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**LABORATORY MANUAL
FOR PHYSICAL CHEMISTRY**

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1st DETERMINATION OF MOLAR MASS FROM FREEZING POINT DEPRESSION

1st1 Theory

A solution may be described as a homogeneous mixture of two (or more) substances. It consists of a single **phase**, or we may say the solution is a one-phase system. The components which constitutes the largest proportion of the solution is called the **solvent**, while the other, the dissolved substance, is referred to as the **solute**. A solution may be gaseous, liquid or solid. This treatment will refer particularly to solutions which are liquid, although the dissolved substance may originally be a solid.

It has been known for many years that when a non-volatile solute is dissolved in a liquid, the vapor pressure of the solution is lower than that of the pure liquid (solvent). Therefore, such solution boils at higher temperature than the pure solvent. Likewise, the solution solidifies (or freezes) at lower temperature than the solvent. The quantitative connection between the lowering of the vapor pressure and the composition of the solution was discovered by F. M. Raoult. If p_A^0 is the vapor pressure of the pure solvent at a particular temperature, and p_A is the vapor pressure of the solvent over the solution at the same temperature, the difference $p_A^0 - p_A = \Delta p_A$ is the lowering of the vapor pressure. The **relative lowering** of the vapor pressure for the given solution is defined by ratio $\Delta p_A/p_A^0$. According to one form of Raoult's law, *the relative lowering of the vapor pressure of the solvent is equal to the mole fraction of the solute in the solution*:

$$\frac{p_A^0 - p_A}{p_A^0} = \frac{\Delta p_A}{p_A^0} = x_B = \frac{n_B}{n_A + n_B}$$

Eq. 1st.1

In equation (Eq. 1st.1), n_A and n_B are the number of moles of solvent (A) and solute (B), respectively. Such solution, which obey Raoult's law exactly at all concentrations and temperatures, are called **ideal solutions**. Actually very few solutions behave ideally, however, for dilute solutions the deviations from Raoult's law are small and can usually be ignored.

The sum of the mole fractions of solvent and solute is equal unity, $x_A+x_B=1$. An alternative form of Raoult's law is obtained by subtracting unity from both sides of equation (Eq. 1st.1):

$$\frac{p_A}{p_A^0} = x_A \text{ or } p_A = p_A^0 x_A$$

Eq. 1st.2

According to the equation (Eq. 1st.2) the vapor pressure of the solvent in a solution is directly proportional to the mole fraction of the solvent, if Raoult's law is obeyed. The proportionality constant is p_A^0 , the vapor pressure of the pure solvent.

The osmotic pressure of solutions connects to the lowering of the vapor pressure too. The lowering of the vapor pressure of the solution, osmotic pressure, ebullioscopic elevation of the boiling point and cryoscopic depression of the freezing point are together called the **colligative** properties of the solution, because they depend only on the concentration (number of particles) of the dissolved substance or substances.

Ebullioscopic and cryoscopic measurement are used to determine molar mass of the dissolved substance. In pharmacy, cryoscopy is also applied at conditioning preparations to the same osmotic pressure as osmotic pressure of blood - isotonization.

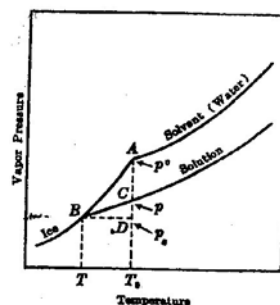


Fig. 1st-1 Temperature effect on vapour pressure

The relationship between the freezing point of the pure solvent and that of a solution may be seen with the aid of the vapor pressure curves in Fig. 1st-1. These curves show the temperature variation of the vapor pressure of the solvent over the pure liquid solvent, the solution, and the solid solvent, respectively. The slope of the vapor pressure curve of the dilute solution in the vicinity of the freezing point is given by the **Clausius-Clapeyron equation**

$$\frac{dp_A}{dT} = \frac{\Delta H_{mv} p_A^0}{RT_0^2}$$

Eq. 1st.3

where T_0 is the freezing point of the solvent. If BC in Fig. 1st-1 is taken to be a straight line, the slope dp_A/dT may be replaced by CB/BD , i.e., by $(p_A - p_s)/\Delta T$, so that

$$\frac{p_A - p_s}{\delta T} = \frac{\Delta H_{mv} p_A^0}{RT_0^2}$$

Eq. 1st.4

The slope of the vapor pressure curve of the solid solvent is also given by another form of the Clausius-Clapeyron equation. This may be written as

$$\frac{dp_A}{dT} = \frac{\Delta H_{ms} p_A^0}{RT_0^2}$$

Eq. 1st.5

where ΔH_{ms} is the molar heat of sublimation of the solid solvent. Again, if AB is treated as linear, the slope is equal to AD/BD . Equation (Eq. 1st.5) becomes

$$\frac{p_A - p_s}{\delta T} = \frac{\Delta H_{ms} p_A^0}{RT_0^2}$$

Eq. 1st.6

Substraction of equation (Eq. 1st.4) from (Eq. 1st.5) the gives

$$\frac{p_A^0 - p_A}{\Delta T} = \frac{(\Delta H_{ms} - \Delta H_{mv}) p_A^0}{RT_0^2}$$

Eq. 1st.7

$$\Delta T = \frac{p_A^0 - p_s}{p_A^0} \frac{RT_0^2}{\Delta H_{mf}}$$

Eq. 1st.8

where $\Delta H_{mf} = \Delta H_{ms} - \Delta H_{mv}$ is the molar heat of fusion of the solid solvent. If Raoult's law is obeyed, the relative lowering of the vapor pressure in equation (Eq. 1st.8) may be replaced by x_B , the mole fraction of solute, so that

$$\Delta T = \frac{RT_0^2}{\Delta H_{mf}} x_B$$

Eq. 1st.9

The most important application of this equation is for the determination of molar mass of dissolved substances, and for this purpose an alternative form is more useful. Since the solution is dilute ($n_B \ll n_A$), the mole fraction x_B may be replaced by the molar ratio n_B/n_A :

$$\Delta T = \frac{RT_0^2}{\Delta H_{mf}} \frac{m_B}{M_B m_A}$$

Eq. 1st.10

In the study of dilute solutions, it has been found convenient to express the concentration of a solution in terms of its molality (this is the number of moles of solute dissolved in 1 kg of solvent). In the solution under consideration m_B/M_B moles of solute are dissolved in m_A kilograms of solvent, and so the molality m is given by

$$m = \frac{m_B}{M_B m_A}$$

Eq. 1st.11

Substitution of these result into equation (Eq. 1st.10) leads to

$$\Delta T = \frac{RT_0^2 M_A}{\Delta H_{mf}} m = K_C m$$

Eq. 1st.12

where K_C is the molal depression constant. It is also called the cryoscopic constant of a given solvent. The depression of the freezing point is thus proportional to the molality of the solution. Cryoscopic constant depends only on the properties of the solvent, for benzene $K_C=5.14 \text{ K kg mol}^{-1}$, for water $K_C=1.86 \text{ K kg mol}^{-1}$ etc.

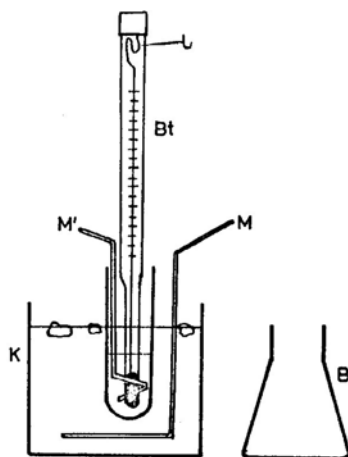


Fig. 1st-2 Apparatus for freezing point determination

1st2 Task

Freezing and melting point will be determined by using the apparatus described on Fig. 1st-2. We will use benzene as the solvent. The dissolved substance (naphtalene) does not dissociate and associates in the solution. We will assume the solution is ideal, Raoult's law is obeyed and the solution is dilute. In this case the molar mass of the dissolved substance can be derived from the expression (see equation (Eq. 1st.11) and (Eq. 1st.12), resp.)

$$M_B = \frac{K_C m_B}{\Delta T m_A}$$

Eq. 1st.13

1st3 Equipment and chemicals

Beckman's thermometer, laboratory thermometer, test tube with a big diameter, metallic spiral stirrer, 1000 ml beaker, Erlenmyer's flask, stop-watch, analytical balance, 20 ml pipette, benzene, sample of naftalene substance, water, ice cubes, alcohol for drying.

1st4 Method

Using water and some pieces of ice-cubes prepare the cooling bath in the beaker. At the cooling process there must be always approx. 2 pcs. of rocks still unmelted. Using clean and dry pipette fill the amount of 20 ml benzene to the dry test tube and check it's temperature with laboratory thermometer. The temperature of the benzene is necessary for the mass (m_A) calculation from its density and volume. Set up the apparatus as it is shown in the figure. Note, that the Beckman's thermometer has to be also dry and must not touch the inner wals of the test tube. Start with gradual cooling by paralel mixing both the benzene and the bath. When the temperature of the bath drops to 5, degrees start the stop watch and write down the temperature in every 10-th second. Check the amount of the unmelted ice. The cooling must be as uniform as it is possible. After reaching the minimum on the cooling curve the bath's temperature will slightly increase for a few seconds (plato on the curve - T_f^B) and then finally goes again down (frozen benzene). The next measurement is the determination of the temperature raise curve. Remove the cooling bath and exchange it with the Erlenmayer's flask (Fig. 1st-2). Continue with mixing and write down the benzene's temperature at every 20-th second. Note that the mixing must be uniform. The temeprature will go trough the plato phase T_m^B (with no or very slight

temperature increases) again. When the temperature reaches 5 degrees, stop the temperature reading. Now weigh a sample of naphthalene (on analytical balances), something between 0.2-0.4 gram. The mass (m_B) of the sample must be determined as precise by as it is possible. Then dissolve the naphthalene in the benzene and repeat the previous cooling and temperature raising process with the prepared benzene solution. Determine the corresponding plateaus (T_f^N, T_m^N) on the temperature-time curves.

1st5 Processing the results

For the pure solvent and solution, respectively, you will find freezing (T_f) and melting (T_m) point from temperature versus time dependence curves. Freezing point depression is given by subtraction of freezing or melting point of the solution from freezing or melting point of the pure solvent:

$$\Delta T_1 = T_f^B - T_f^N$$

Eq. 1st.14

or

$$\Delta T_2 = T_m^B - T_m^N$$

Eq. 1st.15

where index B (or N) is referred to the pure solvent (or solution). Calculate the mass of the solvent m_A as a product of the solvent volume and density at the recorded experiment temperature (Tab. 1st-1 Density of benzene as function of temperature Tab. 1st-1):

$$m_A = V_A \cdot \rho$$

Eq. 1st.16

According to equation (Eq. 1st.13) the molar mass of the dissolved substance - naphthalene is

$$M_B = \frac{K_C m_B}{\Delta T_1 m_A}$$

$$M_B = \frac{K_C m_B}{\Delta T_2 m_A}$$

Eq. 1st.17

where K_C is molar depression constant for benzene ($K_C = 5.14 \text{ Kkg/mol}$) and m_B is the mass of naphthalene which was dissolved in given volume of benzene.

The record (protocol) should include the points:

- Principle of the molar mass determination from freezing point depression
- Working procedure and measurements for determination
- Tables of results, and diagrams of temperature vs. time

Tab. 1st-1 Density of benzene as function of temperature

Temperature $^{\circ}\text{C}$	ρ kg/m^3	Temperature $^{\circ}\text{C}$	ρ kg/m^3
15	884	21	878
16	883	22	877
17	882	23	876
18	881	24	875
19	880	25	873
20	879		

2nd PARTITION COEFFICIENT OF SUCCINIC ACID

2nd1 Theory

Consider a system consisting of two liquid layers (phases) of two immiscible or slightly miscible liquids. If a third substance, which is soluble in both liquids, is added into the system it is found to distribute, or divide, itself between the two layers in a definite manner. It has been shown experimentally that at equilibrium, at constant temperature, the ratio of the concentrations in the two layers has a definite value, independent of the actual amount of the dissolved substance. If c_1 and c_2 are the concentrations of this substance in two layers, then

$$k = \frac{c_1}{c_2}$$

Eq. 2nd.1

In words, therefore, the dissolved substance irrespective of its total amount, distributes itself between the two layers in constant concentration ratio, at constant temperature. The ratio, equal to the constant in equation (Eq. 2nd.1) is referred to as the partition constant or partition coefficient k (or sometime designated as P).

It will be shown below that the distribution law in the form of equation (Eq. 2nd.1) can usually be applied only to dilute solutions. It is also supposed that the partitioned substance undergoes no chemical changes, such as association or dissociation, in any of the two liquid phases.

When two phases are in equilibrium the chemical potential of the partitioned substance will be the same in both phases. The chemical potential of the dissolved substance in any of the two phases may be represented by

$$\mu = \mu_{10} + R.T.\ln a_1 \text{ and } \mu_2 = \mu_{20} + R.T.\ln a_2$$

Eq. 2nd.2

where a_1 and a_2 are the respective activities of the partitioned solute in the two phases. When the system is at equilibrium μ_1 and μ_2 must be equal, so that

$$\mu_2^0 - \mu_1^0 = RT \ln \frac{a_1}{a_2}$$

Eq. 2nd.3

At constant temperature the standard chemical potentials μ_{10} and μ_{20} are constant, and so are R and T; it follows, therefore, that

$$\frac{a_1}{a_2} = \text{constant}$$

Eq. 2nd.4

which is the exact form of the distribution law. For systems which are ideal or do not depart appreciably from ideal behaviour, the ratio of the activities may be replaced by the ratio of the mole fractions, i.e., x_1/x_2 should be constant. Further, for dilute solutions or for gases, the ratio of the concentrations may be used in place of the ratio of the mole fractions, and so in these circumstances c_1/c_2 should be constant, in agreement with the simple form of the distribution law given by equation (Eq. 2nd.1).

2nd2 Task

The partition constant of succinic acid will be measured in system of two immiscible liquids: 1-butanol - water. We will carry out the measurement with various amounts of partitioned substance and various ratio of liquid phases volumes.

2nd3 Equipment and chemicals

Four 100 ml separating funnels, two titrimetric flask, burette, pipettes (5 ml, 10 ml, 25 ml), electric hotplate, thermometer, aqueous solution of succinic acid (20 g/dm^3), aqueous solution of Ba(OH)_2 (0.05 mol/dm^3), phenolphthalein, 1-butanol.

2nd4 Method

Prepare four mixtures of butanol, water and succinic acid into separating funnels according to the following table (Tab. 2nd-1):

Tab. 2nd-1 Mixing table of chemicals

Separating funnel	1	2	3	4
	Pipetted volume of chemicals / ml			
Aqueous solution of succinic acid	25	10	20	20
Distilled water	-	15	-	20
1-butanol	25	25	40	20

Shake the separating funnels with preparing mixtures approximately 20 minutes. Put them to the holder on the laboratory stand and wait few minutes until the mixture is separated into two clear layers. Pour carefully the water phase into a beaker using funnel's cock. Pipette 5 ml of water solution from the beaker to each of the two titrimetric flask for titration. Add 20 ml of distilled water to each flask, warm up the solution to approximately 80°C, add 3 drops of phenophtalein and titrate by the water solution of Ba(OH)₂ with known concentration (0.05 mol/dm³). Use the same process at titration of water phases in the other separating funnels. After titration of water phases, take always 5 ml of butanol solution (organic phase), add 20 ml of distilled water, warm up the solution and titrate.

2nd5 Processing the results

Calculate the concentration of solutions according to following relation

$$c = 0.01 \cdot n \cdot f_{\text{OH}}$$

Eq. 2nd.5

where n means a solution consumption of Ba(OH)₂ in ml and f_{OH} is its analytical correction factor. Now, calculate the partition constant value (k) as the ratio of the concentration of succinic acid in butanol (c_{org}) and its concentration in water (c_{wtr}):

$$k = \frac{c_{\text{org}}}{c_{\text{wtr}}}$$

Eq. 2nd.6

(see equation Eq. 2nd.4 too).

Write your experimental data and the results in the following table (Tab. 2nd-2 Table of measured and calculated partitioning data Tab. 2nd-2):

Tab. 2nd-2 Table of measured and calculated partitioning data

No.	Consumption at titration						C_{org} mol/l	C_{wtr} mol/l	k
	1-butanol solution			water solution					
	I	II	Mean	I	II	Mean			
1									
2									
3									
4									

The record (protocol) should include the points:

- Principle of the partitioning coefficient determination
- Working procedure and measurements
- Tables of results and calculations
- Discussion and conclusions

3rd DETERMINATION OF THE LIQUID-VAPOUR EQUILIBRIUM IN A BINARY SYSTEM OF MISCIBLE LIQUIDS

3rd1 Theory

Solution may be described as a homogeneous mixture of at least two substances, and in most cases, we deal with liquid solutions. The component which represents the largest portion of the solution is usually called the **solvent**, while the dissolved substance is referred to as the **solute**. However, if the solution is made of completely miscible liquids in similar portions, it is not practical to distinguish which component is the solvent and which is the solute. The solutions of miscible liquids are often called **liquid mixtures**.

