

THERMODYNAMIC

Experiment No: 1

Name of the Experiment: Enthalpy of Vaporization

Purpose of the Experiment: The purpose of the experiment is to determine the vaporization enthalpy of diethyl ether, which can easily vaporize at very low temperatures by calorimetric method.

Chemicals:

- Diethyl ether

Materials:

- Calorimetry Set-up
- Dewar Flask
- Heater
- Analytical balance
- Thermometer
- Pipette filler

Experimental

In this method, highly volatile liquid is vaporized by the airflow in the calorimeter set-up and the heat which liquid absorbed from the reaction medium is calculated with the aid of calorimeter constant and measured temperature changes.

First step of the experiment is to determine the calorimeter constant. For this purpose, 100 mL of water filled into the calorimeter set-up and weighted (m_1).

The equilibrium temperature is read by a thermometer placed in the system (T_1).

Heated (to 70-80 °C) and exact temperature determined (T_2) water (30 mL) added to the calorimeter system containing 100 mL of water

After the temperature equilibrium has been established, the temperature is read by the thermometer and the calorimeter set-up is weighed.

With the help of the above data, the calorimeter constant, which is equal to the temperature required to raise the temperature of the calorimeter system by 1 °C, is calculated with using eq 1.1 and $c_{\text{water}} = 1 \text{ cal. K}^{-1} \cdot \text{g}^{-1}$.

$$C(\text{cal. K}^{-1}) = (m_2 - m_3) \cdot (T_2 - T_3) \cdot c_{\text{water}} / (T_3 - T_1) \quad (1.1)$$

Subsequently, the following operations are performed in order to determine the enthalpy of vaporization, respectively.

100 mL of water is added to the calorimeter assembly.

Add 3 mL of diethyl ether to the inner sample flask and read the equilibrium temperature (T_4).

The air is sent to the sample flask with the help of a pipette filler and the diethyl ether is completely evaporated in 2-3 minutes. Then the equilibrium temperature (T_5) of the system is recorded.

Assessment of Results

enthalpy of evaporation of diethyl ether was calculated with using determined calorimeter constant, measured temperatures and calorimeter rule as written;

$$I_{sb}(\text{cal g}^{-1}) = C(T_4 - T_5)/m = C(T_4 - T_5)/v\rho \quad (1.2)$$

m, v and ρ refer to mass, volume and density ($\rho_{\text{ether}} = 0.736 \text{ g/mL}$) of the diethyl ether, respectively.

Questions

- 1) Define the concepts of heat, temperature, work, pressure and chemical potential.
- 2) What is the calorimeter rule? How is calorimeter constant and its value according to water defined?
- 3) Define the concepts of internal energy, enthalpy and entropy.
- 4) Derive their equations $dH = \delta q + Vdp$ and $dH = Tds + Vdp$ based on the basic laws of thermodynamics
- 5) Explain the difference between the vaporization internal energy and the enthalpy of vaporization.
- 6) Derive $H = U + pV$ equality that connects enthalpy and internal energy.
- 7) What is the Trouton rule? Specify the properties of fluids deviating from the Trouton rule.
- 8) Define the concepts of boiling and evaporation. What is the difference between them?

CHEMICAL KINETICS

Experiment No: 2

Name of Experiment: Rate of chemical reaction

Objective: The determination of the reaction rate constant by examining the change of reaction rate over time.

Chemicals:

- 0,06 M saturated potassium persulfate ($K_2S_2O_8$) solution
- 0,4 M potassium iodide (KI) solution
- 0,05 M sodium thiosulfate ($Na_2S_2O_3$) solution
- 1% freshly prepared starch solution (1 g of starch in 100 mL)

Experimental Procedure

The ionic reaction between the iodide and the persulfate in the neutral medium to be examined in this experiment is given below.



20 mL of saturated persulfate solution is diluted to 100 mL. 50 mL of this diluted solution is discharged into an Erlenmeyer flask.

The same volume (50 mL) of 0.4 M KI solution is added to another Erlenmeyer flask.

Mouths of both flasks are sealed and held in a water bath set to 25°C until a temperature equilibrium is established (15-20 minutes).

Before starting the experiment, 0,05 M thiosulphate solution is diluted to 0.005 M (from 20 mL to 200 mL). The diluted solution is filled into the burette.

Then, Erlenmeyers containing 200 mL of pure water are prepared (**Why?**).

After these preparations are completed, the iodide solution is added to the persulfate solution – the solutions in the water bath are used – and the time of mixing is recorded with the stopwatch. Simultaneously, the same amount of 0.4 M KI and diluted $K_2S_2O_8$ is mixed in another flask in a separate place, and the flask is closed with a glass-lid. This solution is immersed in a water bath previously heated to 50 °C and allowed to stand at 50 °C for the duration of the experiment. This experiment should be started at the same time with the other one (**Why such an experiment is done?**).

After 5 minutes of mixing, 10 mL of sample is taken from the reaction mixture using a pipette. The solution in the pipette is poured into the flask containing 200 mL of distilled water (**Why?**).

The same procedure is repeated at previously determined time intervals.

A few drops of 1% starch solution is added to diluted solutions as an indicator and titrated with the thiosulphate solution according to the following equation.



The time interval between samples should be increased as the rate of reaction will decrease over time depending on the concentration of the substance remaining in the environment. After 1 hour, the reaction ends, ie the whole persulfate is reduced.

After these experiments are completed, the solution in the glass-lid flask is cooled. 10 mL of the sample taken from this solution is diluted and titrated with thiosulfate solution. This experiment must be done. Thus, the total amount of persulfate in the reaction is found.

Evaluation of Results

The concentration of I_2 produced in reaction (2.1) and whose molar amount equals to the molar amount of the consumed persulfate (x) can be calculated by using the following equation.

$$[I_2] = M_{(S_2O_3^{2-})} \frac{v_{(S_2O_3^{2-})}}{2.10} = \frac{0.005v}{10} = 0.0005v = x \quad (2.3)$$

During the reaction (2.1) carried out in the glass-lid flask at 50 °C, all of the persulfate ions in the mixture were consumed. Therefore, the molarity of I_2 in the 10 mL sample taken from the mixture in this flask is equal to the initial concentration of persulfate ions. When the volume of $Na_2S_2O_3$ solution used in the titration of 10 mL sample taken from the glass-lid flask where the reaction is completed is v_0 , the molarity of I_2 equal to the initial concentration of persulfate ions is calculated by using the following equation.

$$[I_2] = [S_2O_8^{2-}]_0 = 0.0005v_0 \quad (2.4)$$

The initial concentration of persulfate and the concentration of consumed persulfate in the reaction (2.1) can be determined from the titration with the thiosulfate solution. The persulfate concentration, remaining in the reaction (2.1) can be calculated by the following equation.

$$[S_2O_8^{2-}] = [S_2O_8^{2-}]_0 - [I_2] = [S_2O_8^{2-}]_0 - x = 0.0005(v_0 - v) \quad (2.5)$$

The equation of the first order reaction can be written as follows.

$$\ln([S_2O_8^{2-}]_0/[S_2O_8^{2-}]) = \ln[v_0/(v_0 - v)) = kt \quad (2.6)$$

Hence, the kinetic examination is performed using the volumes of thiosulfate solutions spent during titrations.

To obtain better graphics, it is recommended that the time intervals between the samples are as follows.

t/min	0	5	10	15	20	30	45	60	...	∞
$\Delta t/\text{min}$	0	5	5	5	5	10	15	15	...	∞
v/mL	0	-	-	-	-	-	-	-	...	v_0
$(v_0 - v)/\text{mL}$	v_0	-	-	-	-	-	-	-	...	0

Using the values in this table, $[S_2O_8]^{-2}$ -t ve $\ln ([S_2O_8^{-2}]_0/[S_2O_8]^{-2})$ -t graphs are plotted.

