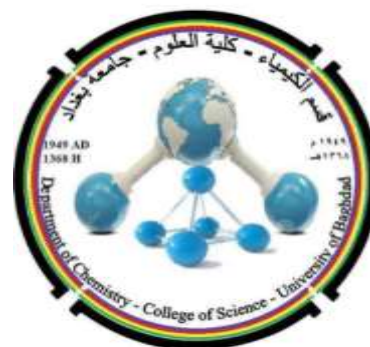


University of Baghdad  
College of science  
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# Practical Physical Chemistry For Second Year Students of Chemistry

**Translated and revised by**

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**&**

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**Experiment No. 1**  
**Part (A)**

# Density

## Determination of the relative and absolute densities of a liquid or solution

**The aim:** Determination the relative and absolute densities of pure liquid.

**Introduction:**

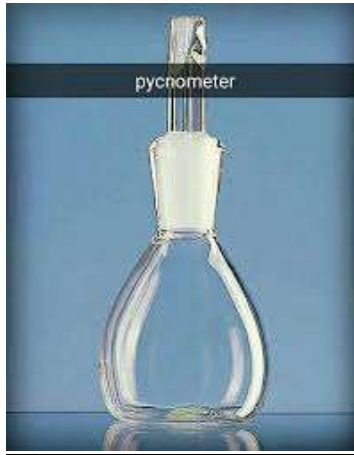
**The absolute density:** of  $\rho$  substance defined as, the mass per unit volume.  $\rho$  (rho) is the symbol most often used for density . Mathematically, density is defined as mass divided by volume.

$$\rho = \frac{m}{V}$$

Where  $\rho$  is the density,  $m$  is the mass, and  $V$  is the volume. From the **SI** (System International) unit of density is: kilogram per cubic meter ( $\text{kg/m}^3$ ) and in **cgs** unit of gram per cubic centimeter ( $\text{g/cm}^3$ ). The density of the material varies with temperature and pressure. This variation is typically small for solids and liquids but much greater for gases. Increasing the temperature of substance decreases its density by increasing its volume. The mass is normally measured with scale or balance while the volume may be measured directly (from the geometry of the object) or by the displacement of fluid.

**"relative density" or "specific gravity"** is the ratio of the density of the material to that of standard material, usually waters, so it has no unit.

$$\text{Relative density} = \frac{\text{density of the material}}{\text{density of the water}}$$



**Experiment Method:**

- 1 . Weight the empty and dried volumetric flask with its cover  $W_1$ .
- 2 . Weight it again after fills it with distilled water  $W_2$ .
- 3 . Remove the water from it, then dried it and rinse with the unknown liquid, weight again  $W_3$ . Wash it with water.

**Calculation:**

Let  $W_2 - W_1$  be the weight of distilled water.

Let  $\rho_1$  be the density of distilled water.

If  $V$  is the volume of volumetric flask.

Let  $W_3 - W_1$  be the weight of liquid that fills the volumetric flasks.

Let  $\rho_2$  be the density of this liquid, then:

$$\rho_1 = \frac{W_2 - W_1}{V} \dots\dots\dots (1)$$

$$\rho_2 = \frac{W_3 - W_1}{V} \dots\dots\dots (2)$$

The relative density of the liquid=  $\frac{\rho_2}{\rho_1} = \frac{W_3 - W_1}{W_2 - W_1} \dots\dots\dots (3)$

**Experiment No. 1**  
**Part (B)**

# Viscosity

## Determination of the relative and absolute viscosities of a liquid and its variation with temperature

**The aim:**

- 1 - Determination the relative and viscosities of a liquid.
- 2 – Calculate the variation of the viscosity with temperature.
- 3 - Calculate the activation energy.

**Introduction:**

Viscosity ( $\eta$ ) is simply defined as the friction between two layers of fluid when the two layers move relative to each other or how resistant that fluid is to flow. Poiseuille (1844) did much work to calculating the viscosity, one important result of his mass transport analysis is the following equation:

$$\eta = \frac{\pi p r^4 t}{8 V \ell}$$

$$\eta_1 = \frac{\rho_1 h g t_1 \pi r^4}{8 v l}$$

$$\eta_2 = \frac{\rho_2 h g t_2 \pi r^4}{8 v l}$$

$$\begin{aligned} \frac{\eta_1}{\eta_2} &= \frac{\frac{\pi r^4 t_1 P_1}{8 L V}}{\frac{\pi r^4 t_2 P_2}{8 L V}} \\ \Rightarrow \frac{\eta_1}{\eta_2} &= \frac{\pi r^4 t_1 P_1}{8 L V} \times \frac{8 L V}{\pi r^4 t_2 P_2} \\ \frac{\eta_1}{\eta_2} &= \frac{t_1 P_1}{t_2 P_2} \end{aligned}$$

V = Volume per second

p = Pressure difference between the two ends

r = Internal radius of the tube

$\eta$  = Absolute viscosity

l = Total length of the tube

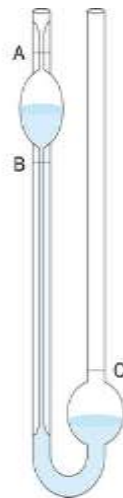
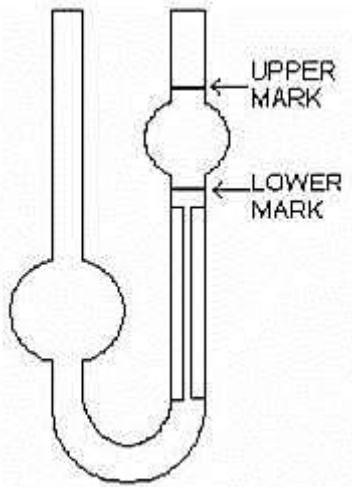
Where  $\eta$  is a proportionality factor known as the coefficient of viscosity. The unit of viscosity is the poise. Its defined as the force necessary to move a layer of liquid of area  $1\text{cm}^2$  with a velocity of 1 cm per second, past another layer at distance of one centimeter. The apparatus commonly used in the laboratory to measured viscosity, is the Ostwald viscometer, also known as U-tube viscometer or capillary viscometer: it is a device used to measure the viscosity of the liquid with a known density. The method of determining viscosity with this instrument consists of measuring the times of flow (t) of equal volume of two liquid through the same capillary tube and measured under the same experimental condition.

