy of electrostatic interaction between ions, formation (or disruption) of the ionic atmospheres.

This energy distinguishes qualities of the real electrolyte solution from the ideal one, that contains uncharged particles. This difference can be expressed with the activity coefficient γ . In such a way it is possible to calculate γ - coefficient with the knowledge of the energy of electrostatic interaction.

The fundamental principles of the Debye–Hückel theory are:

a) strong electrolytes are completely dissociated in the solution;

b) it is excepted, that ions are infinitely - distant in comparison with a size of the ions, that is why the ions are identified with material points, that have particular charge (the own ion volume is neglected);

c) ion distribution in the solution matches with the model of ionic atmosphere, when a transitional statistic distribution of ionic density of opposite charge forms around this ion and this density decreases fast with the distance from the central ion. Ion distribution in the solution is perceived to use the principle by Boltzmann and that forces that function between them are electrostatic by nature, and electrostatic interaction is considered as interaction between an ion and its ionic atmosphere;

d) charge distribution around the ion is supposed to be used with Poisson's equation, that connects charge density with the potential. Strictly speaking, this equation can be applied only to continuous charge. Ion charges in ionic atmosphere are discrete. In this case continuity of the charge can be considered as a result of a statistical distribution;

e) permittivity of solvent which is near the ion is excepted to be equal to permittivity of solution.

In the Debye–Hückel theory the notion of ionic atmosphere plays an important role and it should be observed as average in time predominance of ions of opposite charge near given central ion; as a system, where ionic density is ongoing distance from the center ion. In the same time “radius” of ionic atmosphere is a magnitude multiplied to a characteristic length. It cannot be understood geometrically as a radius of the sphere, where the action of the central ion becomes equal to 0. This magnitude points at the fact that ionic atmosphere creates in the point of the central ion such potential, that could have appeared if the charge of this atmosphere had been arranged on surface on the thinnest shell of charge sphere with radius according to this characteristic length. The radius of the ionic atmosphere $\frac{1}{\chi}$ is defined as

$$\frac{1}{\chi} = \sqrt{\frac{\varepsilon k T 1000}{8 \pi e^2 N_A I}} = 1,9 \cdot 10^{-10} \sqrt{\frac{\varepsilon T}{I}}. \quad (4.27)$$

The radius of the ionic atmosphere decreases with increasing of ionic strength of the electrolyte " I " (i.e. with growth of concentration or ionic charge) and grows with increasing of temperature T (temperature effect is partly compensated with decreasing of permittivity " ε ", electrolyte on heating). The Debye–Hückel theory has helped to find the expression for mean activity coefficient $(\gamma_{\pm})_{z_+, z_-}$ - valence electrolyte:

$$\lg \gamma_{\pm} = -|z_+ \cdot z_-| A \sqrt{I}, \quad (4.28)$$

where $A = 1,825 \cdot 10^6 \cdot (\varepsilon T)^{-3/2}$. This is limiting law of Debye–Hückel.

For instance, in a dilute water solution when $T=298$ and $\varepsilon=78,3$ $A = 0,509$, then for water solution of 1:1 electrolytes the limiting law taking into account (4.28) will look like this: $\lg \gamma_{\pm} = -0,509 \sqrt{c}$.

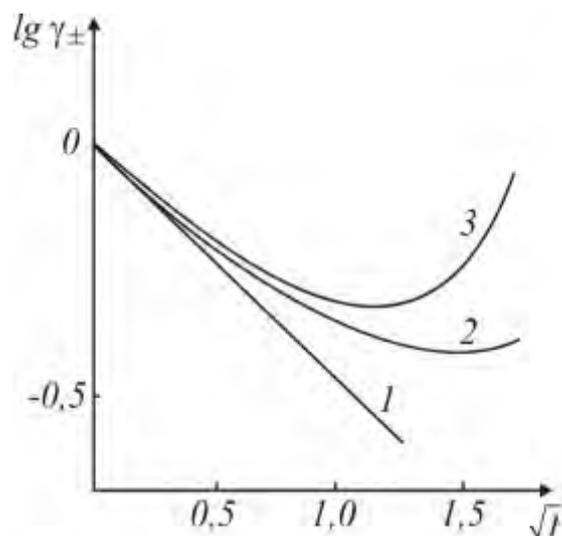


Fig. 4.1 Dependence of $\lg \gamma_{\pm}$ on \sqrt{I}

The limiting law of Debye–Hückel that is accomplished only in case of very dilute ($c \sim 0,01\text{--}0,05$ mol/l) solutions (graph 1 figure 4.1) has theoretically proved the rule of ionic strength– mean activity coefficient of electrolyte for the given ionic strength of the solution is a constant and does not depend on nature of other electrolytes in the solution.

4.2. Conductivity of solutions

Depending on the nature of conductor electrons and ions can be carriers of electric current in the system. In electrolyte solutions electricity conduction is done by transferring ions. The quantitative characteristic of the solutions capacity to conduct electric current is electric conductivity.

Electric conductivity is the quantity reciprocal of resistance. In its turn, the resistance R depends on length of the conductor l , cross-sectional area S and resistivity ρ : $R = \rho \frac{l}{S}$.

They differentiate the specific conductivity and molar conductivity. *The specific conductivity* κ is the conductivity of an electrolyte concluded between electrodes of 1 m^2 each that are at the distance of 1 m from each

other $[\Omega^{-1} \cdot m^{-1}]$. The specific conductivity is the quantity reciprocal of the specific resistance ρ ($\Omega \cdot m$):

$$\kappa = 1/\rho. \quad (4.29)$$

The molar conductivity λ is the conductivity of a 1 cm thick electrolyte placed between electrodes of such an area so that the volume of the electrolyte concluded between them contain 1 gE (gram equivalent) of the substance. The molar conductivity of the electrolyte at such concentration (κ_c) has the following correlation with the specific conductivity at the same concentration (λ_c): $[\Omega^{-1} \cdot m^2 \cdot mol\text{-eq}^{-1}]$

$$\lambda_c = \kappa_c/c, \quad (4.30)$$

where c – concentration of the electrolyte ($mol\text{-eq} \cdot m^{-3}$).

In chemical practice the concentration is often expressed in $mol\text{-eq} \cdot dm^{-3}$ and the resistivity is expressed in $\Omega \cdot m$. In such a case the following coefficient ($\Omega^{-1} \cdot cm^2 \cdot mol\text{-eq}^{-1}$) appears in the correlation between the electric conductivity:

$$\lambda_c = 1000 \cdot \kappa_c / c = \kappa_c / \varphi, \quad (4.31)$$

where φ dilution, the capacity of the solution in which there is 1 gE of the substance. $[\kappa] = 1/\Omega \cdot m$; $[\lambda] = cm^2/\Omega \cdot mol$; $[c] = mol/1000 \cdot cm^3$

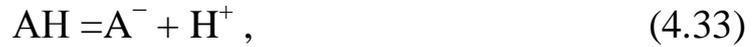
The molar conductivity of solution grows with dilution, it reaches maximum and does not grow anymore in case the dilution is big enough. It is explained by the fact that weak electrolytes have their dissociation degree grown while diluting, which means the increasing number of ions; in case with strong electrolytes the distances between ions are increasing, therefore interactions forces are weakening that increases the velocity of ions motion. The molar conductivity of infinitely diluted solutions is called conductivity at infinite dilution and is denoted:

$$\lambda^0, (\Omega^{-1} \cdot m^2 \cdot mol\text{-eq}^{-1}).$$

According to **Kohlrausch** law

$$\lambda^0 = \lambda_+^0 + \lambda_-^0 \quad (4.32)$$

where λ_+^0 and λ_-^0 – mobilities of a cation and an ion at infinite dilution correspondingly . The values of λ_+^0 and λ_-^0 are taken from the reference table. If a weak electrolyte splits according to the pattern:



the equilibrium (dissociation) constant looks like:

$$K_D = \frac{a_{H^+} \cdot a_{A^-}}{a_{HA}}, \quad (4.34)$$

where a_i – mobilities of the corresponding components.

To calculate the equilibrium of the weak electrolyte solution with relatively small concentration one may use concentrations instead of mobility. If overall concentration is c and dissociation degree is α , equilibrium concentration, equilibrium concentrations are $a_{H^+} = c_{A^-} = c \cdot \alpha$, and if concentration $HA = c$, then

$$K_D = \frac{c_{H^+} \cdot c_{A^-}}{c_{HA}} = \frac{c \cdot \alpha^2}{1 - \alpha}. \quad (4.35)$$

This formula is the analytical expression of *Ostwald's dilution law* (for binary electrolyte), according to which ***the constant of electrolytic dissociation at constant temperature doesn't depend on the concentration (dilution) of the solution.***

As the dissociation degree

$$\alpha_c = \lambda_c / \lambda_0, \quad (4.36)$$

here λ_c – molar conductivity($\text{Ohm}^{-1} \cdot \text{m}^2 \text{mol-eqv}^{-1}$) at the current concentration c ; and λ_0 – equivalent conductivity of the infinite diluted solution,

$$K_D = \frac{\lambda_0^2 \cdot c}{\lambda_0 \cdot (\lambda_0 - \lambda_c)}. \quad (4.37)$$

For strong electrolytes the dependence of molar conductivity on concentration of diluted solutions is characterized by Kohlrausch empirical equation

$$\lambda = \lambda_0 - A\sqrt{c}, \quad (4.38)$$

where A – equation constant. On the basis of this equation one may determine the limiting value of the electrolyte molar conductivity without using reference data on ions mobility if the dependence of molar conductivity on concentration is known. Thermodynamic properties of strong electrolyte solutions differ greatly from those of ideal solutions. To do the necessary calculations for real solutions one uses mobility instead of concentration ($a = \gamma c$).

Velocities of ions at single potential gradient at 1 V/m is called the absolute ion velocities in solutions u_+ and u_- [$\text{cm}^2/\text{s}\cdot\text{V}$]. The absolute velocity multiplied by Faraday constant (96500 Cl) is called the ion mobility V_i and is expressed in the conductivity units, i.e.

$$V_+ = Fu_+; \quad V_- = Fu_-; \quad (4.39)$$

Ions serve as conductors of the current in electrolyte solutions, but as the absolute velocities of anions and cations motions in solutions are not equal, the major part of the current is conducted by faster ions. The quantity, with the help of which one may *express the fraction of electricity that is carried by ions of the given form*, is called the *transport number* and is denoted as t_+ for cations and t_- for anions of the form

$$t_+ = \frac{I_+}{I_+ + I_-}, \quad t_- = \frac{I_-}{I_+ + I_-}, \quad (4.40)$$

There is dependence between transport numbers and ions mobilities in strong electrolytes

$$\frac{\lambda_+}{\lambda_-} = \frac{u_+}{u_-} = \frac{t_+}{t_-} \text{ or } \frac{\lambda_+}{\lambda_+ + \lambda_-} = \frac{t_+}{t_+ + t_-} \text{ and } \frac{\lambda_-}{\lambda_+ + \lambda_-} = \frac{t_-}{t_+ + t_-} \quad (4.41)$$

Considering (4.31) и (4.40)

$$\lambda_+ = \lambda_0 t_+ \text{ and } \lambda_- = \lambda_0 t_- \quad (4.42)$$

Hereby it's obvious that

$$t_+ + t_- = 1. \quad (4.43)$$

Thus, there is succession of calculations to calculate K_D

$$\rho \rightarrow \alpha \rightarrow \lambda \rightarrow \lambda_0 \rightarrow \alpha \rightarrow K_D.$$

Example.