Any liquid substance is more or less volatile, there is certain vapour pressure of this substance above the surface of the pure liquid. When the miscible liquids are mixed together, the vapour pressure of each component above the surface of the formed solution is lowered, in comparison with the pure liquid component. The quantitative expression is given by Raoult's Law, which states that the relative lowering of the vapour pressure of a given component is equal to its molar fraction in the solution. For the ideal two component system (A, B) in the thermodynamical equilibrium at constant temperature we can write the Raoult Law in the following form:

$$p_A = p_A^0 x_A$$

Eq. 3rd.1

$$p_B = p_B^0 x_B,$$

Eq. 3rd.2

where p_A, p_B are the partial pressures of the components above the solution surface, p_A^0, p_B^0 are the pressures of the pure components and x_A, x_B are the respective molar fractions. Solutions that obey Raoult's Law throughout their composition range are called ideal. The total pressure of the gaseous phase is given by Dalton's Law:

$$p = p_A + p_B = p_A^0 x_A + p_B^0 x_B$$

Eq. 3rd.3

$$x_A + x_B = 1$$

Eq. 3rd.4

Composition of the gaseous phase can be obtained as:

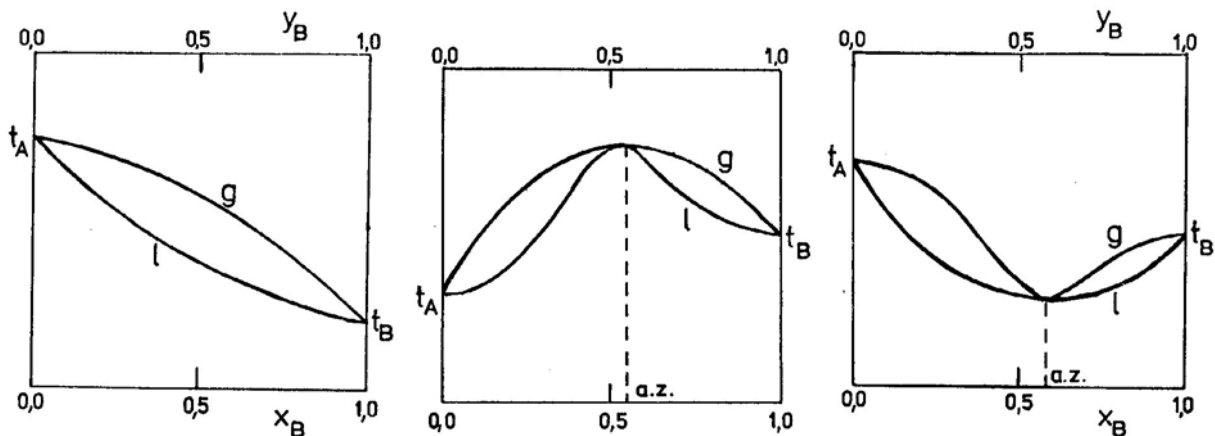
$$y_A = p_A / p$$

Eq. 3rd.5

$$y_B = p_B / p$$

Eq. 3rd.6

where y_A, y_B are the respective molar fractions. If the two components (A, B) of a liquid mixture are different in character, the molecular forces between the A molecules will differ from those acting between the B molecules and the presence of B will affect the evaporation of the A, and vice versa. The observed behaviour of the solution will then differ from the Raoult's law. If the attraction between the B molecules is stronger than between the A type, the escaping tendency of the A will be increased by the presence of B. This phenomenon is known as a **positive deviation from the Raoult's law**, with maximum on the vapour pressure curve and minimum on the isobaric phase diagram. If the two constituents of a liquid mixture attract one another strongly, their total vapour pressure will be less than that required by the Raoult's law. This type of nonideal behaviour is called as the **negative deviation from Raoult's law**. The vapour pressure curve may often have a minimum for a particular composition and there is a maximum on the isobaric phase diagram. Nonideal mixtures with minimum or maximum on the phase diagram cannot be totally separated by a simple **distillation**. When the extreme point on the phase curve is reached the evaporation proceeds without any further change of the composition (**azeotrope**). The composition of the gaseous and liquid phase of the azeotrope is identical.



We can rewrite Rault's law : $p_i = p_i^0 a_i = p_i^0 x_i \gamma_i$ for the ideal gas and nonideal solution, where a_i is the activity of the component i with Rault's standard state, γ_i is the Rault's activity coefficient for the component i . Rault's activity coefficient can be calculated from the following equation:

$$\gamma_i = \frac{p_i}{p_i^0 x_i} = \frac{p y_i}{p_i^0 x_i}$$

Eq. 3rd.7

3rd2 Task

Determination of the liquid-vapour equilibrium for the given real system of two miscible liquids. Construction of its isobaric phase diagram $T = f(x_B, y_B)$. Calculation of the Rault's activity coefficients.

3rd3 Equipment and chemicals

apparatus for the determination of the liquid-vapour equilibrium, Abbe refractometer, thermometer, pure solution components (A,B), test tubes.

Tab. 3rd-1 Pipetting scheme of sample solutions

Sample No.	Volume A/ml	Volume B/ml	Molar fraction A	Molar fraction B
1				
2				
3				
4				
5				
6				

3rd4 Method

The used apparatus (Fig. 3rd-1) has the following main parts: boiling flask, electrical heating device connected to autotransformer, vapour exhausting tubes, temperature meter, cooler, discharging cocks, distillation receiver, overflow tube.

Prepare 4 solutions (samples 2-5) from A,B with volume concentration 20, 40, 60, 80 % (total volume 40 ml). As samples No.1 and No.6 use the pure (100 %) A and B respectively. Record the atmospheric pressure (symbol p [Pa]). At first, pour the sample No.1 into the apparatus through the hole for the thermometer and close it after this step returning the thermometer. The liquid surface above the heating device may not exceed 1 cm.

Set the voltage to 8-12 V on the autotransformer, and gently open the cooler's cock for appropriate cooling. After a little time of boiling hot vapours will pass around the thermometer to the receiver. When the receiver becomes full, the condensate will return to the boiling flask. After establishing the equilibrium the composition of the phases will be equal and the temperature (T_i) of the vapours remains constant.

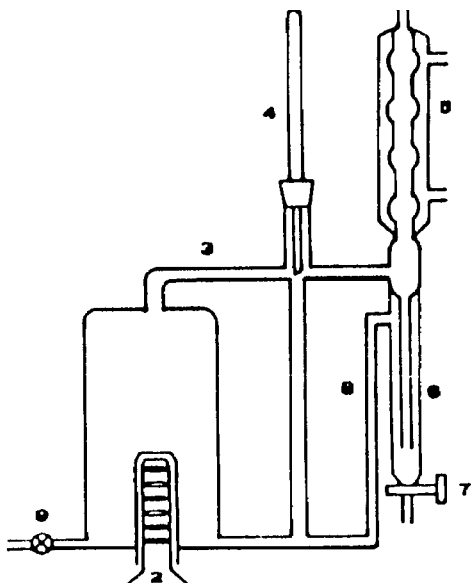


Fig. 3rd-1 Apparatus for liquid-vapour equilibrium determination

Write down the equilibrium temperature, and switch off the electrical heating. Withdraw the condensate and the liquid phase through the outlets (discharging cocks) to the test tubes. Close the test tubes and cool them down. Determine the respective refractive indices (n_{dl} , n_{dg}) and using the attached calibration curve (or solving the appropriate equation) determine the respective composition. Repeat this steps for each sample.

3rd5 Processing the results

Construct the isobaric phase diagram $T=f(x_B, y_B)$ from the measured temperature and composition values. Join the points referring to the liquid solution and mark it as curve "l" - liquidus. Other points define the curve "g" - gaseous. Curves start from the points T_a^0 or T_b^0 , which represent the boiling points of the pure components. Calculate the activity coefficients from the following equation:

$$\ln \frac{p_i^0}{p} = \frac{\delta_{\text{evap}} H_i^0}{R} \left(\frac{1}{T^0} - \frac{1}{T_i} \right)$$

Eq. 3rd.8

where T_i is the boiling point of the given solution, $\delta_{\text{evap}} H$ is the molar evaporation enthalpy, $p_i^0 = p_A^0$ or p_B^0 , and T_i^0 is the boiling point of the pure component in K at pressure 101325 Pa.

The record (protocol) should include the points:

- Theoretical principles of the determination
- Equipment and chemicals
- Working procedure and measurements
- Tables of results, calculations and diagrams

Tab. 3rd-2 Table of results

No.	t °C	T K	n _{dl}	n _{dg}	x _A	x _B	y _A	y _B	p _A ⁰ Pa	p _B ⁰ Pa	γ _A	γ _B
1												
2												
3												
4												
5												
6												

Tab. 3rd-3 Selected physico-chemical properties of substances

Substance	t ⁰ °C	T K	Δ _{evap} H ⁰ kJ/mol	ρ kg/m ³
Acetone	76.5	329.7	20.23	796.0
Ethanol	78.4	351.6	39.39	789.2
Ethylacetate	77.1	350.3	37.63	901.0

4th KINETICS OF DISSOLUTION OF SOLID SUBSTANCES

4th1 Theory

Dissolution of a solid substance is one of the **heterogeneous processes** occurring on the boundary between two phases, which is called the **phase interface**. Obviously one of the phase is solid, so it is the reaction on the solid surface and it can be divided into following steps:

- diffusion of interacting substances to the surface,
- adsorption on the surface,
- reaction on the surface,
- desorption from the surface,
- diffusion of products from the surface.

The total reaction rate of heterogeneous processes is controlled by the rate of the slowest step and in the case of solid/liquid systems the rate determining stage are subprocesses involving diffusion.

The pharmaceutical importance of dissolution of solid substances can be demonstrated on biological accessibility of weakly soluble (or retarded) active compounds in solid peroral formulations. In biological systems, water represents the most frequent liquid environment - solvent. In the process of dissolution of crystalline solid compounds into aqueous solution, the above steps are supplemented with hydration of the surface, and the products of dissolution. Dissolution of the solid substance is controlled by the slowest reaction stage, which is the diffusion of dissolved and hydrated compound from the solid surface. The diffusion transports the dissolved substance across a thin **diffusion layer** δ , where the concentration of dissolved substance continuously decreases from the concentration of **saturated solution** (c_s) at the solid surface to the concentration level (c) in the bulk solution. The **driving force** of diffusion is the spatial concentration gradient in according to First Fick's Law:

$$\frac{dn}{dt} = -D.S. \frac{dc}{dx}$$

Eq. 4th.1,

where dn [mol] is the amount of the dissolved substance within time interval dt [s], D [$m \cdot s^{-1}$] is the **diffusion coefficient**, S [m^2] represents the **total surface** (phase interface) of the dissolved solid substance and finally dc/dx is the mentioned **concentration gradient**. When the mixing is efficient, the diffusion layer is very thin (0.02-0.05 nm) and the concentration gradient may be replaced by a single linear approximation $dc/dx=(c-c_s)/\delta$. For the amount of dissolved substance we can then write $dn=V \cdot dc$, where V is the total volume of the solution and dc is the **concentration increment**. The final shape of the Nernst equation is:

$$\frac{dc}{dt} = \frac{D \cdot S}{V \cdot \delta} (c_s - c)$$

Eq. 4th.2

or $dc/dt=k(c_s-c)$, where k represents the rate constant of dissolution. After separation of variables and integration we obtain the following equation:

$$c = c_s(1 - e^{-kt})$$

Eq. 4th.3

which is formally equivalent to the equation for the first order reaction kinetics.

4th2 Some remarks on chemical kinetics

Chemical kinetics can be defined as a quantitative study on concentration (or pressure) changes with time brought about by chemical reaction. In other words, the chemical kinetics investigates velocities of various chemical reactions. **Reaction rate** is the decrease of the concentration per unit time of one of the reactants. The **rate constant** is a measure of the rate of a given chemical reaction under specified conditions (pressure, temperature). It may be defined in words as the rate of change in concentration of reactant or product with time for a reaction in which all the reactants are at unit concentration. The **order of reaction** is usually a small whole number, but in special cases it may have a fractional value or be zero. It is formally defined as the sum of the powers of the concentration terms that occur in the differential form of the rate law. If the chemical reaction proceeds in a series of sequential stages, then the rate of the reaction is limited by the slowest stage. This stage is referred to as the **rate determining** (controlling) **stage**. **Molecularity** is the number of molecules or ions from which the transition state is formed. The time taken for 50% reaction to occur is called the half life.

4th3 Method

Kinetic measurements are usually performed for determination of reaction rate (or rate constant) or reaction order at a given conditions. Dissolution process of ionic substances can be observed by measuring the conductivity changes with time:

$$G(t) = G_s(1 - e^{-kt})$$

Eq. 4th.4

assuming the surface changes of the dissolved substance are negligible. In the case of less stable organic compounds, precise determination of the conductivity of saturated solution is impossible because of side reactions (e.g. acetylsalicylic acid hydrolyzes to acetic and salicylic acid. Thus the saturated conductivity G_s is handled as unknown quantity and must be determined, too.

The Guggenheim's method of evaluation of the rate constant will be used, because the final concentration is unknown. The essence of the method may be characterized as follows: there are some measurement series constructed within the experiment, where the time shift between the series remains constant. The concentration data are recorded at time "t" and $t+\delta t$ (δt is the appropriate time shift). Using the Guggenheim's method the mentioned kinetic equation for the conductivity dependence may be rewritten as:

$$\ln[G(t + \delta t) - G(t)] = A - kt$$

Eq. 4th.5

where

$$A = \ln[G_s(1 - e^{-k\delta})]$$

Eq. 4th.6

The last equation is used for determination of the unknown saturated conductivity.

The series are not to be taken from the start and the end of the measured process, because the experimental errors are bigger at these points.

4th4 Device and materials

Conductometric cell, commercial conductometer OK-103 (OK-104), electromagnetic stirrer, 400 ml beaker, rinsing bottle, perforated test tube, 4 pcs. of acetylsalicylic acid tablets (max.solubility 2.5 g/l at 15°C), stop-watch.

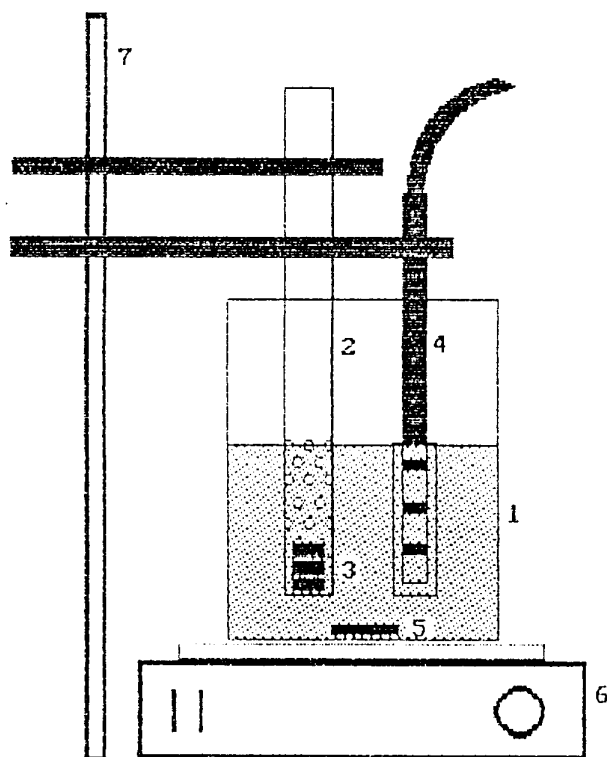


Fig. 4th-1 Apparatus for measurement of tablets dissolution

4th5 Experimental

Place the beaker with 200 ml of redistilled water on the electromagnetic stirrer. Using the laboratory stand fix the perforated test tube and the conductivity cell as it is shown on the Fig. 4th-1. Set the mixing rate on 800 rpm, which is constant for the time of the experiment (Note that no heating is needed). Determine the conductivity of the pure redistilled water (it must be less then $2\mu\text{S}$). Now carefully put the tablets into the test tube and start the stop-watch. Write down the conductivity data every minute and from the 5-th minute every 5 minutes. Repeat the described conductivity determinations for 85 minutes. After finishing the measurements switch off the stirring and conductometer and rinse the conductivity cell with distilled water.

4th6 Processing the results

Plot the graph of function $G=f(t)$ to characterize the overall development of the dissolution in time. Select two series from the measured conductivity data, which differ in reaction times by a constant time shift ($\delta t=40$ min). Then calculate the appropriate quantity: $\ln[G(t+\delta t)-G(t)]$.

The first data set is given by conductivities at reaction time: $t = 5, 10, 15, 20, 25, 30, 35$ min. The second data set is defined likewise: $t+\delta t = 45, 50, 55, 60, 65, 70, 75$.

Using of least squares method determine the parameters for the following linear relationship:

$$\ln[G(t + \delta t) - G(t)] = A - kt$$

Eq. 4th.7

where the slope is negative value of the dissolution rate constant at a given temperature.

The record (protocol) should include the points:

- Theoretical principles of the determination
- Equipment and chemicals
- Working procedure and measurements
- Tables of results, calculations and diagrams

Tab. 4th-1 Table of conductivity dependence on time

Time (t/min)	Conductivity (G(t)/ μ S)
1	14.0
2	24.5
3	48.9
4	81.0
5	101.7
10	150

Tab. 4th-2 The Guggenheim's method of determination of the rate constant

t / min	t+ δt / min	G(t+ δt)-G(t)	$\ln[G(t+\delta t)-G(t)]$
5	45	100.5	4.6101577
10	50	82.5	.
15	55	.	.
20	.	.	.
.	.	.	.

5th DETERMINATION OF ADSORPTION ISOTHERM OF ACETIC ACID ON ACTIVATED CHARCOAL

5th1 Theory

An important property of surfaces is that known as adsorption. This term is used to describe the existence of a higher concentration of any particular substance at the surface of a liquid or solid than is present in the bulk. Molecules can stick to surfaces in two ways.