Knowing the value of viscosity of one liquid, can calculate the viscosity of other liquid by using the following equation: Where  $\eta_1$  and  $\eta_2$  are viscosity coefficients of the liquid and water, and  $\rho_1$  and  $\rho_2$  are the densities of liquid and water, respectively. Viscosity varies with temperature, generally becoming smaller as temperature is elevated and with the size or shape of molecules.

If the time of flow of equal volumes of two liquids through the same capillary is measured under the same experimental conditions, it follows that:

$$\frac{\eta_1}{\eta_2} = \frac{\rho_1 t_1}{\rho_2 t_2} = \dots\dots\dots (4)$$

Where  $\eta_1$  denote the coefficient of viscosity of unknown liquid and  $\eta_2$  denote the coefficient of viscosity of water,  $\rho_1$  and  $\rho_2$  denote their density, and  $t_1$  and  $t_2$  denote their times of flow. This equation is used to calculate the so called relative viscosity. Water is quite generally accepted as the standard of reference in determinations of relative viscosity. If the absolute viscosity of water is known, that of liquid can be calculated.



The viscosity of liquids varies with temperature according to the following equation:

$$\eta = Ae^{E/RT}$$

$$\log \eta = \log A + \frac{E}{2.303RT} \dots\dots\dots(5)$$

A= constant

R = gas constant

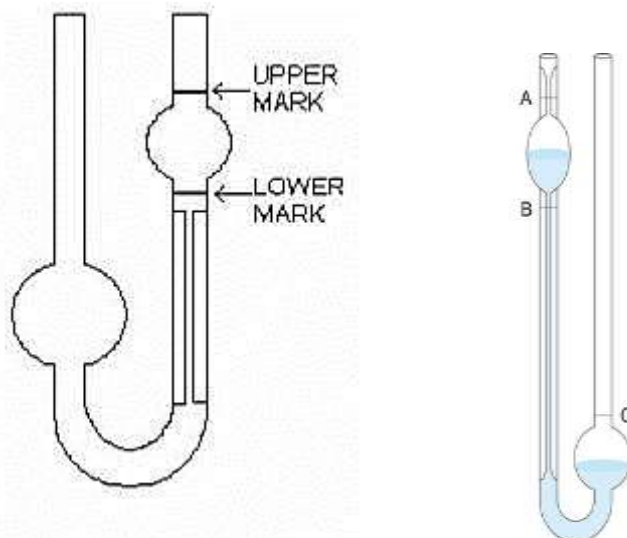
T = absolute temperature

E = activation energy that is necessary for the process of flowing of liquids.

**Experimental method:**

- 1 . Cleaned and dried the viscometer in the same way as described in part A.
- 2 . The viscometer is clamped vertically in a water thermostat. It must be dipped in the thermostat down to the mark (C).
- 3 . An exactly specified volume of liquid (10 ml) is added from pipette.
- 4 . Allowed the liquid 10 min to reach the temperature of thermostat (25 °C)
- 5 . Sucked the liquid up the capillary arm of the viscometer until the surface of the liquid is above the upper mark (a) Fig 1.
- 6 . Allowed the liquid to flow down the capillary arm.
- 7 . The time required for the liquid to pass from the upper mark (a) to lower mark (b) is noted (air bubbles will form in the capillary is affect the time of flow).

- 8 . Weight the empty volumetric flask, filled with  $\eta$  liquid, put it with the viscometer in the water bath, leave it for 10 min .Weight the volumetric flask again
- 9 . Repeat the above steps 5,6,7,8 at (35,45,55) °C
- 10 .on freshly distilled water using exactly the same volume that taken of the liquid and the same temperature.



11 .

Fig 1: Ostwald viscometer

**Calculation:**

- 1 . Let the time of flow of the water be  $t_1$  its density  $d_1$ , and its viscosity  $\eta_1$ . The time of flow of liquid be  $t_2$  its density  $d_2$ , and its absolute viscosity  $\eta_2$ . Then:

$$\frac{\eta_1}{\eta_2} = \frac{t_1 \rho_1 (\text{water})}{t_2 \rho_2 (\text{liquid})}$$

Poise = dynes /cm<sup>2</sup>/unit velocity gradient.

Viscosity of water at 35°C= 0.08937.

- 2 . Put the results as in the following table:

°C	T (K)	t <sub>1</sub> (sec)	t <sub>2</sub> (sec)	$\eta_1$	$\eta_2$	log $\eta_1$	1/T (K <sup>-1</sup> )

- 3 . Plot a curve between  $\log \eta_1$  against  $1/T$  then calculate the activation energy from the slope of the straight line.

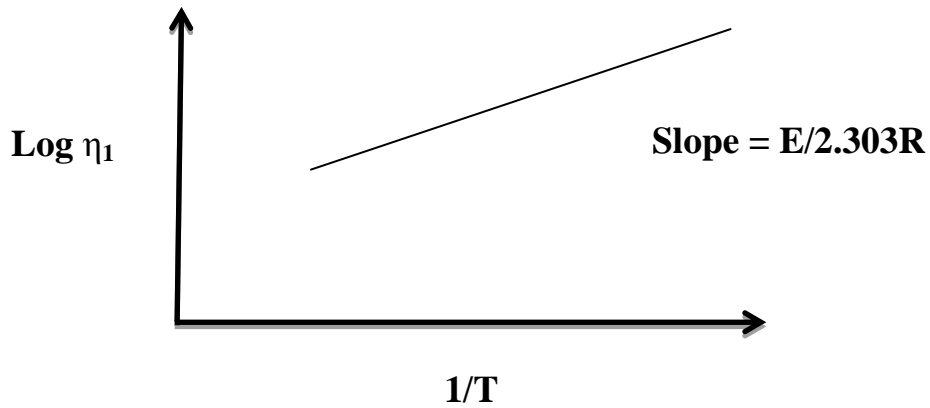


Fig 2: a curve between  $\log \eta_1$  against  $1/T$

**Question for discussion**

- 1- Define the relative and the absolute density. Derive the unit.
- 2- Define the absolute viscosity and the relative viscosity. Derive the unit of it.
- 3- Write the linear equation for the relation between  $\log \eta$  and  $1/T$ . Explain the slope and the intercept.
- 4- Define the activation energy and derive its unit, write the equation use for calculating it?
- 5- What are the factors effected on density and viscosity?