The rate constant for the reaction (2.1) is separately calculated via the graphical method, the differential method and the half-life method and compared with each other. Then, it is discussed why the reaction is first order.

QUESTIONS

- 1) What is the difference between chemical thermodynamics and chemical kinetics?
- 2) Explain the total conversion rate, conversion rate per unit volume, reaction rate, molar conversion rate and molar formation rate.
- 3) According to $N_2 + 3H_2 \rightarrow 2NH_3$ reaction under certain conditions, the rate of formation of ammonia from its elements was determined as $0.10 \text{ mol dm}^{-3} \text{ s}^{-1}$. **a)** Find the reaction rate. **b)** Find the rate of molar consumption of nitrogen per unit volume. **c)** Find the rate of molar consumption of hydrogen per unit volume.
- 4) Explain rate law, reaction rate constant, order of the reaction, and molecularity.
- 5) What is the difference between molecularity and order of reaction?
- 6) Which methods used to determining reaction order? Explain.
- 7) Write the rate laws, the integrated rate laws and half-lives of zero, first, second and third-order simple reactions.
- 8) Explain reaction rate and the temperature dependence of reaction rate.
- 9) For the first-order thermal decomposition of the ethylene oxide at 378.5°C , the half-life and the activation energy is given as 363 minutes and $217\,000 \text{ J mol}^{-1}$, respectively. Find the required time for the decomposition of 75% of ethylene oxide at 450°C .
- 10) Which methods used to determining rate laws of complex reactions? Explain.
- 11) Explain the factors affecting the rate of reaction.
- 12) Explain the phenomenon of catalysis.
- 13) Describe catalyst selectivity and catalyst activity.

CHEMICAL MIXTURES

Experiment No: 6

Name of Experiment: Partial Molar Volumes

Objective: The calculation of partial molar volumes of H_2O - H_2SO_4 mixtures prepared at different concentrations by measuring their densities and the determination of their deviation from the ideal state.

Chemicals: • 20%, 40%, 60% and 80% H_2SO_4 solutions

CAUTION! When preparing the aqueous acid solutions, concentrated sulfuric acid is gradually added on water by continuously stirring. **(Why?)**

Equipment

- Analytical Balance
- Thermometer
- Pycnometer

Background

There are many methods for determining the density of a liquid, however the pycnometer method will be used in this experiment. In this method, the mass of the liquid filled in the containers whose volumes were determined with high sensitivity (± 0.001 mL) is determined. The containers used for this method are called **pycnometer**.

Experimental Procedure

Firstly, we need to determine the volume of the pycnometer. Distilled water is used as a comparison liquid. The pycnometer is washed, dried and weighed. Then, pycnometer is filled with distilled water and capillary tube is placed in the mouth. After the liquids overflowing from the mouth of the capillary, the mouth of the capillary tube are carefully cleaned and the pycnometer is weighed again. The difference between the full and empty pycnometer weighing gives the mass of water in the pycnometer. The mass of water found using with the density of the water ($\rho_{\text{H}_2\text{O}} = 0.9982343 \text{ g cm}^{-3}$) and the volume of the pycnometer. When the same process is performed using 20%, 40%, 60%, 80% H_2SO_4 solutions instead of water, the liquid mass filling the pycnometer and the density of the liquid used by dividing it by the volume of the pycnometer are found. In the experiment, average densities of the liquids was determined using with two pycnometers are used.



Figure 1. Pycnometer

Evaluation of Results

By using experimental data, belirlen partial molar volumes are determined by two different methods and the results are interpreted.

The specific volume ($1/\rho = v$), which is the inverse of the average densities in the experiment, is calculated. v - $\%H_2SO_4$ graph is plotted. To find partial molar volumes, a tangent is drawn from the 50% concentration to the curve. **Partial specific volumes** (\bar{v}_1 and \bar{v}_2) are found from the points where the tangent intersects the H_2O and H_2SO_4 axes. These values are multiplied by the molar mass of water (M_1) and the molar mass of H_2SO_4 (M_2) in order to determine the partial molar volumes (\bar{V}_1 and \bar{V}_2) for 50% H_2SO_4 .

The molar volumes (V) are plotted against the molar fractions (x_2) to determine the partial molar volume of the solutions. The calculated concentrations in the experiment are used to determine the molar volume and molar fraction.

Mole fraction (x_2) molar mass and molar volumes of H_2SO_4 can be found in the following equation.

$$x_2 = \frac{m_2}{M_2} : \left(\frac{100-m_2}{M_1} + \frac{m_2}{M_2} \right) \quad (6.1)$$

$$< M > = x_1 M_1 + x_2 M_2 \quad (6.2)$$

$$V = \frac{<M>}{\rho} = \frac{(x_1 M_1 + x_2 M_2)}{\rho} \quad (6.3)$$

V - x_2 graph is drawn with the found values. In order to find the partial molar volumes of the solutions, the x_2 value corresponding to 50% H_2SO_4 is calculated. The calculated value is marked from the graph and the points where the tangent drawn from this point to the curve cut off the axes give partial molar volumes for water and 50% concentration of sulfuric acid directly.

QUESTIONS

- 1) What is the chemical mixture? Describe the differences between ideal and real mixtures.
- 2) Explain the concept of partial molar feature verbally and mathematically.
- 3) Derive the Gibbs-Duhem equation and write the Gibbs-Duhem equation for a two-component system.
- 4) Write the methods which used to determine the partial molar properties.
- 5) How do you explain the case that the partial molar volume of water in H_2O - H_2SO_4 mixture is equal to zero or has a minus sign?

MIXTURES

EXPERIMENT NO	9
EXPERIMENT NAME	Ebullioscopy
PURPOSE	The aim of this experiment is to determine the molar mass of unknown soluble substance by rising of the boiling point of the solutions.
CHEMICALS	<ul style="list-style-type: none"> • Urea • Water • Unknown Substance
MATERIALS	<ul style="list-style-type: none"> • Scale • Thermometer • Heater • Glass Flask • Dewar Flask

EXPERIMENTAL PROCEDURE

Experiment apparatus consist of heater, dewar flask and thermometer given in Figure 2. For precise temperature measurement is used with 1/10 compartment or a Beckmann thermometer. Before experiment, test tube is washed, dried and tared (m_{tare}). The test tube is filled with enough water to contact with the thermometer. The heater at the bottom of the balloon is opened at medium level and water vapor is sent to the test tube containing water.

After the temperature shown by the thermometer is fixed, boiling temperatures of water are read and recorded at least every three seconds in at least three minutes. Average value is taken as boiling temperature of water (t_o). In order to find the Ebullioscopic constant (K_k), three weights of two grams are taken first from a material (urea) known as molar mass.