1. Construct graphs of dependence of specific and molar conductivity on dilution.

2. Check whether the aqueous solution of the given electrolyte obeys Ostwald's dilution law.

3. If the electrolyte solution is the solution of weak acid or weak base, determine at what concentration the dissociation degree of substance in the solution is 0,1 and what pH this solution has.

4. Determine at what concentration pH of the solution will be 2÷4.

5. Calculate transform numbers (t_+ and t_-) and absolute velocities (v_+ and v_-) of ions H^+ and $(CH_3)_2C_6H_3COO^-$ (A^-) motion in the solution.

The basic data are given in the table 4.3.

Table 4.3. The basic data

The electrolyte solution $(CH_3)_2C_6H_3COOH$									
$\lambda^0,$ $\Omega^1 \cdot cm^2 \cdot mol-eq^{-1}$		Dependence of resistivity ρ , Ohm cm, of the electrolyte solution on concentration c , mol/l							
		Param.	Parameter values						
λ_+^0	λ_-^0	c	0,1	0,05	0,025	0,01	0,005	0,0025	0,001
349,8	2,6	ρ	12,1	17,3	25,1	39,7	57,8	82,0	136,0

Solution.

1. To build graphs do preliminary calculations. Here it should be taken into consideration that dilution (φ) is the quantity that is reciprocal of

concentration and that specific and molar conductivity are calculated according to the formula (4.29) and (4.30) correspondingly. The results of the calculations are put down in the table 4.4 on the basis of which the following graphs (fig.4.2, fig.4.3) are constructed:

Table 4.4 – The results of the calculations:

Parameter	Parameter values (units of measurement of the basic data)						
c	0,1000	0,0500	0,0250	0,0100	0,0050	0,0025	0,0010
ρ	12,1	17,3	25,1	39,7	57,8	82,0	136,0
φ	10,0	20,0	40,0	100,0	200,0	400,0	1000,0
ε	0,08264	0,05780	0,03984	0,02519	0,01730	0,01220	0,00735
λ	0,8264	1,1561	1,5936	2,5189	3,4602	4,8780	7,3529
K_D	4,94E-05	4,88E-05	4,69E-05	4,81E-05	4,66E-05	4,84E-05	4,75E-05

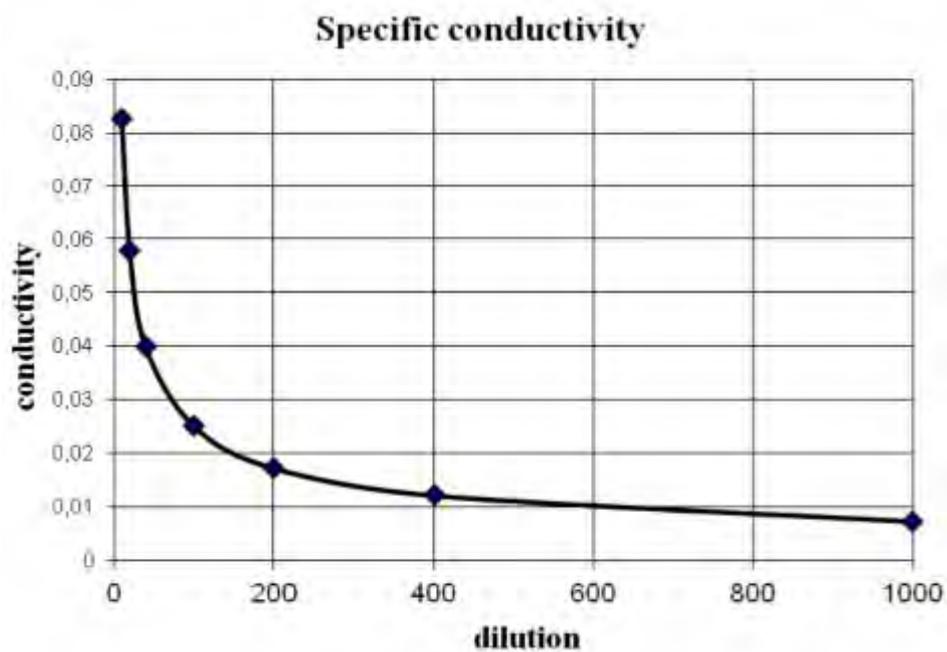


Fig.4.2 Dependence of specific conductivity on dilution

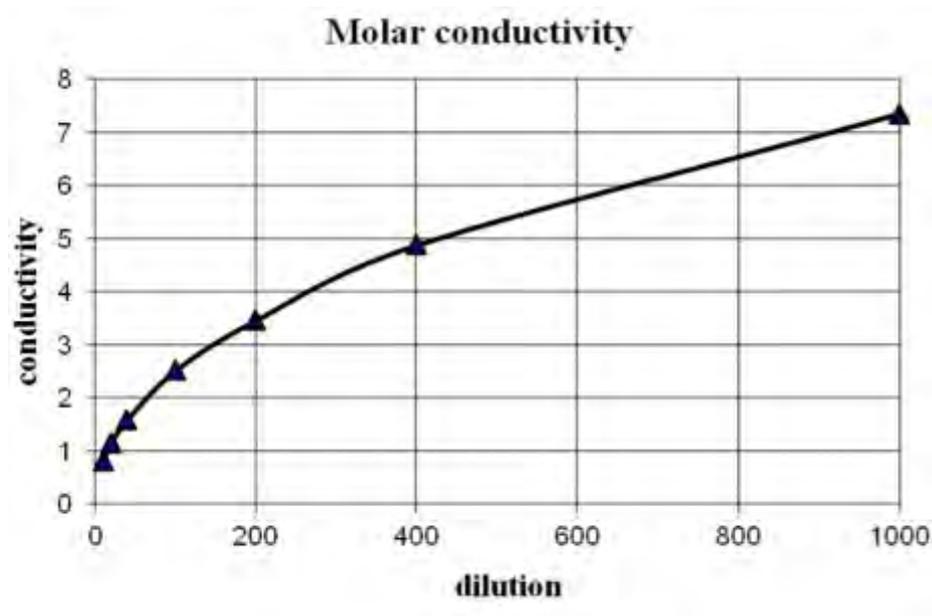
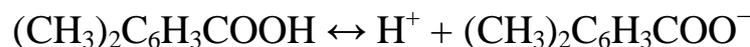


Fig.4.3 Dependence of molar conductivity on dilution

2. Calculate the dissociation constant K_D .

The given electrolyte splits according to the equation

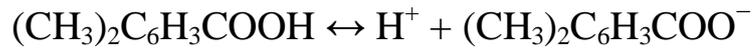


Use the equation (4.36) and calculate the value of the dissociation constant K_D for different basic concentrations. Analyzing the obtained values (the corresponding line in the calculations table) one can see that the dissociation constant K_D saves (within permissible experimental error) its constant value for solutions of different concentration. It means that it obeys Ostwald's dilution law. The solution's obeying Ostwald's dilution law and the small value of the dissociation constant K_D s how that the given electrolyte is weak. The value of the dissociation constant K_D is obtained as the average value for the solutions of different concentration: $K_D = 4,80 \cdot 10^{-5}$.

3. Having solved the equation (4.36) on concentration at the sat value $\alpha = 0,1$, one gets

$$c = \frac{K_D \cdot (1 - \alpha)}{\alpha^2} = \frac{4,80 \cdot 10^{-5} \cdot (1 - 0,1)}{(0,1)^2} \approx 4,75 \cdot 10^{-3}$$

According to the dissociation equation of the given electrolyte



the proton concentration

$$c_{\text{H}^+} = c \cdot \alpha ,$$

so

$$\text{pH} = -\lg(c_{\text{H}^+}) = -\lg(c \cdot \alpha) = -\lg(0,1 \cdot 4,75 \cdot 10^{-3}) = 3,3.$$

As it was found out in point 2 of the example, the given electrolyte is weak so point 5 of the problem for this electrolyte is not realized.

4. For weak electrolyte $\text{pH} = -\lg_{\text{H}^+} c \cdot a$ there are two unknown quantities: concentration and dissociation degree. To solve the problem we express the protons concentration $c_{\text{H}^+} = a \cdot c_{\text{HA}}$ through $a \cdot c_{\text{HA}} = 10^{-\text{pH}}$, then Ostwald's dilution law can be put down in such a way:

$$K_D = \frac{\alpha^2 \cdot c}{1 - \alpha} = \frac{\alpha \cdot 10^{-\text{pH}}}{1 - \alpha}. \quad (4.43)$$

Using this equation one may calculate the dissociation degree of the electrolyte

$$\alpha = \frac{K_D}{K_D + 10^{-\text{pH}}}. \quad (4.44)$$

Knowing the dissociation degree we obtain the concentration as we have already done in point 3.

Provided that $\text{pH} = 3$, then

$$\alpha = \frac{4,8 \cdot 10^{-5}}{4,8 \cdot 10^{-5} + 10^{-3}} = 0,046.$$

Calculate the concentration of the solution for the set α .

$$c = \frac{K_D(1 - \alpha)}{\alpha^2} = \frac{4,8 \cdot 10^{-5}(1 - 0,046)}{0,046^2} = 0,022.$$

Transport numbers are calculated using the values of limiting molar conductivity in such a way:

$$t_+ = \frac{\lambda_{\text{H}^+}^0}{\lambda_{\text{H}^+}^0 + \lambda_{\text{A}^-}^0} = \frac{35,0}{35,0 + 7,55} = 0,82,$$

$$t_- = 1 - 0,82 = 0,18.$$

As absolute velocities are related to mobilities $\lambda_+^0 = Fu_+$, $\lambda_-^0 = Fu_-$, u_+ is calculated like this:

$$u_+ = \frac{\lambda_{\text{K}^+}^0}{F} = \frac{35,0}{96500} = 3,63 \cdot 10^{-4}, \quad u_- = \frac{\lambda_{\text{Cl}^-}^0}{F} = \frac{7,55}{96500} = 7,82 \cdot 10^{-5}.$$

Task 5

On the basis of the values of resistivity ρ that are given in table 4.4 for solutions of different concentration with $T = 298\text{K}$:

- 1) calculate specific and molar conductivities;
- 2) construct the graph of dependence of specific and molar conductivity on dilution ($\varphi = 1000/c$);
- 3) calculate the dissociation degree for all concentrations and check whether Ostwald's dilution law is realized for this electrolyte;
- 4) if the solution of the compound is the solution of weak acid or weak base, determine at what concentration the dissociation degree in the solution is 0,1 and determine the pH of the solution;
- 5) calculate for strong electrolyte the molar conductivity at infinite dilution and the equation constant with the help of graphic method basing on the dependence given in Kohlrausch equation.

Reference data that are necessary for solving the problem are given in annex 2. (resistivity of the solution $\rho \cdot 10^{-2}$, $\Omega \cdot \text{cm}$).