<b>Table 1: Density of Water (0-100) °C</b>	
<b>T °C</b>	<b><math>\rho(\text{g/ml})</math></b>
0	<b>0.9998</b>
4	<b>1.0000</b>
5	<b>0.99999</b>
10	<b>0.99973</b>
15	<b>0.99913</b>
18	<b>0.99862</b>
20	<b>0.99823</b>

<b>Table 2: Viscosity of Water (0-100) °C</b>	
<b>T °C</b>	<b><math>\eta(\text{cp})</math></b>
0	<b>1.7870</b>
4	<b>1.5670</b>
5	<b>1.5190</b>
10	<b>1.3070</b>
15	<b>1.1390</b>
18	<b>1.0530</b>
20	<b>1.0120</b>



25	<b>0.99707</b>
30	<b>0.99567</b>
35	<b>0.99406</b>
38	<b>0.99299</b>
40	<b>0.99224</b>
45	<b>0.99025</b>
50	<b>0.98807</b>
55	<b>0.98573</b>
60	<b>0.98324</b>
65	<b>0.98059</b>
70	<b>0.97781</b>
75	<b>0.97489</b>
80	<b>0.97183</b>
85	<b>0.96865</b>
90	<b>0.96534</b>
95	<b>0.96192</b>
100	<b>0.95838</b>

25	<b>0.9904</b>
28	<b>0.8327</b>
30	<b>0.7975</b>
35	<b>0.7194</b>
38	<b>0.6783</b>
40	<b>0.6529</b>
45	<b>0.5960</b>
50	<b>0.5468</b>
55	<b>0.5040</b>
60	<b>0.4665</b>
65	<b>0.4335</b>
70	<b>0.4042</b>
75	<b>0.3781</b>
80	<b>0.3547</b>
85	<b>0.3337</b>
90	<b>0.3147</b>
95	<b>0.2975</b>
100	<b>0.2818</b>

## Experiment No. 2

### **Heat of Solution**

#### **Determination of heat of solution from solubility measurements**

#### **The aim:**

- 1** - Determination of heat of solution.
- 2** - To calculate the melting point of the solute.

#### **Introduction:**

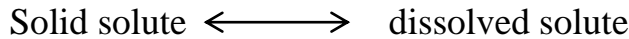
When a solution is dissolved in a solvent, heat may be absorbed or evolved; in general, the heat of solution depends on the concentrate of the final solution. The

integral heat of solution is the enthalpy change for the solution of 1 mole of solute in 1 mole of solvent.

It might be expected that heat would always be absorbed in overcoming the attraction between the molecules or ions of the solid solute. Another process which commonly occurs is  $\eta$  strong interaction with the solvent, referred to as solvate, which evolves heat. With many crystals the heat evolved by solvate is less than the heat absorbed in the separate of the units of the crystal. And so heat is absorbed in the solution process.

The differential heat of solute is the heat of solution of 1 mole of solute in  $\eta$  1000 ml of solvent so large that the additions of one more mole of solute do not change the concentration appreciably. The differential heat of solution depends on the concentration of the solution.

The equilibrium between  $\eta$  solid and its saturated solution may be represented as:



Equilibrium constant  $K_s$  represented as:

$$K_s = \frac{\text{dissolved solute}}{\text{solid solute}}$$

$$K_s \propto \text{Dissolved solute } C_s$$

$C_s$  is the molar concentration of dissolved solute. If  $\Delta H$  is the change in heat content when one mole of solute is dissolved in a large volume of the neatly saturated (heat of solution), then according to **Vant Hoff equation**:

$$\frac{d \ln K_s}{dT} = \frac{\Delta H}{RT^2} \dots\dots\dots(8)$$

$$\frac{d \ln C_s}{dT} = \frac{\Delta H}{RT^2}$$

And by integration:

$$\ln C_s = \frac{-\Delta H}{RT} + H$$

$$\log C_s = \frac{-\Delta H}{2.303RT} + \text{constant}(C) \dots\dots\dots(9)$$

$$\log C_s = \frac{-\Delta H}{2.303R} \left[ \frac{1}{T_m} - \frac{1}{T} \right] \dots\dots\dots(10)$$

Where  $T_m$  melting point of the solute,  $\log C_s$  the solubility at any temperature.

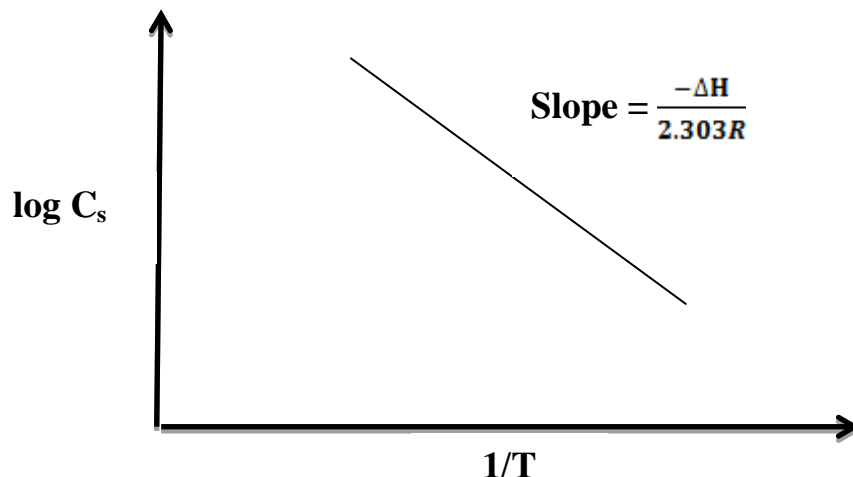


Fig.3: curve between log Cs against 1/T.

