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## EXPERIMENTS IN PHYSICAL CHEMISTRY

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## Experiment no. 1

## PARTIAL MOLAR VOLUME

## 1. PURPOSE

In this experiment we measure densities of NaCl solutions and calculate partial molar volumes as a function of concentration.

## 2. THEORY

Solution volume  $V$ , include  $n_1$  mole of water and  $n_2$  moles of an electrolyte and is given by:

$$V = n_1 \bar{V}_1 + n_2 \bar{V}_2 \quad (1)$$

The apparent molar volume of solute  $\Phi_V$  is defined by:

$$\Phi_V = \frac{V - n_1 \bar{V}_1^\circ}{n_2}, \text{ and} \quad (2)$$

$$V = n_1 \bar{V}_1^\circ + n_2 \Phi_V = n_1 \bar{V}_1 + m n_1 M_1 \Phi_V, \quad (3)$$

Where molality is defined as

$$m = \frac{n_2}{n_1 M_1} \quad (4)$$

$\bar{V}_1^\circ$  - molar volume of pure solvent

$m$  - solution molality

With the

$$V = \frac{n_1 M_1 + n_2 M_2}{\rho_r} \quad \text{and} \quad n_1 \bar{V}_1^\circ = \frac{n_1 M_1}{\rho_1} \quad (5)$$

$\Phi_V$  is expressed as a function of solution density  $\rho_r$ , solvent density  $\rho_1$  and molar mass of solute  $M_2$

$$\Phi_V = \frac{1}{\rho_r} \left( M_2 - \frac{1}{m} \cdot \frac{\rho_r - \rho_1}{\rho_1} \right) \quad (6)$$

Partial molar volumes  $\bar{V}_1$  in  $\bar{V}_2$  are expressed by  $\Phi_V$ :

$$\bar{V}_2 = \left( \frac{\partial V}{\partial n_2} \right)_{n_1, T, P} = \Phi_V + n_2 \left( \frac{\partial \Phi_V}{\partial n_2} \right)_{n_1, T, P} = \Phi_V + m \frac{d\Phi_V}{dm} \quad (7)$$

$$\bar{V}_1 = \frac{V - n_1 \bar{V}_2}{n_1} = \bar{V}_1^\circ - \frac{n_2^2}{n_1} \left( \frac{\partial \Phi_V}{\partial n_2} \right)_{n_1, T, P} = V_1^\circ - m^2 \frac{d\Phi_V}{dm} \quad (8)$$

$\frac{d\Phi_V}{dm}$  can hardly be evaluated graphically, since it is not a linear function of concentration. But the experiments have shown, that for very dissolved solutions of electrolytes,  $\Phi_V$  is a linear function of  $\sqrt{m}$ , in accordance to the Debye-Hückel theory.

$$\Phi_V = \Phi_V^\circ + K\sqrt{m} = \Phi_V^\circ + \sqrt{m} \frac{d\Phi_V}{d\sqrt{m}} \quad (9)$$

$\Phi_V^\circ$  - apparent molar volume of solute, extrapolated to the concentration value 0,  
K – a constant, dependent on the electrolyte. Equations (7) and (8) were transformed, so that  $d\Phi_V/dm$  was changed with the expression  $d\Phi_V/d\sqrt{m}$ , which has a constant value at low concentrations.

$$\bar{V}_2 = \Phi_V^\circ + \frac{3}{2} \sqrt{m} \frac{d\Phi_V}{d\sqrt{m}} \quad (10)$$

$$\bar{V}_1 = V_1^\circ - \frac{1}{2} M_1 m^{\frac{3}{2}} \frac{d\Phi_V}{d\sqrt{m}}, \quad (11)$$

### 3. PROCEDURE

Measure density of 3.2; 1.6; 0.8; 0.4 and 0.2 molal solution of NaCl in water with a densimeter at room temperature.

### 4. APPARATUS

- densimeter DMA

### 5. DATA

Tabulate the results (density) against molality.

### 6. CALCULATION

Calculate  $\Phi_V$  and  $\sqrt{m}$ . Plot a graph of  $\Phi_V$  against  $\sqrt{m}$  and draw carefully a straight line through the points. Find the slope of this curve, which is  $\frac{d\Phi_V}{d\sqrt{m}}$ , then find the  $\Phi_V^\circ$  on the ordinate axis at the point in which  $\sqrt{m}$  equals 0. Also calculate and tabulate  $\bar{V}_1$  and  $\bar{V}_2$

at concentrations  $m = 0, 0.5, 1.0, 1.5, 2.0$  and  $2.5$  mol/kg  $\text{H}_2\text{O}$  and plot graphs of  $\bar{V}_1$  and  $\bar{V}_2$  against  $m$ !

## 7. ACCURACY

$$\frac{\Delta\Phi_V}{\Phi_V} =$$

$$\frac{\Delta(d\Phi_V/d\sqrt{m})}{(d\Phi_V/d\sqrt{m})} =$$

## 8. RESULTS

Present a graph  $\Phi_V$  against  $\sqrt{m}$ , tabulate results and present graphs with  $\bar{V}_1$  and  $\bar{V}_2$  against  $m$ !

$$\Phi_V^\circ =$$

$$\frac{d\Phi_V}{d\sqrt{m}} =$$

**Experiment no.2****CALORIMETRY****1. PURPOSE**

This experiment illustrates the use of a calorimeter which can be used for determination of the enthalpy of solution for salt dissolved in water.

**2. THEORY**

Enthalpy of solution at concentration  $m$ , is heat, which is measured when 1 mol of a salt is dissolved in an amount of solvent, which give us a solution with the concentration  $m$ .

$$\Delta H = H - (n_1 H_1 + n_2 H_2) \dots \text{change in } H \quad (1)$$

$H$  - enthalpy of solution

$H_1$  - enthalpy of solvent

$H_2$  - enthalpy of solute

$$\Delta H_t = \frac{\Delta H}{n_2} \dots \text{enthalpy of solution} \quad (2)$$

$$\Delta H_t = \frac{U \cdot I \cdot t \cdot \Delta T}{m \cdot \Delta T_e} \quad (3)$$

Read from a graph:  $\Delta T$ ,  $\Delta T_e$ .

**3. PROCEDURE**

The body of the calorimeter is in the form of a Dewar flask with lid. Through the lid a heater, a Beckmann thermometer and a pipette are mounted.

Close the pipette with a rubber membrane and fill it with 5 g of sample salt. Put 650 ml of distilled water and the stirrer into the calorimeter.

Observe the temperature change in the calorimeter, by recording its values at 15 seconds intervals. After the temperature arises constantly, perforate the membrane. Salt can now dissolve in water. According to the endothermic reaction, the temperature will

drop due to heat loss in the environment; so, continue the observations until the temperature is constant again. Switch on the heater and observe the temperature rising until it reaches the starting value. Register the time of heating. Turn off the heater and continue the temperature measurements for another 15 minutes. Read the current and potential values of the heater.

#### 4. APPARATUS

- calorimeter
- stirrer
- heater
- Beckmann thermometer
- pipette

#### 5. DATA

Tabulate the results  $T$  (temperature) against  $t$  (time).