In **physisorption**, which is a shortening of **physical adsorption**, there is a van der Waals interaction between the surface and the adsorbed molecule. This is a long-range but weak interaction and the amount of energy released when a molecule is physisorbed is of the order of the enthalpy of condensation. Van der Waals adsorption is characterized by relatively low heats of adsorption, namely about 20 kJmol^{-1} . These energies are insufficient to bond breaking, and so in physisorption the molecule retains its identity, although it might be stretched or bent on account of the proximity of the surface.

In **chemisorption**, which is a shortening of **chemical adsorption**, the molecules stick to the surface as the result of the formation of a chemical, and usually a covalent bond. The energy of attachment is very much greater than in physisorption, and typical values are in the region of 200 kJmol^{-1} . A molecule undergoing chemisorption may be torn apart at the demand of the unsatisfied valencies of the surface atoms, and so it may lose its identity. The existence of molecular fragments on the surface as a result of the chemisorption of whole molecules is one of the reasons why surfaces can exhibit catalytic activity.

5th2 Task

Determine the course of adsorption isotherm of acetic acid using activated charcoal.

5th3 Equipment and chemicals

Six 250 ml boiling flask, six 250 ml Erlenmayers's flask, six funnels, stand for funnels, two 50 ml burettes, stand for burettes, titrimetric flask, some pipettes (50, 25, 10, 5 ml), filtering paper, glazed paper for weighing, spoon, rubber stoppers, activated charcoal, solution of acetic acid (0.4 mol/l), solution of NaOH (0.1 mol/l) and phenolphthalein.

5th4 Method

Prepare aqueous solutions of acetic acid into numbered flasks according to the following scheme:

Tab. 5th-1 Pipetting scheme for acetic acid dilution

Solution / ml	Flask number					
	1	2	3	4	5	6
0.4M CH ₃ COOH	105	55	30	15	10	5
Distilled water	0	55	90	105	150	155
Total volume	105	110	120	120	160	160
	Approximate conc. (mol/l)					
	0.400	0.200	0.100	0.050	0.025	0.012

Titrate prepared solutions using 0.1M aqueous solution of NaOH and phenolphthalein to determine their real concentration. Take off the following amounts of solution (V) from each flask for titration:

Tab. 5th-2 Amounts of solution taken for titration

Flask number	1	2	3	4	5	6
V in ml	5	10	20	20	50	50

Calculate the real concentration of above solutions of acetic acid inserting volume (V) from the table Tab. 5th-1 Pipetting scheme for acetic acid dilution Tab. 5th-1 and consumption of NaOH at titrations (n) into equation (Eq. 5th.1):

$$c_{\text{acetic acid}} = \frac{n c_{\text{NaOH}}}{V}$$

Eq. 5th.1

where c_{NaOH} is real concentration of aqueous solution of NaOH. Take 10 ml from the fifth and sixth flask to obtain the same amount of solution in all six flasks (100 ml).

Weigh 2 g of activated charcoal six times using glazed paper and sift it into solution of acetic acid in the flasks. Cork down the flasks and shake approximately 10 minutes. Filter these solution into the clean and dry flasks. The first drops (approximately 10 ml) of filter liquor you must remove to avoid disturbing effect of adsorption of acetic acid on the filtering paper. After ending filtration mix the flask volume and titrate again 5, 10, 20, 20, 50, 50 ml of filter liquor as before adsorption. Calculate the amount of adsorbed acetic acid from the change of its concentration before and after addition of activated charcoal and table the results.

5th5 Processing the results

Calculate the initial concentration of acetic acid (c_0) and the equilibrium concentration (c) after adsorption using the equation (Eq. 5th.1), and then adsorbed amount of acetic acid per 1 g of activated charcoal according to equation:

$$m = \frac{V_r(c_0 - c)}{b}$$

Eq. 5th.2

where V_r is volume of aqueous solution of acetic acid (100 ml) and b means mass of activated charcoal (2 g).

The plot of $1/m$ against $1/c$ should be a straight line of slope $1/A_{\max}$ and intercept $1/(k.A_{\max})$, where k is adsorption coefficient and A_{\max} is adsorbed amount of acetic acid corresponding to complete surface coverage. Evaluate from above straight line A_{\max} and k using the least-squares method.

The record (protocol) should include the points:

- Theoretical principles of the determination
- Equipment and chemicals
- Working procedure and measurements
- Tables of results, calculations and diagrams

6th ELECTROCHEMICAL CELLS AND ELECTRODES

6th1 Principles and the use of electrochemical cells

Electrochemical cell consists in principle of two **electrodes**, represented by metallic electric conductors, dipping into an **electrolyte**, which is an **ionic conductor**. Electrolyte in the cell is usually represented by a liquid aqueous solution of an ionic compound (e.g. salt, acid, alkali), sometimes it is ionic melt or nearly solid ionic substance. Practically used cells may be more complicated, as described below. Electrochemical cells serve various purposes, as a source of electric energy (galvanic cells) or to carry out electrolysis (electrolytic cells). We consider the electrochemical cell primarily as a basic piece of apparatus for investigation of electrolyte solutions, by means of various electrochemical measurements.

Inside the cell, the two metallic electrodes must not touch each other directly, but they are electrically connected by the electrolyte solution. On the boundary between the electrode and the electrolyte, some chemical and physical processes occur, which are connected with the transfer of the electric charge, so that the electrodes become electrically charged. Each electrode has therefore certain **electric potential**, depending on the chemical composition of the electrode and the respective electrolyte.

The electrode with lower electric potential is a negative terminal (-), the electrode with higher potential is a positive terminal (+) of the cell and they are connected to the respective terminal plugs or cable outlets of the considered cell. The difference between the electric potentials of the two electrodes is the **voltage** of the cell. The SI unit we use to measure both the electric potential and the voltage is **volt**, 1 V, its one thousandth is millivolt, $1 \text{ mV} = 10^{-3} \text{ V}$.

When the cell plugs are put in a closed electric circuit, electric current passes through the cell. The passing current is accompanied by a chemical and sometimes also by physical changes on the boundaries between electrodes and electrolyte, the so called **cell reaction** occurs in the cell. The cell reaction is characteristic for each kind of cells.

The cell reactions often involve **oxidation and reduction**, charging and discharging of ions, or adsorption and desorption of ions. The cell reaction may be either spontaneous, then the cell is a source of electricity (galvanic cell) or the cell reaction is non-spontaneous, driven by

external source of electricity. Regardless of the case, the cell reaction changes the composition of the cell. The passing electric current also affect the voltage of the cell. The cell reaction virtually does not occur and the voltage is stable when no current passes through the cell.

Therefore we recognize the **zero-current voltage** of the cell, measured under such circumstances, when no current, or nearly no current, passes through the cell. The zero-current voltage of the cell is also called the **electromotive force** (EMF) or the **cell potential**, it is an important characteristic of each cell. The electrochemical methods based on measurements of the zero-current voltage, that is on the measurements of the cell potentials, are called **potentiometry**.

There are also other electrochemical methodes, like polarography and voltametry, where external source of electric current is used to drive the cell reaction in the measured electrochemical cell. However, in this article we consider only the **potentiometric measurements** with the cells. It means measurements performed on the conditions when no current passes through the cell. With the potentiometric measurements we can directly determine concentrations of certain ions, oxidizing and reducing species in the solutions, or perform various potentiometric titrations. Very useful are the potentiometric **measurements of pH**.

An electrode dipping in the electrolyte solution is also called the **half-cell**. In this sense, the electrochemical cell is regarded as a unit consisting of **two half-cells**. Sometimes, the two electrodes share the same electrolyte so the whole cell consists of one compartment. More often, each electrode is dipping into its own electrolyte solution, then each half-cell is in a separated compartment.

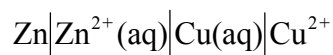
The separation between the two half-cells must prevent free mixing of their electrolyte solutions but, at the same time, it must allowe the **electric contact** between the solutions. Such electric connection between two solutions, which prevents free mixing of the solutions but enables certain migration of ions, is called a **liquid junction**.

In practice, the liquid junction between electrolyte solutions of the two half-cells is conveniently realized by a **porous diafragma** of sintered glas or ceramic between the solutions. If necessary, the solutions of two half-cells may be also electrically connected through a **salt bridge**. The salt bridge is a glass tube, filled by a solution of non-reacting electrolyte, prevented from leaking.

The cell reaction is also regarded as a sum of two processes called **half-reactions**, since one process occurs in one half-cell and the other occurs in the second half-cell. Another name for the half-reaction is the **electrode reaction**, because it is a process which occurs on one electrode.

6th2 Cell diagrams, cell potential and standard potentials

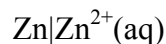
Simple example of the electrochemical cell is the zinc-copper cell (Daniel cell). It consists of a zinc strip dipping in aqueous solution of ZnSO_4 (the first half-cell) and a copper strip dipping in equally concentrated aqueous solution of CuSO_4 (the second half-cell). The cell can be diagrammed as follow:



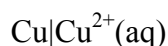
Chem. 6th-A

Only the species important for the cell reaction are written in the diagram. The boundaries between electrode and electrolyte (phase boundaries) or between two electrolytes are marked by a single vertical line, |. The vertical line in the middle of the diagram stands for the liquid junction. If a salt bridge is used, it is marked by a double vertical line.

The cell (Chem. 6th-A) consists of two half-cells, the left-hand side (zinc) half-cell

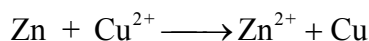


and the right-hand side (copper) half-cell:



In practice, when we say electrode, we very often mean the whole half-cell.

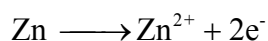
When the cell (Chem. 6th-A) is put in an electric circuit and operates spontaneously, the following cell reaction occurs:



Chem. 6th-B

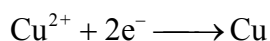
The cell reaction (Chem. 6th-B) is an oxidation-reduction reaction and it may be regarded as a sum of two half-reactions.

In the zinc half-cell the atom of zinc metal is **oxidized** to zinc ion, two electrons are left on the electrode and the ion is dissolved:



Chem. 6th-C

In the copper half-cell, the copper ion takes two electrons from the electrode so the ion is discharged and **reduced** to atom of copper metal and deposited on the copper electrode:



Chem. 6th-D

The whole cell reaction (B) is the sum of the two half-reactions, or electrode reactions (Chem. 6th-C) and (Chem. 6th-D). Due to the half-reaction (Chem. 6th-C) the zinc electrode gains a negative charge, it becomes the negative terminal of the cell. On the other side, due to the half-reaction (Chem. 6th-D) the copper electrode becomes a positive terminal of the cell, it has higher electric potential than the zinc electrode. The electrons released on the zinc electrode by the half-reaction (Chem. 6th-C) pass through the circuit to the copper electrode where they are bound by the half-reaction (Chem. 6th-D).

When precautions are taken that no current is passing through the cell, then no reaction virtually occurs, and the cell is in a state called the electrochemical equilibrium. In this condition, the measured voltage (zero-current voltage, EMF) is the cell potential E . The cell potential is equal to the difference of the electrode potentials:

$$E = E_{\text{right}} - E_{\text{left}}$$

Eq. 6th.1

By an accepted agreement (convention), we always subtract the potential of the left-hand side electrode (E_{left}) from the potential of the right-hand side electrode (E_{right}) in the cell diagram. After this convention, the cell potential E is a positive number, when $E_{\text{right}} > E_{\text{left}}$, that is, when the electrode written on right-hand side of the cell diagram is a positive terminal of the cell and the left-hand side electrode is a negative terminal. If possible, we write the cell diagrams by this way.

After Eq. 6th.1, we can write for the potential E of the cell (Chem. 6th-B):

$$E = E_{\text{Cu}} - E_{\text{Zn}}$$

Eq. 6th.2

The cell potential depends on the nature of the cell and on its thermodynamic state - the purity of the metal electrodes, electrolyte concentrations, temperature etc. Therefore a **standard**

state is defined for each cell or half-cell. The cell (Chem. 6th-B) is in the standard state when the respective electrodes are made of pure zinc and copper, the concentration (precisely activity) of the respective solutions of ZnSO_4 and CuSO_4 is 1 M (1 mol dm^{-3}), and the standard temperature is 25 °C. The **standard cell potential** E° is again the difference of the respective standard electrode potentials:

$$E = E_{\text{Cu}}^\circ - E_{\text{Zn}}^\circ$$

Eq. 6th.3

The standard potential of the Daniel cell is $E^\circ = 1.1 \text{ V}$.

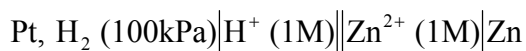
Every electrode (half-cell) is characterized by the standard electrode potential and every cell by the standard cell potential. The reference cell used as a voltage standard for potentiometric measurements is the **Weston cell**, its accurately known cell potential is $E_{\text{W}} = 1.0181 \text{ V}$ at 25 °C.

6th3 Electrode potentials and the Nernst equation

It is important to stress that the electrochemical measurements are always done with whole cell, not with a single electrode (half-cell). The real electric potential between an electrode and the solution cannot be measured, but the potential difference between two electrodes is readily measured as the cell potential. Therefore the sensing electrode is always combined with a suitable reference electrode into a cell and the cell potential (electromotive force) is measured.

In spite of it, we use so called **electrode potentials** based on another accepted agreement. After this agreement, the potential of a chosen electrode is assigned at any temperature as exactly zero volt, 0 V (by a similar way as the sea level is established zero elevation). The chosen zero potential reference electrode is the **standard hydrogen electrode**. The hydrogen electrode is a gas electrode, indeed it is a half-cell. It is set up by a platinum foil covered with very finely divided platinum, immersed in a solution and bubbled around by the hydrogen gas. In the standard hydrogen electrode, the hydrogen pressure is 101.3 kPa (normal barometric pressure) and strong acid (e.g. HCl) is dissolved in the solution, so that the concentration (more accurately activity) of the hydrogen ions H^+ is 1 M (1 mol dm^{-3}).

When, for example, we wish to determine the potential of the standard zinc electrode, then a salt bridge is used to combine the standard hydrogen electrode (left-hand side) with the examined electrode (right-hand side) and the following cell is set up:



Chem. 6th-E

The potential E° of the cell (Chem. 6th-E) can be readily measured and, after eq (Eq. 6th.1), it is

$$E = E_{\text{Zn}}^\circ - E_{\text{H}}^\circ$$

Eq. 6th.4

where E_{Zn}° and E_{H}° are the respective potentials of the standard zinc electrode and the standard hydrogen electrode. Since by the accepted agreement $E_{\text{H}}^\circ = 0$, it follows $E_{\text{Zn}}^\circ = E^\circ$, the potential of the standard zinc electrode is identified with the measured potential of the cell (Chem. 6th-E).

The standard hydrogen electrode is rarely used in practice, but the electrode potentials (and redox potentials) determined by the described procedure are collected in various tables. They are in fact cell potentials (EMF), determined with cells analogous to the cell (Chem. 6th-E).

Electrode potentials are often expressed and calculated by the **Nernst equation**, derived from thermodynamics of the electrochemical cell. If a metal electrode (M) is immersed in the solution of the salt of its ions (M^{z+}), the electrode reaction (half-reaction) is:



Chem. 6th-F

The potential E_{M} of this metal electrode is given by the Nernst equation in the form:

$$E_{\text{M}} = E_{\text{M}}^\circ + 2.303 \frac{RT}{zF} \log a_{\text{M}^{z+}}$$

Eq. 6th.5

where

E_{M}° is the standard potential of the electrode,

$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ the gas constant, T (K) the temperature,

$F = 96485 \text{ C mol}^{-1}$ the Faraday constant, z is a charge number of the ion M^{z+} and a number of electrons in the electrode reaction (Chem. 6th-F),

$a_{M^{z+}}$ is the **activity of the ion M^{z+}** , in the diluted solutions the activity can be replaced by the concentration of the ion, denoted as $[M^{z+}]$.

When the potential of an electrode is given by Eq. 6th.5, we say that the electrode is reversible with respect to the M^{z+} ion, or that the electrode gives Nernst response to the M^{z+} ion. The Nernst equation is often used in more simple form, obtained after inserting numerical values R , T and F . For the potential of the electrode with Nernst response to the cation M^+ (charge number $z = 1$) at 25°C (298.15 K) the simplified Nernst equation is:

$$E_M = E_M^0 + 0.0592 \log a_{M^+} \text{ (Volt)}$$

Eq. 6th.6

At 20°C , the coefficient in the equation is 0.0582 V .

There are also electrodes with Nernst response to anions. The Nernst equation for the potential of the electrode with response to the anion X^- (charge number $z = -1$) at 25°C holds in the form:

$$E_X = E_X^0 - 0.0592 \log a_{X^-} \text{ (Volt)}$$

Eq. 6th.7

Symbols a_{M^+} and a_{X^-} are again activities of the respective ions M^+ and X^- , in diluted solutions they can be replaced by the respective concentrations $[M^+]$ and $[X^-]$.

The response for metal cations is exhibited by corresponding metal electrodes and a number of ion-selective membrane electrodes. The hydrogen electrode and glass electrode (glass membrane electrode) give response to the H^+ cation, so they are used for the potentiometric pH measurements. The calomel electrode and the silver chloride electrode give response to the chloride anion (Cl^-) and there are also numerous ion-selective membrane electrodes responding to various anions.