$C_s$  = dissolved solute.

T= absolute temperature.

$\Delta H$  = heat of solution.

R= gas constant =  $8.314 \text{ J K}^{-1} \text{ mole}^{-1}$  or  $R = 1.987 \text{ cal.K}^{-1} \text{ .mole}^{-1}$ .

Integration of Vant Hoff equation between two different temperatures (limited integration) will give the following equation:

$$\log \frac{C_{s(2)}}{C_{s(1)}} = \frac{-\Delta H}{2.303R} \left( \frac{T_1 - T_2}{T_1 T_2} \right) \dots\dots\dots(11)$$

**Experiment Method:**

1. Prepare 100 ml of standard solution of 0.05 M NaOH.
2. Put 75 ml of distilled water in a large test tube is saturated with benzoic acid crystals at about  $80^\circ \text{C}$ , adjust the temperature by the use of thermostat.
3. After equilibrium is reached, at  $70^\circ \text{C}$  transfer by means of a pipette 5 ml (which warmed by washing it with hot distilled water) of the clear supernatant liquid into a conical flask, the tip of the pipette is plugged with a small roll of cotton wool so as to prevent withdrawal of fine crystals with the solution, then wash the pipette again with hot distilled water to be sure that all the acid is pour.

4. Titrate the solution against 0.05 H NaOH, using few drops of ph.ph. as an indicator.
5. Repeat the above steps at the temperatures (60°C, 50°C, 40°C, and 30°C).

### Calculation:

- 1 . Calculate the normality concentration (M)at each temperature.
- 2 . Arrange your data as the following table:

H (°C)	T (K)	Volume of NaOH (ml)	Mormality (M)	Solubility (C <sub>s</sub> )	log C <sub>s</sub>	1/T (K <sup>-1</sup> )

- 3 . Calculate the solubility C<sub>s</sub> by:

$$M = \frac{wt(C_s)}{M.wt} * \frac{1000}{V}$$

- 4 . Plot (log C<sub>s</sub>) against (1/T) as in equation No.9.
- 5 . From the slope of the straight line. Calculate ΔH practically.
- 6 . Calculate ΔH theoretically from two temperatures by equation No.11 then compare it with the value of ΔH practically.
- 7 . Calculate the melting point of the solute (T<sub>m</sub>) from equation No. 10.

### Question for discussion

- 1- Define the solubility. What is the unit it?
- 2- Define the saturated solution?
- 3- Why is the pipette must washed by hot water before using?
- 4- Write the linear equation for the experiment. Explain the slope and the intercept?
- 5- What are the factors effected on the solubility?

## Experiment No. 3

# Molecular Weight Determination

## Freezing points, cooling curves, and cryoscopy determination of molecular weight

**The aim: 1-**To calculate the molar depression constant and molecular weight

**2 -** Plot the cooling curves to determine the freezing points of water and, solution.

### Introduction:

The freezing point of a liquid is the temperature at which the solid and the liquid are in equilibrium. Freezing points of pure liquids are used to identify materials and as a criteria of purity.

When a liquid consisting of one component (pure) is cooled the plot of temperature versus time (cooling curve) has a nearly constant slope. At the temperature at which the solid crystallized out, the cooling curve becomes horizontal if the cooling is slow enough. The halt in the cooling curve results from the heat evolved when liquid solidified (fig. 4).



**Fig. 4:** The halt in the cooling curve results from the heat evolved when the liquid solidified.

The dip below the freezing point is due to super cooling. Freezing points are usually, but not always, depressed by the presence of solutes. This fact is used in molecular weight determinations. If solution is ideal, the following relation may be applied:

$$T_0 - T = \Delta T = K_f * \frac{w_1 * 1000}{w_2 M_1} \dots\dots\dots(12)$$

$$\Delta T = K_f * M \dots\dots\dots(13)$$

M<sub>1</sub>: molecular weight of solute.

W<sub>1</sub>: weight of dissolved solute.

W<sub>2</sub>: weight of solvent.

M: Molarity of the solution.

K<sub>f</sub>: is called the molal depression constant. It is a constant characteristic of a certain solvent, and is defined as the lowering of the freezing point cause by dissolved 1g molecular of solute in 1000 ml of solvent.

The cooling curve for the solution (fig. 5) shows no horizontal portion, because the solution becomes more concentrated as the solvent freezes out and the freezing point drops continuously. Line a-b is extrapolated back to interact line a-d. The intersection is the true freezing point of the solution.