#### 6. CALCULATION

Draw a graph of temperature versus time. Find  $\Delta T$  and  $\Delta T_e$ . From these data calculate the value of  $\Delta H_t$

#### 7. ACCURACY

$$\ln \Delta H_t = \ln U + \ln I + \ln t + \ln \Delta T - \ln m - \ln \Delta T_e$$

$$\frac{\Delta(\Delta H_t)}{(\Delta H_t)} = \frac{\Delta U}{U} + \frac{\Delta I}{I} + \underbrace{\frac{\Delta t}{t}}_{k_{st}=0} + \underbrace{\frac{\Delta(\Delta T)}{(\Delta T)}}_{k_{st}=0} - \frac{\Delta m}{m} - \underbrace{\frac{\Delta(\Delta T_e)}{(\Delta T_e)}}_{k_{st}=0}$$

$$\frac{\Delta(\Delta H_t)}{(\Delta H_t)} =$$

#### 8. RESULTS

$$\Delta H_t =$$

## Experiment no.3

# VAPOUR PRESSURE AND ENTHALPY OF VAPORIZATION

## 1. PURPOSE

This experiment involves the measurement of vapour pressure over the range of temperatures and the calculation of enthalpy of vaporization.

## 2. THEORY

Consider a system comprising a liquid and its vapour at equilibrium which undergoes a very small reversible change. Equalizing the changes in free energy in the liquid and gaseous phases gives:

$$\frac{dP}{dT} = \frac{S_p - S_t}{V_p - V_t} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T\Delta V} \quad (1)$$

Since the two phases are in equilibrium

$$\Delta G_{vap} = \Delta H_{vap} - T\Delta S_{vap} = 0, \quad (2)$$

where  $T$  is the temperature of the equilibrium, i.e. the boiling point at the pressure under consideration.

$$\Delta S_{vap} = \Delta H_{vap}/T \quad (3)$$

From that we can obtain the Clapeyron equation which is exact for a system at equilibrium:

$$\frac{dp}{dT} = \Delta H_{vap}/T \Delta V_{vap} \quad (4)$$

To a good approximation, the term  $\Delta V_{vap} = V_g - V_l$  may be replaced by  $V_g$  because the volume of gas is much larger than the volume of the liquid. If the vapour is assumed to obey the perfect gas equation, then for one mole

$$V_p = RT/P. \quad (5)$$

Therefore from eq. (4) and (5)

$$\frac{dp}{dT} = \frac{\Delta H_{vap}}{RT^2}, \quad (6)$$

from which the Clausius – Clapeyron equation is obtained

$$\frac{d \ln P}{dT} = \frac{\Delta H}{RT^2}, \text{ or in the integral shape: } \ln P_2 - \ln P_1 = -\frac{\Delta H}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad (7)$$

In graph  $\ln p$  against  $1/T$  (in  $K^{-1}$ ), the obtained slope of the line equals  $-\Delta H/R$ .

### 3. PROCEDURE

Fill the isoteniscope with the sample liquid. Connect the isoteniscope with the cooler and the ballast vessel, than put it into the thermostated liquid. The starting temperature must be  $25^\circ C$ . Reduce the pressure, until the liquid boils gently, thus removing the air from the narrow tube. Close the tube that leads to the vacuum pump and let the air into the isoteniscope until you get the same level in both parts of the U tub. Note the temperature of the stirred water, and read pressure data from the manometer. Repeat the observations at intervals of  $5^\circ C$  up to the boiling point of the liquid.

### 4. DATA

Measure the ambient atmospheric pressure  $p_{atm}$  with a barometer.

Tabulate the results:  $T$  ( $^\circ C$ ),  $1/T$  ( $K^{-1}$ ),  $p_1$  (mbar),  $p_2$ (mbar),  $p_{vap}$  (mbar),  $\ln p$

### 5. APPARATUS

- isoteniscope
- thermostat
- ballast volume
- Mercury manometer
- vacuum pump

- thermometer

## 6. CALCULATION

From the slope of the line in graph calculate:  $\Delta H = - \operatorname{tg} \alpha \cdot R$

## 7. ACCURACY

$$\frac{\Delta(\Delta H)}{\Delta H} =$$

## 8. RESULTS

$$\Delta H =$$

**Experiment no. 4****BINARY PHASE DIAGRAM****1. PURPOSE**

To discuss distillation we can construct a liquid/vapour temperature-composition (T-x) phase diagram for a binary mixture of water and sample, in which the boundaries show the compositions of the phases that are in equilibrium at various temperatures.

**2. THEORY**

Binary mixtures of two volatile liquids exhibit a range of boiling behaviour from ideal, with a simple continuous change in boiling point with composition, to non ideal, showing the presence of an azeotrope and either a maximum or minimum boiling point. In this experiment, the properties of a binary mixture will be investigated by studying the change in boiling point with composition.

For ideal mixtures of liquids, the composition of the vapour phase is always richer in the component with the higher vapour pressure. According to Raoult's Law, the vapour pressure of component A is given by

$$P_A = x_A P_{A^*} \quad \text{and} \quad P_B = x_B P_{B^*} \quad (1)$$

where  $x_A$  ( $x_B$ ) is the mole fraction of A (B) in solution and  $P_{A^*}$  ( $P_{B^*}$ ) is the vapour pressure of pure A (B)

$$x_A + x_B = 1 \quad \text{and total pressure equals} \quad P = P_A + P_B,$$

$$P = P_{B^*} + x_A (P_{A^*} - P_{B^*}) = P_{A^*} + x_B (P_{B^*} - P_{A^*}) \quad (2)$$

Composition of the vapour which is in equilibrium with the solution does not equal the composition of solution:

$$x_{A'} / x_{B'} = x_A P_{A^*} / x_B P_{B^*} \quad (3)$$

where  $x_{A'}$  ( $x_{B'}$ ) is the mole fraction of A (B) in vapour. From eq.:

$$x_A = x_{A'} P_{B^*} / (x_{A'} P_{B^*} + x_{B'} P_{A^*}) \quad (4)$$

and from equations (4) and (2) we get:

$$P = P_{B^*} P_{A^*} / [P_{A^*} + x_{A'} (P_{B^*} - P_{A^*})] \tag{5}$$

Equations can be used for the construction of vapour pressure diagrams (Fig.1). With the distillation at constant pressure, we can determinate the boiling points for different compositions in the solution and construct the phase temperature – composition diagrams (Fig.2).