7th POTENTIOMETRIC MEASUREMENT OF PH USING HYDROGEN ELECTRODE

7th1 Theory - pH of aqueous solutions

Aqueous solutions always contain certain concentration of hydrogen ions and this property is conveniently expressed in the form of pH. Value of pH is the negative decadic logarithm of the **activity of hydrogen ions** in the solution:

$$\text{pH} = -\log a_{\text{H}^+}$$

Eq. 7th.1

Activity a_{H^+} of the hydrogen ions in aqueous solution is regarded as the product of their concentration $[\text{H}^+]$ and the mean activity coefficient γ_{\pm} :

$$a_{\text{H}^+} = [\text{H}^+] \gamma_{\pm}$$

Eq. 7th.2

In sufficiently diluted solution the activity coefficient is however close to unity ($\gamma_{\pm} \sim 1$) and when it is neglected, pH can be written as the negative decadic logarithm of the concentration of the hydrogen ions:

$$\text{pH} = -\log [\text{H}^+]$$

Eq. 7th.3

In mathematical formulae we write hydrogen ions as H^+ for brevity. But they are reactive species, in liquid water and aqueous solutions they are strongly hydrated and should be written as H_3O^+ ($\text{H}^+\cdot\text{H}_2\text{O}$). In spite of it we sometimes call them free hydrogen ions, to distinguish them from the undissociated protons of weak acids.

Larger concentrations of hydrogen ions are produced by the dissociation of the dissolved acids. In a small extent, hydrogen ions are also produced together with hydroxide ions by the self-ionization (autoprotolysis) of water molecules, $2\text{H}_2\text{O} \longrightarrow \text{H}_3\text{O}^+ + \text{OH}^-$. For that reason the hydrogen ions are always present in the aqueous solutions and the product of the

concentrations of H^+ (i.e. H_3O^+) and OH^- ions in water and diluted solutions is constant and it is called the **ionic product** of water K_w :

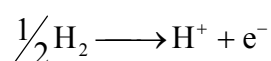
$$K_w = [\text{H}^+][\text{OH}^-] = 1 \times 10^{-14}, \text{ or } \text{p}K_w = -\log K_w = 14 \text{ (25 } ^\circ\text{C)}$$

In pure water and **neutral solutions**, the concentrations of the hydrogen and hydroxide ions are thus the same, $[\text{H}^+] = [\text{OH}^-] = 1 \times 10^{-7} \text{ mol dm}^{-3}$ and **pH = 7**. In the **acidic solutions** (solutions of acids), the concentration of hydrogen ions is bigger and they have **pH < 7**. On the other hand, in the **alkaline solutions** (solutions of bases), the concentration of hydrogen ions is smaller and they have **pH > 7**.

7th2 Theory of hydrogen electrode

Hydrogen electrode (gas electrode) used for the potentiometric pH measurements is a half-cell set consisting of a platinum foil covered with very finely divided platinum (so called platinized platinum), immersed in the measured solution and bubbled around by the hydrogen gas. In principle the electrode is the same like the above mentioned standard hydrogen electrode, the hydrogen gas is also bubbled under the normal barometric pressure, but the measured solutions are of various kinds.

The hydrogen gas is adsorbed on the surface of the platinum foil and due to the catalytic effect of the finely divided platinum the following electrode reaction (half-reaction) occurs on the boundary between the platinum and the solution:



Chem. 7th-A

With respect to the stated electrode reaction, the potential E_{H} of the hydrogen electrode is given by the Nernst equation Eq. 6th.5 in the following form (25 °C):

$$E_{\text{H}} = E_{\text{H}}^0 + 0.0592 \log a_{\text{H}^+} \text{ (Volt)}$$

Eq. 7th.4

The standard potential E_{H}^0 in Eq. 6th.6 is identical with the potential of the standard hydrogen electrode, which is assigned as zero, see 15.3. Inserting $E_{\text{H}}^0 = 0 \text{ V}$ and $\log a_{\text{H}^+} = -\text{pH}$ into Eq. 6th.6, a simple relationship between the hydrogen electrode potential and the pH of the measured solution is obtained:

$$E_H = - 0.0592 \log \text{pH}$$

Eq. 7th.5

However, the potentiometric measurements cannot be done with a single electrode (half-cell) but an **electrochemical cell** with two electrodes is necessary. Therefore we combine the sensing **hydrogen electrode** with a suitable **reference electrode**, to set up a complete cell and to measure the cell potential. We use a saturated calomel electrode as the reference and by this way the following complete cell is set up:

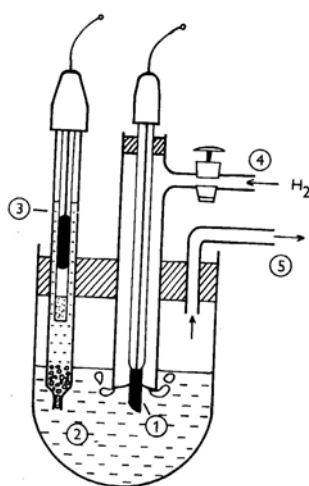


Fig. 7th-1 Hydrogen electrode

In the diagrammed cell, the hydrogen electrode (Pt) is the negative terminal (-) and the calomel electrode (Hg) the positive terminal (+) of the cell, since the potential E_{cal} of the calomel electrode is higher than the potential E_H of the hydrogen electrode. After the basic Eq. 6th.1, the measured **cell potential** E (electromotive force) is the potential difference between the right hand side (E_{cal}) electrode and the left hand side (E_H) electrode:

$$E = E_{\text{cal}} - E_H$$

Eq. 7th.6

Inserting for E_H from Eq. 7th.5 we get a simple formula for calculation of the pH of the solution from the measured cell potential E (V):

$$\text{pH} = \frac{E - E_{\text{cal}}}{0.0592}$$

Eq. 7th.7

The potential gradient 0.0592 V (see 15.3) is valid at 25 °C and at this temperature the potential of the saturated calomel electrode $E_{\text{cal}} = 0.241$ V. At 20 °C the gradient is 0.0582 V and $E_{\text{cal}} = 0.244$ V, at another temperature the proportional values are used.

The hydrogen electrode is regarded as a primary standard for the pH measurements, other methods are in fact based on the data measured by the hydrogen electrode. It can measure the whole range of the pH scale, from pH 0 to 14. With special arrangement the hydrogen electrode can measure the hydrogen ion activity even in a broader scale, in the solutions of concentrated strong acids as well as strong alkalies, where other methods fail. The electric resistance of the cell with the hydrogen and calomel electrodes is not too high, so the cell potential (EMF) can be easily measured, also by older compensation potentiometers.

On the other hand, there are some severe limitations of the pH measurements with the hydrogen electrode. The hydrogen catalyzed by the platinum is highly reactive, it can react with a long list of the oxidizing agents, which must not be present in the measured solutions: peroxides, salts of heavy metals, nitrates, reducible organic compounds, H_2S and sulphides, cyanides, ammonia etc. The tedious maintenance and operation of the hydrogen electrode are also impractical and unsuitable for routine use.

The main purpose of the hydrogen electrode is the accurate measurement of the primary pH standards, the buffer solutions by which other pH electrodes, such as glass electrodes, are standardized (calibrated). The more practical and routine methods of pH measurements are thus in fact based on the data measured with the hydrogen electrode.

7th3 Device and materials

The potentiometer (pH meter) for the measurements of the cell potential (electromotive force), the platinized platinum electrode, the electrolytic (pure) hydrogen gas in the steel cylinder with outlet valve and manometers, tubings, saturated calomel electrode, thermometer, measuring cell with water closure. Measured solutions of acids, alkalies, buffers.

The platinized platinum electrode (hydrogen electrode) must always be kept immersed in distilled water. When not used, it must never get dry. The calomel electrode is to be kept immersed in the saturated KCl solution.

7th4 Experimental

Manipulations with the hydrogen gas valve may be done by the instructor only, or under his (her) supervision!

Prepare the electrodes, pour the sample of the measured solution into the measuring cell (vessel) and close it. About half of the platinum foil (or platinum wire) and the liquid junction (tip) of the calomel electrode must be immersed in the measured solution. Connect the electrodes with the potentiometer (pH meter), remember the hydrogen electrode is the negative terminal (-) and the calomel electrode the positive terminal (+) of the set up electrochemical cell.

When the whole set up is checked, the instructor will help you to start the hydrogen gas to bubble around the foil of the platinum electrode. After 10 - 15 minutes of bubbling the cell potential E (electromotive force) is measured and the measurement is repeated in 2 - 3 minutes till the constant value of E (within 0.5 mV). Before starting measurement of another solution and after the measurements, the cell and the electrodes must be thoroughly cleaned with distilled water.

7th5 Processing the results

From the measured cell potentials E (V), the respective pH value of the measured solutions are calculated after Eq. 7th.7. The number of decimal places in the resulting pH values must correspond to the accuracy of the measurement. After Eq. 7th.7, approximately 59 mV of the measured cell potential (EMF) corresponds to 1 pH unit and if the accuracy of the measurement is about 0.5 mV, the accuracy of pH is about 0.01.

The record (protocol) should include the points:

- Theory of pH and its measurement by the hydrogen electrode.
- Working procedure
- Calculations and the table of results:

Tab. 7th-1 Table of measured and calculated results

Solution	$t(^{\circ}\text{C})$	$E(\text{V})$	$E_{\text{cal}}(\text{V})$	pH

8th POTENTIOMETRIC MEASUREMENT OF PH USING GLASS ELECTRODE

8th1 Theory

Potentiometric measurement of pH of various solutions by the **glass electrode** is a practical and often used method of the pH determination. The glass electrode is one of the numerous **membrane electrodes** or ion-selective electrodes, they are sophisticated electrode systems based on the existence of the **membrane potential** between the solution and a suitable membrane. The membrane potential is due to the selective ion-exchange, that is adsorption and desorption of a certain kind of ions on the membrane surface. Due to the selective ion-exchange the membrane exhibits potential response in the presence of certain ion and the membrane potential can also be expressed by the Nernst equation.

Membrane of the glass pH electrode is a thin glass layer, made of a special sodium glass, which exhibits selective potential response to the hydrogen ions in the solution. The membrane is shaped as a small **glass bulb** and inside the bulb is internal solution with the **internal reference electrode**. The cable outlet (terminal) of the glass electrode is connected just to the internal reference electrode. In the most cases, it is the silver-silver chloride electrode, indeed a silver wire covered by AgCl, and dipped in the internal solution of diluted aqueous HCl. The potential of the sealed internal system of the glass electrode is relatively constant but when the glass bulb is dipped in the various measured solutions, potential of the whole glass electrode changes, according to the activity of hydrogen ions in the measured solution.

The sensing glass electrode must be combined with an **external reference electrode** to set up an electrochemical cell. The external reference electrode may be also the silver-silver chloride electrode or the calomel electrode. Modern **combination glass electrodes** have the external reference electrode housed together with the glass electrode in one body (shaft), and there is a one co-axial (dual) outlet cable from the two electrodes. In the case of the combination electrode, the liquid junction of the external reference electrode is placed just above the glass bulb of the glass electrode (small greyish spot). Both the glass bulb and the liquid junction must be dipped in the measured solution.

The complete electrochemical cell necessary for measurements of pH using glass electrode is thus represented by the following diagram:



The glass electrode is written on the left-hand side of the diagram (to the left from the measured solution), the external reference electrode is on the right-hand side.

Potential E_g of the **glass electrode** dipped in the measured solution can be expressed by a modified Nernst equation, at 25 °C it is:

$$E_g = E_g^* + 0.0592 \log a_{\text{H}^+}, \text{ (Volt)}$$

Eq. 8th.1

a_{H^+} is the activity of the hydrogen ions (H^+) in the measured solution,

E_g^* is here a sum of several potential contributions, it includes the potential of the internal Ag|AgCl electrode and a so called **asymmetrical potential** of the glass membrane.

The measured property is the **cell potential** E , that is the EMF of the diagrammed cell with the glass electrode. After Eq. 6th.1, it is the difference of the potential E_{ref} of the external reference electrode (right) and the potential E_g of the glass electrode (left):

$$E = E_{\text{ref}} - E_g$$

Eq. 8th.2

In Eq. 8th.1, the activity of the hydrogen ions can be replaced by $\text{pH} = -\log a_{\text{H}^+}$, and inserting into Eq. 8th.2, we receive the relationship between the cell potential and pH of the measured solution:

$$E = E_{\text{ref}} - E_g^* + 0.0592 \text{ pH}$$

Eq. 8th.3

One of the disadvantages of the glass electrode is the potential E_g^* is not known beforehand and only relatively constant. As the glass electrode is ageing, it may change somewhat, mainly due to the time variations of the asymmetrical potential of the glass membrane. Therefore the glass electrode must be **repeatedly standardized** (calibrated) by the standard buffer solutions with known value of pH.

At the standardization procedure the electrodes are dipped in the standard buffer solution with the known pH_{st} and the corresponding cell potential (EMF) E_{st} is measured. The

standard solution is then replaced by the measured solution with unknown pH and here the cell potential is E . After inserting into Eq. 8th.3, the operational expression for the unknown pH of the measured solutions is obtained (25 °C):

$$\text{pH} = \text{pH}_{\text{st}} + \frac{E - E_{\text{st}}}{0.0592}$$

Eq. 8th.4

The calculation after Eq. 8th.4 is done by the used pH-meter (potentiometer) measuring the cell potential in the course of the standardization procedure and the instrument shows the resulting pH value of the measured solution.

For high quality pH measurements, the standardization by two (or more) standard buffers is recommended, one buffer with lower pH and one with higher pH than the expected measured value are required. The **accuracy** of the measured pH always depends on the accuracy of the standardization of the glass electrode and on the quality of the instrumentation, for the high quality measurements it is about 0.01 pH unit.

The **potential gradient** $\Delta E/\Delta \text{pH}$ of the properly operating glass electrode follows from the Nernst equation, it is therefore the same as with other pH sensing electrodes. After Eq. 8th.3 and Eq. 8th.4, $\Delta E/\Delta \text{pH} = 0.0592 \text{ V}$ (25 °C), the potential change $\Delta E = 0.0592 \text{ V}$ (59.2 mV) thus corresponds to the pH change $\Delta \text{pH} = 1$, at 20 °C the gradient is 0.0582 V. For accurate measurements, temperature of the solutions should be measured and the pH-meter adjusted, more advanced instruments are equipped with automatic temperature measurement and adjustment. The gradient can be also checked by the standardization procedure with two or more buffers.

Another disadvantage of the glass electrodes is a very high electric resistance of the glass membrane, about 10^8 W with electrodes of the recent production. This disadvantage is easily overcome by the electronic pH meters (potentiometers), they are in principle high-sensitive volt meters, some of them are small and easily portable. Without the electronic instrumentation the measurements of pH by the glass electrode are not possible.

The common types of glass electrodes are used for practical measurements of aqueous solutions in the broad range of pH 1 - 12, in too acidic and too alkaline solutions the measurements of pH may become erroneous. For the extreme pH ranges, as well as for some non-aqueous solutions, special glass electrodes are constructed. The main advantage is the versatility of the glass electrode and its insensitivity to the oxidation and reduction agents, like

salts of heavy metals etc., thus they do not interfere with the pH measurements by the glass electrode. However the electrode can be disabled by the glass damaging agents (strong alkalies, fluorides, HF) and fouling substances like fats and, of course, the electrode is **very fragile**. Because of the necessity of the standardization by a solution with known pH, the glass electrode is not a primary standard.

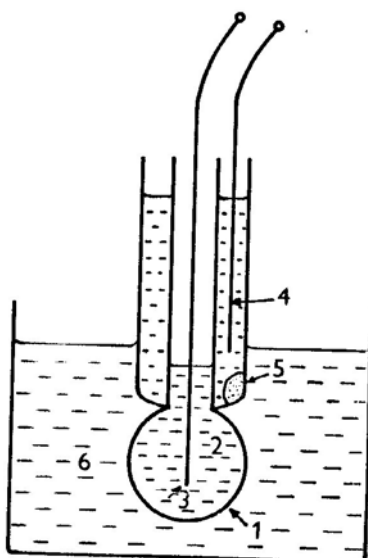


Fig. 8th-1 Combination glass electrode

8th2 Device and materials

pH-meter with combination glass electrode, measured solutions, rinsing bottle. If the electrode has to be standardized, the standard aqueous buffer solutions are necessary, eg.:

Potassium hydrogenphthalate 0.05 mol dm^{-3} , pH = 4.00

Disodium tetraborate 0.01 mol dm^{-3} , pH = 9.18 (25 °C)

8th3 Experimental

The pH measurements using the glass electrode is quite simple but the technical details depend on the kind of the used pH-meter. Therefore follow the advice of the instructor. The fragile glass electrode must be handled with care, it should be rinsed carefully before and after the use and dipped in distilled water when not used.

a) Standardization - when the electrode was not already standardized. Similar procedure as measurement but the standard buffer solution is used, instead of the measured solution.

b) Measurement. Pour the measured solution in the clean beaker, dip carefully the bulb of the combination glass electrode in the solution, the liquid junction of the external reference electrode (a greyish spot above the bulb) must be also just submerged. Read the measured pH after the instructions. Clean the electrode and the beaker after each measurement.

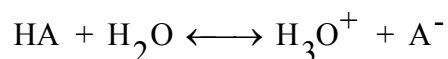
The record (protocol) should include the points:

- Theory of the measurement of pH the glass electrode.
- Working procedure and the table of results.

9th POTENTIOMETRIC DETERMINATION OF THE DISSOCIATION CONSTANT OF WEEK ACID

9th1 Theory

Dissociation of a week acid represents one of the proton exchange reactions, they are also called the acid-base reactions. The Bronsted-Lowry classification defines an acid as a proton donor (protogenic substance) and a base as a proton acceptor (protofilic substance). The acid HA generates the following equilibria in the water:



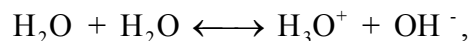
Chem. 9th-A

$$K_a = \frac{a(\text{H}^+) a(\text{A}^-)}{a(\text{HA})}$$

Eq. 9th.1

We have assumed that the activity of the water is constant and have absorbed it into the definition of the acid dissociation constant K_a . The species A^- (anions of the week acid) acts as a proton acceptor in the equilibrium. Therefore it is a base according to the Bronsted-Lowry definition, and it is called the conjugate base of the acid HA. The hydrated hydrogen ions H_3O^+ are written as H^+ in mathematical formulae, for brevity.