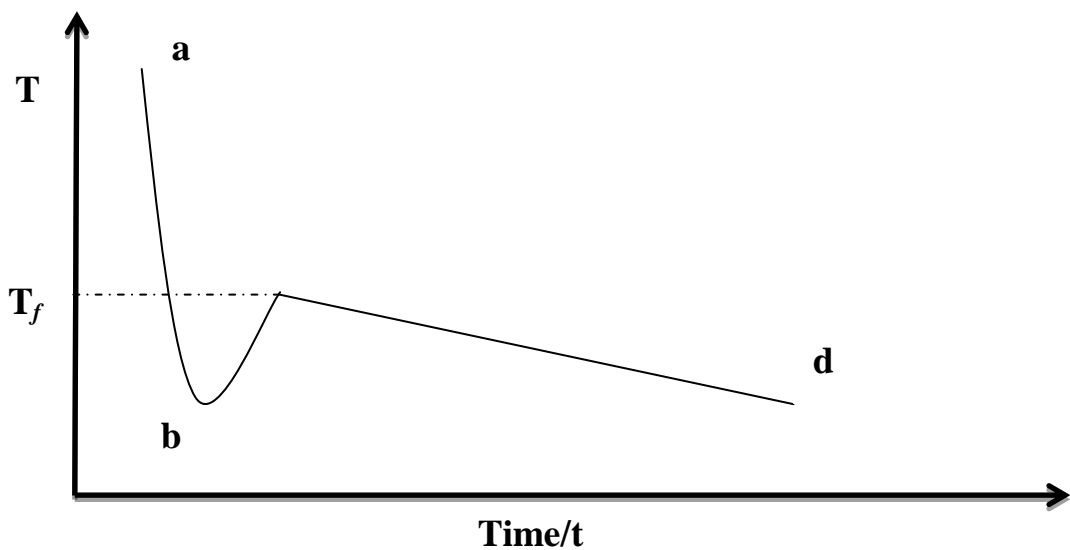
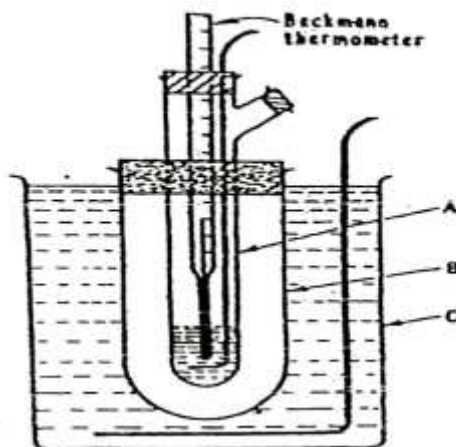


Fig. 5: The cooling curve for the solution shows no horizontal portion.

**Experiment Method:**

1. Introduce 10 ml of water in tube (A) fitted with a Beckmann thermometer as shown in the Fig 7.. This tube inserted in the air jacket in the air jacket (B), and the whole arrangement is placed in cooling mixture of ice and common salt. The cooling mixture is contained in the glass vessel (C) covered with metallic lid carrying (B) and another stirrer to maintain the temperature uniform.

2. Record the water temperature each minute with stirring it continually.
3. Dissolve about 1g of known substance, then repeat step 2 and determine the freezing of the solution.
4. Repeat the above steps by using unknown substance.



**Fig. 6: Beckmann's fp. depression apparatus.**

### **Calculation:**

- 1 . Plot the cooling curves to determine the freezing points of pure water  $T_0$ .
- 2 . Plot the cooling curves to determine the freezing points of solution  $T$ .
- 3 . Calculate  $\Delta T$ :

$$\Delta T = T_0 - T$$

- 4 . Use the formula given above equation (12) to estimate  $K_f$  for water.
- 5 . Repeat steps 2,3. Then calculate the molecular weight of unknown substance.

### **Question for discussion**

- 1- Define the molal freezing constant. Derive its unit.
- 2- What are the factors effected on lowering the freezing point?
- 3- Write the mathematic equation for calculating the molal freezing constant. Define the symbols.

## Experiment No. 4

# Density of Gases and Vapors

## Molecular weight determination by Victor Meyer method

**The aim:** To Determine the Molecular weight of a volatile liquid.

### Introduction:

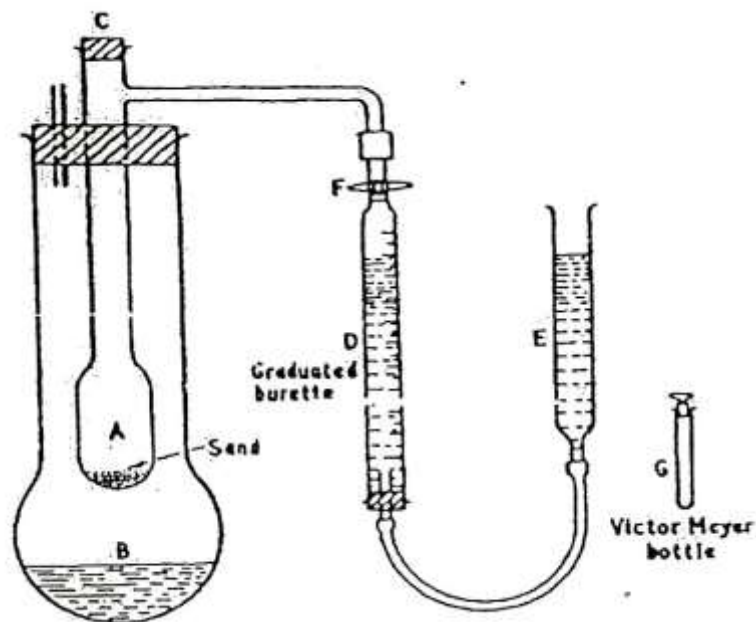
The density of a gas or vapor is defined as the weight of unit volume measured under specified conditions of temperature and pressure (0°C and 1 atmospheric pressure).

Relative densities are the ratio of the density of the gas to that of a reference gas, usually Hydrogen or Oxygen at the same temperature and pressure.

Avogadro's hypothesis states that equal volumes of gases at the same temperature and pressure contain equal numbers of molecules; the relative gas density is equal to the ratio of the molecular weights of the two gases.

The two well-known classic methods of determining the density of vapor of a substance which is liquid at normal temperature are those of Dumas and of Victor Meyer.

In Victor Meyer's method the vaporized liquid displaces air from a vessel maintained at a high constant temperature, but the volume of air is measured at ordinary temperature.