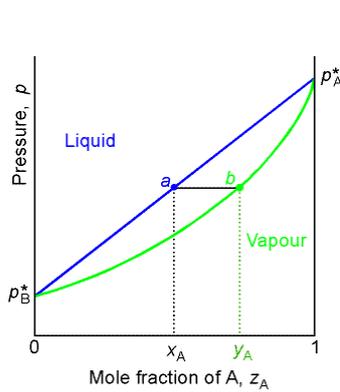


Fig. 1

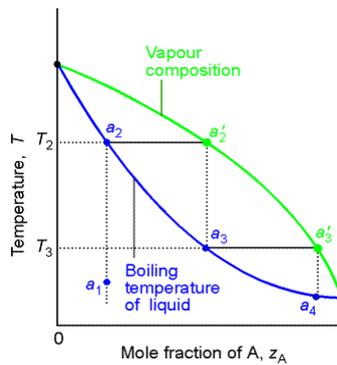


Fig.2

Actual vapour pressures can be greater or less than those predicted by Raoult's Law, indicating negative and positive deviations from ideality. In some cases, the deviations are large enough to produce maxima or minima in the boiling point and vapour pressure curves. At the maximum (Fig.3) or minimum (Fig.4), the compositions of the liquid and vapour phases are the same, but the system is not a pure substance. This results in an azeotrope, a mixture which boils with constant composition.

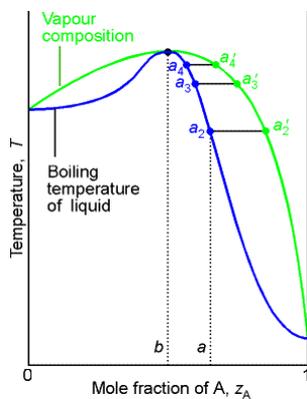


Fig. 3

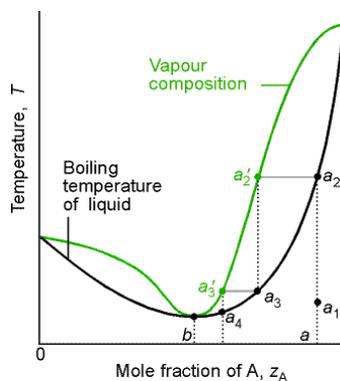


Fig.4

Simple distillation can be used to obtain a boiling point diagram as long as some method exists to analyze both the distillate and the residue. In practice, several mixtures of differing composition of the two liquids are distilled and samples of both the distillate and residue are taken. The temperature (boiling point) of each distillation is recorded and the composition of both the distillate and residue is determined. The analysis method should provide a measurement which changes significantly and continuously over the entire range of concentration, from one pure liquid to the other pure liquid. In many cases, the refractive index provides a suitable measure of concentration. A calibration curve must be obtained using known data of mixtures.

### 3. PROCEDURE

Use the boiling tube device with reflux condenser. Measure the boiling point of pure component which is water. Take a small sample (app. 3 ml) of a distillate through the condenser and a small sample of distillate residue from a round bottom flask. Put the samples into test tubes and close them with stoppers. Add 5 ml of a sample and boil the mixture again. Note the boiling point of mixture and collect the sample of distillate and the residue. Repeat the process until 25 ml of a sample is added.

Repeat all the procedure from the beginning with a sample and add water as a second component.

Measure the refractive index of each sample and draw a calibration curve of refractive index against mole fraction from the already measured data.

### 4. APPARATUS

- boiling tube device
- test tubes
- pipette
- refractometer

## 5. DATA

Tabulate the results of boiling points against refractive index. Construct a plot of temperature versus mole fraction.

## 6. RESULTS

Present a phase temperature – composition diagram.

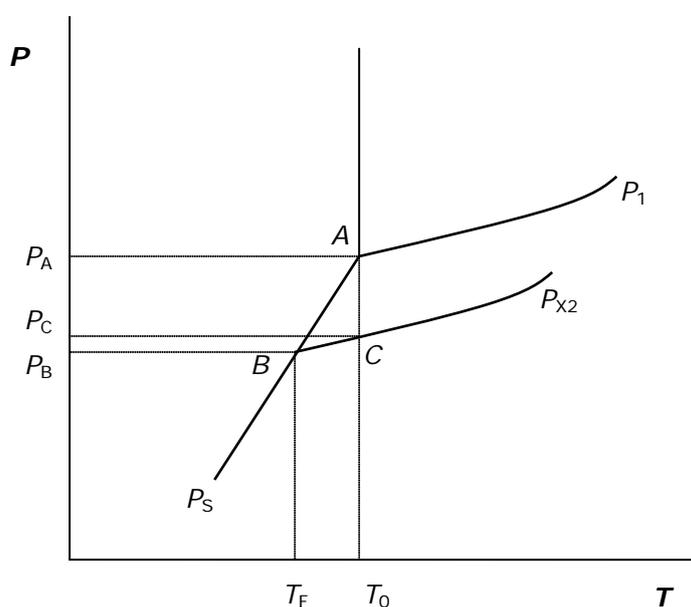
## Experiment no. 5

## CRYOSCOPIC METHOD

## 1. PURPOSE

In this experiment we determine the molar mass of a sample from depression of the freezing point.

## 2. THEORY



The simple phase diagram for solvent and solute shows: the curve  $P_1$  shows the dependence of vapour pressure for pure solvent at equilibrium against temperature and the curve  $P_S$  shows the dependence of vapour pressure of solid solvent (sublimation pressure) against temperature. The curve  $P_{X_2}$  shows the dependence of vapour pressure of solvent with the  $x_2$  fraction amount of solute against temperature.  $T_0$  is freezing point of pure solvent with the vapour pressure  $P_A$  and  $T_F$  is the freezing point of solution with the vapour pressure  $P_B$ .

The dependence of vapour pressure versus shown temperature by curves  $P_S$  and  $P_{X_2}$  is obeying the Clausius – Clapeyron equation. In this case we assume that a vapour has a property of ideal gas, the molar volume of condensed phase is negligible in comparison with the molar volume of vapour and the enthalpy of phase transformation is independent on temperature.

For points A and B we obtain:

$$\ln \frac{P_A}{P_B} = \frac{\Delta H_{sub}}{R} \left( \frac{1}{T_z} - \frac{1}{T_o} \right), \quad (1)$$

and for points C and B:

$$\ln \frac{P_C}{P_B} = \frac{\Delta H_{izp}}{R} \left( \frac{1}{T_z} - \frac{1}{T_o} \right) \quad (2)$$

where  $\Delta H_{sub}$  is the sublimation enthalpy and  $\Delta H_{vap}$  is the enthalpy of vaporization for one mole of solvent.

For vapour pressure  $P_C$  we use Rault' law:  $P_C = x_1 P_A = (1 - x_2) P_2$ , where  $x_2$  is the mole fraction of solute:

$$\ln \frac{P_A}{P_B} = \frac{\Delta H_{sub}}{R} \left( \frac{1}{T_z} - \frac{1}{T_o} \right) \quad (3)$$

From equations (1) and (3) we obtain:

$$-\ln(1 - x_2) = \frac{\Delta H_{sub} - \Delta H_{izp}}{R} \left( \frac{1}{T_z} - \frac{1}{T_o} \right) \quad (4)$$

Links are:

$\Delta H_{tal} = \Delta H_{sub} - \Delta H_{izp}$  and  $\Delta T = T_o - T_z$ , where  $\Delta T$  is the freezing point depression and  $\Delta H_{fus}$  is the enthalpy of fusion of the solvent. The equation is usually simplified by various approximations:

$$\ln(1 - x_2) \equiv -x_2$$

$$T_o \cdot T_z \approx T_o^2$$

$$\text{So we obtain: } x_2 = \frac{\Delta H_{tal}}{2T_o} \Delta T \quad (5)$$

At cryoscopic measurements we obtain the concentration of solute with the molality  $m$ :

$$x_2 = \frac{m M_1}{m M_1 + 1} \quad (6)$$

At low concentrations  $m M_1$  is much lower than 1, so, we can negligible this product and obtain

$$m = \frac{\Delta H_{fus}}{RT_o^2 M_1} \Delta T, \quad (7)$$

$$\Delta T = K_k \cdot m, \quad K_k = \frac{RT_o^2 M_1}{\Delta H_{fus}}, \quad (8)$$

$K_k$  is a cryoscopic constant and depends on the nature of solvent.