Table 4.5 – Variants of tasks

№	Electrolyte	Concentration, mol/l					
		0,05	0,02	0,01	0,005	0,002	0,001
1	HF	4,55	7,44	10,9	16,3	28,5	45,1
2	HCl	0,501	1,23	2,43	4,28	11,9	23,7
3	HCOOH	8,55	13,8	19,9	28,8	48,4	72,3
4	LiCl	2,00	4,78	9,33	18,3	44,9	88,5
5	KCNS	1,60	3,81	7,46	14,6	36,0	72,0
6	HNO ₂	5,70	9,23	13,4	19,8	33,8	52,7
7	KCl	1,50	3,66	7,10	13,9	34,3	70,0
8	HJ	0,50	1,22	2,43	4,82	12,0	23,8
9	CH ₃ COOH	27,6	48,9	62,5	89,0	144	207
10	KBrO ₃	1,78	4,24	8,26	16,3	40,0	79,2
11	C ₆ H ₅ COOH	16,7	23,5	33,6	48,4	79,0	116
12	CH ₃ COOK	1,97	4,73	9,22	18,1	44,5	87,8
13	(CH ₃) ₂ CHCOOH	31,1	40,8	70,4	101	162	233
14	HJO ₃	0,645	1,45	2,78	5,41	13,2	26,0
15	CH ₃ COONa	2,60	6,18	12,0	23,4	57,0	113
16	HNO ₃	0,514	1,25	2,47	4,90	12,1	24,1
17	C ₂ H ₅ COOH	32,0	50,8	72,3	103	165	238
18	NaBrO ₃	2,21	5,24	10,2	20,0	48,6	95,5
19	CH ₂ ClCOOH	3,25	5,59	8,34	12,7	23,2	28,2
20	AgNO ₃	1,74	4,12	8,02	15,7	38,6	76,2
21	NH ₄ OH	39,4	62,5	88,6	127	205	295
22	CsOH	0,794	1,95	3,80	7,25	18,7	37,2
23	NH ₄ Cl	1,50	3,63	7,10	13,9	34,3	68,0
24	CH ₂ CNCOOH	2,23	3,81	5,85	9,25	18,1	31,7
25	KJ	1,49	3,59	7,05	13,8	34,1	67,7

4.3. Electrode processes. Voltage for a galvanic cell

A device in which the electric current derives as the result of the oxidation-reduction reaction is called a galvanic cell. The galvanic cell consists of half cells: a cathode and an anode, the reduction reaction proceeds on the cathode, the oxidation reaction proceeds on the anode. Processes of oxidation and reduction are separated in the galvanic cell (processes proceed on different electrodes). If liquid-junction potential is neglected, the electromotive force (EMF) of the galvanic element E is defined as the difference between electrode potentials of the anode and the cathode $E = E_+ - E_-$ where E_+ is the potential of a more positive electrode (cathode). The value of the electrode potential is obtained with the help of Nernst equation.

$$E = E_+^0 + \frac{RT}{zF} \ln \frac{a_{ox}}{a_{red}}, \quad (4.45)$$

where E_+^0 – standard electrode potential of the cathode (taken from a reference book); a_{ox} , a_{red} – activities of the oxidized and reduced forms, z – amount of electrodes in the electrode reaction equation, R – gas constant that is equal 8,31 J/mol·K.

Electrode potential of the electrode of the first kind that is reversible to the cation M^{z+} on which the reaction proceeds $M^{z+} + ze = M^0$ (according to Nernst equation) is calculated in such a way:

$$E_+ = E_+^0 + \frac{RT}{zF} \ln a_+, \quad (4.46)$$

As it was stated before, the ions activity is connected with their concentration in such a correlation: $a_+ = c_+ \cdot \gamma_{\pm}$ and $a_- = c_- \cdot \gamma_{\pm}$ where γ_{\pm} – average ion coefficient of the electrolyte activity that depends on the solution concentration, c_+ and c_- – ion concentrations of cations and anions correspondingly. Generally ion concentrations for an electrolyte of the K_xA_y form are calculated on the basis of the equation in such a way:

$$c_{\pm} = c \cdot \gamma_{\pm} \cdot (x^x \cdot y^y)^{\frac{1}{v}} = c \cdot \gamma_{\pm} \cdot L, \quad (4.47)$$

where x – number of cations, y – number of anions in the formula of the compound, $n = x + y$.

At 298K the equation for binary electrolyte Nernst equation may be written like this:

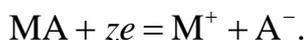
$$E = E^0 + \frac{0,059 \cdot \lg a_{+}}{z}, \quad (4.48)$$

Electrodes of the first kind include gas electrodes (hydrogen, chloric, oxygen etc.). The potential of hydrogen electrode

$$E = \frac{0,059}{\lg a_{+}} = -0,059 pH \quad (4.49)$$

where $pH = -\lg a_{H^{+}}$.

On electrodes of the II type, which consist of the metal M, covered with its poorly soluble salt MA, and dipped into the solution, which includes anions, identical to the anions of poorly soluble salt, the electrode reaction proceeds



The electrode potential

$$E_{M|MA|A^{-}} = E_{M|MA|A^{-}}^0 - \frac{RT}{zF} \ln a_{z^{-}} \quad (4.50)$$

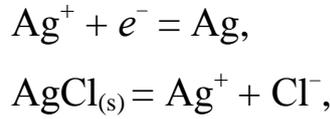
At 298K for the binary electrolyte the Nernst equation can be written as

$$E = E^0 + \frac{0,059 \cdot \lg a^{z^{-}}}{z}, \quad (4.51)$$

where $a^{z^{-}}$ is the ionic activity.

Electrodes of the II type are reversible to the anion. But electrodes of the II type can be also considered as electrodes of the I type, reversible to the cation. Two equilibria are established in such electrodes: one is between the metal atoms and the cations of poorly soluble salt, the other

one is between the anions of poorly soluble salt and the anion in the solution. The oxidized form is poorly soluble salt, the reduced form is the metal atom and the anion of the solution. Silver chloride electrode can be used as an example



where the first step is the potential-defining process. The activity of silver ions in the solution is defined by the solubility product of poorly soluble salt ($K_{\text{sp AgCl}}$), constant at the given temperature. If the silver chloride electrode is considered as reversible to the cation, then its potential can be calculated by the Nernst equation $E_1 = E_{\text{Ag}^+|\text{Ag}}^0 + 0,059 \lg a_{\text{Ag}^+}$, where $E_{\text{Ag}^+|\text{Ag}}^0 = 0,799 \text{ V}$ (standard potential of the silver electrode at $a_{\text{Ag}^+}=1$), a_{Ag^+} – the activity of silver ions.

On the other hand, according to (4.51) the potential of the silver chloride electrode

$$E_2 = E_{\text{Cl}^-|\text{AgCl, Ag}}^0 - 0,059 \lg a_{\text{Cl}^-}; E_{\text{Cl}^-|\text{AgCl, Ag}}^0 = 0,222 \text{ V}.$$

The electrode potentials E_1 and E_2 are equal, since they define the potential of the same electrode at $T=298\text{K}$.

Equating right parts, we get $E_{\text{Ag}^+|\text{Ag}}^0 + 0,059 \lg a_{\text{Ag}^+} = E_{\text{Cl}^-|\text{AgCl, Ag}}^0 - 0,059 \lg a_{\text{Cl}^-}$.

Taking into account that $K_{\text{sp}} = a_+ \cdot a_-$, after simple transformations we get:

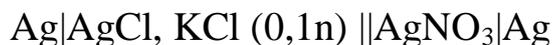
$$0,059 \lg a_{\text{Ag}^+} \cdot a_{\text{Cl}^-} = 0,059 \lg K_{\text{sp AgCl}} = E_{\text{Cl}^-|\text{AgCl, Ag}}^0 - E_{\text{Ag}^+|\text{Ag}}^0 \quad (4.52)$$

or

$$\lg K_{\text{sp AgCl}} = (E_{\text{Cl}^-|\text{AgCl, Ag}}^0 - E_{\text{Ag}^+|\text{Ag}}^0) / 0,059.$$

Thus the solubility product of the slightly soluble compound is connected with the potential of electrodes of the II type.

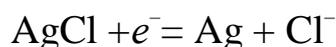
Example. An electrochemical circuit with a given concentration of silver ions in silver nitrate solution can serve for determining the K_{sp} of AgCl:



The overall reaction in the element: $\text{AgCl} = \text{Ag}^+ + \text{Cl}^-$.

The left electrode is an electrode of the II type, and the right one is an electrode of the I type.

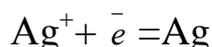
The reaction proceeds on the silver chloride electrode:



Let's write the expression for the potential:

$$E_{\text{Cl}^-|\text{AgCl}, \text{Ag}} = E_{\text{Cl}^-|\text{AgCl}, \text{Ag}}^0 - 0,059 \lg a_{\text{Cl}^-}; E_{\text{Cl}^-|\text{AgCl}, \text{Ag}}^0 = 0,222 \text{ V.}$$

The reaction proceeds on the silver electrode:



$$E_{\text{Ag}^+|\text{Ag}} = E_{\text{Ag}^+|\text{Ag}}^0 + 0,059 \lg a_{\text{Ag}^+}; E_{\text{Ag}^+|\text{Ag}}^0 = 0,799 \text{ V.}$$

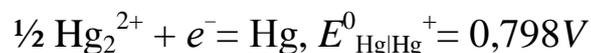
Knowing the concentration of silver ions and having used the tables of ionic activity coefficients according to the Nernst equation, we determine the cathode potential. Knowing the EMF of the circuit and the cathode potential, we find the anode potential. Then according to the previously discussed technique we find the K_{sp} AgCl.

$$\lg K_{sp} \text{ AgCl} = (E_{\text{Cl}^-|\text{AgCl}, \text{Ag}}^0 - E_{\text{Ag}^+|\text{Ag}}^0) / 0,059 = (0,222 - 0,799) / 0,059 = -9,78;$$

$$K_{sp} = 1,7 \cdot 10^{-10} \text{ g.ion/l.}$$

The other method of potentiometric definition the solubility product of slightly soluble salt is based on the calculation of the electrode potential, reversible to one of the ions of this salt (anion).

For an example let's calculate the solubility product of calomel (Hg_2Cl_2) at $T = 298\text{K}$. From tables of the standard potential we find the potential of the mercury electrode of the I type, where the following reaction proceeds:



and the calomel electrode with the reaction



The number of equivalents in the calomel molecule $n = 2$.

Hence by the equation:

$$\lg K_{\text{sp}(\text{Hg}_2\text{Cl}_2)} = \frac{2 \cdot \left(E_{\text{Cl}^-|\text{Hg}_2\text{Cl}_2|\text{Hg}}^0 - E_{\text{Hg}^{2+}|\text{Hg}}^0 \right)}{0,059} = 2 \cdot \frac{(0,286 - 0,798)}{0,059} = -17,97$$

$$K_{\text{sp} 298} = 1,1 \cdot 10^{-18}.$$

Electrodes of the II type are used as reference electrodes. The most known reference electrodes are silver chloride ($\text{KCl}|\text{AgCl}|\text{Ag}$) and calomel electrodes ($\text{Hg}|\text{Hg}_2\text{Cl}_2|\text{Hg}$), the potentials of which E_{sc} and E_{cal} are equal respectively:

$$E_{\text{sc}} = 0,2224 - 6,4 \cdot 10^{-4} (T - 298), \quad (4.53)$$

$$E_{\text{cal}} = 0,2438 - 6,5 \cdot 10^{-4} (T - 298). \quad (4.54)$$

As a rule, redox electrodes consist of inert metal (for example, platinum) dipped in a solution, containing a substance with a different oxidation number *Ox* and *Red*. The equation of a potential-defining reaction has this form $\text{Ox} + ne = \text{Red}$. In the first place to the redox elements belong electrodes, oxidized and reduced forms of which are represented by ions, and besides an electrode reaction lies in an alteration of their oxidation number. The potential of the redox electrode ($E_{\text{Red/Ox}}$):

$$E_{\text{Red/Ox}} = E_{\text{Red/Ox}}^0 + \frac{RT}{zF} \ln \frac{a_{\text{Ox}}}{a_{\text{Red}}}, \quad (4.55)$$

With the help of the EMF of a galvanic cell with one electrolyte, reversible to the cation and the anion of this electrolyte, one can also determine the average ionic activity coefficient γ_{\pm} of this electrolyte:

$$\ln \gamma_{\pm} = + \frac{RT}{zF} (E - E^0) + \ln L \cdot c, \quad (4.56)$$

where $L = v_{\pm} = \sqrt[v_{+}^{v_{+}} \cdot v_{-}^{v_{-}}]$; c – concentration of the electrolyte.