**Fig. 7:** Victor Meyer's apparatus for determination of vapor densities.



**Experiment Method:**

- 1 . Take off the stopper (C) as shown in Figure 8
- 2 . Boil the water in the outer jacket (B), continue boiling noticing that bubbles are set free at the open end of the side tube (C).
- 3 . Meanwhile, weight the Victor Meyer bottle, first empty, then filled with the given liquid; taking care that no air bubbles should exist after weighting. Let the weight of liquid be  $W_1$
- 4 . Judging that all excess air in (A) has been expelled, release momentarily stopper (C) and quickly throw Victor Meyer bottle to the bottom of (A). The liquid evaporation and equal volume of air is displaced up to the graduated jar.
- 5 . When evaporation is complete, both water surfaces in the two jars are adjusted to the same level. The volume of gas enclosed  $V$  is then recorded.
- 6 . The atmospheric pressure is  $P$  and the vapor pressure of water  $P^\circ$  at the working temperature ( $T$ ) is found from tables.

**Calculation:**

$$V_o = \frac{P - P^\circ}{760} * \frac{273}{273 + tC} * V_3 \quad \dots\dots\dots 14$$

$W_1$  (g): Weight of Victor Meyer bottle empty.

$W_2$  (g): Weight of Victor Meyer bottle with liquid.

$W_2$  (g) -  $W_1$  (g) =  $W_3$  (g) Weight of the liquid.

$V_1$ : Initial reading at the graduated bottle.

$V_2$ : Final reading at the graduated bottle.

$V_2 - V_1 = V_3$  volume of the displaced air which equal to the volume of liquid vapor.

$T$  °C: Experiment temperature.

$P$ : Atmospheric pressure.

$P^\circ$ : Water vapor pressure at the experimental temperature.

$V_o$ : The correct volume (at S.T.P).

$W_o$ : Weight of the same volume of Hydrogen at  $H_2$

$$W_o = V_o * \frac{0.09g}{1000 \text{ cm}^3} \quad \dots\dots\dots 15$$

$$\text{Relative density} = \frac{\text{Wt of unknown } (w_3)}{\text{Wt of the same volume of } H_2 (w_o)} \quad \dots\dots\dots 16$$

M.wt of unknown = Relative density\* M.wt of Hydrogen .....17

**Question for discussion**

- 1- Write the Avogadro's hypothesis.
- 2- For which kind of liquid can Victor Mayer method be used?
- 3- Enumerate the exception that applied in this experiment.
- 4- Calculate the molecular weight of a volatile liquid using the following data:  
The weight of volatile liquid = 0.26 g, the volume of vapor of a volatile liquid = 18ml, and the vapor pressure of water = 15.477mmHg at 18°C.

## Experiment No. 5:

### Part (A):

# Refractometry

## Determination of refractive index of some alcohols

### **The aim:**

- 1 - Determination of refractive index of some alcohols.
- 2 - Calculate the molecular refractivity for pure liquid
- 3 - Calculate the molecular refractivity for a mixer

### **Introduction:**

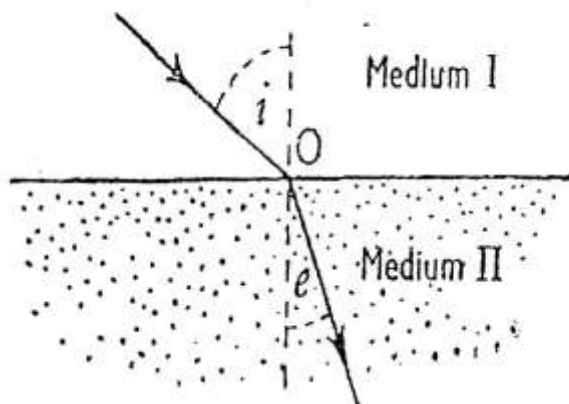
When a ray of monochromatic light passes from a less dense to a more dense medium, it is bent or refracted towards the normal.

In (fig. 8) if I is the less dense and II is the more dense medium, a ray of light passing from I to II will be bent so that the angle of refraction  $e$  will be less than the angle of incidence  $i$  and according to the law of refraction, the relation between these two angles will be such that:

$$\frac{\sin i}{\sin e} = \frac{N}{n}$$

$n$ : Index of refraction of the less dense medium.

$N$ : Index of refraction of the denser medium.



**Fig. 8: Refraction and the critical angle principle.**

The expression:

$$R = \frac{n^2 - 1}{n^2 + 2} * \frac{1}{\rho}$$

Remains nearly constant at different temperature, whereas the refractive index n of a substance varies with the temperature ( $\rho$ : the density).

The value of R dependent only on the nature of the substance and is characteristic of it, and it is called refractivity of the substance.

If the refractivity is multiplied by the molecular weight of the substance, one obtains the molecular refractivity.

$$[R]_D = \frac{n^2 - 1}{n^2 + 2} * \frac{M}{\rho} \dots\dots\dots(18)$$

M: Molecular weight.

R: Have the dimensions of a volume.

Refractometer measurement may be used, very advantageously for the quantitative determination of the composition of binary solutions.

The molecular refractivity is related to the composition of solution according to the following equation:

$$\begin{aligned} [R_{A,B}] &= X_A R_A + X_B R_B \\ &= X_A R_A + (1 - X_A) R_B \\ &= X_A (R_A - R_B) + R_B \dots\dots\dots(19) \end{aligned}$$

For solution the molecular refractivity is:

$$[R_{A,B}] = \frac{n_{AB}^2 + 1}{n_{AB}^2 + 2} \left[ \frac{X_A M_A + X_B M_B}{\rho_{AB}} \right] \dots\dots\dots(20)$$

$R_A$ : Molecular refractivity of liquid A.

$R_B$ : Molecular refractivity of liquid B

$R_{AB}$ : Molecular refractivity of liquid solution of (A+B).

$X_A, X_B$ : Mole fractions of A and B in solution.