In this exercise we will use eq.:

$$m = \frac{m_2}{M_2 \cdot m_1}, \quad (9)$$

and

$$M_2 = \frac{m_2 \cdot K_k}{m_1 \cdot \Delta T} \quad (10)$$

### 3. PROCEDURE

Fill the Dewar flask with several pieces of ice mixed with one fourth of kitchen salt. Put the 10 ml of distilled water into the tube. Inside the tube there must also be a stirrer and the sensor for measuring the temperature. Stir the solution uniformly and continuously. Observe the temperature every 30 minutes until the value is constant. Remove the freezing tube from the Dewar flask and melt the ice in hot water. Then add 1,0000 gram of a sample salt into the tube and after all the sample is melt, repeat the experiment with the solution.

### 4. APPARATUS

- tube, thermometer
- stirrer
- Dewar flask
- pipette

## 5. DATA

Tabulate the results  $T$  (temperature) versus  $t$  (time).

## 6. CALCULATION

Draw a graph of temperature against time. Find the  $\Delta T$ . From data calculate the value of  $M_2$ .

$K_k = 1,860 \text{ K mol}^{-1} \text{ kg}$  is the cryoscopic constant for water.

## 7. ACCURACY

$$\frac{\Delta M_2}{M_2} = \frac{\Delta T}{T} + \frac{\Delta m_2}{m_2} + \frac{\Delta m_1}{m_1} =$$

## 8. RESULTS

$M_2 =$

**Experiment no. 6****HETEROGENEOUS EQUILIBRIA****1. PURPOSE**

In this experiment we intend to investigate the distribution of  $\text{CH}_3\text{COOH}$  between water and buthanol.

**2. THEORY**

The equilibrium distribution is reached, when the chemical potential is equal in all phases, at constant pressure and temperature. For distribution of two phases we obtain:

$$\mu_i' = \mu_i'' \quad (1)$$

where  $\mu_i'$  and  $\mu_i''$  are chemical potentials for the corresponded phase. The dependence between concentration  $c^0$ , chemical potential and activity coefficient  $y$ , is:

$$\mu_i = \mu_i^0 + RT \ln \frac{c_i}{c^0} y. \quad (2)$$

$\mu_i^0$  is a constant that depend on temperature and pressure. Thus from eq. (1) and (2),

$$\frac{c_i'}{c_i''} = \left( \frac{f_i''}{f_i'} \right) \exp \left( \frac{\mu_i^{\circ''} - \mu_i^{\circ'}}{RT} \right).$$

For diluted solutions, the ratio of activity coefficients is independent on concentration, so we can obtain:  $\frac{c_i'}{c_i''} = K_i$ , where  $K_i$  is a distribution coefficient with a constant value at lower concentrations, up to 0.1 M.

**3. PROCEDURE**

Put a 60 ml of 2M  $\text{CH}_3\text{COOH}$  and 40 ml of buthanol into the Erlenmeyer flask (basic cell) with a graduated cylinder. Stir the flask for 10 minutes and then let the phases to separate.

With a 25 ml bulb pipette deliver the upper alcoholic layer into the pure Erlenmeyer flask with a cup for the alcoholic phase. Add also 25 ml of water and some drops of phenolphthalein.

With another 25 ml bulb pipette deliver the lower water layer from the cell into the other Erlenmeyer flask and add phenolphthalein. Titrate contents of both flasks with 1M NaOH until the violet colour appears.

The distribution coefficient  $K_{\text{water/alcohol}}$  is a ratio between concentrations of acetic acid in water and the alcoholic phase. It is calculated by dividing equivalent volumes of used NaOH at both titrations.

In the mean time, add 25 ml of buthanol and 25 ml of water to the rest of the liquid in the Erlenmeyer flask (basic cell) and shake the flask for 10 minutes.

When the phases separate, deliver 25 ml of both alcoholic and water layers (add 25 ml of water to the buthanol phase), into separate flasks, add phenolphthalein into both of them and titrate with a NaOH.

Repeat the procedure with addition of 20 ml of buthanol and 30 ml of water into the rest of the basic cell.

#### 4. APPARATUS

- Erlenmeyer flask with a cup as a basic cell
- Erlenmeyer flask with a cup for an alcoholic phase
- Erlenmeyer flasks for water phase
- bulb pipettes
- burette

#### 5. DATA

Tabulate the results  $V$  (volume) for alcoholic and water phases.

#### 6. CALCULATION

Calculate the  $K_{\text{water/alcohol}}$  which is an average value of all three  $K$  values.

**7. ACCURACY**

$$\frac{\Delta K}{K} = \left| \frac{\bar{K} - K_{\max}}{\bar{K}} \right|$$

**8. RESULTS**

$$\bar{K} =$$

## Experiment no. 7

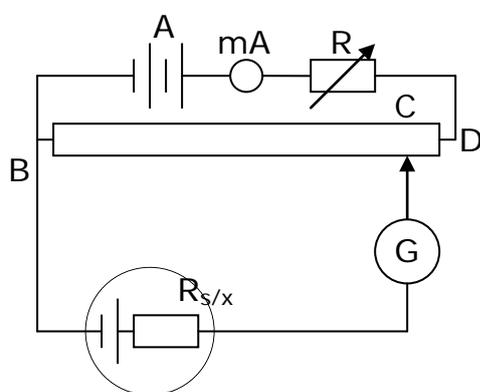
## GALVANIC CELL POTENTIAL AND pH

### 1. PURPOSE

In this experiment we prepare a galvanic cell and determine its potential with a compensation method.

### 2. THEORY

Galvanic cell potential is measured by the compensation method.