Water can play the role of both acid and base. Therefore even in pure water the autoprotolysis equilibrium occurs:



Chem. 9th-B

with the equilibrium constant

$$K_w = a(\text{H}^+) a(\text{OH}^-) ,$$

Eq. 9th.2

in which both water activities have been absorbed into the K_w . At 25°C, $K_w=1.008 \times 10^{-14}$, and this very small value indicates that only very few water molecules are dissociated. Both in pure water and in the diluted aqueous solutions the activities (concentrations) of H_3O^+ and OH^- ions are mutually interdependent by the equation for K_w .

The strength of an acid is measured by its dissociation constant. Strong acids are strong proton donors, and then the K_a is then large. Weak acids have low values of K_a because the proton equilibrium lies in favour of HA (at room temperature acetic acid has $K_a=1.8 \times 10^{-5}$).

The concentration of protons plays an important role in many applications of chemistry and it can vary over many orders of magnitude. The pH scale is defined as:

$$pH = -\log a(H^+),$$

Eq. 9th.3

and it is a convenient measure of proton activity. In a similar way, the value of $pK_a=-\log K_a$ is usually introduced. Transformation of the definition equation of the dissociation constant of the weak acid HA gives:

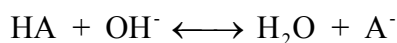
$$pK_a = pH + \log \frac{[HA]}{[A^-]}$$

Eq. 9th.4

where the pK_a value is alternative measure of the acid strength (acids with $pK_a > 2$ are labelled as weak acids) - terms in the brackets represent the equilibrium concentrations.

The measurement of the pH of a solution is the key to the determination of the strengths of acids and bases. The neutralization plot of weak acid shows the dependence pH of the solution on the percentage of the neutralized acid. The pK_a can be estimated from the plot at $p=50\%$ (halfway of neutralization), which corresponds to equal concentrations $[HA]=[A^-]$ and so at this point it holds $pH=pK_a$.

Consider the neutralization reaction of weak acid HA by a strong hydroxide MeOH (e.g. KOH, NaOH, LiOH ...). The latter is a strong electrolyte, completely dissociated into the Me^+ and OH^- ions in diluted aqueous solutions. The OH^- anions are regarded as a strong base and they react with the acid HA:



Chem. 9th-C

Therefore we can write the following mass balance equations for each step of the titration from 10% to 90% of neutralization between the initial point and the end point:

$$[\text{HA}] = c(\text{HA}) - c(\text{MeOH})$$

Eq. 9th.5

$$[\text{A}^-] = c(\text{MeOH})$$

Eq. 9th.6

where $c(x)$ denotes the analytical concentration of the component x (acid and the hydroxide).

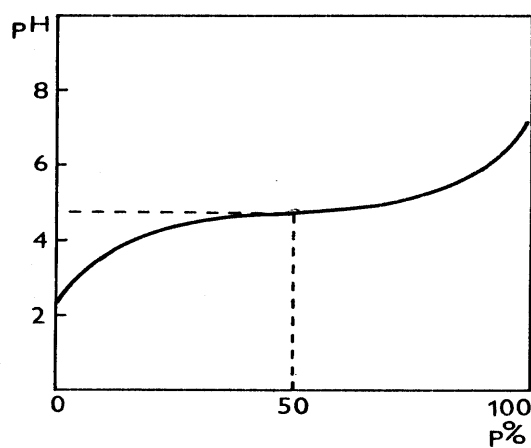


Fig. 9th-1 Neutralization plot of weak acid

9th2 Equipment and chemicals

precision pH-meter, combination glass electrode (or glass and calomel reference electrodes), standard buffer solutions, 10 ml and 20 ml pipette, 9 graduated flasks (50 ml), 2 beakers, factorized solutions of CH_3COOH (0.1M), NaOH (0.1M), NaCl (0.2M)

9th3 Task

Determination of the dissociation constant of acetic acid and statistical comparison of the experimental and table values. The procedure is based on the pH measurement of the set of prepared acetic acid solutions partially neutralized with NaOH at constant ionic strength.

9th4 Preparation of solutions

Pipette 20 ml of 0.1 M CH_3COOH to the clean and labelled 50 ml flasks. Add solution of 0.1 M NaOH in following amounts:

2ml (No.1), 4 ml (No.2) ..18 ml (No.9) and 0.2 M solution of NaCl 12 ml (No.1), 11.5 ml (No.2) ..8 ml (No.9). Complete the samples with water to the total volume of 50 ml. Shake the flasks to homogenize the solutions.

Tab. 9th-1 Pipetting scheme of the sample solutions

Sample	1	2	3	4	5	6	7	8	9
Solution	Pipetted volume of solutions in ml								
CH_3COOH	20	20	20	20	20	20	20	20	20
NaOH	2	4	6	8	10	12	14	16	18
NaCl	12.0	11.5	11.0	10.5	10.0	9.5	9.0	8.5	8.0
H_2O	16	14.5	13.0	11.5	10.0	8.5	7	5.5	4
Total volume	50 ml								

9th5 Potentiometric determination of pH

Connect the electrode(s) to the precision pH-meter (combination electrode should be connected to the G-terminal; in case of using the glass electrode-calomel electrode system connect the glass electrode to the G-terminal and the other one to the R-terminal. Calibrate the electrode using the standard solution if is it necessary. Carefully clean and dry the electrode(s). Dipp it into the measured sample. Wait 2-3 minutes and record the displayed pH. Repeat the outlined procedure for each sample (1-9).

9th6 Processing of the measured data

Calculate the analytical concentration of acetic acid (it should be equal in each samples) and the analytical concentration of NaOH in the samples using equation:

$$c(x) = \frac{v(x) \cdot c(x)_{\text{prec}}}{V_{\text{total}}}$$

Eq. 9th.7

where $c_{\text{prec}}(x)$ is the precise concentration of the stock solutions of CH_3COOH or NaOH (given as a following product: $c_{\text{nominal}} \cdot \text{factor}$), $v(x)$ is the pipetted volume and V_{total} is the total volume of the sample (50 ml).

Determine the equilibrium concentrations of the acid and the base ($[\text{CH}_3\text{COOH}]$, $[\text{CH}_3\text{COO}^-]$) using the following equations:

$$[\text{CH}_3\text{COOH}] = c(\text{CH}_3\text{COOH}) - c(\text{NaOH})$$

Eq. 9th.8

$$[\text{CH}_3\text{COO}^-] = c(\text{NaOH})$$

Eq. 9th.9

$$c(\text{CH}_3\text{COOH}) > c(\text{NaOH})$$

Eq. 9th.10

The final equation of acetic acid's pK_a is given:

$$\text{pK}_a = \text{pH} + \log \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$$

Eq. 9th.11

Calculate the pK_a for each sample and from the K_a s determine the mean $\langle \text{K}_a \rangle$. Using the mean $\langle \text{K}_a \rangle$ recalculate the mean $\langle \text{pK}_a \rangle$ as following:

$$\langle \text{K}_a \rangle = \frac{\sum_i^N 10^{-\text{pK}_a^{(i)}}}{N}$$

Eq. 9th.12

If N is the number of the samples and $\text{K}_a^{(i)}$ defines the i -th dissociation constant then finally we get:

$$\langle \text{pK}_a \rangle = -\log \langle \text{K}_a \rangle$$

Eq. 9th.13

Read the table value of the acetic acid's pK_a (for the nearest temperature) and calculate the relative error of your measurement.

$$\delta (\%) = 100\% \frac{|\langle \text{pK}_a \rangle - \text{pK}_a^{\text{TABLE}}|}{\text{pK}_a^{\text{TABLE}}}$$

Eq. 9th.14

Plot the neutralization diagram (pH versus percentual amount of the neutralized acid - p). Read the pH function value for p=50%.

$$p = 100\% \frac{c(\text{NaOH})}{c(\text{CH}_3\text{COOH})}$$

Eq. 9th.15

The protocol should include the points:

- Definition of the dissociation constant and related terms
- Experimental procedure, calculations
- Tables of the results, neutralization diagram
- Statistics of the results

Tab. 9th-2 Calculated and measured quantities

No.	c(NaOH) mol.dm ⁻³	c(CH ₃ COOH) mol.dm ⁻³	log([HA]/[A ⁻])	p %	pH	pK _a	K _a
1.							

10th CHECKING THE FUNCTION OF THE BROMIDE ION-SELECTIVE ELECTRODE

10th1 Theory - bromide ISE

The bromide ion-selective electrode (bromide ISE) is a **membrane** electrode exhibiting the **potential response** to bromide anions (Br^-) in the aqueous solutions. It is used as the sensing electrode for potentiometric titrations of various bromides or for the direct potentiometric estimation of the concentration of the free bromide anions in the solution.

The construction of the **bromide ISE** is analogous to the glass electrode (see 8th) and other membrane ion-selective electrodes. There are internal reference electrode and internal solution in the electrode body, and the ion-sensitive membrane in the bottom of the ISE. When the ISE is in operation, the membrane is dipped in the measured solution. We use the bromide ISE with the **solid membrane**, it is a thin pressed plastic disc with the admixture of the insoluble salt AgBr. The internal reference is silver-silver bromide electrode dipped in the internal solution of bromide ions (e.g. KBr). The **diagram** of the used bromide ISE, including the measured solution, is following:



The sensing bromide ISE must be again combined with a suitable external reference electrode, usually with a saturated calomel electrode, to complete an electrochemical cell for measurements of the **cell potential** (EMF). This time we write the bromide ISE on the right hand-side and the external reference electrode (REF) on the left-hand side of the abbreviated **cell diagram**:



Chem. 10th-A

After the accepted convention (see Eq. 6th.1), the cell potential E is here equal to the difference between the potential E_{Br} of the bromide ISE (to the right) and the potential E_{ref} of the reference electrode REF (to the left):

$$E = E_{\text{Br}}^* - E_{\text{ref}}$$

Eq. 10th.1

With respect to the cell diagram (Chem. 10th-A), the measured cell potential E is taken as a **positive** number when the bromide ISE is the positive terminal (+) of the measured cell (when $E_{\text{Br}} > E_{\text{ref}}$), and when the bromide ISE is the negative terminal (-) of the cell (when $E_{\text{Br}} < E_{\text{ref}}$), then the measured cell potential E is taken as a **negative** number.

The **potential** E_{Br} of the bromide ISE can be derived from the Nernst equation (see Eq. 6th.3Eq. 6th.5). The charge number of the Br^- anions $z = -1$, so that at 25 °C the expression for E_{Br} is analogous to Eq. 6th.7:

$$E_{\text{Br}} = E_{\text{Br}}^* - 0.0592 \log a_{\text{Br}^-} \text{ (Volt)}$$

Eq. 10th.2

E_{Br}^* is a certain constant potential and a_{Br^-} is the **activity** of the bromide anions in the measured solution. Inserting for E_{Br} in we receive the operational relationship for the cell potential E of the cell (Chem. 10th-A) with bromide ISE

$$E = E^* - 0.0592 \log a_{\text{Br}^-} \text{ (Volt)}$$

Eq. 10th.3

where $E^* = E_{\text{Br}}^* - E_{\text{ref}}$.

In analogy with pH, value of $\text{pX} = -\log a_{\text{X}}$ is conveniently used for any ion X, when working in potentiometry with ion-selective electrodes. For bromide anions Br^- it is:

$$\text{pBr} = -\log a_{\text{Br}^-}$$

Eq. 10th.4

With this symbolics, the Eq. 10th.2 for the potential of the cell (Chem. 10th-A) with bromide ISE can be rewritten as:

$$E = E^* + 0.0592 \text{pBr} \text{ (Volt)}$$

Eq. 10th.5

The potential E^* is a characteristic quantity for the cell (Chem. 10th-A) or for a similar cell with ISE. It is relatively constant and, if necessary, it must be found (or excluded from calculations) by means of standardization, in a similar way like with the glass electrode.

10th2 Activity and activity coefficient of a strong electrolyte

Potassium bromide KBr is a **strong electrolyte**, in the diluted aqueous solutions it is practically completely dissociated into the cations K^+ and anions Br^- . Due to the mutual interactions of the ions, the solutions of electrolytes behave non-ideally. As a consequence, activities instead of concentrations has to be inserted in the thermodynamic equations, like the Nernst equation, for accurate calculations of various properties. The **thermodynamic activity** (a_i) of a certain species (i) is in general a product of the concentration (c_i) and the activity coefficient (γ_i), $a_i = c_i\gamma_i$.

For solutions of electrolytes we use so called **mean activities** and **mean activity coefficients**, which are found by experimental measurements or by theoretical calculations. The mean activity coefficient γ_{\pm} of an electrolyte is a geometric mean of the activity coefficients of the respective cations and anions. It is supposed that in the diluted solutions of such electrolytes like KBr, activities of cations and anions are practically equal.

The activity a_{Br^-} of bromide ions can be calculated from their concentration (written as c_{Br^-} or $[Br^-]$) and the corresponding mean activity coefficient

$$a_{Br^-} = c_{Br^-} \gamma_{\pm}, \text{ or it can be written as } a_{Br^-} = [Br^-] \gamma_{\pm}.$$

In the solutions of KBr, which is a well dissociated **strong electrolyte**, the concentration of bromide anions is practically equal to the concentration of KBr, $[Br^-] = c_{KBr}$. The activity a_{Br^-} of the bromide anions can be therefore calculated as follow:

$$a_{Br^-} = c_{KBr} \gamma_{\pm}$$

Eq. 10th.6

The necessary mean activity coefficients γ_{\pm} of KBr in the aqueous solution at various concentrations c_{KBr} are listed in Tab. 10th-2.

10th3 Practical task

The **practical task** is to **check the potential gradient** $\Delta E/\Delta p_{Br}$ of the bromide ISE. After Eq. 10th.5, the theoretical value of the gradient at 25 °C is $\Delta E/\Delta p_{Br} = 0.0592$ V (59.2 mV), at 20 °C it is 0.0582 V. The theoretical value follows from the Nernst equation (Eq. 6th.6). The experimentally observed gradient of the properly functioning ISE should be close to the theoretical value, within several mV. Substantial deviation of the potential gradient $\Delta E/\Delta p_{Br}$

from the theoretical value indicates the electrode malfunction, caused by ageing or by damage of the electrode membrane by chemical agents. The presence of interfering ions in the solution may also change the potential gradient of ISE. It is therefore recommended to check the potential gradient regularly.

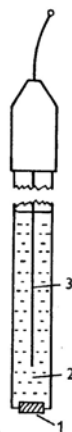


Fig. 10th-1 ISE electrode

The gradient can be checked by measuring series of the cell potentials (EMFs) of the cell (Chem. 10th-A) with the tested bromide ISE. The measured solutions are aqueous solutions of potassium bromide (KBr), for which the activity of bromide anions (a_{Br^-}) can be calculated after Eq. 10th.6 from the known mean activity coefficients γ_{\pm} listed in Tab. 10th-2. The concentration of the measured solutions of KBr have to be variable, in our practical task in the approximate range 10^{-1} - 10^{-3} mol dm⁻³.

10th4 DEVICE AND MATERIALS

Precision electronic potentiometer (pH-meter), bromide ion-selective electrode, saturated calomel electrode, two aqueous solutions of KBr, $c_{\text{KBr}} = 0.1$ mol dm⁻³ and 0.01 mol dm⁻³, pipettes 5 cm³, 10 cm³, and 20 cm³, graduated pipette, beakers (150 cm³), rinsing bottle, filtration paper, electromagnetic stirrer - if possible.

10th5 EXPERIMENTAL

Instrumentation and measurement of the cell potential. The used potentiometer (pH meter) is to be switched over to the mV range, the bromide ISE connected to the G-terminal (+ terminal) and the calomel electrode connected to the R-terminal of the potentiometer. The sign

on the potentiometer display (+ or -) then agrees with the sign of the measured cell potential E (EMF).

The bromide ISE and especially the calomel electrode should be carefully rinsed and dried by a strip of filtration paper. When not in operation, the calomel electrode is dipped in the saturated solution of KCl, so the traces of chlorides must be washed away before use. The clean electrodes are dipped (ca 1 cm) in the measured solution of KBr and by this way, the electrochemical cell after the diagram (Chem. 10th-A) is prepared for the repeated measurements of the cell potential, while the measured solution is gradually diluted.

Dilution of the KBr solution on the measurements. The measured solutions of KBr are diluted by water in the course of the repeated measurements of the cell potential. The dilution scheme is in the Tab. 10th-3 Scheme of dilution of the measured solution of KBr Tab. 10th-3, at the end of the instructions. At first, 10.00 cm^3 of the solution $c_{\text{KBr}} = 0.1 \text{ mol dm}^{-3}$ is pipetted in the clean dry beaker, the electrodes are dipped in the solution, stirring is started and, after 5 min, the cell potential is measured. Then water is gradually added as stated in Tab. 10th-3, after each dilution and 5 min of stirring the measurement of the cell potential is repeated. When the electrodes are too much dipped in the increasing volume of the solution, it is necessary to elevate them somewhat. The temperature of the measured solution must be recorded, at least at the end of the series of measurements.