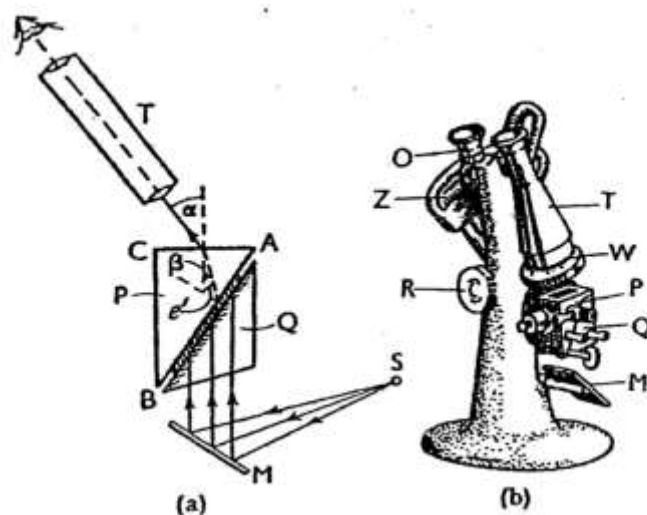
$n_{A,B}$ : Refractive index of solution of (A+B).

$n_A$ : Refractive index of pure A.

$n_B$ : Refractive index of pure B.

The abbe refractometer is the most commonly used instrument in chemical laboratories. The principle of operation is illustrated diagrammatically. The appearance of the instrument is shown in (fig. 9).

The optical system consist of three parts: a mirror M a prism-box PQ which can be rotated as a whole by means f a knob- R and a fixed telescope, T.



**Fig. 9: The Abbe refractometer**

**(a) Optical principle.**

**(b) General view of the instrument.**

### **Experiment Method:**

- 1- Clean the glass surface of refractive index by using alcohol or acetone.
- 2- In order to carry out a determination of refractive index of a liquid, open the prism box and place a few drops of the liquid on the ground surface of the lower prism.
- 3- Close and fasten- the prism box again, taking care that the liquid dose not flow away. a film of liquid ill thus be enclosed between the two prisms.
- 4- Focus the cross-wire of the telescope by rotating the eyepiece and adjust so as to get good illumination. .
- 5- By means of the knob H, turn the prism box slowly backwards and forwards until the field of view becomes partly light and partly dark.

- 6- When a white light is used the edge of the light band will show a colored fringe. By the means of the ring w on the telescope, rotate the "compensator" until the fringe disappears and the light band shows a sharp edge.
- 7 -Now rotate the prism box until this sharp edge is in coincidence with the intersection of the cross-wire in the telescope.
- 8 -Read off directly the index of refraction on the scale through eyepiece O the third decimal place can be read directly, and the fourth can be estimated with an accuracy of about 0.0002.
- 9 -Use the density bottle to measure the density of liquid as in experiment No. 1, part (A).
- 10 -repeat the above steps by using another alcohol.

### Calculation:

- 1-Calculate R for each liquid replacing  $n_D$  in equation No. 18.
- 2-Calculate R for methylene group  $-CH_2-$  by subtract value of  $R_B$  from value of  $R_A$  to get  $R_{-CH_2-}$ .

### Experiment No. 5

#### Part (B):

#### **Determination of molecular refractivity of solutions**

#### Experiment Method:

- 1-Propose a series of solution of unknown composition of A and B according to the following table:

$V_A$	$V_B$	$W_A$	$W_B$	No. of A moles $n_A$	No. of B moles $n_B$	No. of total moles $n_{AB}$	Molar fraction for $X_a$	Molar fraction for $X_B$
1	4							
2	3							
3	2							
4	1							

2-Read the refractive index of each solution as in part (H) and also determine its density as in experiment no. 1, then arrange your data as the following table:

Mixture AB	Density of mixture $\rho_{AB}$	$n_{AB}$	Molecular refractivity of mixture $R_{AB}$
1			
2			
3			
4			

**Calculation:**

- 1-Calculate  $[R_{A,B}]$  by the use of equation (20).
- 2-Plot graph between the molecular refractivity of  $[R_{A,B}]$  as ordinate and the mole fraction  $X_A$  as abscissa according to equation (19).
- 3-From graph calculate the slope and  $R_B$ .
- 4-Compare the result obtained from this plot and the result obtained by the direct calculation of the molecular refractivity of a pure liquid by the use of equation (18).

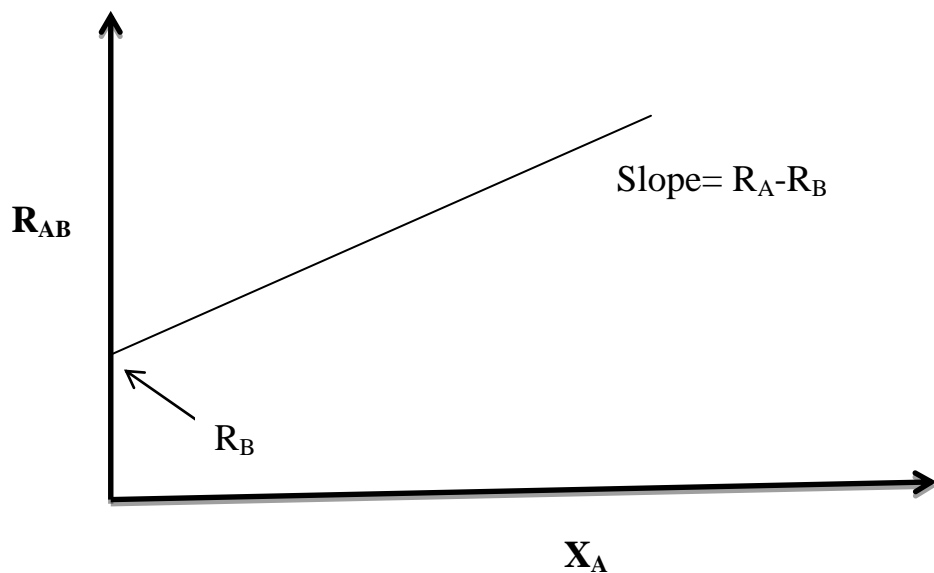


Fig 10: graph between the molecular refractivity of  $R_{A,B}$

### **Question for discussion**

- 1- Define the refraction index and the molar refraction index. Derives the units.
- 2- Write the mathematic equation for calculating the molar refraction index for pure and mixture liquid?
- 3- Write the linear equation for the relation between  $R_{AB}$  and  $X_{AB}$ . Explain the slope and the intercept.
- 4- Calculate the molar refraction of amixture of (7 ml of A) and (3 ml of B). Knowing that the M.wt of A is 154 g/mol, M.wt of Bis 46 g/mol, density of A is 1.594 g/ml, density of B is 0.785 g/ml, the density of mixture is 1.09 g/ml, and refraction index of mixture is 1.4122.
- 5- Calculate the molar refraction for butane and methanol, if the molar refraction of ethanol and propanol are 12 and 15 respectively.