The main point of this method is that the potential of known value and with the same attitude but with the opposite direction is connected to the measured potential. The current through the galvanometer therefore equals zero. With this, the reversibility condition is satisfied and the measured potential equals the reversible potential of the cell. The simplified circuit diagram is shown in the upper figure. On the d.c. supply (A) the potentiometer is connected, presented by a resistive wire with a slide contact C. The current  $I$  through the potentiometer is defined by a potential of supply and all resistances in the circuit ABDA. The potential drop on the resistor between the points B and C equals the product of  $I$  and  $R$  in accordance to Ohm's law. By shifting the position of a contact C, we can change  $R$ , but the potential always equals  $IR$ . One side of the measured cell  $R_{s/x}$  is connected through the galvanometer to the slide contact. A slide contact is adjusted in such a position, that no current flows through the galvanometer. In that point, the potential drop on the resistor equals the reversible potential of the cell:

$$E_x^\circ = I \cdot R_x^\circ \quad (1)$$

First we connect the standard galvanic cell with a known potential  $E_S^\circ$

$$\text{and} \quad E_S^\circ = I \cdot R_S^\circ \quad (2)$$

If we set the same for the sample galvanic cell, we obtain at the end

$$E_x^\circ = E_S^\circ \cdot \frac{R_x^\circ}{R_S^\circ}, \quad R \propto l, \quad (3)$$

$$E_x^\circ = E_S^\circ \cdot \frac{l_x}{l_s} \quad (4)$$

Where  $l_s$  is the length of the calibrated wire for the standard galvanic cell and  $l_x$  is the length of the calibrated wire for the sample galvanic cell.

### 3. PROCEDURE

Connect the circuit as shown in the former figure. For determining  $R_{s/x}$ , first use the standard galvanic cell with known potential. Measure the length of  $l_s$  at different current values: 100, 120, 150, 170, 200, 220 and 250 mA, so that the current flow through the galvanostat equals zero.

Prepare a sample galvanic cell by using two beakers filled with a different sample of ionic solutions. Dip the corresponding electrode into each solution and connect them into the circuit. Connect the solutions with a salt bridge. Repeat the measurement of length of  $l_x$  at the same different current values as before, so that the current flow through the galvanostat equals zero.

### pH MEASUREMENTS

pH is defined by:

$$pH = -\log [H^+]_{aktiv} \quad (5)$$

In the system:

Saturated calomel electrode    |    Sample solution    |    Glass electrode

we can obtain the potential of a cell. For the glass electrode potential we get

$$E_{St} = E_{St}^{\circ} + \frac{RT}{F} \ln [H^+]_{aktiv} \quad (6)$$

where  $E_{St}^{\circ}$  is the standard potential value. Since the potential value of saturated calomel electrode is constant, we can obtain:

$$E = E_{St}^{\circ} + \frac{RT}{F} \ln a_{H^+} - E_{NKE} + E_{dif} \quad (7)$$

$E_{dif}$  is the diffusion potential, which appears on the interface of both liquid phases. The pH measurement is performed by using the pH meter which has been calibrated with a buffer solution.

Measure the pH of a sample.

#### 4. APPARATUS

- d.c. supply (a battery)
- mA meter
- resistor
- calibrating wire
- galvanometer
- standard cell
- bakers
- electrodes
- salt bridge
- pH meter

**5. DATA**

Tabulate the results  $I_s$  and  $I_x$  at different current values. Measure the pH for a given solution.

**6. CALCULATION**

$$E_x^\circ = E_S^\circ \cdot \frac{I_x^\circ}{I_S^\circ}$$

$$\bar{E}_x^\circ =$$

**7. ACCURACY**

$$\frac{\Delta E_x^\circ}{E_x^\circ} = \frac{\Delta E_S^\circ}{\underbrace{E_S^\circ}_{k_{st}=0}} + \frac{\Delta I_x^\circ}{I_x^\circ} + \frac{\Delta I_S^\circ}{I_S^\circ}$$

**8. RESULTS**

$$\bar{E}_x^\circ =$$

$$pH =$$

**Experiment no. 8****TRANSPORT NUMBER****1. PURPOSE**

At this exercise the transport number of Hydrogen ion is measured by a moving boundary method.

**2. THEORY**

The transport number  $t_{\pm}$  is defined as the fraction of total current carried by the ions of a specified type. For a solution of two kinds of ions, the transport numbers are:

$$t_{\pm} = \frac{I_{\pm}}{I} \quad (1)$$

where  $I_{\pm}$  is the current carried by the cation or anion, and  $I$  is the total current through the solution. It follows as the total current is the sum of the cation and anion currents, it follows:

$$t_{+} + t_{-} = 1 \quad (2)$$

The limiting transport number  $t_{\pm}^{\circ}$  is defined in the same way but for the limit of zero concentration of the electrolyte solution, so we can avoid the problem of ionic interactions. The current that can be ascribed to each type of ion is related to the mobility of the ion  $u_{+}$  and  $u_{-}$ , hence the relation between transport number and mobilities:

$$t_{\pm}^{\circ} = \frac{Z_{\pm} \nu_{\pm} u_{\pm}}{Z_{+} \nu_{+} u_{+} + Z_{-} \nu_{-} u_{-}} \quad (3)$$

$$\text{Since } Z_{+} \nu_{+} = Z_{-} \nu_{-} \quad (4)$$

, This equation simplifies for all ionic species to:

$$t_{\pm}^{\circ} = \frac{u_{\pm}}{u_{+} + u_{-}} \quad (5)$$

Moreover, the ionic conductivities are related to the mobilities, so it follows:

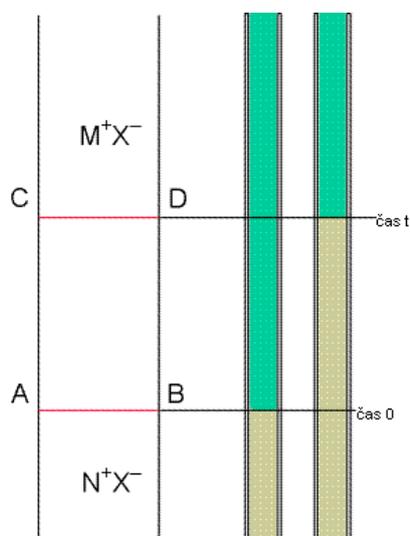
$$t_{\pm}^{\circ} = \frac{\nu_{\pm} \lambda_{\pm}}{\nu_{+} \lambda_{+} + \nu_{-} \lambda_{-}} = \frac{\nu_{\pm} \lambda_{\pm}}{\Lambda_m^{\circ}} \quad (6)$$

And hence, for each type of ion the relation exists:

$$\nu_{\pm} \lambda_{\pm} = t_{\pm}^{\circ} \Lambda_m^{\circ} \quad (7)$$

Consequently, because there are independent ways of measuring transport numbers of ion, we can determine the individual ionic conductivities and ionic mobilities.

### Moving boundary method



MX is the salt of interest and is called leading solution, and NX a salt giving a denser solution which is called an indicator solution. There is a sharp boundary between the two solutions. After the cell is connected to a d.c. potential, the anode begins to solute leading to the formation of  $N^+X^-$ . All the M ions in the volume between AB and CD must have passed through CD if the boundary moves from AB to CD. In the volume ABCD the solution  $M^+X^-$  is

substituted by  $N^+X^-$ . The transport number is

therefore:

$$t_{+} = \frac{c V F}{I t} \quad (8)$$

and the mobility:

$$u_{+} = \frac{\kappa V}{I t} \quad (9)$$

### 3. PROCEDURE

The moving boundary tube is sealed by a Cd electrode at the bottom and by an Ag/AgCl electrode at the top. Prepare 0.1 M solution of HCl and add the indicator. Put the solution

into the tube. Connect the electrodes with a power supply giving constant current of 10 mA. Record the times taken for boundary to move through successive volumes of 0.5 ml.