If EMF of the galvanic cell E is calculated at various temperatures, its main thermodynamic properties (the isobaric potential ΔG , enthalpy ΔH and entropy ΔS) can be determined for the reaction, which proceeds in the given element.

EMF of the element is determined by the decrease of the isobaric potential of the reversible process:

$$-\Delta G = zFE \text{ and } \ln K_a = \frac{zF}{RT} E^0, \quad (4.57)$$

where K_a – a constant of chemical equilibrium; z – quantity of electrons, which participate in an electrode process; F – the Faraday constant, equals 96500 C.

Having used the Gibbs–Helmholtz equation

$$\Delta G = \Delta H + T \left(\frac{\partial \Delta G}{\partial T} \right)_p \text{ and } \Delta G = \Delta H - T \Delta S, \quad (4.58)$$

we can calculate the alteration of the entropy and enthalpy:

$$\Delta S = zF \left(\frac{\partial E}{\partial T} \right)_p; \Delta H = zFE + zFT \left(\frac{\partial E}{\partial T} \right)_p. \quad (4.59)$$

Thus, if the potential of one of the electrodes and the EMF element is known, one can determine the potential of the second electrode, find the ionic activity in solutions, calculate pH of the solution or the solubility product of the poorly soluble compounds and calculate the average ionic activity coefficient of γ_{\pm} electrolyte.

Examples of calculation of main properties of galvanic cells

Write electrode reactions and calculate the EMF of the galvanic cells given in the table 4.5. Concentrations of electrolytes are expressed in mol/L. The gas pressure in gas electrodes equals 1 atmosphere. The temperature is 298K. The average activity coefficients and standard

electrode potentials should be taken from the application (table 4.2 and 4.3). Junction potentials should be ignored.

Example.

To write an electrode reaction and calculate the EMF of the galvanic cell $\text{Pt} \mid \text{H}_2 \mid \text{HCl} \mid \text{Hg}_2\text{Cl}_2 \mid \text{Hg}$.

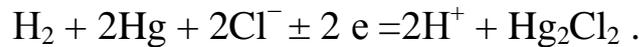
The concentration of the electrolyte equals 0,15 mol/L. In gas electrodes the gas pressure equals 1 atmosphere. The temperature is 298K. Junction potentials should be ignored.

Solution. First method

Let's write the reactions, which proceed on electrodes. The following reaction proceeds on the negative electrode: $\text{H}_2 + 2\text{e} = \text{H}^+$,

On the positive one: $\text{Hg}_2\text{Cl}_2 + 2\text{e} = 2\text{Hg} + 2\text{Cl}^-$.

We obtain the general equation of the reaction that proceeds in the galvanic cell using the algebraic addition of electrode reactions:



We find standard potentials in reference data:

$E_{\text{Hg}|\text{Hg}_2\text{Cl}_2|\text{Cl}^-}^0 = 0,286\text{V}$, $E_{\text{Pt}|\text{H}_2|\text{H}^+}^0 = 0$, thus, the EMF of the galvanic cell $E^0 = 0,268 - 0 = 0,286\text{V}$.

For the given reaction according to the Nernst equation

$$E = E^0 + \frac{RT}{nF} \ln \frac{a_{\text{Hg}}^2 \cdot a_{\text{H}^+}^2 \cdot a_{\text{Cl}^-}^2}{a_{\text{H}_2} \cdot a_{\text{Hg}_2\text{Cl}_2}} = E = E^0 + \frac{0,059}{nF} \ln \frac{a_{\text{Hg}}^2 \cdot a_{\text{H}^+}^2 \cdot a_{\text{Cl}^-}^2}{a_{\text{H}_2} \cdot a_{\text{Hg}_2\text{Cl}_2}} .$$

The activities of Hg, solid Hg_2Cl_2 and H_2 equal 1, so the EMF of the cell equals

$$E = 0,268 - \frac{0,059}{2} \lg(a_{\text{H}^+} \cdot a_{\text{Cl}^-}) .$$

As $a_+ \cdot a_- = a(a_{\text{H}^+} \cdot a_{\text{Cl}^-}) = a_{\pm}^2$, then $E = 0,268 - \frac{0,059}{2} \lg(a_{\pm}^2)$.

According to the reference data, the average activity coefficient in

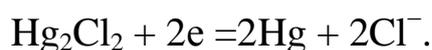
the HCl solution with the concentration $c = 0,15 \text{ mol/L}$, $\gamma_{\pm} = 0,8895$. $a_{\pm} = c_{\pm} \cdot \gamma_{\pm}$ and $c_{\pm} = c \cdot (x^x y^y)^{\frac{1}{n}}$ $a_{\pm} = 0,15 \cdot 1 \cdot 0,8895 = 0,133$. Thus,

$$E = 0,268 - 0,059 \lg (0,133)^2 = 0,371 \text{ V.}$$

Solution. Second method

This exercise can be solved in another way, by calculating the potential of each electrode separately using the Nernst formula. The EMF of the circuit will be equal to the difference between the anode and cathode potentials. Since the same equation has been used for solving, the results should match.

The following reaction proceeds on the cathode



At $T = 298\text{K}$ the standard electrode potential of the calomel electrode $E_{\text{Hg}|\text{Hg}_2\text{Cl}_2|\text{Cl}^-}^0 = 0,268\text{V}$. Let's determine the potential of the calomel electrode in this solution by the Nernst equation.

$$E_+ = E^0 + \frac{RT}{2zF} \ln a_{\text{Cl}^-}^2 = 0,268 - 0,059 \lg (0,15 \cdot 0,8895) = 0,3196 \text{ V.}$$

Similarly let's calculate the anode potential (the standard potential of the hydrogen electrode is equal to zero): $E_- = 0,059 \cdot \lg 0,133 = -0,0516 \text{ V}$.

EMF of the whole circuit: $0,3195 - (-0,516) = 0,371 \text{ V}$.

The given cell is the chemical cell without transference. It consists of the gas electrode and the electrode of the II type.

Exercise 6

To write electrode reactions and calculate the EMF of the galvanic cell. Concentrations of the electrolytes are expressed in mol/l. In gas electrodes gas pressure equals 1 atm. The temperature is 298K. The average activity coefficients and the standard electrode potentials should

be obtained in the applications 3 and 4. Junction potentials should be ignored.

In the table 4.5 of galvanic cells, schematically depicted in the table 4.4, the EMF-temperature equation $E = f(T)$ is known.

It's required: within the range of temperatures 270 – 360K with a step of 10 degrees to determine the EMF of the galvanic cell E , the alteration of the Gibbs energy (ΔG), the temperature EMF coefficient (dE/dT), the alteration of entropy (ΔS) and the alteration of enthalpy (ΔH) in the reaction, proceeding reversibly in the galvanic cell.

1. To characterize the galvanic cell (chemical, concentrational, with and without transference) and determine the type of the electrode (I type, II type, redox or gas). To write reactions, which proceed on the electrodes and an overall reaction, which proceeds in the galvanic cell.

2. To calculate the value given in the last column of the table 4.6: the equilibrium constant K_a , the average ionic activity coefficient of the electrolyte (γ_{\pm}) at the given concentration c , the solubility product of the poorly soluble salts (K_{sp}), activity of one of the ions a , the value of the electrode potential (E_+ or E_-), pH of the solution. Required values of the standard potentials are listed in the application.

Example

Dependence of the EMF on the temperature of the element, where the reaction $Zn + Hg_2SO_4 = ZnSO_4 + 2Hg$ proceeds, is described by the equation

$$E = 1,4328 - 0,00119 (T-298) - 7 \cdot 10^{-6} (T-298)^2.$$

To determine ΔH , ΔS , ΔG и ΔF ($T = 303K$) for this reaction.

Solution.

The EMF of the element at $T = 303K$ equals:

$$E_{303} = 1,4338 - 0,00119 (303 - 298) - 7 \cdot 10^{-6} (303 - 298)^2 = 1,413 \text{ V}.$$

In accordance with (1.32):

$$\Delta G = -nFE = 2 \cdot 96500 \cdot 1,413 = -272,78 \cdot 10^3 \text{ J/mol.}$$

$$\Delta F = \Delta G - p \cdot \Delta v.$$

Since $\Delta v = 0$, then $\Delta G = \Delta F = -272,78 \cdot 10^3 \text{ J/mol.}$

In the Gibbs–Helmholtz (1.31) equation we make substitutions

$\Delta G = -nFE$, and $\left(\frac{\partial \Delta G}{\partial T}\right) = nF\left(\frac{\partial E}{\partial T}\right)$. We determine enthalpy with the help

of the equation (1.34):

$$\Delta H = nF \left[T \left(\frac{\partial E}{\partial T} \right) - E \right]. \text{ For determining } \Delta H \text{ we find } \left(\frac{\partial E}{\partial T} \right):$$

$$\left(\frac{\partial E}{\partial T} \right) = -0,00119 - 7 \cdot 10^{-6} \cdot 2 (T - 298) = -0,00119 - 7 \cdot 10^{-6} \cdot (303 - 298) = -1,26 \cdot 10^{-3}.$$

$$\Delta H = 2 \cdot 96500 \cdot 10^3 [303 \cdot (-0,00126) - 1,41337] = 346,46 \text{ kJ/mole.}$$

$$\Delta S = nF \cdot 10^3 \left(\frac{\partial E}{\partial T} \right) = 2 \cdot 96500 \cdot (-0,00141) = -243,18 \text{ J/mole} \cdot \text{K.}$$

$\gamma_{\pm}(\text{ZnSO}_4)$ at $c = 0,5$ has to be calculated additionally in the given exercise. For its calculation we should know the standard EMF of the circuit and calculate the EMF of the circuit at $T=298\text{K}$ and $c = 0,5$ (in our case an electrolyte of 1:2 type; $L = 1,59$; $z = 2$; $\nu = 3$) by the given equation. Consequently, in accordance with the formula (4.56)

$$\ln \gamma_{\pm} = \frac{2 \cdot 96500}{3 \cdot 8,31 \cdot 298} \cdot (1,4328 - 1,378) + \ln(0,5 \cdot 1,59) = -1,6788$$

The given galvanic cell is the chemical one without transference. It is constituted of electrodes of the I and II type.