2 grams of urea dissolved ($\approx 25 \text{ cm}^3$) in water and the boiling temperature of the solution with the average of the recorded temperatures (t). After that, the test tube is removed and the tap water is cooled externally for a period of time and then it is dried and weighed (m_{tot}). Urea, 2 grams is

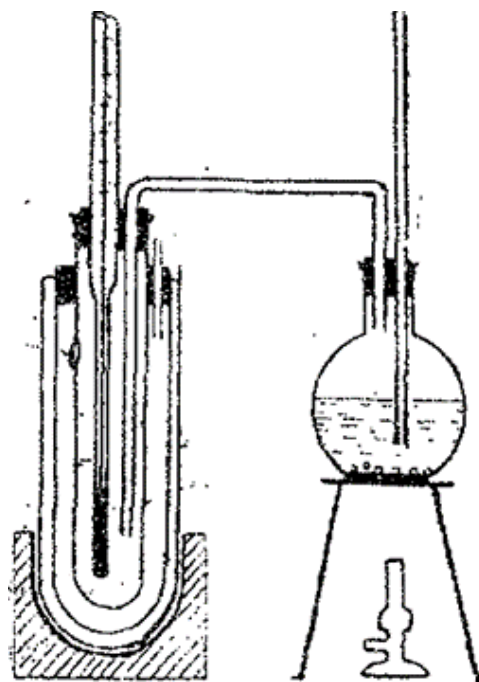


Fig. 2. Ebullioscopic diagram

added two times in succession to this solution, boiling temperature elevations of solutions are found with containing 2, 4 and 6 grams urea as above, respectively. For the molar mass unknown substance, experiments with urea are repeated exactly. Experiments are repeated for the unknown substance exactly.

Evaluation of Results

First, the ebullioscopic constant (K_b) of the solvent is determined by the following equation. The average value of this K_b constant is determined by three experiments with urea.

$$\Delta T_b = K_b \times m \quad (9.1)$$

Molalities of urea solutions,

$$m = 1000 \, n_2 / m_1 \quad (9.2)$$

$$m = 1000 \, m_2 / M_2 m_1 \quad (9.3)$$

from equation, $m_1 = m_{\text{water}}$, $m_2 = m_{\text{urea}} = 2, 4$ and 6 grams, $M_2 = M_{\text{urea}} = 60 \, \text{g mol}^{-1}$ and $m_{\text{water}} = m_{\text{tot}} - (m_{\text{tare}} + m_{\text{urea}})$ was calculated. Accordingly, for each of the three experiments is found molality values. In equation $\Delta T_b = K_b \times m$, for each experiments was calculated $\Delta T_b = (T - T_o)$ values and m values are replaced and K_b values and their average are calculated.

The K_b constant, on the other hand, can also be obtained from the temperature difference graph against the molarity and from the slope of the line passing through the origin ($\Delta T_b / m = K_b$).

The results of the experiments performed for the unknown substance of molar mass are calculated by substituting the equilibrium of 9.3 and the M_x molar mass is calculated.

The arithmetic average of the molar mass in the three experiments is taken as more accurate molar mass.

QUESTIONS

- 1) Explain the colligative properties of a solution.
- 2) What kind of substances can be used instead of urea? Give an example.
- 3) What is the van't Hoff factor and how is it determined?
- 4) Explain the methods of ebullioscopy and cryoscopy.
- 5) Is the ebullioscopic constant dependent on the type of solute? Why is that?
- 6) Derive $\Delta T_b = K_b \times m$ the equation from the thermodynamic equilibrium condition between phases.
- 7) Explain the events caused by the vapor pressure of a solution being less than the vapor pressure of

the pure solvent.

- 8) How is the vapour sent from the balloon of the experiment to heat the solution above its own temperature?
- 9) How is the freezing point drop and boiling temperature rise measured with the Beckmann thermometer? What is the difference of this thermometer from other thermometers?
- 10) Identify the osmotic event and osmotic pressure. What does reverse osmosis mean?
- 11) Identify the osmosis event and osmotic pressure. What does reverse osmosis mean?
- 12) What are the other molar mass determination methods?

ELECTROCHEMISTRY

EXPERIMENT NO : 14

EXPERIMENT NAME : Potentiometric Titration and Determination of pH by Kinhidron Electrode
Potentiometric Titration

PURPOSE : The purpose of this experiment is to determine the turning point of the reaction in the cell by measuring the electromotor force (EMF) of a galvanic cell composed of a reference and an indicator electrode.

CHEMICALS :

- Solution of solid iron (II) ammonium sulfate salt in H_2SO_4
- 0.017 M potassium bichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) solution
- Saturated KCl solution

MATERIALS :

- Potentiometer
- Reference electrode
- Indicator electrode
- Salt bridge
- Beherglas
- Buret

Information

Potentiometric titration is based on measuring the potential after each addition of the reagent. The solution to be titrated is connected to the reference electrode by means of a salt bridge. Immerse the indicator electrode into the solution and measure the electromotor force (EMF) of the solution. Since the potential of the reference electrode remains constant during the measurement, the change in EMF is only changed by the addition of the reagent. This change is due to the change in the potential of the indicator electrode. This method can be applied to any color, colorless and type solution.

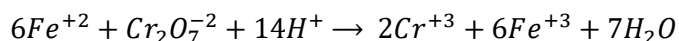
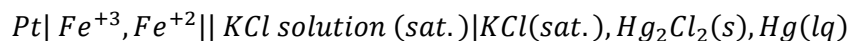
EXPERIMENTAL PROCEDURE

A 10-15 mL of acid (II) ammonium sulfate solution taken into a beherglas is diluted 1/5. The indicator electrode is immersed into the beaker and is connected to the reference electrode (Calomel Electrode) by means of a salt bridge.

The EMF of the cell is read before any reagent is added. Then add 1 mL of reagent and read the EMF by mixing the solution thoroughly. As the turning point is approached, the volume of reagent added should be reduced to 0.5 mL and the turning point should be correctly. It is important to

mix and add 1-2 minutes after each addition. The turning point is determined by the sudden increase in EMF. This process is continued until the turning point exceeds 4-5 mL.

In this experiment, a redox reaction is occurred in the solution after each addition of the reagent. This redox event continues until the turning point. Since there is no ion to be oxidized from this point, the redox event ends. The schema of the galvanic cell used and the redox reaction during the titration in this cell, respectively, are as follows.



Evaluation of Results

Three different graphs are derived from each other in order to find the turning point with the evaluation of the data obtained.

- $E(\text{potential}) - v(\text{added reactive volume})$
- $\Delta E / \Delta v (\text{first differential}) - v_{\text{average}}$
- $\Delta^2 E / \Delta v^2 (\text{second differential}) - v_{\text{average}}$

The sensitivity of the method depends on the exact location of the turning point.

The slope of the titration curve is greatest at the equivalence point. If the slope is small, the equivalence point cannot be determined exactly (a). In such cases, the slope of the curve is plotted against the average of the added reagent volume (b). This curve is called **the first derivative curve**. The peak of this curve is the equivalence point. The presence of both turning points is based on the symmetrical curves around the equivalence point. However, this may not always be seen. In this case, the second derivative of the change of the potential with the volume is taken. This is called **the second derivative curve**. The point where the $\Delta^2 E / \Delta v^2 - v_{\text{ort}}$ line drawn from here intersects the horizontal axis is the point of equivalence (c).