After the first series of the measurements, the beaker is again cleaned, dried with the strip of filter paper and the whole measuring procedure is repeated with 10.00 cm^3 of the solution with the initial concentration $c_{\text{KBr}} = 0.01 \text{ mol dm}^{-3}$. In this second series the concentrations of KBr are ten times lower, than stated in Tab. 10th-3. If the added volume of water declines from the stated dilution scheme, the true concentration of KBr must be calculated. When the measurements are finished, all the devices should be put in order.

Procession of the results. From the concentrations c_{KBr} of the measured solutions, activities a_{Br^-} and values of $p\text{Br}$ are to be calculated, using Eq. 10th.3, Eq. 10th.5 and the mean activity coefficients γ_{\pm} from Tab. 10th-2, or their interpolated values. Arrange the processed values and the measured cell potentials E (EMF) in two tables, the first table is for the measured solution with the initial concentration $c_{\text{KBr}} = 0.1 \text{ mol dm}^{-3}$, the second one for the solution with the lower initial concentration $c_{\text{KBr}} = 0.01 \text{ mol dm}^{-3}$. Be careful with the correct sign of the E values. The following pattern of the tables is recommended:

Tab. 10th-1 Measured solutions of KBr

V cm ⁻³	c _{KBr} mol dm ⁻³	γ_{\pm}	pBr mV	E mV
10.00	0.1	0.770	1.114	-108.5

The potential gradient $\Delta E/\Delta pBr$ is calculated from the dependence of the measured E values on pBr by the least squares method, on a personal computer using the program FIT. After eq. (4), the gradient $\Delta E/\Delta pBr$ is an angular coefficient of the linear function $E = f(pBr)$. The computer also calculates the statistical parameters and draws the diagram of the function.

The record (protocol) should include the points:

- Principle of the bromide ISE, its use and checking of its function.
- Working procedure and measurements for determination of the potential gradient of the given bromide ISE.
- Tables of results, computer results and diagram of E vs. pBr, comparison of the evaluated gradient $\Delta E/\Delta pBr$ with the theoretical value, conclusion.

Tab. 10th-2 Mean activity coefficients of KBr in aqueous solutions at 25 oC

c _{KBr} mol dm ⁻³	γ_{\pm}	c _{KBr} mol dm ⁻³	γ_{\pm}
0.10	0.770	0.009	0.906
0.09	0.777	0.008	0.910
0.08	0.785	0.007	0.915
0.07	0.794	0.006	0.921
0.06	0.804	0.005	0.927
0.05	0.816	0.004	0.934
0.040	0.830	0.0035	0.937
0.035	0.838	0.0030	0.942
0.030	0.847	0.0025	0.946
0.025	0.857	0.0020	0.952
0.020	0.869	0.0015	0.958
0.015	0.884	0.0010	0.965
0.010	0.901	0.0005	0.975

Tab. 10th-3 Scheme of dilution of the measured solution of KBr

$\delta V, \text{cm}^3$	V, cm^3	$c_{\text{KBr}}, \text{mol dm}^{-3}$
-	10.0	0.1000
1.1	11.1	0.0901
1.4	12.5	0.0800
3.1	15.6	0.0641
9.4	25.0	0.0400
15.0	40.0	0.0250
20.0	60.0	0.0167
20.0	80.0	0.0125
20.0	100.0	0.0100
25.0	125.0	0.0080

11th EXERCISES

11th1 Molecular weight, molar mass, amount of substance, molar volume concentration of solutions

Problems

1.1 With the help of chemical tables write down the relative **molecular weights** M_r and molar masses M (kg mol^{-1} , g mol^{-1}) of a) water, b) methane.

Calculate also:

- c) **Molar volume** (V_m) of liquid water at the temperature $25\text{ }^\circ\text{C}$, when its density is 997.0 kg m^{-3} .
 d) **Amount of substance** (n) and the number of molecules (N) in the 200 mg sample of methane
 e) Volume (V) of that sample of methane at the temperature $25\text{ }^\circ\text{C}$ and the pressure 101.3 kPa , providing the ideal gas behavior of methane.

1.2 Describe, how to prepare the following aqueous solutions of K_2SO_4 :

- a) 500 cm^3 of the solution with **molarity** $c = 0.02\text{ mol dm}^{-3}$.
 b) The solution with $250\text{ g H}_2\text{O}$ and **molality** $m = 0.01\text{ mol kg}^{-1}$.
 Notice the ambiguity of symbol m .

1.3 Consider the preparation of the solution (mixture) of two liquids, acetone (1) and methanol (2); $M_1 = 58.8\text{ g mol}^{-1}$, $M_2 = 32.04\text{ g mol}^{-1}$.

- a) If we mix 5 g of each of them, what are the **molar fractions** (x_1 , x_2) of these components in the prepared mixture?
 b) What is x_2 in the mixture with $x_1 = 0.4$? How to prepare 0.5 mol (total amount) of this mixture?

1.4 Concentrated hydrochloric acid is aqueous solution of about 36% HCl (m/m) and its density is 1180 kg m^{-3} . The molecular weights are HCl 36.46 and H_2O 18.02 , respectively.

Calculate: a) molality (mol kg^{-1}), b) molarity (mol dm^{-3}), c) molar fractions of HCl and H_2O in the concentrated solution.

d) Using the concentrated solution, how to prepare 1 dm^3 (1 l) of the aqueous solutions of HCl with following molarities: 0.5 , 0.1 , 0.05 etc. e) Calculate the approximate pH of the prepared diluted solutions.

Answers

1.1 a) $M_r = 18.02$, $M = 0.001802\text{ kg mol}^{-1} = 18.02\text{ g mol}^{-1}$, b) $M_r = 16.04$ etc., c) $V_m = 1.807 \times 10^{-5}\text{ m}^3\text{ mol}^{-1} = 18.07\text{ cm}^3\text{ mol}^{-1}$, d) $n = 0.01247\text{ mol} = 12.47\text{ mmol}$, $N = 7.509 \times 10^{21}$ molecules, e) $V = 3.051 \times 10^{-4}\text{ m}^3 = 0.3051\text{ dm}^3$

1.2 a) 1.1743 g of K_2SO_4 for 500 cm^3 of **final solution**, b) $0.4357\text{ g K}_2\text{SO}_4$ and 250 g water

1.3 a) $x_1 = 0.3554$, $x_2 = 0.6446$, b) $x_2 = 0.6$, 11.62 g acetone and 9.61 g methanol

1.4 a) $m = 15.43\text{ mol kg}^{-1}$, b) $c = 11.65\text{ mol dm}^{-3}$, c) $x_{\text{H}_2\text{O}} = 0.7825$, $x_{\text{HCl}} = 0.2175$, d) cm^3 of concentrated acid: 42.92 , 8.58 , 4.29 etc., e) pH 0.3 , 1.0 , 1.3 etc.

11th2 RADIOACTIVITY, RADIOACTIVE DECAY

Problems

2.1 One of the artificially prepared radioactive isotopes of iodine is the nuclide $^{131}_{53}\text{I}$, it is an β^- and γ emitter, and its **half-life** is $t_{1/2} = 8.07\text{ d}$ (days).

- a) What nuclide arises by the radioactive decay of $^{131}_{53}\text{I}$?
 b) Define and calculate the **decay constant** λ of $^{131}_{53}\text{I}$.

The **activity** (A , Bq) of a sample of the radiotherapeutic drug containing $^{131}_{53}\text{I}$ was $A_0 = 5.0$ MBq, at the time of preparation (initial activity).

- What was the initial number of atoms (N_0) and mol (n_0) of the radionuclide in the sample (at the time of preparation).
- At what time the content of radionuclide and the activity of the sample decrease to one half, one fourths etc.
- Calculate the number of the radioactive atoms (N) and the activity of the sample 10 days after the preparation.
- For how long the prepared radiotherapeutic drug may be used, if only 20% decrease of its original activity is acceptable.
- How old is the prepared drug, if its activity decreased to one hundredth of the original value.

2.2 Radionuclide $^{99m}_{43}\text{Tc}$ used in diagnostics emits gamma radiation (I.T.), it has **half-life** $t_{1/2} = 6.02$ h (hours) and its daughter nuclide is nearly non-radioactive $^{99}_{43}\text{Tc}$. Aqueous solutions of the salts of $^{99m}_{43}\text{Tc}$ with certain **volume activity** a_v (activity per volume, $a_v = A/V$) are produced in laboratory from the so called technetium generator. When the fresh solution has volume activity $a_{0v} = 60$ MBq dm^{-3} (time $t = 0$, initial activity), calculate:

- The concentration (mol dm^{-3}) of $^{99m}_{43}\text{Tc}$ in the fresh solution and after 6.02 h, 12.04 h etc.
- The volume activity a_v of the solution after 6.02 h, 12.04 h etc. Draw a diagram of the time-dependence of the calculated volume activity.
- For how long the solution may be stored if the minimum required volume activity is 10 kBq cm^{-3} .
- What will be the volume activity exactly 3 days after preparation?
- For how long the solution must be stored before its volume activity drops below the safety limit of radioactivity, which is 500 Bq dm^{-3} .

2.4 The radionuclide $^{99m}_{43}\text{Tc}$ emits photons with energy $e = 142.7$ keV. What is the name of the emitted radiation, what is its frequency (ν) and wavelength (λ). Notice the ambiguity of the symbol l .

Answers

- 2.1** a) Non-radioactive $^{131}_{54}\text{Xe}$, $\lambda = 0.08589$ $\text{d}^{-1} = 9.941 \times 10^{-7}$ s^{-1} , c) $N_0 = 5.03 \times 10^{12}$ atoms, $n_0 = 8.35 \times 10^{-12}$ mol, d) after 8.07 d, 16.14 d etc., e) $N = 2.13 \times 10^{12}$ atoms, $A = 2.12$ MBq, f) 2.6 d = 62.4 h, g) 53.6 d
2.2 a) $c = 3.11 \times 10^{-12}$ mol dm^{-3} , 1.56×10^{-12} mol dm^{-3} etc, b) $a_v = 30$ MBq dm^{-3} , 15 MBq dm^{-3} etc., c) 15.6 h, d) 15.1 kBq dm^{-3} , e) for 4.2 days.
2.4 $\nu = 3.450 \times 10^{19}$ Hz, $l = 8.69 \times 10^{-12}$ m = 8.69 pm

11th3 ATOMIC SPECTRA, MOLECULES, SPECTROPHOTOMETRY, MOLECULAR SPECTRA

Problems

3.2 Atomic spectrum of hydrogen atom. Calculate the wavenumber $\tilde{\nu}$ and wavelength l of the corresponding spectral lines, emitted by the excited H-atom due to the electron transitions $n' \rightarrow n$:

- $n' = 2$, $n = 1$
- $n' = 4$, $n = 2$
- $n' = 3$, $n = 2$
- $n' = 4$, $n = 3$

What are the spectral regions of these lines?

3.3 Molar refraction R_m is an **additive** property, sometimes it is regarded as a sum of the increments of chemical bonds, e.g.: C-C 1.21 $\text{cm}^3 \text{mol}^{-1}$, C=C 4.15 $\text{cm}^3 \text{mol}^{-1}$, C-H 1.7 $\text{cm}^3 \text{mol}^{-1}$.

- Liquid hydrocarbon C_6H_{12} has density $\rho = 778.4$ kg m^{-3} and refractivity index $n = 1.4260$. Using the molar refraction, decide if it is hexene or cyclohexane.
- Another non-aromatic hydrocarbon $\text{C}_{10}\text{H}_{16}$ with no triple bond has density 855.0 kg m^{-3} and refractivity index 1.4823. Using the molar refraction, propose its structural formula.

3.4 Molar refractions R_m ($\text{cm}^3 \text{mol}^{-1}$) of several compounds are as follow: CH_3I 19.5, CH_3Br 14.5, HBr 9.9 and CH_4 6.8. Assuming the additivity of the molar refractions of atoms and atomic groups, calculate the molar refraction of:

- HI , b) CHBr_3 , c) CH_2BrI .

3.6 Absorbance $A = 0.875$ of the aqueous solution of K_2PtCl_6 , with concentration $c = 2.5 \times 10^{-4} \text{ mol dm}^{-3}$, was measured by a spectrophotometer in a cell with the **optical path length** $b = 2.0 \text{ cm}$ at the wavelength $\lambda = 264 \text{ nm}$. Calculate:

- Transmittance** (T) and of the measured solution at the used wavelength.
- Molar absorption coefficient** ϵ of in the units $\text{m}^2 \text{ mol}^{-1}$ and $\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$.
- Concentration of another K_2PtCl_6 solution, with absorbance $A = 0.700$, measured at the same wavelength in the cell with $b = 0.5 \text{ cm}$.
- Absorbance of the solution of K_2PtCl_6 with concentration $c = 4.0 \times 10^{-5} \text{ mol dm}^{-3}$ in the cell with $b = 5.0 \text{ cm}$.

3.7 In the **infrared (IR) absorption spectrum** of hydrogen chloride, the absorption band of the stretching vibration H-Cl (isotopes ^1H and ^{35}Cl) is located at wavenumber $\nu = 2991 \text{ cm}^{-1}$.

- What is the wavelength of the band and the frequency of the stretching vibration?
- Calculate the **force constant** k of the H-Cl bond.
- Calculate the wavenumber of the analogous absorption band of D-Cl ($^2\text{H}^{35}\text{Cl}$) with the same force constant.
- The force constants of the stretching vibration of H-Br and H-I are not too different from that of H-Cl. What is the sequence of the wavenumbers of the corresponding absorption bands of these compounds?
- When a photon with the above stated wavenumber 2991 cm^{-1} is absorbed by the molecule of HCl, what is the increase of the vibration energy of the molecule? Calculate this energy for one molecule (ΔE_v , J and eV) and for 1 mol (ΔE_{mv} , J mol^{-1}).

Answers

3.2 a) $\nu = 0.8230 \times 10^7 \text{ m}^{-1} = 82300 \text{ cm}^{-1}$, $\lambda = 1.215 \times 10^7 \mu = 121.5 \text{ nm}$, UV region, b) $\nu = 20580 \text{ cm}^{-1}$, $\lambda = 486 \text{ nm}$, VIS region, c) $\nu = 15240 \text{ cm}^{-1}$, $\lambda = 656 \text{ nm}$, VIS region, d) $\nu = 5335 \text{ cm}^{-1}$, $\lambda = 1846 \text{ nm}$, IR region.

3.3 a) The stated values of r and n give $R_m = 27.70 \text{ cm}^3 \text{ mol}^{-1}$, while from the bond increments, hexene has $R_m = 29.39 \text{ cm}^3 \text{ mol}^{-1}$ and cyclohexane $R_m = 27.66 \text{ cm}^3 \text{ mol}^{-1}$, make a decision by yourself. b) From r and n it results $R_m = 45.45 \text{ cm}^3 \text{ mol}^{-1}$, and $C_{10}H_{16}$ can be here dekatriene, cyclodekadiene or bicyclodekaene, the respective molar refractions calculated from the bond increments are 46.91, 45.18, and 43.45 $\text{cm}^3 \text{ mol}^{-1}$, decide.

3.4 R_m is a) 14.9, b) 29.9, c) 27.2 $\text{cm}^3 \text{ mol}^{-1}$.

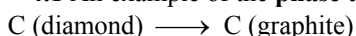
3.6 a) $T = 0.133$, $T\% = 13.3\%$, b) $\epsilon = 175 \text{ m}^2 \text{ mol}^{-1} = 1750 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$, c) $c = 8.0 \times 10^{-4} \text{ mol dm}^{-3}$, d) $A = 0.350$.

3.7 a) $\lambda = 3343 \text{ nm}$, $\nu = 89.67 \times 10^{12} \text{ Hz}$, b) $k = 516 \text{ N m}^{-1}$, c) $\nu = 2143 \text{ cm}^{-1}$, d) the sequence of wavenumbers is the opposite than the sequence of atomic masses Cl, Br, I, e) $\Delta E_v = 5.942 \times 10^{-20} \text{ J} = 0.371 \text{ eV}$, $\Delta E_{mv} = 35.78 \text{ kJ mol}^{-1}$.

11th4 THERMODYNAMICS - PHASE EQUILIBRIA, SOLUTIONS AND PARTITION EQUILIBRIA

Problems - Phase equilibria and transitions

4.1 An example of the **phase transition** is the following change of the crystalline modification of carbon:



At $25 \text{ }^\circ\text{C}$ and normal pressure the molar **enthalpy change** (heat per one mol) of this transition is $\Delta H_{\text{mtr}} = -1.90 \text{ kJ mol}^{-1}$. In the temperature range between $25 \text{ }^\circ\text{C}$ and $250 \text{ }^\circ\text{C}$, the molar **heat capacities** (C_{mp}) of diamond and graphite are 6.06 and $8.64 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively.

a) Is the considered transition at $25 \text{ }^\circ\text{C}$ **endothermic** or **exothermic** process?

Calculate the respective changes of the molar enthalpy of b) diamond, c) graphite, when they are heated from $25 \text{ }^\circ\text{C}$ to $250 \text{ }^\circ\text{C}$ (the heat required for the temperature change).

d) From the previous results, calculate the molar enthalpy of the considered phase transition at the temperature $250 \text{ }^\circ\text{C}$ (Kirchhoff law).

4.2 The molar **entropy change** of the phase transition from diamond to graphite is $\Delta S_{\text{mtr}} = 3.255 \text{ J K}^{-1} \text{ mol}^{-1}$, at $25 \text{ }^\circ\text{C}$ and normal pressure. Using data and results also from Problem 4.1, calculate:

a) The molar **Gibbs free energy** ΔG_{mtr} of the transition at $25 \text{ }^\circ\text{C}$, and decide in what direction the process is spontaneous.