Table 4.6 – Exercise variants

№	Galvanic cell	№	Galvanic cell
1	Zn ZnBr ₂ PbBr ₂ Pb 0,1	1	Pt H ₂ HBr AgBr Ag
2	Pt H ₂ KOH KCl Hg ₂ Cl ₂ Hg 0,010,1	4	0,1
3	Cu CuSO ₄ AgNO ₃ Ag 0,010,1	1	Ag AgCl LiCl LiCl AgCl Ag
4	Zn ZnSO ₄ PbSO ₄ Pb 0,001	5	0,1 0,01
5	Hg Hg ₂ Cl ₂ KCl Cl ₂ Pt 0,5	1	Zn ZnCl ₂ Cl ₂ Pt
6	Cd CdSO ₄ NaJ PbJ ₂ Pb 0,010,1	6	0,02
7	Zn ZnSO ₄ ZnSO ₄ Zn 0,01 0,1	1	Cd CdI ₂ AgJ Ag
8	Pt, H ₂ HCl KCl Cl ₂ Pt 0,01 0,01	7	0,005
9	Pt H ₂ HCl HCl Cl ₂ Pt 0,1 0,1	1	Ni NiSO ₄ KCl AgCl Ag
10	Ag AgCl CuCl ₂ Cu 0,005	8	0,10,1
11	Pb PbCl ₂ HCl H ₂ Pt 0,01	1	Pt H ₂ HCl HCl H ₂ Pt
12	Zn ZnSO ₄ CdSO ₄ Cd 0,001 0,01	9	0,001 0,1
13	Ni NiSO ₄ Hg ₂ SO ₄ Hg 0,2	2	Pb PbCl ₂ KCl Cl ₂ Pt
		0	0,1
		2	Hg Hg ₂ Cl ₂ KCl AgNO ₃ Ag
		1	0,1 0,001
		2	Pb PbSO ₄ H ₂ SO ₄ H ₂ Pt
		2	0,01
		2	Cd CdCl ₂ AgCl Ag
		3	0,002
		2	Pt H ₂ HBr Hg ₂ Br ₂ Hg
		4	0,1
		2	Zn ZnCl ₂ Hg ₂ Cl ₂ Hg
		5	0,01

Table 4.7 – Exercise variants

Nº	Galvanic cell	Equation of dependence $E = f(T)$	M	A
1	Zn ZnSO ₄ Hg ₂ SO ₄ Hg	$E = 1,4328 - 0,0012 \cdot 10^{-4} T$	0,5 ÷ 2	$\gamma_{\pm}(\text{ZnSO}_4)$
2	Pb PbI ₂ KI AgI Ag	$E = 0,259 - 1,38 \cdot 10^{-4} T$		K _a
3	Ag AgCl LiCl Fe(SO ₄) ₃ , Fe(SO ₄) ₂ Pt	$E = 0,455 + 1,02 \cdot 10^{-3} T$		E ₊
4	Hg Hg ₂ O KOH KCl Hg ₂ Cl ₂ Hg	$E = 0,1636 + 8,37 \cdot 10^{-4} (T - 298)$	0,5 ÷ 2	$\gamma_{\pm}(\text{KOH})$
5	Zn ZnCl ₂ AgCl Ag	$E = 1,125 - 4,02 \cdot 10^{-4} T$	0,5 ÷ 2	$\gamma_{\pm}(\text{ZnCl}_2)$
6	Cd CdCl ₂ AgCl Ag	$E = 0,869 - 6,5 \cdot 10^{-4} T$	0,5 ÷ 2	$\gamma_{\pm}(\text{CdCl}_2)$
7	Cd CdCl ₂ PbCl ₂ Pb	$E = 0,331 - 4,8 \cdot 10^{-4} T$	0,1 ÷ 0,3	$\gamma_{\pm}(\text{ZnCl}_2)$
8	Ag AgCl KCl Hg ₂ Cl ₂ Hg	$E = 0,0566 - 3,338 \cdot 10^{-4} T$		K _a
9	Ag AgCl KCl AgNO ₃ Ag (m _{AgNO₃} =0,1)	$E = 0,45 + 1,49 \cdot 10^{-3} (T - 298)$		K _{sp}
10	Zn ZnSO ₄ KCl Hg ₂ Cl ₂ Hg	$E = 1 + 0,94 \cdot 10^{-4} (T - 298)$	0,5 ÷ 2	$\gamma_{\pm}(\text{ZnCl}_2)$
11	Pb PbCl ₂ KCl AgCl Ag	$E = 0,49 - 0,186 \cdot 10^{-3} (T - 298)$		K _{sp}
12	Pb PbCl ₂ KCl Hg ₂ Cl ₂ Hg	$E = 0,5353 + 1,45 \cdot 10^{-4} T$		K _{sp}
13	Zn ZnSO ₄ CuSO ₄ Cu	$E = 1,096 + 0,33 \cdot 10^{-4} (T - 298)$		K _a
14	Cd CdSO ₄ Hg ₂ SO ₄ Hg	$E = 1,0183 - 4,06 \cdot 10^{-5} (T - 298)$	0,5 ÷ 2	$\gamma_{\pm}(\text{CdSO}_4)$
15	Hg Hg ₂ Cl ₂ KCl HCl C ₆ H ₄ O ₂ , C ₆ H ₄ (OH) ₂ Pt	$E = 0,3385 + 2,6 \cdot 10^{-4} (T - 298)$		pH
16	Zn (Hg) a ₁ ZnSO ₄ ZnSO ₄ Zn (Hg) a ₂ =0,1	$E = 0,04227 + 1,485 \cdot 10^{-4} (T - 284,6)$		a ₁
17	Pb Pb(CH ₃ COOH) ₂ Cu(CH ₃ COOH) ₂ Cu	$E = 0,4764 + 0,41 \cdot 10^{-3} (T - 298)$	a _{Cu} ²⁺ = 0,2	a _{pb} ²⁺
18	Pt H ₂ HCl HCl C ₆ H ₄ O ₂ , C ₆ H ₄ (OH) ₂ Pt	$E = 0,699 - 7,4 \cdot 10^{-4} (T - 298)$		pH
19	Pt H ₂ HCl KCl Hg ₂ Cl ₂ Hg	$E = 0,266 - 0,32 \cdot 10^{-4} (T - 298)$		pH
20	Pb PbCl ₂ KCl Cl ₂ Pt	$E = 1,75 - 6,2 \cdot 10^{-4} T$		E ₋

Chapter 5. CHEMICAL KINETICS

5.1 Kinetic characteristics at the constant temperature

For an elementary homogeneous reaction



where A_1, A_2, A_3 – reactants; n_1, n_2, n_3 – stoichiometric coefficients. According to the law of mass action for elementary reactions (C. M. Guldberg and P. Waage), the rate of a chemical reaction is proportional to the concentration of reactants raised to the power equal to their stoichiometric coefficients

$$w = -\frac{dc}{d\tau} = k \cdot c_1^{n_1} \cdot c_2^{n_2} \cdot c_3^{n_3} \dots, \quad (5.2)$$

where $w = -\frac{dc}{d\tau}$ – the rate of a chemical reaction; c_1, c_2, c_3 – concentration of reagents, k – a reaction rate constant, i.e. the reaction rate at the single concentration of reagents.

The power exponent n_i at concentrations in the kinetic equation (5.2) is called a reaction order with respect to a given reagent, i.e. n_1, n_2, n_3 – the reaction order with respect to the first, second and third reagent correspondingly. It reflects the reacting pattern of reagents in a chemical reaction.

The overall order of a reaction is equal to the sum of the orders with respect to all reactants:

$$n = n_1 + n_2 + n_3 + \dots, \quad (5.3)$$

The order of a chemical reaction is one of the most important characteristics of it; it can be expressed as an integer as well as a fraction and have values from 0 to 3. Complex chemical reactions that go through a number of intermediate phases can have a fractional order; in a zero-order reaction the rate of it remains constant in time.

The reaction order with respect to each reactant predominantly (except for elementary reactions that occur in one stage) does not coincide with the number of molecules that participate in the reaction according to the stoichiometric equation because the last-mentioned describes the process in general, i.e. its mass balance, but does not reflect the actual reaction mechanism.

Thus, the determination of reaction order contributes to the determination of its mechanism.

The order of a reaction can be found using several methods:

1. substitution of experimental values of the concentrations of reactants into a kinetic equation;
2. by the time of a half-reaction;
3. method of the construction of graphical (linear) dependencies of the reactants concentration on the time of the reaction;
4. determination of reaction rates at different initial concentrations of reactants (Van't Hoff method);
5. by the isolation method (Ostwald's method).

Example:

Determine the reaction order and the rate constant of hydrolysis of 17 % sucrose solution in 0,1M HCL aqueous solution at 35°C for the following obtained data on reaction path.

Table 5.1 – The obtained data

Time, min	9,82	59,60	93,18	142,90	294,80	589,40
Current sucrose concentration, %	96,5	80,3	71,0	59,1	32,8	11,1

Solution: Determine the reaction order.

Analytical method: We substitute the experimental data into the equations (5.4-5.6) for the rate constant for different orders and compare the values of the constants obtained for each kinetic equation. For

$$\text{first-order reaction} \quad k_1 = \frac{1}{\tau} \ln \frac{c_0}{c_\tau}, \quad (5.4)$$

$$\text{second-order reaction} \quad k_2 = \frac{1}{\tau} \left(\frac{1}{c_\tau} - \frac{1}{c_0} \right), ; \quad (5.5)$$

$$\text{third-order reaction} \quad k_2 = \frac{1}{\tau} \left(\frac{1}{c_\tau^2} - \frac{1}{c_0^2} \right), . \quad (5.6)$$

Where k_1, k_2, k_3 – rate constants of the corresponding order; c_0 – the concentration of the reactant at the initial time; c_τ – the concentration of the reactant remaining at time τ .

Having calculated each of the given above equations, we have the following set of values of the rate constants:

$$k_1 = (3,63; 3,68; 3,67; 3,68; 3,78; 3,73) \cdot 10^{-3} \text{min}^{-1};$$

$$k_2 = (3,69; 4,12; 4,38; 4,84; 6,95; 13,50) \cdot 10^{-5} \text{conc}^{-1} \cdot \text{min}^{-1};$$

$$k_3 = (3,76; 4,62; 5,02; 5,65; 14,0; 56,8) \cdot 10^{-7} \text{conc}^{-2} \cdot \text{min}^{-1}$$

According to the calculated data, it can be seen that the value of the rate constant for the second- and third-order reaction systematically changes during the reaction path, whereas the calculated values for the first-order reaction fluctuate around a certain average value. I.e. the experimental data obey the equation (5.4). Hence it follows that the reaction is a first-order reaction.

Example:

During the reaction $(\text{CH}_3)_2\text{CO} = \text{C}_2\text{H}_4 + \text{H}_2 + \text{CO}$ at $V = \text{const}$, $T = 298\text{K}$ the total pressure changes in this way:

Table 5.2 – The obtained data

τ, min	0	6,5	13,0	19,9
$p_{\text{total}}, \text{Pa}$	41589	54386	65050	74914

Determine the reaction order.

Solution:

We use the graphical solution method. Please note that kinetic equations are derived for one of the reactants. Therefore, sometimes (as in this particular case) the experimental data should be recalculated (applying chemical and physical laws) in such a way that we would be able to use them to determine the order.