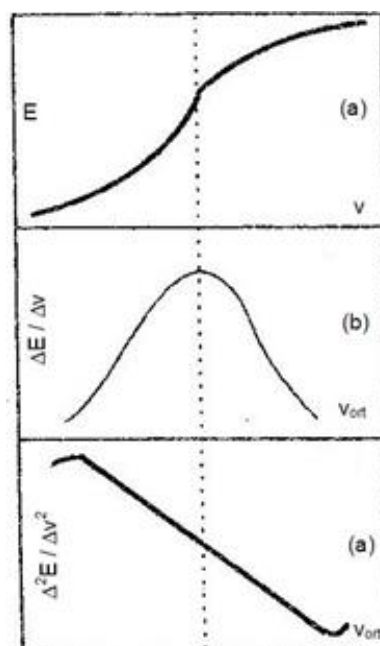


Fig. 5. First and second derivative curves obtained from the potential-volume curve

Drawing of the second derivative curve from the first derivative curve

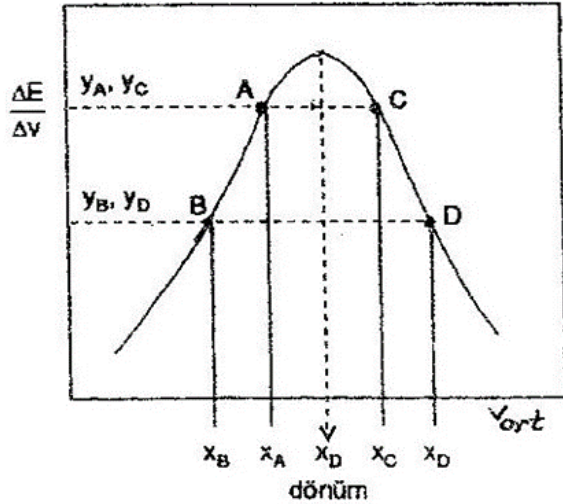


Fig. 6. First derivative curve

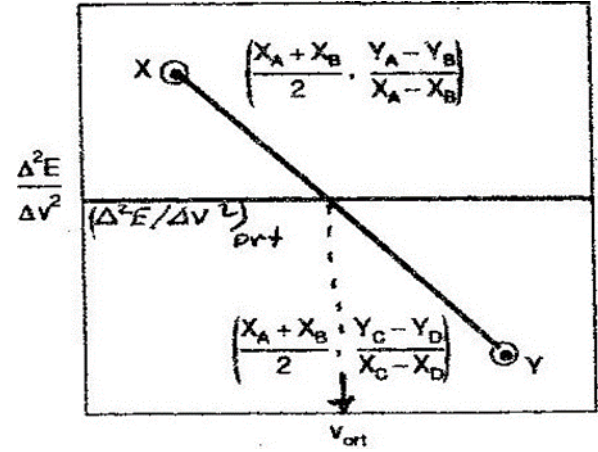


Fig. 7. Second derivative curve

Two points are selected from the left and right side of the curve as shown in Fig. 6 (A, B, C, D)

Using the points that are read from the chart of these points $\Delta^2 E / \Delta v^2$ ve v_{average} respectively.

$$\Delta^2 E / \Delta v^2 = (Y_A - Y_B) / (X_A - X_B) \text{ ve } \Delta^2 E / \Delta v^2 = (Y_C - Y_D) / (X_C - X_D),$$

$$V_{\text{ort}} = (X_A + X_B) / 2 \quad \text{and} \quad V_{\text{ort}} = (X_C + X_D) / 2$$

are calculated from equations. The X and Y points found using these calculated points are marked as shown in Fig. 7, the point where the line joining these points crosses the horizontal axis is found.

Determination of pH by Kinhidron Electrode

PURPOSE :

The electrode potential is the determination of the pH of the solution by the quinhydrone electrode, which is dependent on the hydrogen ion activity.

CHEMICALS :

Saturated solution of quinhydrone in water

MATERIALS :

- Potentiometer
- Reference electrode
- Indicator electrode
- Salt bridge
- Thermometer
- Buret

EXPERIMENTAL PROCEDURE

The saturated solution of the quinhydrone is prepared and the Pt electrode immersed into this solution and combined with the calomel electrode with a salt bridge.

The EMF of the cell is read from the potentiometer. Also, read the temperature by immersing a thermometer into the solution.

An equimolar amount of quinone (Q) and quinhydrone (QH₂) is released by dissolution of the quinhydrone in water. This reaction is a reversible redox reaction.

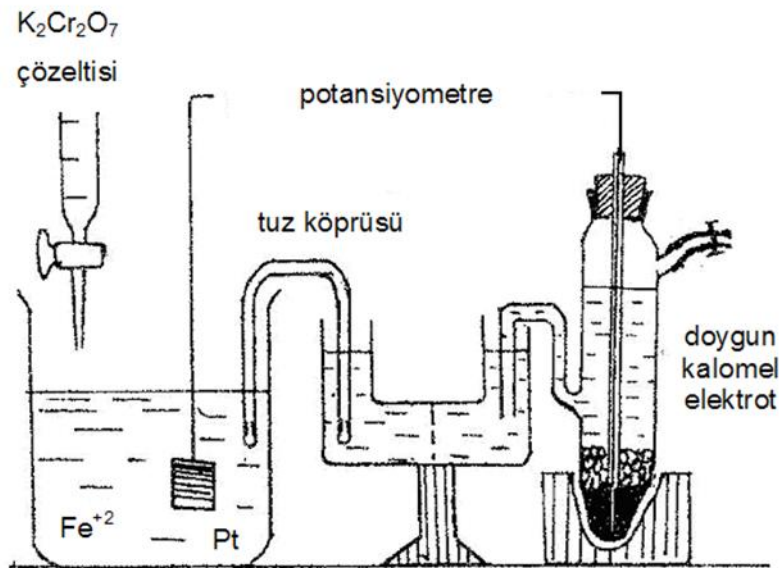
The electrode potential of the reaction is as follows.

$$E_Q = E_{Q/Q_2}^\theta + \frac{RT \ln}{2F} \frac{a(Q)a(H_3O^+)^2}{a(QH_2)}$$

in the oversaturation state is to be $a(Q) = a(QH_2)$ from the last equation

$$E_Q = E_{Q/Q_2}^\theta + \frac{RT}{F} 2,303 \log a(H_3O^+)$$

equality is obtained.



Evaluation of Results

Since E_Q and E_{SCE} are depened on temperature, the temperature read from the thermometer is replaced by the following values. these values are found in the following relations.

$$E_{kin} = 0,6994 - 7,36 \times 10^{-4} (t-25)$$

$$E_{kal} = 0,2425 - 76 \times 10^{-4} (t-25)$$

Electromotor, E, in a cell

$$E = E_{cathod} - E_{anode} = E_{right} - E_{left}$$

the following equations are written for the EMF and pH value of the above mentioned cell respectively.

$$E = E_Q - E_{SCE}$$

$$E = E_Q^0 + \frac{RT}{F} 2,303 \log a (H_3O^+) - E_{SCE}^0$$

$$E = E_Q^0 - \frac{RT}{F} 2,303 pH - E_{SCE}^0$$

$$pH = (E_Q^0 - E_{SCE}^0 - E) / (2,303 RT/F)$$

The E value read from the potentiometer and the calculated E_Q / E_{SCE} values are calculated in the equation above and the pH of the solution is calculated.

QUESTIONS

- 1) Explain what is the EMK, reference electrode, indicator electrode, anode, cathode.
- 2) Describe the Faraday laws verbally and mathematically.
- 3) Since the mass of Au^{3+} ions in the gold electrodes is electrolyzed for 10 minutes with a constant current, as the mass of the cathode increases by 1,314 g, find the current number and current intensity of the electricity passing through the circuit.
- 4) What are the duties of the Salt Bridge?
- 5) What are the advantages of potentiometric titration?
- 6) Before the turning point in potentiometric titration, explain the sudden potential change in the turning point by typing the reactions that are going on at the turning point and after the turning point.

Potansiyometrik titrasyonda dönüm noktasından önce, dönüm noktasında ve dönüm noktasından sonra yürüyen tepkimeleri yazarak dönüm noktasındaki ani potansiyel değişimini açıklayınız. Why does the potential remain nearly constant after the turning point?