#### 4. APPARATUS

- moving boundary tube
- power supply
- milliamperemeter
- thermostat
- watch

#### 5. DATA

Tabulate the results  $V$  (volume) against  $t$  (time).

$$\chi_{(25^{\circ}\text{C})} = 3,913 \cdot 10^{-2} \text{ cm}^{-1}\Omega^{-1}$$

$$I = (10.0 \pm 0.1) \cdot 10^{-3} \text{ A}$$

#### 6. CALCULATION

Draw a graph of volume versus time. Find the slope  $\frac{\tilde{V}}{t}$ .

Calculate  $t_+$  and  $u_+$ .

#### 7. ACCURACY

$$\frac{\Delta t_+}{t_+} = \frac{\Delta c_1}{c_1} + \frac{\Delta\left(\frac{V}{t}\right)}{\frac{V}{t}} + \frac{\Delta I}{I} =$$

$$\frac{\Delta u_+}{u_+} = \frac{\Delta \chi}{\chi} + \frac{\Delta \left( \frac{V}{t} \right)}{\frac{V}{t}} + \frac{\Delta I}{I} =$$

## 8. RESULTS

$$t_+ =$$

$$u_+ =$$

## Experiment no.11

**CONDUCTANCE OF STRONG ELECTROLYTES****1. PURPOSE**

In this exercise the molar conductivity is measured by showing its variation by concentration.

**2. THEORY**

The resistance of a sample increases with its length  $l$  and decreases with its cross-sectional area  $S$ . We therefore write:

$$R = \rho \frac{l}{S}, \rho \text{ is resistivity.} \quad (1)$$

Conductance is the inverse of resistance:

$$\frac{1}{R} = \frac{S}{\rho \cdot l} = \chi \frac{S}{l}, \chi \text{ is conductivity} \quad (2)$$

$\kappa$  in electrolytes depends on the concentration and increases with the increasing concentration. The conductivity of a solution depends on the number of ion present and therefore we introduce the molar conductivity  $\lambda$  :

$$\lambda = \frac{\chi}{c}, \quad (3)$$

Molar conductivity of a simple electrolyte ( $z_+ = z_- = 1, c_+ = c_- = c$ ) is given by the equation:

$$\lambda = F (u_+ + u_-) = \lambda_+ + \lambda_- \quad (4)$$

and is a sum of ionic conductivities  $\lambda_j$ , which can be determinate trough transport numbers:

$$t_+ = \frac{u_+}{u_+ + u_-} = \frac{\lambda_+}{\lambda} = 1 - t_- \quad (5)$$

Molar conductivity varies for strong electrolytes linearly with the square root of the concentration:

$$\lambda = \lambda^\circ - A \sqrt{c}, \quad (6)$$

$\lambda^\circ$  is the limiting molar conductivity, the molar conductivity in the limit of zero concentration,  $c = 0$ , (when the ions are effectively far apart and do not interact with each other).

$A$  is a constant, and depends on sort the of ions, valence number, dielectric constant, temperature, viscosity, etc.

### 3. PROCEDURE

Check with an independent thermometer that the water is 25°C and measure its temperature accurately. Before each resistance measurement, wash the conductivity probe with a little of the sample solution. Rinse the electrode in a similar manner. Allow the samples at least 15 minutes to attain the thermal equilibrium before taking any readings. First measure the resistance of 0.02 M KCl. With a 100 ml bulb pipette deliver the 0.08 M sample into the 200 ml volumetric flask and dilute it to the mark. Prepare and measure the resistance for the concentrations 0.08 M, 0.04 M, 0.02 M, 0.01 M and 0.005 M!

### 4. APPARATUS

- conductometer
- Wheatson bridge
- pipettes, volumetric flasks.

### 5. DATA

Tabulate the results  $R$  against  $c$ .

### 6. CALCULATION

$$\chi_{0,02M_{KCl}} = 2,768 \cdot 10^{-3} \Omega^{-1} cm^{-1}$$

$$\frac{1}{R} = \kappa_{KCl} \cdot \frac{S}{l}, \quad \frac{l}{S} = k_{cell}, \text{ cell constant}$$

$$\kappa = k_{cell} \cdot \frac{1}{R}$$

Tabulate calculated values for  $c$ ,  $c^{1/2}$ ,  $R$ ,  $\kappa$ ,  $\lambda$ .

Draw a graph of  $\lambda$  against  $c^{1/2}$ . Find the  $\lambda^\circ$  at  $c = 0$  and slope  $A$ .

## 7. ACCURACY

$$\frac{\lambda^\circ - \lambda'}{\lambda^\circ} =$$

$$\frac{A - A'}{A} =$$

## 8. RESULTS

$$\lambda^\circ =$$

$$A =$$

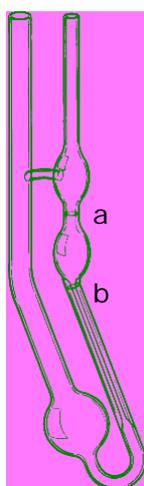
## Experiment no.12

## VISCOSITY OF LIQUIDS

## 1. PURPOSE

In this experiment we measure the viscosity of a sample with a Cannon - Fenske viscometer.

## 2. THEORY



Two types of glass capillary viscometer are in common use for the characterization of dilute solutions. The simple Ostwald or Cannon – Fenske viscometer is a constant volume device. There are calibration marks at positions a and b (see figure). The liquid flows through the marked volume in time  $t$  through the tube with a radius  $r$ . Therefore:

$$\eta = \frac{\pi r^4 g \bar{h}}{8 V l} \rho t \quad (1)$$

where  $\bar{h}$  is a time average of height difference between the liquid area in upper and lower flask,  $g$  is a gravitational acceleration.

The Cannon – Fenske viscometer is used for the relative determination of viscosity. Therefore it is necessary, first measure the time for the flow of liquid with the known viscosity  $\eta_0$  and density  $\rho_0$ , and then for the unknown, with the density  $\rho$ .

Therefore we can obtain:

$$\eta = \eta_0 \frac{\rho \cdot t}{\rho_0 \cdot t_0} \quad (2)$$

## 3. PROCEDURE

Place the viscometer in the constant temperature bath. Rinse the viscometer with distilled water using a vacuum pump. With a pipette deliver the 10 ml of distilled water into the viscometer. Now bring the liquid level in the viscometer above upper graduation mark. This can be done by a vacuum pump. Allow the liquid to drain down the capillary tube. Start the time measurement as the meniscus passes the upper graduation mark,

and stop as the meniscus passes the lower mark. Make repeated determinations for water three to five times and the same for the sample liquid.

Leave the viscometer clean and dry at the end of the experiment.

#### 4. APPARATUS

- thermostat at 20°C
- Cannon - Fenske viscometer
- 10 ml bulb pipette

#### 5. DATA

Tabulate the results  $t$  for water and sample.