Suppose the partial pressure of reactants at the baseline at $\tau = 0$ is respectively: acetone $p_{(\text{CH}_3)_2\text{CO}} = p_0$, ethylene $p_{\text{C}_2\text{H}_4} = 0$, hydrogen $p_{\text{H}_2} = 0$, carbon monoxide $p_{\text{CO}} = 0$. Then at any specific time the partial pressure of the components will be:

$$p_{\text{C}_2\text{H}_4} = p_{\text{H}_2} = p_{\text{CO}} = x, p_{(\text{CH}_3)_2\text{CO}} = p_0 - x$$

the total pressure

$$p_{\text{tot}} = p_0 - x + 3x = p_0 + 2x.$$

From here it follows that $x = \frac{p_{\text{tot}} - p_0}{2}$ and

$$p_{(\text{CH}_3)_2\text{CO}} = p_0 - x = \frac{3p_0 - p_{\text{tot}}}{2}, c_{(\text{CH}_3)_2\text{CO}} = \frac{n}{v} = \frac{p}{RT} = \frac{3p_0 - p_{\text{tot}}}{2RT}.$$

Taking into account the obtained equation, we have a new data table.

Table 5.3 – The new data table

c_τ	16,79	14,21	12,06	10,07
$\ln c$	2,82	2,65	2,49	2,31
$1/c$	$5,954 \cdot 10^{-2}$	$7,037 \cdot 10^{-2}$	$8,294 \cdot 10^{-2}$	$9,934 \cdot 10^{-2}$
$1/c^2$	$3,545 \cdot 10^{-3}$	$4,952 \cdot 10^{-3}$	$6,878 \cdot 10^{-3}$	$9,869 \cdot 10^{-3}$

Based on this data, we construct a plot on coordinates that correspond to the first-, second- and third-order reactions (fig. 5.1, fig. 5.2 and fig. 5.3).

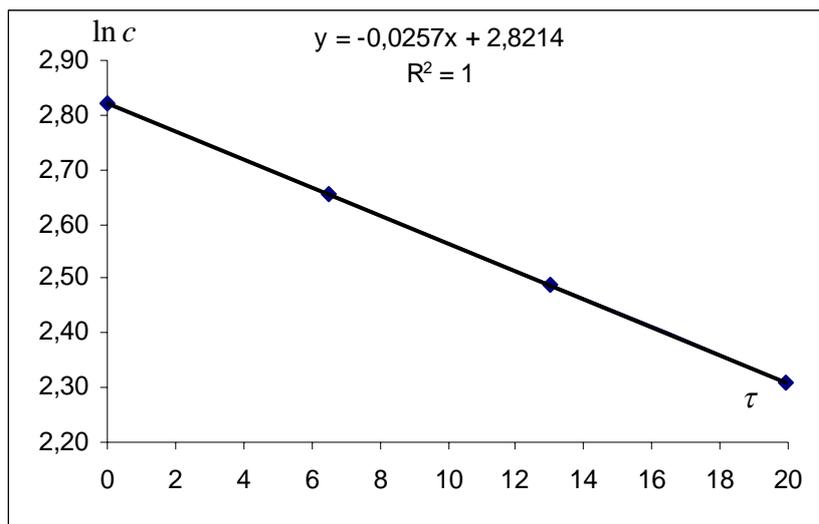


Fig. 5.1. Dependence of $\ln c$ on time

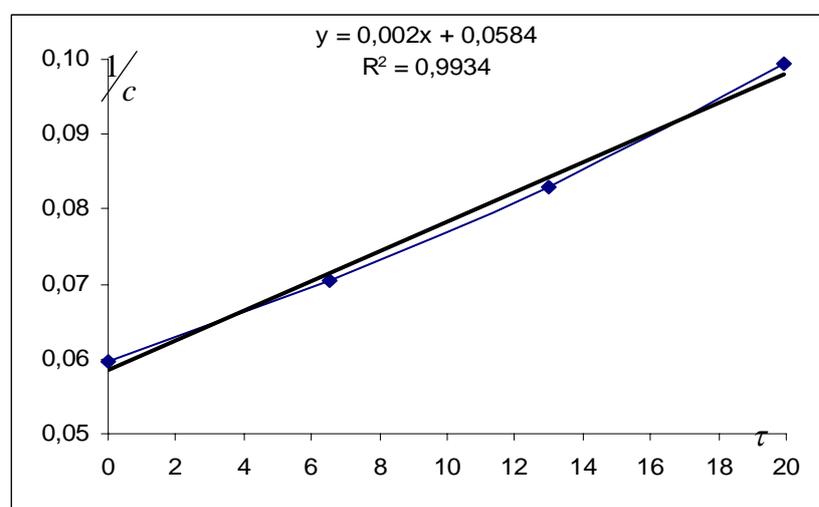


Fig. 5.2. Dependence of $1/c$ on time

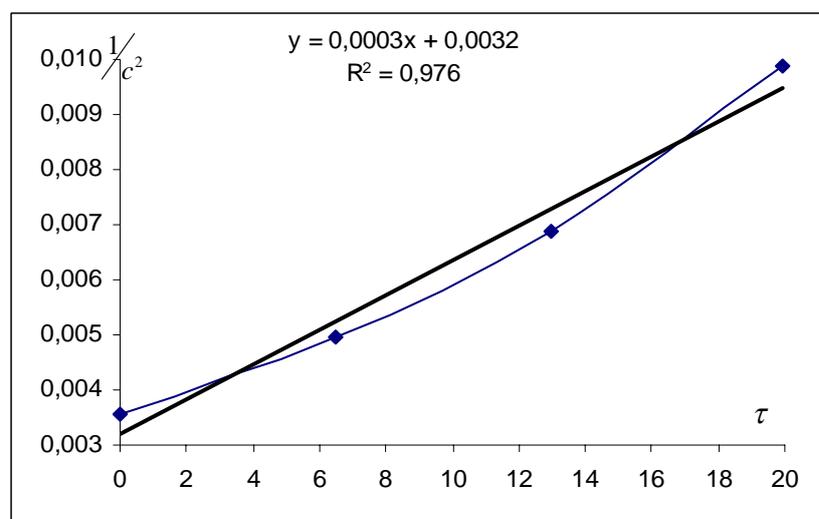


Fig. 5.3. Dependence of $1/c^2$ on time

Taking into account the value of the correlation coefficient, the best subordination of the experimental data is observed to the coordinates that correspond to the first-order reaction.

Example:

Determine the reaction order using the experimental data that are given in the form of kinetic curve.

Solution:

In that case, it is better to use the half-reaction method.

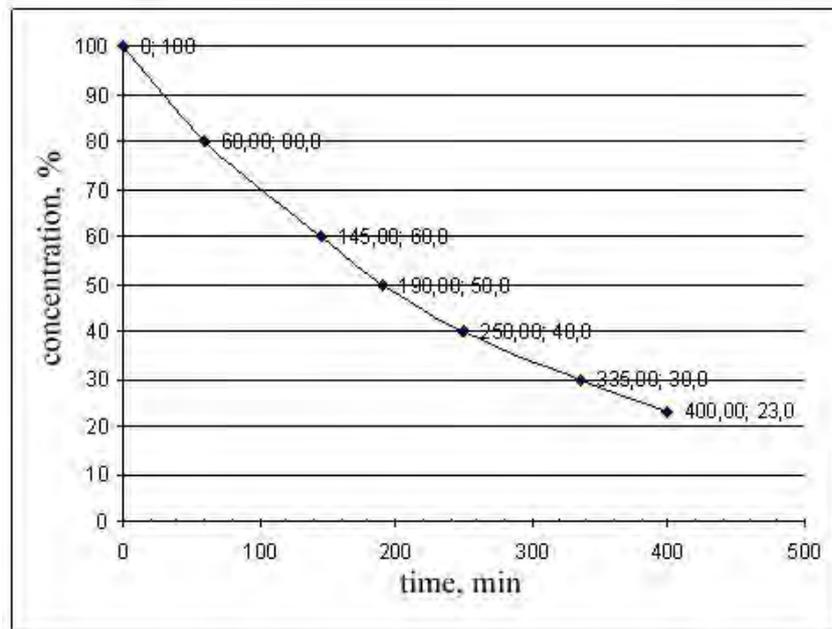


Fig.5.4. Dependence of the concentration of starting materials on time

We choose some derivative values for c_0 and find the time that corresponds to the concentration of $c_{0/2}$, taking into account the plot shift ($\tau=0$) along the time axis:

$$c_0 = 100$$

$$\tau_{1/2} = 190 \text{ min};$$

$$c_0 = 80$$

$$\tau_{1/2} = 250 - 60 = 190 \text{ min};$$

$$c_0 = 60$$

$$\tau_{1/2} = 335 - 145 = 190 \text{ min}.$$

The calculation data have shown that the reaction time of 50% of the starting materials does not depend on the initial concentration. This

shows that the reaction belongs to the first-order reactions.

Sometimes it is convenient to use the half-reaction method in analytical form, especially when the order of a reaction is fractional. In that case, the extended equation for the half-transformation time:

$$\tau_{1/2} = \frac{\text{const}}{c_0^{n-1}} \text{ or } \ln(\tau_{1/2}) = \ln(\text{const}) - (n-1)\ln c_0. \quad (5.7)$$

Having a half-transformation time at two different initial concentrations, we determine n according to the formula:

$$n = \frac{\ln(\tau'_{1/2}) - \ln(\tau''_{1/2})}{\ln(c'_0) - \ln(c''_0)} + 1. \quad (5.8)$$

During the determination of the reaction order, in most methods a rate constant is simultaneously obtained. In analytical methods it is an average value of the constants obtained in the kinetic equation, which the experimental data is obeyed to. Thus, the rate constant for the reaction analyzed in the example 1 is:

$$k_{aver}^1 = 3,70 \cdot 10^{-3} \text{ min}^{-1}.$$

In the graphical solution method the rate constant is obtained using the tangent of the slope of a straight line (in the corresponding coordinates for each reaction order):

–for the first-order reaction $k_1 = -\text{tg}\alpha$;

–for the second-order reaction $k_2 = \text{tg}\alpha$;

–for the third-order reaction $k_3 = \frac{\text{tg}\alpha}{2}$.

The rate constant for the reaction analyzed in the example 2 is:

$$k_1 = -(-0,0257) = 0,0257 \text{ c}^{-1}.$$

When the reaction order and the rate constant are determined, it means that the differential and integrated rate laws are established, i.e. these rate laws are equations that can be used to calculate the rate of a reaction and the current concentration of a substance at any time.

Task 7

For the reactions given in Table 5.4 :

1) Determine the reaction order and the rate constant using the data on process during the time τ (from the beginning of the reaction). For gases the pressure can be used in calculations instead of concentration, if the reaction under study is the first-order reaction. Indicate the dimension of the calculated rate constant;

2) Calculate the reaction time for B %.