- 7) What is the relationship between concentration and activity?
- 8) Derive the Nernst equation.
- 9) What is observed when the opposite EMF is applied directly to the systems with and without self-galvanic cells?
- 10) What are the differences between an electrolysis cell and an galvanic cell?
- 11) Calculate the theoretical decomposition voltage of water.
- 12) $Pb_{(s)} | PbSO_4 (s) | Na_2SO_4 \cdot 10H_2O (sat. sol.) | Hg_2SO_4 (s) | Hg (lq)$ the standard electromotor force of this cell was 0.9647 V, while the rate of change of the electromotor force with

temperature at constant pressure was measured as 1.74×10^{-4} . a) Write down the reduction reactions in the semi-cells and the total reaction in the battery. b) For the reaction in the battery, find the standard reaction free enthalpy, the standard reaction entropy, the standard reaction enthalpy, the reversible heat exchange and the equilibrium constant.

CORROSION

Deney No: 29

Deneyin Adı: Determination of Corrosion Rate

Deneyin Amacı: The aim of this experiment is to determine the corrosion rate of iron and steel in the acidic medium by using the current-potential curve.

Kullanılan Kimyasallar:

- 1L 0.5 M HCl solution (to be prepared in laboratory)
- Materials to determine the Corrosion Rate (Iron and Steel)

Information

Corrosion is the most important data corrosion rate. It is found by the following methods.

- 1- By measuring the loss of mass,
- 2- By measuring the amount of product formed during corrosion,
- 3- Extrapolation of the current-potential curves in the anodic and cathodic Tafel regions to the corrosion potential, A
- 4- From the slope of the linear polarization change around the corrosion potential,
- 5- It can be found by using the equivalent electrical circuit (AC-impedance diagram) of the metal / solution interface (from the load transfer resistance).

Corrosion can occur in a variety of ways,

- 1- General corrosion
- 2- Pitting corrosion
- 3- Galvanic corrosion
- 4- Stress-Cracking corrosion
- 5- Erosion corrosion
- 6- Intergranular corrosion
- 7- Welding corrosion
- 8- Hydrogen cracking corrosion

Corrosion rate can be prevented by various methods. These;

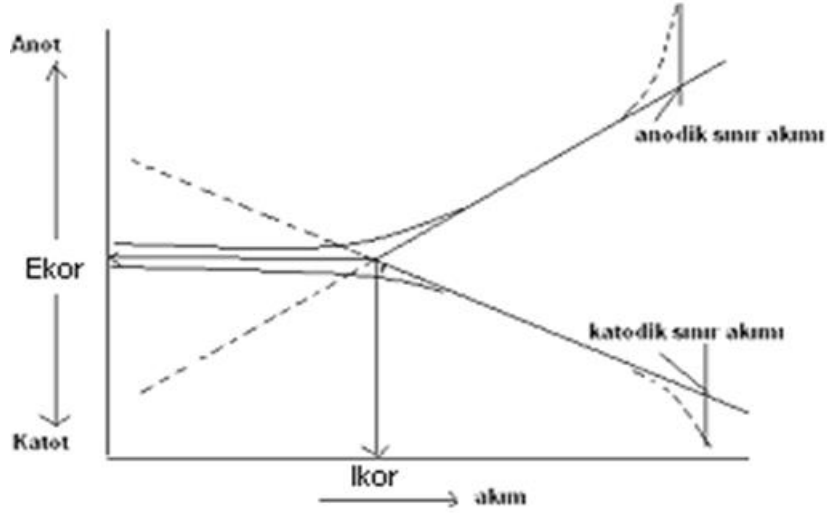
- 1- Cathodic protection
- 2- Alloying metal
- 3- Remove from corrosive environments
- 4- To increase the resistance of metal
- 5- Metal and non-metal coatings
- 6- Sacrificed anode method
- 7- Selection of suitable materials

Corrosion formation conditions

- 1- Formation of anodic and cathodic regions
- 2- Potential difference

3- Current transmission

Corrosion does not occur if one of these conditions is missing. Corrosion can be reduced by using inhibitors, these inhibitors are anodic, cathodic and carbon inhibitors.



F'g/ 8. Current-Potential Curve (Tafel Curve)

Experimental Procedure

In this experiment, the current-potential curve is taken for both electrodes with the help of three electrode system using electrochemical method. These electrodes are 0,3 cm diameter and 5 cm long iron and steel sheet. Üçlü elektrot sistemi sırayla karşıt elektrot (Pt), referans elektrot (kalomel elektrot) ve çalışma elektrotudur (demir ve çelik çubuklar). Bu üç elektrot önceden hazırlanmış korozi (aşındırıcı) ortam olarak önceden hazırlanmış 100 mL'lik kapta bulunan 0,5 M HCl çözeltisine daldırılır. Sisteme akım verilmeksizin elektrotların denge potansiyelleri belirlenir. Sistemden akım geçmesi suretiyle alınan veriler $\log (A/cm^2)$ -Volt eğrisine geçirilerek katodik Tafel bölgedeki doğrularının denge potansiyeline ekstrapolasyonu ile birim yüzey alanda geçen akım A/cm^2 yani korozyon hızı her iki metal için bulunur.

Evaluation of Results

By comparing the corrosion rates found in the current-potential curves, the material that is susceptible to corrosion is determined. The reason for the different corrosion rates should be explained.

QUESTIONS

- 1) How to prevent corrosion?
- 2) Why is corrosion important?
- 3) Explain the types of corrosion.
- 4) Describe cathodic protection.
- 5) Describe the oxygen concentration battery.
- 6) Explain atmospheric corrosion.
- 7) Explain the corrosion in the soil.
- 8) Which methods does the corrosion rate find?
- 9) How to find the anode and cathode regions in corrosion?
- 10) Give an example to the reference electrode and derive the electrode potential expression.
- 11) Is the cathode size or anode magnitude more effective in corrosion?
- 12) Describe the factors that increase corrosion in the aqueous environment.
- 13) Explain the potential-pH diagram.
- 14) Find out whether zinc in an oxygen-free aqueous medium has a corrosion value of pH 7 and the ion concentration is 10^{-3}M .
- 15) Explain the effect of temperature on the corrosion rate.

KAYNAKLAR

Bu elektronik föy, Fizikokimya Deneyleri (Yüksel Sarıkaya, Ankara Üniversitesi Basımevi, 2009) başlıklı föyün elektronik versiyonu olup, korozyon ve polimer kimyası konularına ilişkin teorik bilgi ve deneyler sonradan eklenmiştir.

1. Y. Sarıkaya, Fizikokimya Deneyleri, Ankara Üniversitesi Basımevi, 2009.
2. Y. Sarıkaya, Fizikokimya, Gazi Kitabevi, 2006.
3. M. Saçak, Polimer Kimyası, Gazi Kitabevi, 2010.
4. M. Saçak, Kimyasal Kinetik, Gazi Kitabevi, 2010.
5. E. Hetiz, R. Henkhaus ve A. Rahmel, Korrosionskunde im Experiment, Verlag Chemie, 1983.
6. Handbook of Corrosion Experiments, NACE.
7. S. Üneri, Korozyon ve Önlenmesi, Korozyon Derneği, 1998.
8. A. A. Aksüt, Ders Notları, 2017.

ÖNEMLİ NOT

Bu elektronik föyde sadece Korozyon ve Polimer Kimyası alanlarında özet şeklinde teorik bilgiler bulunmaktadır. Deneyleri yapacak öğrencilerimizin deney konusu ile ilgili teorik bilgileri mutlaka diğer kaynaklardan çalışarak laboratuvara gelmesi gerekmektedir. Aksi halde deney öncesi yapılacak olan sözlü sınavdan geçmeleri mümkün olmayacaktır.