#### 6. CALCULATION

Calculate  $\eta = !$

#### 7. ACCURACY

$$\frac{\Delta\eta}{\eta} = \frac{\Delta t_o}{t_o} + \frac{\Delta t}{t} =$$

#### 8. RESULTS

$$\eta =$$

## Experiment no. 11

## SURFACE TENSION

## 1. PURPOSE

In this experiment we measure the surface tension of a sample by two methods, manometric and stalagmometric.

## 2. THEORY

Every molecule inside the liquid is attracting by a force of a neighbor molecule. These forces are strong but have a short range. The resultant of all forces deep inside the homogenous liquid equals zero. But the strong forces of inner molecules, influence the molecules on the surface of liquid, and cannot be compensate by very dilute molecules in the vapour phase. Because of that, the resultant of all forces which act on any molecule on the surface, has a direction which points to the inside of the liquid. Molecules on the surface follow this resultant and pass over from the surface to the inner of liquid all the time. Therefore the liquid occupy the smallest possible surface. The surface force between the vapor and liquid phase on the liquid surface which act rectangular on the length unit of liquid edge is called surface tension:

$$\gamma = \frac{F}{l} \quad (1)$$

The surface tension decreases with increasing temperature and reaches zero at critical temperature, when the surface disappears.

The surface tension can be measured with a:

- **Manometric method:** Through the capillary, which is connected with a manometer and immersed into the liquid, the air is pushed into the liquid. We measure the pressure which is needed for bubble formation. When the air flows thru the capillary into the liquid, the pressure in the bubble increases, its radius decreases, but the product  $r\Delta P$  remains constant. Close before the bubble detaches, the pressure in it is the largest. It equals the pressure on the outer side of bubble  $P_0 + \rho g l$  enlarged

by a  $\Delta P = \frac{2\gamma}{r}$ , so:

$$P = P_0 + \rho g l + \frac{2\gamma}{r} \quad (2)$$

where  $P_0$  is the air pressure over the liquid,  $\rho$  is the liquid density,  $l$  is the height of immersed capillary and  $r$  the inner radius of the capillary. We can avoid the determinacy of a capillary radius by the compensation method, so that we first measure the values for water and than for the sample:

$$\gamma = \gamma_0 \frac{\rho_0 \cdot h - \rho \cdot l}{\rho_0 \cdot h_0 - \rho_0 \cdot l_0} \quad (3)$$

$\gamma_0$  for water at 20°C is  $72.78 \cdot 10^{-3}$  N/m

- **Stalagmometric method:** here we measure the volume of a liquid drop. When the small drop of liquid falls through the capillary with a diameter  $2r$ , the drop weight is  $m_i \cdot g$  and equals the surface tension in the moment in which it detaches:

$$m_i g = 2 \pi r \gamma \quad (4)$$

Since only a part of a drop falls, the weight of the drop is for  $m \cdot g$  smaller than the ideal drop  $m_i \cdot g$ . The ratio  $\Phi = m/m_i$  depends on  $r/V_{drop}$ . The best results are given when  $r/V^{1/3}$  lies between 0.7 and 0.9. When  $m_i$  in the equation (4) is changed by  $m$ , we obtain:

$$\gamma = \frac{m g}{2 \pi r \Phi} \quad (5)$$

Instead of measuring volume, the number of drops  $n$  in the defined volume  $V$  is counted:

$$V = n \cdot v. \quad (6)$$

With the comparative method using a calibrating liquid (water) we get the equation:

$$\frac{\gamma}{\gamma_0} = \frac{n_0 \cdot \rho}{n \cdot \rho_0} \quad (7)$$

### 3. PROCEDURE

#### Manometric method

The apparatus contains the cylindrical vessel filled with water, a small tube with a capillary and the U – manometer with a coloured liquid. Fill the small tube with water and note the height  $h_0$  on the capillary. Open the tap on the bottom of the cylindrical

vessel. The outflowing liquid creates an underpressure. Read  $h_0$  on the manometer when the outgoing bubble flow into the liquid is uniform.

Repeat the procedure with a sample to determinate  $l$  and  $h$ .

### Stalagmometric method

Suck the water into the stalagmometer. Regulate the velocity of outflowing liquid so, that a drop can only detach by its own weight. Count the number of drops in which all the marked volume for water decay. Repeat the procedure with the sample.

## 4. APPARATUS

- U - manometer
- Stalagmometer

## 5. DATA

Tabulate the results  $l_0$ ,  $l$ ,  $h_0$ ,  $h$ ,  $n$  and  $n_0$  for water and sample.

## 6. CALCULATION

Calculate  $\gamma$  for both of method.

## 7. ACCURACY

- Manometric method

$$\frac{\Delta\gamma}{\gamma} = \frac{\Delta l_0}{l_0} + \frac{\Delta l}{l} + \frac{\Delta h_0}{h_0} + \frac{\Delta h}{h} =$$

- Stalagmometric method

$$\frac{\Delta\gamma}{\gamma} = \frac{\Delta n_0}{n_0} + \frac{\Delta n}{n} =$$

## 8. RESULTS

- Manometric method,  $\gamma =$
- Stalagmometric method,  $\gamma =$

**Experiment no. 12****ADSORPTION****1. PURPOSE**

In this experiment we determine for the system acetic acid – charcoal the adsorption isotherm and constants **a** and **b** for a modified Freundlich equation.

**2. THEORY**

Adsorption is the process whereby atoms or molecules of adsorbate become attached to a surface. Adsorption may in principle occur at all surfaces, but its magnitude is particularly noticeable when a porous solid such as charcoal, which has a high surface area, is in contact with gases or liquids. At the interphase between the gas and a solid state, the concentration of gas molecules at the solid surface is always higher than the concentration of molecules inside the gas – that phenomenon is called adsorption. The forces which bind the foreign particles to the surface may be either physical or chemical in nature, and the adsorption processes are sometimes referred to as physisorption (weak Van der Waals forces) and chemisorption (strong valence forces). Adsorption increases with the active area of adsorbent and with the attraction forces. The gas adsorption is a spontaneous process:  $\Delta G < 0$  and  $\Delta S < 0$ .

From the equation:

$$\Delta H = \Delta G + T \Delta S \quad (1)$$

We can obtain by using the former criteria ( $\Delta G < 0$  and  $\Delta S < 0$ ), that  $\Delta H < 0$ .

The amount of adsorbed substance decreases with temperature. The adsorption and pressure dependence at constant temperature is obtained by:

$$\frac{x}{m} = a \cdot P^b, \text{ Freundlich empirical equation} \quad (2)$$

$x/m$  is the amount of adsorbed gas per mass unit of adsorbent,  $a$  and  $b$  are empirical constants, and  $P$  is pressure.