Table 5.4 – Task variants

№	Reaction	τ , time	Result of the reaction path control, A	B , %
1	$H_2 + I_2 \rightarrow 2HI$ A – concentration I_2 , mol/l	0 200 4006 00	0,022 0,0168 0,0136 0,0114	80
2	Isomerization of cyclopropane to propylene $\begin{array}{c} CH_2 \\ / \quad \backslash \\ CH_2-CH_2 \end{array} \rightarrow CH_2=CH-CH_3,$ A – concentration of propylene, mol/l	0 40 60 120	1,0 0,985 0,977 0,955	25
3	$C_2H_4 + H_2 \rightarrow C_2H_6$ A – ethylene concentration, mol/l time, c	0 120 300 400	0,02 0,0173 0,0144 0,0132	50
4	$C_6H_5C \equiv CCOOH + I_2 \rightarrow C_6H_5IC = CICOOH$ (equal initial concentrations, $T = 298K$) A – iodine concentration, mol/l	0 10 23	0,1 0,052 0,032	40
5	$2 C_2H_5OH + 2 Br_2 \rightarrow CH_3COOC_2H_5 + 4 HBr$ (great excess of ethanol, $T = 298K$) A – concentration of $Br_2 \cdot 10^3$, mol/l	0 4 14,5	$8,1 \cdot 10^{-3}$ $6,1 \cdot 10^{-3}$ $3,7 \cdot 10^{-3}$	90
6	$SO_2Cl_2 \rightarrow SO_2 + Cl_2$ $T = 600K$ A – total pressure, $p \cdot 10^{-7}$, Pa	0 60 120 500	1,122 1,131 1,140 1,195	25
7	$2 H_2O_2 \rightarrow 2 H_2O + O_2$ (in aqueous solution, $T = 303K$) A – concentration of hydrogen peroxide, mol/l	0 11,5 27,1	0,342 0,207 0,124	75
8	$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$ ($T = 298K$) A – sugar concentration, mol/l	0 57,5 147	0,65 0,63 0,60	20
9	$CH_3COOH_3 \rightarrow C_2H_4 + H_2 + CO$ (gas phase reactions) A – total pressure of all gases, atm.	0 0,11 0,33	0,41 0,54 0,74	90
10	$2 N_2O_5 = 2 N_2O_4 + O_2$ ($T = 298K$) A – concentration of N_2O_5 , mol/l	0 182 319	2,33 2,08 1,91	15

Continuation of Table 5.4

№	Reaction	τ , time	Result of the reaction path control, A	B, %
11	$\text{CH}_3\text{COOC}_2\text{H}_5 + \text{OH}^- \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{CH}_3\text{COO}^-$ <i>A</i> – concentration of alkali, mol/l	0 30 60 200	0,2 0,174 0,154 0,10	80
12	$\text{CCl}_3\text{CH}_3 \rightarrow \text{CCl}_2 = \text{CH}_2 + \text{HCl}$ ($T = 298\text{K}$) <i>A</i> – total pressure, $p \cdot 10^{-5}$, Pa	0 500 600 700	0,506 0,239 0,712 0,683	60
13	$\text{H}_2 + \text{S}_{(\text{ж})} \rightarrow \text{H}_2\text{S}$ (molten sulphur, in excess; $T = 583\text{K}$; H_2S absorbed by alkali) <i>A</i> – pressure of hydrogen, atm.	0 24 36	0,956 0,651 0,538	30
14	$2 \text{PH}_3 \rightarrow 3 \text{H}_2 + 2 \text{P}$ ($T = 298\text{K}$) <i>A</i> – partial pressure PH_3 , mm Hg	0 1 2	700 427,5 261	70
15	$2 \text{AsH}_3 = 2 \text{As}_{(\text{TB})} + 3 \text{H}_2$ ($T = 283\text{K}$) <i>A</i> – total pressure, mm Hg	0 5,5 8,1	733 806 836	60
16	$\text{Cu} + (\text{NH}_4)_2\text{S}_2\text{O}_8 = (\text{NH}_4)_2\text{SO}_4 + \text{CuSO}_4$ (initial concentration $(\text{NH}_4)_2\text{S}_2\text{O}_8$ – 0,219 mol/l) <i>A</i> – concentration of CuSO_4 , mol/l	0,5 1,0	0,054 0,095	95
17	$\text{NH}_4\text{CNO} \rightarrow (\text{NH}_2)_2\text{CO}$ (in aqueous solution; $T = 298\text{K}$) <i>A</i> – concentration of NH_4CNO , mol/l	0 5 7,6	0,20 0,13 0,105	85
18	$\text{CO}_2\text{Cl}_2 \rightarrow \text{CO} + \text{Cl}_2$ <i>A</i> – total system pressure, $p \cdot 10^{-7}$, Pa time, c	0 60 500	1,122 1,132 1,203	65
19	$\text{CH}_3\text{J} + \text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{CH}_3\text{NaS}_2\text{O}_3 + \text{NaJ}$ (in aqueous solution) <i>A</i> – concentration of $\text{Na}_2\text{S}_2\text{O}_3$, mol/l, (equal initial concentrations)	0 0,18 0,51	0,02 0,014 0,009	35
20	$2 \text{NO}_2 \rightarrow 2 \text{NO} + \text{O}_2$ (thermal decomposition at high temperature and low pressure) <i>A</i> – concentration of $\text{NO}_2 \cdot 10^2$, mol/l; (time, c)	0 20 60	17,5 10,5 5,8	40

Continuation of Table 5.4

No	Reaction	τ , time	Result of the reaction path control, A	B, %
21	$\text{CH}_3\text{Br} + \text{NaJ} \rightarrow \text{CH}_3\text{J} + \text{NaBr}$ A – concentration of ethyl bromide, mol/l	0 511 879	0,002 0,00184 0,00174	90
22	$\text{CH}_2\text{-CH}_2 \rightarrow \text{CH}_4 + \text{CO}$ $\begin{array}{c} \backslash \ / \\ \text{O} \end{array}$ (in the gas phase, $T = 688\text{K}$) A – total pressure, mm Hg	0 0,2 0,5	116 133 154	95
23	$\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{C}_2\text{H}_5\text{OH}$ (equal initial concentrations of ether and alkali, $T = 293\text{K}$), time, sec A – concentration of the starting material is decreased, mol/l	0 300 2100 7200	0,02 0,0072 0,01574 0,01862	70
24	$\text{C}_2\text{H}_5\text{Br} \rightarrow \text{C}_2\text{H}_4 + \text{HBr}$ A – total pressure $p \cdot 10^{-5}$, Pa $T = 650\text{K}$	0 100 200 300	1,013 1,029 1,045 1,061	90
25	$\text{CH}_3\text{COH} \rightarrow \text{CH}_4 + \text{CO}$ (in the gas phase, $T = 700\text{K}$) A – aldehyde concentration, mol/l: time, c	0 80 120 160	1,00 0,53 0,43 0,36	40

5.2. The effect of temperature on the rate of a chemical reaction

Temperature is one of the main factors that affects the rate and the rate constant of a reaction. If in the analyzed temperature range the reaction mechanism does not change, the reaction rate always increases with increasing temperatures. According to the Van't Hoff's empirical rule for low temperatures, the reaction rate increases 2 or 4 times for every ten degree rise in temperature, i.e.

$$\gamma = \frac{w_{T+10}}{w_T} = \frac{k_{T+10}}{k_T} = 2 \div 4, \quad (5.9)$$

where γ – temperature coefficient of the reaction rate that characterizes the increase of the reaction rate for every 10°C rise in temperature.

For an arbitrary temperature interval an average temperature coefficient of the reaction rate can be determined using the formula:

$$\gamma^{\frac{T_2-T_1}{10}} = \left(\frac{w_{T_2}}{w_{T_1}} \right) = \left(\frac{k_{T_2}}{k_{T_1}} \right). \quad (5.10)$$

Example:

Determine the average coefficient of the rate of the autoxidation reaction of hydroxylamine, for which the rate constant changes from $0,237 \cdot 10^{-4} \text{s}^{-1}$ to $2,64 \cdot 10^{-4} \text{s}^{-1}$ if the temperature rises from 0°C to 25°C, and determine whether this reaction conforms with the Van't Hoff's law.

Solution:

On the basis of equation (5.10) we have $\gamma = \left(\frac{2,64}{0,237} \right)^{\frac{10}{25}} = 2,62$.

The obtained Van't Hoff coefficient lies in the interval $2 \div 4$, indicating that for this reaction the Van't Hoff's law is satisfied.

More accurate data on the effect of temperature on the reaction rate are given by the theory of chemical kinetics.

According to the Arrhenius collision model, only collisions of active molecules i.e. those molecules that have the necessary excess of energy, lead to chemical transformations.

The minimum excess energy (compared to the average), that is enough for performing a chemical action, is called activation energy. It describes how the temperature affects the rate constant.

The relation between activation energy and rate constant gives the Arrhenius equation:

$$k = B e^{-\frac{E}{RT}}, \quad (5.11)$$

where E is the activation energy, J/mol; R is the universal gas constant, J/mol K; T is the temperature, K; B is the pre-exponential factor; k is the rate constant at the temperature T .

A closer look at the Arrhenius equation reveals that the larger the activation energy, the smaller the rate constant, which means that the reaction proceeds more slowly.

Taking two values of the rate constants at two different temperatures yields the activation energy value:

$$E = \frac{RT_1T_2}{T_2 - T_1} \ln \frac{k_{T_2}}{k_{T_1}}, \quad (5.12)$$

where k_{T_1} and k_{T_2} are the rate constants at the temperatures T_1 and T_2 , respectively.

One can determine the pre-exponential factor using the values given for the activation energy and the rate constant at any temperature:

$$B = k \cdot e^{\frac{E}{RT}}. \quad (5.13)$$

In the Arrhenius equation the pre-exponential factor is the total number of collisions per unit volume per unit time.

In the absolute reaction rate theory the elementary act of chemical interaction is considered as simultaneous and gradual breaking of old bonds and formation of new ones. This situation is realized if a quasi-molecule is unstable (it has a high energy level), which refers to an activated complex. The theory supposes that the rate constant is determined according to the following equation:

$$k = \frac{RT}{Nh} e^{\frac{\Delta S^*}{R}} \cdot e^{-\frac{\Delta H^*}{RT}}, \quad (5.14)$$

where k is the rate constant; R is the universal gas constant; h is the Planck constant; N is the Avogadro constant; ΔS^* is the entropy of activation (the entropy change involved in the formation of the activated complex by the collisions of the reacting molecules); ΔH^* is the enthalpy of activation (the enthalpy change involved in the formation of the activated complex by the collisions of the reacting molecules).

The enthalpy of activation is related to the experimental value of the energy of activation, which is represented by the following ratio:

$$\Delta H^* = E_A - RT. \quad (5.15)$$

Example.

Calculate the energy of activation, pre-exponential factor, entropy and enthalpy of the formation of the activated complex under standard conditions using the experimental data derived for the reaction of the auto-oxidation of hydroxylamine if a temperature increase from 0 °C to 25 °C changes the rate constant – its values are ranging from $0,237 \cdot 10^{-4} \text{ c}^{-1}$ to $2,64 \cdot 10^{-4} \text{ c}^{-1}$.

Solution. Determination of the activation energy for the reaction.

Substitute the experimental values into the Arrhenius equation (5.12).

$$E = \frac{8,31 \cdot 273 \cdot 298}{273 - 298} \ln \frac{2,64 \cdot 10^{-4}}{0,237 \cdot 10^{-4}} = 65,18 \text{ kJ/mol.}$$

Deduce the pre-exponential factor from the equation (5.13):

$$B = 2,64 \cdot 10^{-4} \cdot e^{65180/8,31 \cdot 298} = 7,1 \cdot 10^7$$

Calculate the enthalpy of activation from the equation (5.14):

$$\Delta H_{298}^{\#} = 65180 - 8,31 \cdot 298 = 62,7 \text{ kJ / mol.}$$

Derive the entropy of activation from the transformed equation (5.15):

$$\Delta S^\# = R \left(\ln \frac{k \cdot N \cdot h}{RT} + \frac{\Delta H^\#}{RT} \right),$$

$$\Delta S_{298}^\# = 8,31 \cdot \left(\ln \frac{2,64 \cdot 10^{-4} \cdot 6,02 \cdot 10^{23} \cdot 6,63 \cdot 10^{-34}}{8,31 \cdot 298} + \frac{62700}{8,31 \cdot 298} \right);$$

$$\Delta S_{298}^\# = -102,8 \text{ J/mol} \cdot \text{K}.$$

Exercise 8

Calculate the missing values in Table 8 using the data on the kinetics of a reaction.