MIXTURES

Experiment No:	10
Name of the Experiment:	Solubility of Ammonium Oxalate
Purpose of the Experiment:	The aim of this experiment is to determine the enthalpy of dissolution by examining the change in solubility of ammonium oxalate in water with temperature.
Reagents:	<ul style="list-style-type: none">• Ammonium oxalate ($(\text{NH}_4)_2\text{C}_2\text{O}_4$)• 0.02 M aqueous potassium permanganate (KMnO_4) solution• 0.05 M aqueous sulfuric acid (H_2SO_4) solution
Equipment:	<ul style="list-style-type: none">• Landolt pipette• Thermometer• Heater• Cotton• Glassware (Test tube, beaker, erlenmeyer, stirring rod, burette)• Puar• Ice-water bath

Experimental Procedure

In this experiment, the solubility of ammonium oxalate will be determined at different temperatures.

Solubility at 0 °C: 3 g of ammonium oxalate is dissolved by gradually addition of 25-30 mL water. An amount of undissolved particles must remain in the solution. This saturated solution at room temperature is transferred to a test tube. The tube is immersed into an ice-water bath for 30 minutes. The tube is frequently stirred with a glass bagette, and the temperature of the solution is measured. This solution is sampled with Landolt pipette whose tar is m_1 , and after drying its outer surface, it is again weighed (m_2). The weight of the solution is calculated from $m = m_2 - m_1$ equation. The solution in Landolt pipette is placed in an erlenmeyer, and after the addition of 5-10 mL of sulfuric acid

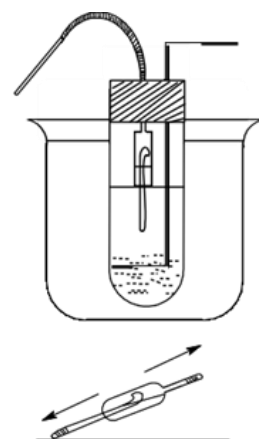


Figure 3.
Experimental set-up at high temperatures

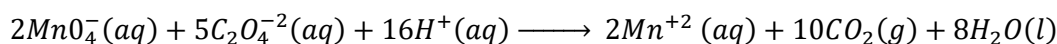
solution, it is heated. This solution is titrated with a permanganate solution until a light pink color is observed. The volume of titrant KMnO_4 is determined (v_y).

Solubility at 100 °C: 11 g of ammonium oxalate, 25 mL of water and a thermometer are placed in a test tube. The tube is immersed into a water bath. The tube is stirred with a glass bagette and heated up to the boiling point at the same time. When the desired temperature is reached, the solution is stirred for at least 10 minutes. The sample is taken from the solution with the Landolt pipette and pipette is cooled down with water. Cooled solution precipitates in the pipette. Landolt pipette is weighted again (m_2). The difference in weight is the amount of the solution. Then pipette is dipped into 40 mL of dilute sulfuric acid solution which is heated to 50-60°C, downstream of the upper pipe and the pipette is moved up and down to dissolve the salt. This liquid is transferred to a 250 mL flask and the tube washed with distilled water and all of the washing water is poured into the flask and completed to 250 mL with distilled water. 25 ml of this solution is added to the same volume of heated H_2SO_4 solution and titrated with KMnO_4 . The volume of used KMnO_4 is determined (v_y).

Same procedures are repeated at 25°C, 50°C and 75°C.

Assessment of Results

The titration equation to determine the solubility is given below.



The oxidant permanganate and reductant oxalate are represented with y and i, respectively. The mass and the mole fraction of ammonium oxalate are calculated with the equations given below.

$$2n_i = 5n_y \quad , \quad 2v_i C_i = 5v_y C_y \quad , \quad C_i = \frac{5v_y C_y}{2v_i} = \frac{\left(\frac{m_i}{M_i}\right) 1000}{v_i} = \frac{m_i 1000}{v_i M_i}$$

$$m_i = (5/2) \times (M_i C_y v_y / 1000) = [(5/2) \times 124 \times 0,02 / 1000] v_y = 6,2 \times 10^{-3} v_y$$

$$x_i = (m_i / M_i) \sum m_i / M_i$$

The $\ln x$ values of the solubilities (x) are plotted versus $1/T$ and the solubility at the desired temperature is measured from the graph. The Dissolution Enthalpy (ΔH_2) is calculated from the slope.

$$\ln x = -\Delta H_2 / RT + C$$

Questions

- 1) Explain the solubility and the factors that affecting the solubility.
- 2) What is the unit of solubility?
- 3) Explain the reasons for the change in the solubility of solids and gases in liquids with temperature.
- 4) How can the enthalpy of dissolution be found using from the solubility value of a solid, in a liquid?
- 5) How can the enthalpy of dissolution be found with graphical method?
- 6) Derive the law of ideal solubility.
- 7) Derive the solubility expression of gases with changing temperature.

STATES OF MATTER

Deney No: 11
Deneyin Adı: Viscosity Measurement
Deneyin Amacı: The aim of the experiment is the determination of viscosity energy by monitoring the change of viscosity with temperature for different liquids.

Kullanılan Kimyasallar:

- Acetone
- Ethyl alcohol

Kullanılan Malzemeler:

- Ubbelohde Viscosimeter
- Termometer
- Heater
- Stopwatch
- Water bath

Deneyin Yapılışı

The lower chamber of the viscosimeter is first filled with water of known viscosity. The viscosimeter is immersed in the water bath which is set to the specified temperature. Then, the water in the viscosimeter is applied to the upper chamber of the viscometer with a liquid volume by means of the puarin. The flow time (t_1) is then determined by the stopwatch. The same experiment is repeated with fluids of unknown viscosity. The flow times of all liquids are determined in similar ways at 30 °C, 40 °C, 50 °C and 75 °C.

Sonuçların Değerlendirilmesi

The flow times measured in the experiment are calculated using the equation 11.1 given below, to calculate the viscosities at different temperatures and the $\eta(2) - T$ graph is plotted. Then the logarithm of equality 11.2 is taken and the $\ln \eta / T$ graph is drawn according to the equation. From the slope of this correct graph, the viscosity energy is determined. Viscosity energies are interpreted for the results of the determined liquids.

$$\eta'_2 = \eta_2 / \eta_1 = \rho_2 t_2 / \rho_1 t_1 \quad (11.1)$$

$$\eta = 1/\phi = Ae^{Ev/RT} \quad (11.2)$$

SORULAR

- 1) Explain the concepts of viscosity and fluency.
- 2) Write down the viscosity coefficient and the unit.
- 3) Explain laminar and turbulent fluency. Describe the Reynolds number and explain what it does.
- 4) Explain the methods of measuring the viscosity.
- 5) What is a fluid, compressible fluid, and non-compressible fluid? Please explain.
- 6) How does the viscosity of gases and liquids change with temperature?
- 7) How is the viscous energy of liquids found?
- 8) What is the viscosity of liquids?
- 9) What is rheology?

What is Newtonian and non-Newtonian flow?

Deney No: 13

Deneyin Adı: Change in Vapor Pressure With Changing Temperature

Deneyin Amacı: The aim of this experiment is to determine the enthalpy of evaporation by monitoring the vapor pressure of a liquid by temperature change.