Calculate the respective changes of molar entropy of b) diamond, c) graphite, when they are heated from $25 \text{ }^\circ\text{C}$ to $250 \text{ }^\circ\text{C}$.

Calculate d) ΔS_{mtr} , e) ΔG_{mtr} of the considered transition at temperature $250 \text{ }^\circ\text{C}$.

4.3 Gibbs phase rule. What is the necessary number of the intensive quantities defining the state of the following systems (in equilibrium):

- Hydrogen gas pressurized in a cylinder.
- Mixture of two gases, eg. $N_2 + O_2$.
- The system of two perfectly miscible liquids and their vapors.
- The system of pure liquid water and steam (saturated steam without the presence of air).
- Is it possible to derive unequivocally the temperature of the system d) from its pressure? Consider, if the co-existence of the following phases in one equilibrium system is possible:
- Water steam, liquid water (pure) and one crystalline modification of ice.
- Water steam, liquid water and two crystalline modification of ice.
- Liquid water and two modification of ice.
- Water steam and one modification of ice etc.

4.5 The pressure of the **saturated vapor** of benzene (vapor in equilibrium with liquid) is 101.32 kPa at 80 °C and 4.81 kPa at 5.5 °C, respectively. The latter pressure and temperature correspond to the **triple point** of benzene.

- Calculate the approximate molar **heat of vaporization** ΔH_{mv} of benzene (Clausius - Clapeyron equation).
- What is the **normal boiling point temperature** of benzene? Calculate the boiling point under a reduced pressure 10 kPa.
- Under what pressure benzene boils at 10 °C.
- What is the saturated vapor pressure over solid benzene in the triple point (5.5 °C).

Colligative properties of solutions

4.8 Cryoscopic constant of benzene is $K_k = 5.10 \text{ K kg mol}^{-1}$. The solidifying temperature of the solution of 150 mg of the investigated compound in 20 g benzene was measured and it was by 0.444 lower than the solidifying temperature of pure benzene. Calculate a) the molar mass and b) the relative molecular weight of the investigated compound.

4.9 Water has **ebullioscopic constant** $K_e = 0.52 \text{ K dm}^3 \text{ mol}^{-1}$ and **cryoscopic constant** $K_k = 1.86 \text{ K dm}^3 \text{ mol}^{-1}$. The 0.710 g sample of Na_2SO_4 ($M_r = 142.0$) was dissolved in water, so that 250 cm^3 of the aqueous solution was prepared. Disregarding the osmotic coefficient, calculate a)-c):

- Boiling temperature of the solution at normal pressure.
- Freezing temperature of the solution. Is the solution isoosmotic with the blood plasma?
- Osmotic pressure** of the solution (p) at 0 °C and 25 °C.
- Aqueous solution of KCl with concentration 0.5 $mol dm^3$ freezes at -1.66 °C. Calculate the osmotic coefficient (j) of this solution.

4.10 The hypotonic aqueous solutions used for injections and collyria have to be isotonized by the addition of suitable auxiliary substance into the solution. Using the cryoscopic constant of water from Problem 4.9, calculate the amount (mass) of the auxiliary substance, necessary for the isotonization of the following solutions:

- 1 dm^3 of 0.5% $MgSO_4$ ($M_r = 120.4$), auxiliary substance NaCl ($M_r = 58.4$).
- 200 cm^3 of 1% $ZnCl_2$ ($M_r = 136.3$), auxiliary NaCl.
- 200 cm^3 of the solution of vitamin B₁, conc. 20 mg in 1 cm^3 (thiaminium dichloride, $B^{2+}(Cl)_2$, $M_r = 337.3$), auxiliary galactose ($M_r = 180.2$).

Partition equilibria

4.11 The solubility of iodine in CCl_4 (c_o) is 18.8 $g dm^{-3}$ and in water (c_w) only 0.22 $g dm^{-3}$ (20 °C).

- What is the partition coefficient (k) of iodine in the system CCl_4 /water. Solution of 0.1 g of iodine in 0.5 of water was prepared. How much % of iodine is extracted into CCl_4 , if this aqueous solution is shaken for sufficient time
- once with 50 cm^3 of CCl_4 ,
- two times with 25 cm^3 of CCl_4 ,
- five times with 10 cm^3 of CCl_4 in each run.

Answers

4.1 a) Exothermic, because $\Delta H_{mtr} < 0$, b) $\Delta H_m = 1.364 \text{ kJ mol}^{-1}$, c) $\Delta H_m = 1.944 \text{ kJ mol}^{-1}$, d) $\Delta H_{mtr} = -1.32 \text{ kJ mol}^{-1}$.

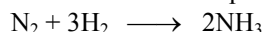
4.2 a) $\Delta G_{mtr} = -2.87 \text{ kJ mol}^{-1}$, the transition is spontaneous from diamond to graphite, since $\Delta G_{mtr} < 0$, b) $\Delta S_m = 3.41 \text{ J K}^{-1} \text{ mol}^{-1}$ c) $\Delta S_m = 4.86 \text{ J K}^{-1} \text{ mol}^{-1}$, d) $\Delta S_{mtr} = 4.71 \text{ J K}^{-1} \text{ mol}^{-1}$, e) $\Delta G_{mtr} = -3.78 \text{ kJ mol}^{-1}$.

- 4.3 a) 2 quantities, e.g. p, T, b) 3 quantities, e.g. p, T and concentration, c) 2, d) 1, e) yes, f) yes - triple point, g) no, h) yes, i) yes.
- 4.5 a) $\Delta H_{mv} = 33.47 \text{ kJ mol}^{-1}$, b) $80 \text{ }^\circ\text{C}$ and $20.4 \text{ }^\circ\text{C}$, c) 6.05 kPa , d) 4.81 kPa .
- 4.8 a) $M = 0.0861 \text{ kg mol}^{-1}$, b) $M_r = 86.1$.
- 4.9 a) $100.03 \text{ }^\circ\text{C}$, b) $-0.112 \text{ }^\circ\text{C}$, the solution is hypotonic, b) $p = 136 \text{ kPa}$ ($0 \text{ }^\circ\text{C}$) and 149 kPa ($25 \text{ }^\circ\text{C}$), d) $j = 0.892$.
- 4.10 a) 5.74 g NaCl , b) 0.34 g NaCl , d) 3.67 g galactose .
- 4.11 a) $k = 85.5$, b) 89.5% , c) 96.4% , d) 99.3% .

11th5 THERMODYNAMICS - CHEMICAL REACTIONS AND EQUILIBRIA

Problems

5.1 There is an example of the **stoichiometric equation** of the chemical reaction:

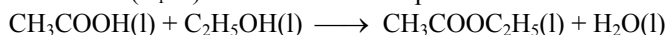


- a) Write down the **stoichiometric coefficients** n_i of the respective **reaction components** (reactants and products).
 b) Write down a formula for the **reaction extent** x (mol).

At the start of the reaction $x = 0$, calculate x when in the reaction course:

- c) 1 mol of N_2 was consumed, d) 2 mol of NH_3 was formed, e) 3 mol of H_2 was consumed, f) 0.3 mol of NH_3 was formed.

5.2 The stoichiometric equation of esterification and the corresponding **standard enthalpies** (heats) of **formation** ($D_f H^\circ$) of the reaction components are as follow

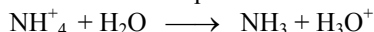


$-484.2 \quad -277.0 \quad -486.6 \quad -285.7 \text{ kJ mol}^{-1}$

The symbol (l) denotes the liquid state and the corresponding $\Delta_f H^\circ$ (kJ mol^{-1}) at the standard temperature $25 \text{ }^\circ\text{C}$ are given bellow each of the reaction component.

- a) Calculate the standard reaction enthalpy $\Delta_r H^\circ$ (reaction heat) of the esterification.
 b) What is the standard enthalpy of the opposite reaction, the hydrolysis of ester.
 c) In what direction the reaction is exothermic or endothermic.

5.5 In diluted aqueous solution the ammonium cation NH_4^+ **dissociate** after equation:



At $25 \text{ }^\circ\text{C}$ the ammonium cation has $\text{pK}_A = 9.245$ and the standard dissociation enthalpy (heat) is $\Delta_r H^\circ = 52.01 \text{ kJ mol}^{-1}$.

- a) Consider, without calculation, if ammonia (NH_3) is stronger or weaker base at higher temperature.
 b) Calculate pK_A of the ammonium cation at $70 \text{ }^\circ\text{C}$.
 c) Calculate $\Delta_r G^\circ$ and $\Delta_r S^\circ$ of dissociation at $25 \text{ }^\circ\text{C}$.

Results

5.1 a) $n_{\text{N}_2} = -1$, $n_{\text{H}_2} = -3$, $n_{\text{NH}_3} = 2$, b) $x = \Delta n_i / n_i$, c) $x = 1 \text{ mol}$, d) 1 mol , e) 1 mol , f) 0.15 mol .

5.2 a) $\Delta_r H^\circ_{\text{est}} = -11.1 \text{ kJ mol}^{-1}$, b) $\Delta_r H^\circ_{\text{hydr}} = -\Delta_r H^\circ_{\text{est}} = 11.1 \text{ kJ mol}^{-1}$, c) esterification is exothermic, and the reverse.

5.5 a) Since $\Delta_r H^\circ > 0$, the dissociation is shifted to the right at higher temperature, which means weakening the ammonia basicity, b) $\text{pK}_A = 8.050$ at $70 \text{ }^\circ\text{C}$, c) $\Delta_r G^\circ = 52.77 \text{ kJ mol}^{-1}$, $\Delta_r S^\circ = -2.55 \text{ J K}^{-1} \text{ mol}^{-1}$.

11th6 ELECTROCHEMISTRY - SOLUTIONS OF ELECTROLYTES

Problems

6.1 The sublimation enthalpy (heat) of potassium iodide (KI) is $\Delta H_{\text{subl}} = 644 \text{ kJ mol}^{-1}$ and the enthalpy of its dissolution in large excess of water is $\Delta H_{\text{sol}} = 20.3 \text{ kJ mol}^{-1}$. What is the approximate enthalpy of **hydration** ΔH_{hydr} of potassium iodide (i.e. the K^+ and I^- ions) in diluted aqueous solution? Explain the calculation.

Electric conductivity of strong electrolytes

6.2 The **electric resistance** of several **strong electrolyte** solutions was measured at 25 °C in the same conductivity cell. The following resistances of the respective solutions were found, HCl 468 W, NaCl 1580 W, NaNO₃ 1650 W, while the concentration of the solutions was the same, $c = 0.002 \text{ mol dm}^{-3}$. The **molar conductivities** of the very diluted strong electrolytes are nearly independent of concentration and the known molar conductivity of NaNO₃ at 25 °C is $\lambda = 12.1 \text{ mS m}^2 \text{ mol}^{-1}$. Calculate approximately:

- Specific conductivity** (conductance, k) of the measured solution of NaNO₃.
- Specific conductivities (k) of the measured solutions of HCl and NaCl, and the corresponding molar conductivities (λ).
- Molar and specific conductivity of solution of HNO₃, $c = 0.002 \text{ mol dm}^{-3}$, which was not measured.
- Specific conductivity of a solution in which two strong electrolytes are dissolved, HCl $0.001 \text{ mol dm}^{-3}$ and NaCl $0.002 \text{ mol dm}^{-3}$.
- The resistance of another solution of NaNO₃ was measured at the same conditions and it was 275 W. Calculate the concentration of NaNO₃.

Conductivity and dissociation of weak electrolytes

6.3 The **limiting ionic conductivities** (at very large dilution) of the hydrogen ion (H⁺) and of the anion of butyric acid (A⁻) are $\lambda_0(\text{H}^+) = 34.98 \text{ mS m}^2 \text{ mol}^{-1}$ and $\lambda_0(\text{A}^-) = 3.26 \text{ mS m}^2 \text{ mol}^{-1}$, respectively (25 °C).

- Calculate the **limiting molar conductivity** $\lambda_0(\text{HA})$ of butyric acid (HA, weak electrolyte).
The respective specific conductivities (k) of two solutions of butyric acid with different concentrations were measured, in the first solution $c = 0.001 \text{ mol dm}^{-3}$, $k = 4.436 \text{ mS m}^{-1}$ and in the second one $c = 0.01 \text{ mol dm}^{-3}$, $k = 14.31 \text{ mS m}^{-1}$.
Calculate the respective molar conductivities $\lambda(\text{HA})$ and the **degrees of dissociation** α of butyric acid
- in the 1st and c) 2nd solution.
- Calculate pH of the two solutions.
- Calculate the dissociation constant K_A and $\text{p}K_A$ of butyric acid from the data for the two solutions.

Ionic strength, activity coefficient, solubility product

6.4 The general formula for the **ionic strength** I (mol dm^{-3}) of the strong electrolyte solution is $I = 0.5 \sum c_i z_i^2$, where c_i and z_i are the respective concentrations and charge numbers of all the **ions** in the solution. Derive the simplified formulae for the calculation of the ionic strength of the following electrolytes from their respective concentrations c :

- KCl, NaCl, HNO₃, etc., b) CaCl₂, Na₂SO₄, c) MgSO₄, ZnSO₄,
d) K₄[Fe(CN)₆], f) Cr₂(SO₄)₃.
- Calculate the ionic strength of the solutions of the electrolytes a)-e) at concentration $c = 0.01 \text{ mol dm}^{-3}$.
- Three salts are dissolved in one solution: Mg(NO₃)₂ 0.003, MgSO₄ 0.005, K₂SO₄ 0.007 mol dm^{-3} . Calculate the ionic strength of the solution.

6.5 By means of the **Debye-Hückel limiting law** calculate the mean activity coefficients γ_{\pm} of the solutions of strong electrolytes from **6.4** a), b), at concentration $c = 0.001 \text{ mol dm}^{-3}$ (25 °C).

6.6 Consider solutions of hydrochloric acid (HCl, strong acid) with the respective concentrations
a) 0.0001, b) 0.001, c) 0.01 mol dm^{-3} .

By the same way as in **6.5**, calculate the respective $\log \gamma_{\pm}$ of HCl and then pH values of the solutions, corresponding to the **activities**.

6.7 The **solubility product** of silver chloride (AgCl) in water is $K_s = 1.56 \times 10^{-10}$ (25 °C). Calculate the respective **solubilities** s (mol dm^{-3}) of AgCl:

- In pure water. Is the activity coefficient important in this case?
- In the solution of MgSO₄ 0.01 mol dm^{-3} , using the mean activity coefficient calculated after the Debye-Hückel limiting law.
- In the solution of NaCl 0.02 mol dm^{-3} , neglecting the activity coefficient.
- In the same solution of NaCl, more precisely, using the mean activity coefficient, calculated as in b).
- Convert the solubilities s (mol dm^{-3}) calculated in a)-d) into mg of silver in 1 dm^3 of solution (Ag: $M_r = 107.9$)

Weak acids and bases, pH, buffers

6.8 Acetic acid (HA) is often used **weak acid** with $\text{p}K_A = 4.75$ (at 25 °C and negligible ionic strength).

- Write down the equation of the **dissociation** of the weak acid HA, derive the formulae for the dissociation constant K_A and $\text{p}K_A$.
- Calculate pH of the diluted solution of acetic acid with concentration $c = 0.05 \text{ mol dm}^{-3}$ (and similar examples).

- c) What is the approximate pH of the acetate **buffer solution**, where acetic acid (HA) and sodium acetate (NaA) are mixed in the same concentrations? What is the working range of pH of acetate buffers?
- e) Acetate buffer can be also prepared by the partial **neutralization** of HA with NaOH: 20 cm³ of the solution of NaOH, 0.1 mol dm⁻³, were added to 50 cm³ of the solution of HA with the same concentration, and the mixture was filled up by water to 100 cm³. Calculate the equilibrium concentrations [HA] and [A⁻] and pH of the final buffer solution.
- f) Write down the equation of **hydrolysis** of sodium acetate in aqueous solution and calculate pH of the solution of NaA 0.01 mol dm⁻³ (pK_w = 14.00)

6.9 Phosphoric acid H₃PO₄ is a **triprotic acid**, so that its dissociation is described by three pK_A values, namely pK_{A1} = 2.12, pK_{A2} = 7.21 and pK_{A3} = 12.6 (25 °C).

- b) What are the working ranges of pH of the often used phosphate buffer solutions?
Several phosphate buffers were prepared by partial neutralization of H₃PO₄ with NaOH. The solution of H₃PO₄, 0.1 mol dm⁻³, 25 cm³, was mixed with certain volume of the solution of NaOH, 0.1 mol dm⁻³, and the mixture was filled up by water to 250 cm³. Calculate pH of the final buffers if the used volumes of the NaOH solutions were:
c) 15 cm³, d) 35 cm³, e) 65 cm³.

6.10 Tris-(hydroxymethyl)aminomethan (THAM) is a **weak base** B and together with its hydrochloride salt BHCl (BH⁺Cl⁻) it is used for the preparation of various buffer solutions. The protonated cation BH⁺ has pK_A = 8.01 (25 °C).

- a) What is the working range of pH of the THAM buffers?
b) Write down equations for K_A and K_B, calculate pK_B of the base B (pK_w = 14.00).
c) Calculate pH of the solution of the salt BHCl 0.02 mol dm⁻³.
d) Calculate pH of the solution of the base B 0.02 mol dm⁻³.
e) How to prepare 1 dm³ of the buffer solution with pH = 7.5 and the total concentration c_B + c_{BHCl} = 0.02 mol dm⁻³, if both the base B (M_r 121.14) and the salt BHCl (M_r 157.6) are available.
f) Another THAM buffer was prepared by dissolving 0.727 g of the base B in 25 cm³ of the solution of HCl, 0.1 mol dm⁻³ (partial neutralization), and filling up the solution with water to 200 cm³. Calculate pH of the prepared buffer solution.