Plot the graphs of:

- 1) the temperature dependence of the rate constant;
- 2) $\ln k$ versus $1/T$.

In Table 5.5 k_1 , k_2 and k_3 correspond to the rate constants of a reaction at the temperatures T_1 , T_2 and T_3 ; E_A is the activation energy of the reaction, kJ/mol; γ is the temperature coefficient of a chemical reaction rate.

Table 5.5 – Variants of the Tasks

№	T_1	k_1	T_2	k_2	T_3	k_3	E_A	γ
1	298	0,002	338	0,03	320			
2	283	1,0	305	7,15	315			
3	320	4,0	350		370			2,1
4	273	0,002	313	0,10		0,50		
5	303	0,004	353		323		70	
6	300	75	325		350		85	
7	873	83		132	938	210		
8	879	12	933	52		95		
9	600	66	645	850	630			
10	328	0,01	298	0,001	343			
11	273	0,27	303			1,5		2,5
12	283	0,68	273		298		57	
13	298	0,009	303	0,013	308			
14	273	2,5	293	48	323			
15	333	5500	313	570	293			
16	273	1,2	293			50	44	
17	823	2,5	843	8,2		12,3		
18	893	92	873	35	850			
19	293	0,7	313	3,5	333			
20	560	5,5	520		500		210	
21	750	0,15	800	0,35	770			
22	480	320		150	450		180	
23	298	6,3	273			40	210	
24	900	1,6	880		660			1,9
25	273	140		250	298		160	

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APPENDIXES

Appendix 1

Thermodynamic Quantities for Elementary Substances and Compounds

Substance	ΔH_0 , kJ/mol	ΔS_0 , J/(mol·K)	C_p , J/(mol·K)	Coefficients of an equation $C_p = a + bT + cT^2 + C'T^{-2}$, J/(kmol·K)			
				a	$b \cdot 10^3$	$c \cdot 10^{-5}$	$c \cdot 10^6$
Cl ₂ (r)	0	223,0	33,84	36,69	1,05	-2,52	-
H ₂ (r)	0	130,6	28,83	27,28	3,26	0,502	-
I ₂ (r)	62,24	260,58	36,9	37,40	0,59	-0,71	-
O ₂ (r)	0	205,03	29,36	31,46	3,39	-3,77	-
S ₂ (r)	129,1	227,7	32,47	36,11	1,09	-3,52	-
CO(r)	-110,5	197,4	29,15	28,41	4,10	-0,46	-
CO ₂ (r)	-393,51	213,6	37,13	44,14	9,04	-8,53	-
COCl ₂ (r)	-223,0	289,2	60,67	67,16	12,11	-9,03	-
CaCO ₃ (Kp)	-1206	92,9	81,85	104,5	21,92	-25,94	-
CaO (Kp)	-635,1	39,7	42,80	49,63	4,52	-6,95	-
Ca(OH) ₂ (Kp)	-986,2	(83,4)	87,5	105,2	12,0	-19,0	-
HCl (r)	92,30	186,70	29,16	26,53	4,60	1,09	-
HI (r)	25,94	206,30	29,16	26,32	5,94	0,92	-
H ₂ O(r)	-241,84	188,74	33,56	30,00	10,71	0,33	-
H ₂ S (r)	-20,15	205,64	33,93	29,37	15,40	-	-
MgCO ₃ (Kp)	-1096,2	65,69	75,52	77,91	57,74	-17,41	-
Mg(OH) ₂ (Kp)	-924,66	63,14	76,99	54,56	66,11	-	-
MgO (Kp)	601,24	26,94	37,41	42,59	7,28	-6,19	-
NO (r)	90,37	210,62	29,83	29,58	3,85	-0,59	-
NO ₂ (r)	33,89	240,45	37,11	42,93	8,54	-6,74	-
N ₂ O ₄ (r)	9,37	304,3	78,99	83,89	39,75	-14,9	-
PCl ₃ (r)	-277,0	311,7	72,05	80,12	3,1	-7,99	-
PCl ₅ (r)	-369,45	362,9	111,9	129,5	2,92	-16,4	-
SO ₂ (r)	-296,9	248,1	39,87	42,55	12,55	-5,65	-
SO ₂ Cl ₂ (r)	-358,7	311,3	77,4	53,72	79,50	-	-
SO ₃ (r)	-395,2	256,23	50,63	57,32	26,86	-13,05	-
CH ₄ (r)	-74,85	186,19	35,79	17,45	60,46	-	-1,117
C ₂ H ₄ (r)	52,28	219,4	43,63	4,196	154,59	-	-81,09
C ₂ H ₆ (r)	-84,67	229,5	52,70	4,494	182,26	-	-74,86
C ₆ H ₆ (r)	82,93	269,2	81,67	33,90	471,87	-	-98,34
C ₆ H ₁₂ (r)	-123,1	298,2	106,3	51,72	598,8	-	-230,0
CH ₂ O ₂ (r)	-376,7	251,6	48,7	19,4	112,8	-	-47,5
CH ₄ O (r)	-201,2	239,7	43,9	15,28	105,2	-	-31,04
CH ₃ I (r)	20,5	253,0	44,1	19,16	92,67	-	-32,28
C ₂ H ₅ Cl (r)	-105,0	274,8	62,3	13,07	188,5	-	-71,94

Appendix 2
Ionic Limiting Molar Conductivity ($C \rightarrow 0$) $T=298K$

Cation	λ_0^+ (cm^2/Ω (mol equiv))	Anion	λ_0^- (cm^2/Ω (mol equiv))
Ag^+	61,9	BrO_3^-	55,4
Cs^+	77,2	Cl^-	76,35
H^+	349,8	F^-	55,4
K^+	73,5	I^-	76,85
Li^+	38,6	IO_3^-	40,8
NH_4^+	73,5	NO_2^-	71,4
Na^+	50,1	NO_3^-	71,4
		OH^-	198,3
		SCN^-	66,0
		HCOO^-	54,6
		CH_3COO^-	40,9
		$\text{CH}_2\text{ClCOO}^-$	39,8
		$\text{CH}_2\text{CNCOO}^-$	41,8
		$\text{C}_2\text{H}_5\text{COO}^-$	35,8
		$(\text{CH}_3)_2\text{CHCOO}^-$	34,2
		$\text{C}_6\text{H}_5\text{COO}^-$	32,3

Appendix 3
The Activity Coefficient γ_{\pm} of Strong Electrolytes at 298 K

Electrolyte	Concentration, mol/1000 g of water								
	0,001	0,002	0,005	0,01	0,02	0,05	0,1	0,2	0,5
AgNO_3	–	–	0,925	0,897	0,860	0,793	0,734	0,657	0,536
CdCl_2	0,819	0,743	0,623	0,524	0,456	0,304	0,228	0,161	0,101
CdI_2	–	–	0,490	0,379	0,281	0,167	0,106	0,068 5	0,037 6
CdSO_4	0,726	0,639	0,505	0,399	0,307	0,206	0,150	0,102	0,061
CuCl_2	0,888	0,849	0,783	0,723	0,659	0,577	0,508	0,455	0,411
CuSO_4	0,74	–	0,573	0,438	0,317	0,217	0,154	0,104	0,062
HBr	0,966	–	0,930	0,906	0,879	0,838	0,805	0,782	0,789
HCl	0,965	0,952	0,928	0,904	0,875	0,830	0,796	0,767	0,757
H_2SO_4	0,830	0,757	0,639	0,544	0,453	0,340	0,265	0,209	0,156
KCl	0,965	0,952	0,927	0,902	0,869	0,816	0,770	0,718	0,649
KI	0,952	–	0,928	0,903	0,872	0,820	0,778	0,733	0,676
KOH	–	–	–	–	–	0,824	0,798	0,760	0,723
LiCl	0,963	0,948	0,921	0,896	0,865	0,819	0,790	0,757	0,739
NaI	–	–	–	–	–	–	0,787	0,751	0,723
NaOH	–	–	–	0,905	0,871	0,818	0,766	0,727	0,690
NiSO_4	–	–	–	–	–	–	0,150	0,105	0,063
ZnBr_2	–	–	–	–	–	–	0,547	0,510	0,511
ZnSO_4	0,700	0,608	0,477	0,387	0,298	0,202	0,150	0,104	0,063
ZnCl_2	0,88	0,84	0,77	0,71	0,64	0,56	0,515	0,462	0,394

Appendix 4
Standard Electrode Potentials in Aqueous Solutions at 298 K

№	Electrode	Reaction	E^0 , V
1	$H^+ H_2$	$H^+ + e \rightarrow 1/2 H_2$	0,00
2	$Zn^{2+} Zn$	$Zn^{2+} + 2e \rightarrow Zn$	- 0,763
3	$Cd^{2+} Cd$	$Cd^{2+} + 2 e \rightarrow Cd$	-0,403
4	$Ni^{2+} Ni$	$Ni^{2+} + 2 e \rightarrow Ni$	-0,250
5	$Pb^{2+} Pb$	$Pb^{2+} + 2 e \rightarrow Pb$	- 0,126
6	$Cu^{2+} Cu$	$Cu^{2+} + 2 e \rightarrow Cu$	0,337
7	$Ag^+ Ag$	$Ag^+ + e \rightarrow Ag$	0,799
8	$Cl_2 Cl^-$	$1/2 Cl_2 + e \rightarrow Cl^-$	1,360
9	$Pb PbI_2 I^-$	$PbI_2 + 2e \rightarrow Pb + 2 I^-$	- 0,365
10	$Pb PbBr_2 Br^-$	$PbBr_2 + 2e \rightarrow Pb + 2 Br^-$	- 0,284
11	$Pb PbCl_2 Cl^-$	$PbCl_2 + 2e \rightarrow Pb + 2 Cl^-$	- 0,268
12	$Ag AgI I^-$	$AgI + e \rightarrow Ag + I^-$	- 0,152
13	$Hg Hg_2I_2 I^-$	$1/2 Hg_2I_2 + e \rightarrow Hg + I^-$	- 0,040
14	$Ag AgBr Br^-$	$AgBr + e \rightarrow Ag + Br^-$	0,071
15	$Hg Hg_2Br_2 Br^-$	$1/2 Hg_2Br_2 + e \rightarrow Hg + Br^-$	0.140
16	$Ag AgCl Cl^-$	$AgCl + e \rightarrow Ag + Cl^-$	0,222
17	$Hg Hg_2Cl_2 Cl^-$	$1/2 Hg_2Cl_2 + e \rightarrow Hg + Cl^-$	0,268
18	$Hg Hg_2SO_4 SO_4^{2-}$	$Hg_2SO_4 + 2e \rightarrow 2Hg + SO_4^{2-}$	0,615
19	$H_2 OH^- Pt$	$2 H_2O + 2e \rightarrow H_2 + 2 OH^-$	- 0,828

Навчальне видання

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