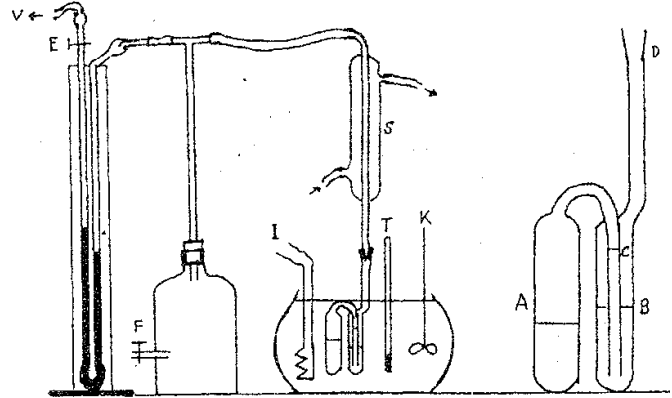
Kullanılan Kimyasallar: • Polar protic liquids with low boiling temperatures

Kullanılan Malzemeler: • Isoteniscope
• manometer
• condenser
• heater
• waterbath

Deneyin Yapılışı

With the help of an isoteniscope, the vapor pressures of liquids at different temperatures can be measured and the enthalpy of evaporation can be calculated. The device used in the experiment is shown in Figure 4.1.

The B part of the isoteniscope is filled with liquid and moved up and down to allow the liquid to pass in an equal volume to the A chamber. The isoteniscope is placed in the water bath and the condenser is connected. When the two-way tap F is open to the air, the tap E is pulled from the tap E until the mercury in the pressure gauge is just over the tap and the tap is closed.



Şekil 4. İzoteniskop

After the manometer is prepared for the experiment, the pump is operated and the system is vacuumed by means of the two-way tap F. After the mercury level remains constant, it is continued to vacuum for a while and the air in tube A is removed. It should be observed that the mercury levels in the manometer are approximately equalized and remain constant. After closing tap F, the vacuum pump is also switched off.

If the mercury levels are not constant, the system may have leakage and the system must be shut down. After there is no leakage, the mixer is operated and the bath temperature is read. Air is slowly inflated to the system until the fluid reaches to C level. When levels B and C are equalized, the difference in mercury levels in the manometer gives the vapor pressure at the measured bath temperature of the test liquid. After this first reading, the heater and the mixer are activated together and the vapor pressures are read in a similar way at the manometer.

NOTE: The most important point to be considered when equalizing B and C levels is opening the tap F carefully and giving air to the system carefully. Otherwise, air is escaped into tube A and the value read from the manometer is not equal to the vapor pressure. Also, it is not allowed to boil the liquid in the tube to prevent air leakage into tube A.

Sonuçların Değerlendirilmesi

The test results are evaluated by plotting p - T and $\ln p$ - $1/T$ plots. The slope of the graph matching the Classius-Clappeyron equation is ΔH_{sb} . Then according to the Trouton rule, the evaporation entropy is determined. As a result, the type of examined liquid is determined according to the enthalpy of evaporation value.

SORULAR

- 1) Explain the concepts of vapor pressure, steam, gas, critical point and triple point.
- 2) What is the chemical potential? What thermodynamic quantification is indicated?
- 3) What is the Trouton rule? What is its effect, on the interaction of the molecules?
- 4) In the p - T diagram of water, how you explain the negative fluid curve.
- 5) What are the other methods used to determine the vapor pressure?
- 6) Explain the equilibrium conditions between phases.
- 7) Derive Clapeyron and Clasius-Clapeyron equations.
- 8) Explain the temperature dependence of the enthalpy of evaporation.
- 9) Can a pure substance have more than 1 triple point? Please explain.
- 10) The temperature change of the vapor pressure of the liquid benzene is given as $\ln (p / \text{Nm}^{-2}) = -3883 / T + 22,516$. Find the molar evaporation entropy, the normal boiling temperature and the entropy of evaporation at this temperature. Compare the enthalpy and enthalpy of vaporization with the results you will find in the Trouton rule.

POLYMER CHEMISTRY

Deney No: 16

Deneyin Adı: Polymer Synthesis and Determination of Viscosity Average Molecular Weight of a Polymer

Conversion of Polymerization and Polymerization Rate

Deneyin Amacı: The aim of this experiment is to determine the percentage of polymerization and polymerization rate by weighing the polymer formed in a certain period of time in the reaction system.

Kullanılan Kimyasallar:

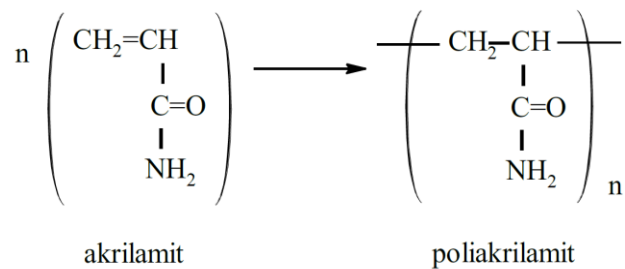
- Acrylamide
- Benzoyl peroxide (Bz₂O₂)
- Distilled water
- Acetone
- Methyl alcohol

Kullanılan Malzemeler:

- glass rod
- beher glass
- watch glass
- pipette (10 mL ve 25 mL)
- roun bottom flask (polymerization tube)
- Waterbath

Bilgi

In this experiment, the chain polymerization of acrylamide will be examined. Polyacrylamide polymer formation from acrylamide;



is occurred with chain polymerization.

Deneyin Yapılışı

0.71 g of acrylamide and 18 mL of distilled water are added to the reaction vessel and placed in a thermostated water bath at 75 ° C. It is waited until temperature equilibrium is established (10 minutes). After the temperature equilibrium is established, a solution of 0.0484 g of Bz₂O₂ in 2 mL of acetone is added to the reaction vessel. From this moment on, the time is recorded and the mixture is allowed to polymerize for 1.5 hours. At the end of this period, the reaction mixture is cooled and the polymerization is stopped. The solution is decanted into the beaker. After cooling has been completed, the methanol is slowly added by mixing with a glass rod and the polyacrylamide is precipitated. The upper part of the solution is discarded and the polyacrylamide baguette on the bottom is dried and then dried. Dried polyacrylamide is weighed and the polymer conversion (%) and polymerization rate are calculated.

Sonuçların Değerlendirilmesi

The conversion of polymerization P % is calculated from the following relations as m g polymer is formed at the end of t minute with m_o monomer mass.:

$$\% P = (m/m_o) \times 100 \quad (16.1)$$

Concentration of monomer [M]_o and rate of polymerization r_p

$$[M]_o = (m_o/M_o) \times 1000/v \quad (16.2)$$

$$r_p / \text{mol L}^{-1} \text{dk}^{-1} = (\%P) \times [M]_o / 100 t \quad (16.3)$$

can be calculated, respectively. Here, M_o is the molecular weight of monomer, v is the total volume of the solution and t show the polymerization duration.

Determination of Viscosity Average Molecular Weight of a Polymer

Deneyin Amacı: The aim of this experiment is to determine the viscosity average molar weight of the polymer by measuring the viscosity of dilute solutions of a polymer with unknown molar weight.

Kullanılan Kimyasallar: • poly(acrilamide) – (PAam)

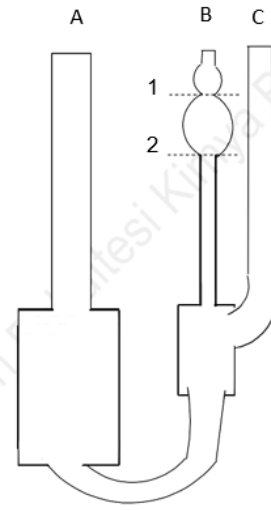
Kullanılan Malzemeler: • Waterbath
• Heater
• Ubbelohde viscometer

- stopwatch
- puar

Deneyin Yapılışı

Dilute solutions of PAAm with unknown molecular weight are prepared less than 1 g / 100 mL. Measurements are taken at the same temperature as the Ubbelohde viscometer. The advantage of using the Ubbelohde viscometer in the experiment is that the dilution of the polymer solution is carried out in the viscometer.