There are many adsorption theories, which depend on models. The Langmuir theory includes a Langmuir adsorption isotherm:

$$\frac{x}{m} = k \cdot \Theta = \frac{k \cdot P}{u+P}, \quad (3)$$

$\Theta$  is the surface area of the adsorbent, covered by gas molecules,

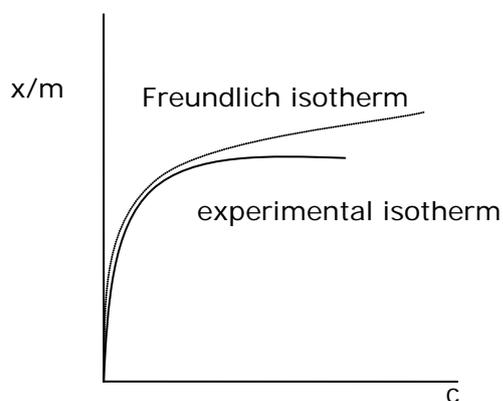
$k$  is a temperature dependent constant.

Adsorption increases also with the increasing concentration of solution. In many cases the experimental results matches the Freundlich empirical equation:

$$\frac{x}{m} = a \cdot c^b, \quad (4)$$

$$\log \frac{x}{m} = \log a + b \log c \quad (5)$$

where  $x$  is the amount of adsorbed substance,  $m$  is the mass of adsorbent;  $c$  is the concentration of solution at equilibrium. At high concentrations the adsorbent becomes saturated, since the Freundlich equation demands unlimited increasing of adsorbed substance with increasing temperature. At lower concentrations the experimental isotherm is linear.



### 3. PROCEDURE

Put 3 g of charcoal into the neck of six dry Erlenmeyer flasks and add 100 ml of prepared acetic acid solutions with concentrations:

0,4 M            0,2 M            0,1 M            0,05 M            0,025 M            0,0125 M

Shake solutions for 1,5 hours. In the time between define the exact concentrations of solutions of  $\text{CH}_3\text{COOH}$  with 0,1 M and 0,0125 M KOH by titration. As indicator use Phenolphthalein. Into the Erlenmeyer flask put:

5 ml 0,4 M                      10 ml 0,2 M                      20 ml 0,1 M  $\text{CH}_3\text{COOH}$

5 ml 0,05 M                      10 ml 0,025 M                      20 ml 0,0125 M  $\text{CH}_3\text{COOH}$

Titrate the upper solutions with 0,1 M KOH and the lower solutions with 0,0125 M KOH.

After the flasks were shaken for 1,5 hours, filtrate the solutions into dry flasks. Reject the first 10 ml of solution. Put the same amount of acid into the flasks as you did before. By titration define the concentrations of solutions.

#### 4. APPARATUS

- burettes
- Erlenmeyer flasks
- pipettes
- funnels

#### 5. DATA

Tabulate the volumes of KOH used by titration with acetic acid before and after the adsorption.

#### 6. CALCULATION

$$x = C_0 - C$$

Calculate the concentrations in mmol/100ml of solution

Tabulate the results:

$c_0$ (m mol/100 ml)	$\log c_0$	$c$ (m mol/100 ml)	$\log c$	$x$	$x/m$	$\log (x/m)$
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From a graph define:

$\log a =$  ,  $a =$

$b =$

### 7. ACCURACCY

$$\frac{\Delta a}{a} =$$

$$\frac{\Delta b}{b} =$$

### 8. RESULTS

$a =$

$b =$

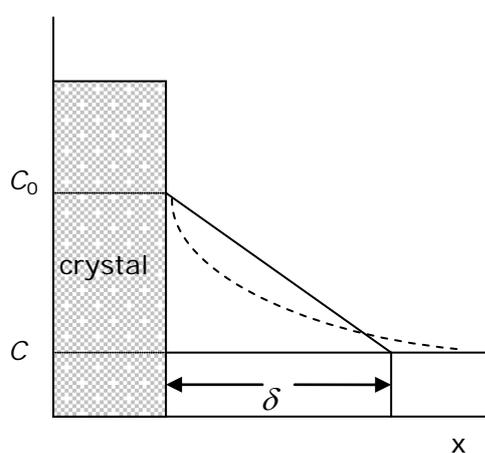
## Experiment no.13

## KINETICS OF A SALT DISSOLUTION

## 1. PURPOSE

In this experiment we study the physical process - diffusion. Gypsum is a relatively weak soluble salt, so we can easily use measurements of conductivity to study changes in concentration of salt solutions.

## 2. THEORY



When a crystal is dissolving, a layer of saturated solution lies on its surface. From this layer the dissolving salt diffuses into the solution which is not yet saturated. Under normal condition of stirring, the diffusion process appears in the thin diffusion layer with the thickness  $\delta$  (0.1 – 0.01 mm) at the crystal surface. In time  $dt$ , only so much salt can dissolve as it can diffuse into the solution. By Fick's first law of diffusion, we obtain:

$$dn = D S \frac{dc}{dx} dt, \quad (1)$$

where  $D$  is the diffusion constant,  $dc/dx$  is the concentration gradient,  $S$  is the crystal surface area,  $t$  is the time and  $n$  the amount of substance that diffuses into the solution. In the upper figure the line represents the approximate, and the dashed line the real concentration change.

Concentration gradient is:

$$-\frac{dc}{dx} = \frac{c_0 - c}{\delta}. \quad (2)$$

If we consider that  $dc = dn/V$ , the diffusion equation becomes:

$$\frac{dc}{dt} = \frac{DS}{\delta V} (c_0 - c) = k (c_0 - c), \quad k = \frac{DS}{\delta V}, \quad (3)$$

With integration we obtain:

$$\ln \frac{c_0}{c_0 - c} = k t \quad (4)$$

We use measurements of conductivity to study change in concentration of salt solution. Conductivity of diluted solution is proportional to the concentration, so we obtain:

$$\ln \frac{\chi_k}{\chi_k - \chi} = k t, \quad (5)$$

where  $\chi$  is the conductivity in time  $t$  and  $\chi_k$  in time  $t = \infty$ , at the saturated solution. Conductivity can be measured indirectly through resistance, so:

$$\ln \frac{R}{R - R_k} = k t \quad (6)$$

where  $R$  is the resistance of solution in time  $t$  and  $R_k$  in time  $t = \infty$ .

### 3. PROCEDURE

Because it takes many hours, before the solution become saturated, it is recommended, that you first measure the  $R_k$  value of the already prepared saturated solution. After that, rinse the baker, electrode and crystal with distilled water. Put gypsum, stirrer, electrode and water into the baker. Note the time ( $t = 0$ ) at which you pour the water (cca. 600 ml) upon the crystal. Measure the resistance of the solution at exactly thirty – seconds intervals, and then increase the interval from 1.5 to 10 minutes.

### 4. APARATUS

- conductometer
- conductometric cell (beaker with the electrode)
- stirrer
- a gypsum crystal

## 5. DATA

Tabulate the resistance  $R$ ,  $t$ ,  $R/R - R_k$  and  $\ln R/R - R_k$

## 6. CALCULATION

Calculate  $\ln R/R - R_k$ .

Draw a graph of  $\ln R/R - R_k$  against time. Find the slope  $k$ .

## 7. ACCURACY

$$\frac{\Delta k}{k} =$$

## 8. RESULTS

$k =$

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