Results

- 6.1** $\Delta H_{\text{hydr}} = \Delta H_{\text{sol}} - \Delta H_{\text{subl}} = -624 \text{ kJ mol}^{-1}$ (cyclus).
6.2 k = 0.0242 S m⁻¹ = 24.2 mS m⁻¹, b) HCl: k = 85.3 mS m⁻¹, $\lambda = 42.7 \text{ mS m}^2 \text{ mol}^{-1}$, NaCl: k = 25.3 mS m⁻¹, $\lambda = 12.6 \text{ mS m}^2 \text{ mol}^{-1}$, c) l = 42.1 mS m² mol⁻¹, k = 84.2 mS m⁻¹, d) k = 67.9 mS m⁻¹, e) c = 0.012 mol dm⁻³.
6.3 a) $\lambda_0(\text{HA}) = 38.24 \text{ mS m}^2 \text{ mol}^{-1}$, b) $\lambda(\text{HA}) = 4.436 \text{ mS m}^2 \text{ mol}^{-1}$, a = 0.116, c) $\lambda(\text{HA}) = 1.431 \text{ mS m}^2 \text{ mol}^{-1}$, a = 0.0374, d) pH = 3.93 and 3.43, e) K_A = 1.52 × 10⁻⁵, pK_A = 4.82 and K_A = 1.45 × 10⁻⁵, pK_A = 4.84.
6.4 a) I = c, b) I = 3c, c) I = 4c, d) I = 6c, f) I = 0.01, 0.03 mol dm⁻³, etc., g) I = 0.05 mol dm⁻³.
6.5 a) $\gamma_{\pm} = 0.96$, b) $\gamma_{\pm} = 0.82$.
6.6 a) $\log \gamma_{\pm} = 0.005$, pH = 4.005, b) $\log \gamma_{\pm} = 0.016$, pH = 3.016, c) $\log \gamma_{\pm} = 0.051$, pH = 2.051.
6.7 a) s = 1.25 × 10⁻⁵ mol dm⁻³, activity coefficient can be neglected, b) $\gamma_{\pm} = 0.39$, s = 3.2 × 10⁻⁵ mol dm⁻³, c) s = 7.8 × 10⁻⁹ mol dm⁻³, d) $\gamma_{\pm} = 0.85$, s = 10.8 × 10⁻⁹ mol dm⁻³, f) 1.35 mg, 3.45 mg, 0.84 × 10⁻³ mg = 0.84 mg, 1.2 × 10⁻³ mg = 1.2 mg.
6.8 a)... K_A = ([H⁺][A⁻])/[HA], pK_A = -log K_A, b) pH = 3.02, c) pH = pK_A = 4.7, working range of pH 4.7 ± 1, e) [HA] = 0.03 mol dm⁻³, [A⁻] = 0.02 mol dm⁻³, pH = 4.57, f)... pH = 8.37.
6.9 b) Three working ranges of pH: 2.1 ± 1, 7.2 ± 1, 12.6 ± 1, frequently used is the range of pH 6.2–8.2, c) pH = 2.30, d) pH = 7.03, e) pH = 12.08.
6.10 a) pH 8.0 ± 1, b)... pK_B = pK_w - pK_A = 5.99, c) pH = 4.85, d) pH = 10.35, e) 0.572 g of the base B and 2.408 g of the salt BHCl dissolve in water and fill up to 1 dm³, f) pH = 8.16.

11th7 ELECTROCHEMISTRY - CELLS AND ELECTRODES

Problems

- 7.1** The described electrochemical cell (concentration cell) was set up :
Cu|CuSO₄ (c₁) || CuSO₄ (c₂)|Cu
Determine which electrode is the positive terminal (+) of the cell and calculate the **cell potential** (E, electromotive force) for the given concentrations of the electrolyte (25 °C):

- a) $c_1 = 0.01 \text{ mol dm}^{-3}$, $c_2 = 1 \times 10^{-4} \text{ mol dm}^{-3}$,
 b) $c_1 = 1 \times 10^{-4} \text{ mol dm}^{-3}$, $c_2 = 0.01 \text{ mol dm}^{-3}$.

7.2 **Potentiometric measurements** of pH were carried out at 25 °C using the hydrogen electrode immersed in the examined solution (left hand side electrode of the cell) and saturated calomel reference electrode (right hand side). Calculate pH of the examined solution from the measured cell potential:

a) $E = 359 \text{ mV}$, b) $E = 1.000 \text{ V}$

Other measurements of pH were carried out with quinhydrone electrode (right hand side electrode of the cell) and saturated calomel electrode (left hand side). Calculate pH from the measured cell potential:

c) $E = 400 \text{ mV}$, d) $E = -80 \text{ mV}$

Is the last measurement reliable?

Potential of the saturated calomel electrode $E_{\text{cal}} = 0.241 \text{ V}$ and the standard potential of quinhydrone electrode $E^{\circ}_{\text{QH}} = 0.700 \text{ V}$ (25 °C).

Results

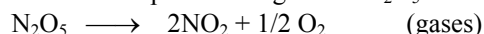
7.1 a) $E = -0.0592 \text{ V}$, left hand side electrode (+), b) $E = 0.0592 \text{ V}$, right hand side electrode (+).

7.2 pH values a) 1.99, b) 12.83, c) 1.00, d) 7.76, less reliable measurement, too high pH for quinhydrone electrode.

11th8 CHEMICAL KINETICS

Problems

8.1 Decomposition of gaseous N_2O_5 is a monomolecular **reaction of the 1st order**:

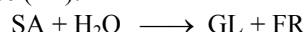


Because all the components are gases, the reaction kinetics is conveniently investigated by the measurements of the pressure changes in the reaction course and the **rate constant** of the reaction is $k = 4.8 \times 10^{-4} \text{ s}^{-1}$ (25 °C). Assume the reaction takes place in a constant volume vessel at 25 °C and the initial pressure of the gaseous N_2O_5 is 100 kPa. Calculate the fraction (%) of the decomposed N_2O_5 and the pressure of the reaction mixture after the time

a) 10 s, b) 10 min, c) 1 h.

d) In what time 50% of N_2O_5 is decomposed, does this reaction **half-life** ($t_{1/2}$) depend on the initial pressure (or concentration) of the reactant?

8.2 Inversion of saccharose (SA) is a bimolecular reaction with water, producing glucose (GL) and fructose (FR):



a) What is the **reaction order** if the reaction takes place in **diluted** aqueous solution.

Half-lives $t_{1/2}$ of the reaction were measured polarimetrically at various temperatures, in diluted acidified aqueous solutions, with the initial concentration of saccharose 0.2 mol dm^{-3} , and it was found:

50 °C, $t_{1/2} = 23.0 \text{ s}$; 25 °C, $t_{1/2} = 673 \text{ s}$; 10 °C, $t_{1/2} = 111.7 \text{ min}$.

Calculate

b) rate constants (k) of the reaction,

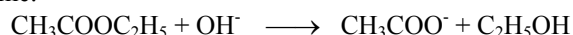
c) time of 90% inversion of saccharose, at the given conditions and temperatures.

d) From the reaction constants at 10 °C and 50 °C, calculate the **activation energy** (E) of the reaction.

e) Calculate the rate constant and half-life of the reaction at 40 °C.

Examples of kinetics of the 1st order see also in Problems 2.1 and 2.2 on radioactive decay.

8.3 Saponification of ethylacetate (ester) takes place in diluted aqueous solution of NaOH after the reaction scheme:



The reaction kinetics is of the **2nd order** and the rate constant $k = 0.11 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ (25 °C).

Assume the initial concentrations of both the ester and NaOH are the same, $c_0 = 0.1 \text{ mol dm}^{-3}$, and calculate the decreasing concentration of the ester (c), as well as the increasing concentration of the produced acetate anion (x), after the time

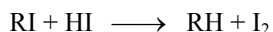
a) 10 s, b) 10 min.

Calculate the **reaction rate** (v), which is the velocity of the decrease of the concentration of the ester, $v = -dc/dt$:

c) the initial rate (v_0), d) after 10 s, e) after 10 min.

f) Calculate the reaction **half-life**, does it depend on the initial concentration?

8.4 The scheme of the reaction of elimination of iodine from organic molecule is



where R is an aliphatic radical. The reaction is of the 2nd order, at 25 °C the rate constant is $k = 1.9 \times 10^{-11} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ and the activation energy of the reaction is $E = 106 \text{ kJ mol}^{-1}$.

Calculate the rate constant and how much the reaction is accelerated, when the temperature is raised from 25 °C to a) 35 °C, b) 20 °C, c) 125 °C.

Results

8.1 a) 0.48%, $p = 100.72 \text{ kPa}$, b) 25.0%, 137.5 kPa , c) 82.2%, 223.4 kPa , d) $t = 1440 \text{ s}$, for the reaction of the 1st order t does not depend on the initial pressure or concentration of the reactant.

8.2 a) The 1st order - pseudounimolecular reaction, b) 50 °C: $k = 0.0301 \text{ s}^{-1}$, 25 °C: $k = 1.03 \times 10^{-3} \text{ s}^{-1}$, 10 °C: $k = 0.103 \times 10^{-3} \text{ s}^{-1}$, c) 50 °C: 76.5 s , 25 °C: 37.2 min , 10 °C: 6.2 h , d) $E = 108 \text{ kJ mol}^{-1}$, e) $k = 8.3 \times 10^{-3} \text{ s}^{-1}$, $t_{1/2} = 83 \text{ s}$.

8.3 a) $c = 0.090 \text{ mol dm}^{-3}$, $x = 0.01 \text{ mol dm}^{-3}$, b) $c = 0.013 \text{ mol dm}^{-3}$, $x = 0.087 \text{ mol dm}^{-3}$, c) $v_o = 1.1 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$, d) $v = 0.89 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$, e) $v = 1.9 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$, f) $t_{1/2} = 90.9 \text{ s}$, it is inversely proportional to the initial concentration.

8.4 a) $k = 7.6 \times 10^{-11} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, 4times, b) $k = 2.8 \times 10^{-10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, 15times, c) $k = 8.8 \times 10^{-7} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, 46000times faster.

12th APPENDIX A – CRYOSCOPIC DETERMINATION OF MOLAR MASS OF NONELECTROLYTES

12th1 Task

Cryoscopic determination of molar mass of unknown non dissociating substance (nonelectrolyte), in aqueous solution.

12th2 Equipment

Apparatus for cryoscopic measurements as it is shown in Fig. 1st-2: Beckman's thermometer (Bt), test tube with thick walls (S), mixer (M), vessel containing cooling mixture (K); magnifying glass, 3 pcs of weighing bottle, 20 cm³ pipette, beaker, laboratory thermometer, stop watch.

12th3 Chemicals

Cooling mixture (solution of 5 deals of ice brash and 1 deal of NaCl swiped with water), sample of the unknown substance, alcohol for drying.

12th4 Procedure

Step I. Preparation of cryoscopic test tube

Using analytical balances weigh 3 portions of unknown substance in clean and dry weighing bottles, each sample with 0.5 grams of approximate weight. Clean the cryoscopic test tube using distilled water and dry it up after applying a little amount of alcohol. Using the pipette add 20 cm³ of distilled water with known temperature t (record it into the table 2). After insertion of the mixer place the adjusted Beckman's thermometer (Bt) so that it's whole reservoir, containing mercury, is immersed in the solution and it is not touching inner walls of the test tube. Insert the prepared cryoscopic test tube into the cooling mixture. The surface of the cooling bath should be set 2-3 cms above the solvent's level.

Step II. Measurements with pure solvent

Record the initial temperature of the liquid inside the cryoscopic test tube when it drops to 5 degrees. Start the stop watch and record the temperature every 5 seconds. Because the Beckman's thermometer displays relative temperature and the thermometer's scale is given in degrees (which numerically equals to 1 Kelvin), the temperature depression will be given in Kelvins. The temperature will decrease until the solid phase starts to precipitate from the solution which is indicated with sharply increasing temperature. Curve of undercooling looks as it is shown in Fig. 1st-1. As a freezing point (T_0) will be regarded that temperature, which represents the highest value on flat part on the mentioned curve (point A in Fig. 1st-1). Record this temperature in Table 2. Move out the cryoscopic test tube from the cooling bath into the baker which is filled with warmish water and mix the content until the freezed solvent becomes fully melted. Determination of freezing point of the pure solvent, described in step II, should be repeated 3 times. It is assumed that the determined values of freezing points will be close.

Step III. Measurements with aqueous solution of unknown sample

After the last repetition of the measurement with pure solvent heat up the test tube again, so the Beckman's thermometer could be gently removed from the liquid. Add the first portion of weighed sample substance into the solvent and mix it. After the sample dissolution the Beckman's thermometer should be restored back to its original place in the test tube and the previous procedure should be repeated as it was described for pure solvent (see again step II.). The maximum temperature, measured after undercooling, will be considered again as the freezing point of the solution (T_i). Repeat the measurement for 3 different concentrations given with gradually added portions of weighed unknown sample. Record the determined freezing points of these solutions in Table 3. The total mass of added sample is given as sum of the masses of all previous additions. Each temperature determination for the given concentration must be repeated 2 times and the results should be averaged.

Step IV. Completion the measurements

After the measurements are finished discharge the solution from the apparatus. The cryoscopic test tube, thermometer and mixer should be carefully cleaned and dried up. Finally weight the masses of empty weighing bottles and record the results in Table 1.

Tab. 1 Weighing the samples

Sample No:	1	2	3
weighing bottle+sample (g)			
empty weighing bottle (g)			
mass of the sample μ_B (g)			

Tab. 2 Solvent data

Solvent	K_K K.kg.mol ⁻¹	μ_A g	t °C	T_{01} °Bk	T_{02} °Bk	T_{03} °Bk
water	1,859					
<T ₀ >, average freezing point (°Bk)						

12th5 Processing the results

- Using Table 2 calculate the average temperature <T₀> from the columns T₀₁, T₀₂, T₀₃.
- Using Table 3 calculate step by step <T_i> and ΔT_{ki} as difference between the average freezing point of pure solvent <T₀> and that of the solutions <T_i>:

$$\Delta T_{ki} = \langle T_0 \rangle - \langle T_i \rangle$$

Tab. 3 Solution data

Run No	Mass of the sample μ_{Bi} (g)		Freezing points of samples, °Bk		<T _i > °Bk	ΔT_{ki} K	M_{bi} g.mol ⁻¹	ratio $\mu_B/\Delta T_K$
	individua l	total	T _{i1}	T _{i2}				
1								
2								
3								

3. Calculate the molar mass of unknown substance as follows

3.A Direct calculation from a formula

$$M_{Bi} = \frac{K_K \times \mu_B}{\Delta T_{ki} \times \mu_A} \quad (1)$$

μ_{Bi} is the mass of the unknown sample in grams

μ_A is the mass of the solvent in grams calculated from volume density data

Calculate the average value of molar mass <M_B> and the appropriate standard deviation s using formulae:

$$\langle M_B \rangle = \frac{\sum_{i=1}^N M_{Bi}}{N},$$

$$s = \sqrt{\frac{\sum_{i=1}^N (M_{Bi} - \langle M_B \rangle)^2}{N - 1}}$$

and N is the number of readings.

Tab. 4 Density of water at various temperatures

Temperature [°C]	Density [kg.m ⁻³]	Temperature [°C]	Density [kg.m ⁻³]
15	999.129	21	998.022
16	998.972	22	997.801
17	998.804	23	997.569
18	998.625	24	997.327
19	998.435	25	997.075
20	998.234	26	996.823

3.B Calculation of the limit value

In case of solutions which differ from the ideal (Equation 1 does not hold for them) it is necessary to extrapolate to zero weight. The unknown molar mass should be calculated from Equation 2. Process the dependence $f(\mu_{Bi}) = \mu_{Bi} / \Delta T_{Ki}$ using the least square method. The intersection data, on the axis of dependent variable (parameter „p2“ in application program FIT), represents the requested limit value:

$$\lim_{\mu_{Bi} \rightarrow 0} (\mu_{Bi} / \Delta T_{Ki})$$

This limit can be obtained also from diagram of function dependence $f(\mu_{Bi}) = \mu_{Bi} / \Delta T_{Ki}$ using graphical extrapolation method to zero weight ($\mu_{Bi} \rightarrow 0$) and can be read from function value at $\mu_{Bi} = 0$.

The molar mass is then determined using the following equation:

$$M_B = \left[\frac{K_K}{\mu_A} \right] \times \lim_{\mu_{Bi} \rightarrow 0} (\mu_{Bi} / \Delta T_{Ki}) \quad (2)$$

The experimental error of molar mass should be calculated in %, so called relative error, where the table value of molar mass represents the reference (100%) data:

$$\delta (\%) = \frac{|\langle M_B \rangle - M_B^{TAB}|}{M_B^{TAB}} \times 100\%$$

Include in your protocol the following points:

- Theoretical principles of the molar mass determination using cryoscopy
- Brief description of the used device and procedure
- Tables of measured data
- Calculations of molar mass (procedures A and B), standard deviation, relative error

- Diagrams:
 - Time dependence of temperature for simple measurement of pure solvent and solution of unknown substance (1st addition)
 - dependence $f(\mu_{Bi}) = \mu_{Bi}/\Delta T_{Ki}$ for determination of $\mu_{Bi} \rightarrow 0$
- Discussion and conclusions