The viscometer is placed in a fixed water bath at 25 °C. Transferring 10 mL of solvent through the A tube allows a short time to set the temperature balance. The puar is then inserted into tube B (Fig. 9). The mouth of the C-pipe is closed with the finger and is pulled up with the help of the pin until the solvent passes to the first bubble in the B-pipe. The finger that closes the hole on the pad and the finger in the C pipe are pulled at the same time. Thus, the free flow of solvent from the capillary tube is provided.



Şekil 9. Ubbelohde Viskozimetresi

The stopwatch is run while the solvent level is at full 1. The stopwatch is stopped while passing through level 2. Thus t_0 is measured. Then the solvent is discharged. 8 ml of a 1% polymer solution is placed in the viscometer and placed in a 25 °C water bath. t_1 is measured as in the determination of solvent flow time. Without pouring the 1% polymer solution through the viscometer, the second dilute solution is prepared by adding an appropriate amount of solvent (pure water) from the A-tube.

Polimer çözeltisi derişimi/g(100 cm ³)	İlave edilen çözücü miktarı/mL	Viskozimetre içindeki çözücü miktarı/mL
1		8
0,8	2	10
0,6	3	13
0,5	3	16
0,4	4	20

while determination of the flow time of the solvent and polymer solutions (t_1 , t_2 , t_3 , ...), each measurement must be taken at least 3 times.

Dilution should be done properly. After the addition of solvent, tube C should be closed and thoroughly mixed with air through the viscometer.

Once the test is completed, the viscometer should be drained and thoroughly rinsed, especially with the capillary solvent removed, and then dried.

Sonuçların Değerlendirilmesi

Using the data obtained from the experiment, the following quantities are calculated.

$$\text{relative viscosity} = \eta_b = \eta/\eta_o = t/t_o \quad (16.4)$$

$$\text{specific viscosity} = \eta_{sp} = \eta_b - 1 \quad (16.5)$$

$$\text{Limit (intrinsic) viscosity} = [\eta] = (\eta_{sp}/c)_{c=0} \quad (16.6)$$

Herer, η_o and η are the viscosity values of the solvent and solution, $(\eta_{sp}/c)_{c=0}$ is the ratio of η_{sp}/c obtained while concentration is close to zero.

The relation between the viscosity average molar weight of the linear polymers, $\langle M_v \rangle$ with limit viscosity is given below:

$$[\eta] = k \langle M_v \rangle^\alpha \quad (\text{Mark-Houwink equation}) \quad (16.7)$$

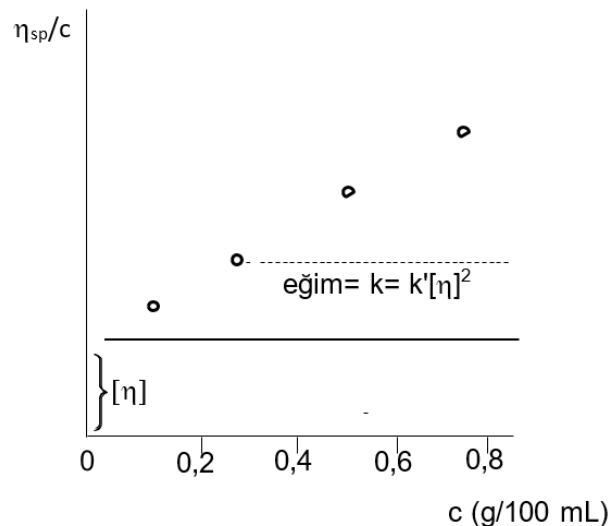
Here, k and α are constants depend on polymer, type of solvent and temperature.

At $T = 30^\circ\text{C}$ the Mark-Houwink constants of PAAm are given as:

$k \text{ dL/g}$	α
$12,5 \times 10^{-5}$	0,78

In the Polimer- solvent system, the change of η_{sp}/c with c is given with

$$\eta_{sp}/c = [\eta] + kc \text{ equation.}$$



Şekil 10. Change of η_{sp}/c with c

We can briefly summarize the ways to determine the viscosity average molar mass as follows:

- 1) η_{sp} / c values are plotted against c .
- 2) It is extrapolated to zero concentration and read from the y axis $[\eta]$.
- 3) The k and α values are found in the tables for the same polymer, solvent and temperature at which the viscosities are measured.
- 4) Mark-Houwink equation $\langle M_v \rangle$ is calculated.

SORULAR

- 1) Explain the concepts of initiator, monomer, mer, polymer, copolymer.
- 2) What is condensation and chain polymerization? Please explain. Give examples of polymers synthesized in both ways.
- 3) What is the initiator? Specify the name and the open formula of an initiator you know.
- 4) How is branching in the polymer chain?
- 5) Specify the name, open formula and properties of a polymer we use in daily life.
- 6) Write the initiation, growth and termination reactions for the radical polymerization of a suitable monomer with the help of a suitable initiator.
- 7) Why does the mean mean mass of moles be used for polymers?
- 8) What are the molar masses of polymers?
- 9) Write the synthesis reactions of the 3 addition and condensation polymers you know and the names of the substances in the reactions.

STATES OF MATTER

Exp. No	12
Exp. Name	Surface Tension
Aim	The purpose of this experiment is to investigate the relation between alcohol concentration and surface tension.
Chemicals	<ul style="list-style-type: none"> • 0,2 - 0,1 ve 0,05 M isopropyl alcohol solutions • 0,2 - 0,1 ve 0,05 M butyl alcohol solutions
Materials	<ul style="list-style-type: none"> • Beaker • Pipette pump • Pipette

Experimental

First of all we need to find a drop of liquid corresponds to how many fractional capillary lengths. It named as “s”. After than the number of drops in a known volume (v) is counted. After the last drop has fallen, the difference between the end of the volume v and the point at which the drop ends is determined (Δs).

Same experiments are performed with water and alcohol solutions in different solutions and the number of drops corresponding to the v volume is found. The surface tension of water is taken as $72,8 \text{ dyn cm}^{-1}$ at 25°C and the surface tensions of other alcohol solutions is calculated with the help of the following equation,

$$\sigma_2/\sigma_1 = n_1/n_2$$

Measurements and calculations during the test should be carried out according to the table below.

Experiment No	s	n	Δs	$n \pm \Delta s/s$	σ	Δn
1						
2						

PS: Since the surface tension depends on the temperature according to Eötvös relation, the temperature should be kept constant at 25°C during the measurements.

Evaluation of the Results

Calculated surface tensions plotted against alcohol concentrations.

Substances that decrease the surface tension of water when it is dissolved is called as surfactants or capillary active.

Questions

- 1) What is the surface tension and its units.
- 2) What are the surface tension determination methods.
- 3) How does the surface tension change with temperature?
- 4) How does the surface free enthalpy change during the growth or shrinkage of the surface?
- 5) What do you know about the electrical double layer?
- 6) Drop counts of water and another liquid are 30 and 60 respectively. The surface tension of the water at the experiment temperature is $72,8 \text{ dyn cm}^{-1}$. What is the surface tension of the another liquid.
- 7) Derive the equation which gives the temperature dependence of the molar surface energy.
- 8) Explain the dependence of the number of drops of liquids close to each other on the surface tension.