## Experiment No. 6

### Part (A)

# Thermochemistry

## Determination of calorimetric constant

### The aim:

- 1 -To calculate the calorimetric constant.
- 2 –Draw the calibration curve.
- 2 -To calculate the liberated or absorb heat.

### Introduction:

Most chemical process is accompanied by measurable absorption or evolution of heat. It follow from the first law of thermodynamics that the magnitude of the heat change is proportional to the quantity of substance involved and depends also on the physical state of the reactants and the products, but it is independent on the path by which the reaction is brought about.

The heat change accompanying a physical or chemical process is measured by some form of calorimeter, the measured rise or fall of temperature multiplied by the total heat capacity of the calorimeter gives the quantity of the heat in calories.

$$q = C\Delta T \dots\dots\dots (21)$$

The technique of calorimetry presents two principal difficulties firstly, how to determine the heat capacity of the calorimeter and all its contents, and secondly, how to deal with die inevitable exchange of some heat between die calorimeter and its surroundings.

The calorimeter constant may be measured by carries out a reaction in it and observes the temperature change  $\Delta T$  for this reaction.

The calorimeter consists of an isolated vessel {thermos} with a compact cover pass through it a thermometer and stirrer.

Exothermic reactions evolve heat and have negative values of  $\Delta H$ , and endothermic reactions absorb heat and have positive values of  $\Delta H$ .

### Experiment Method:

1. Clean Dewor's flask (calorimeter) and put 100 ml of distilled water, stir and record the temperature for 10 minute in a 1 minute interval, be careful that the thermometer bulb immersed in water before starting.

- Rise up the cover and add quickly 1.5 ml of concentrated sulfuric acid and cover again then record the temperature for 5 minute in a half a minute interval.
- Plot the temperature as ordinate and the time as abscissa for a graphical correction for the heat exchange in calorimetry (calculate  $\Delta H$ ) as in Fig. 13.
- Draw 10 ml of a solution in the calorimeter, put it in a conical flask, add two drops of phenolphthalein indicator, and titrate with 1N NaOH.
- To determine  $\Delta H$  which is equivalent to this normality, plot a graph between  $\Delta H$  and normality N, data in table. And obtain it from this graph. Fig. 12.

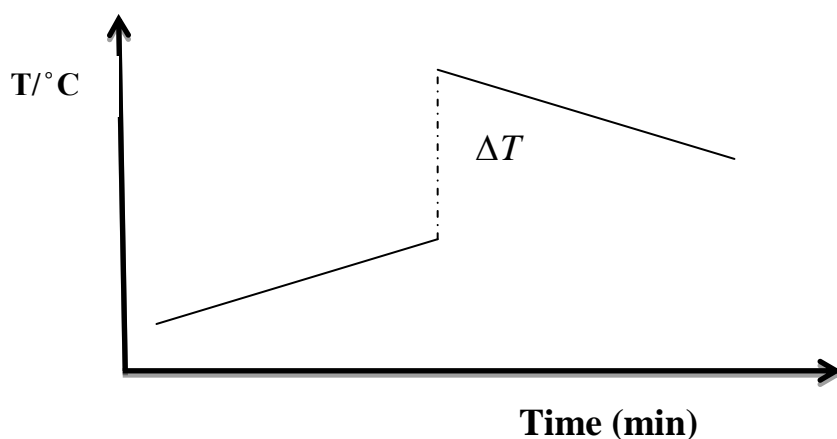
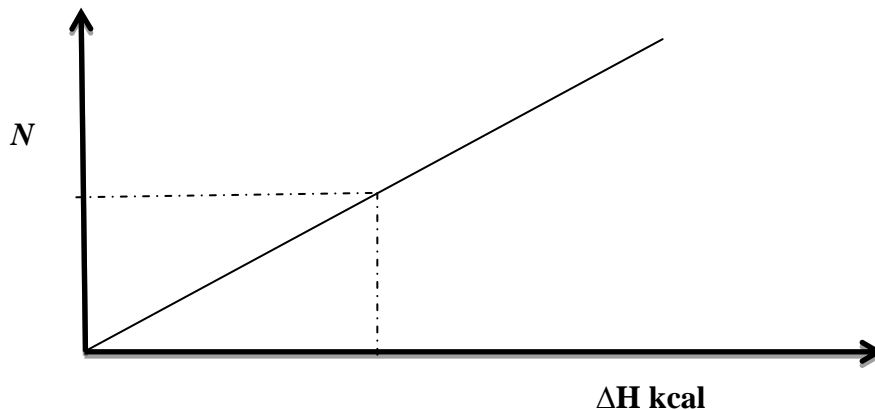


Fig. 11: A graph of the temperature as ordinate and the time as abscissa for a graphical correction for the heat exchange in calorimetry.

Acid added (ml) H=1.84	Normality of final solution (H)	Heat liberated $\Delta H$ (kcal)
3.0	1.100	0.946
2.5	0.918	0.780
2.3	0.842	0.718
1.5	0.552	0.473
0.75	0.227	0.242
0.6	0.217	0.191



**Fig. 13 : A graph between  $\Delta H$  and normality N.**

6 -Calculate the calorimeter constant from the following equation:

$$C = \Delta H * (V/100) * (1/\Delta T) \dots\dots\dots 22$$

V: Volume of solution in the calorimeter.

$\Delta T$ : The change in temperature.

C: Calorimeter constant.

$\Delta H$ : Heat liberated (from calibration curve).

## **Experiment no. 6**

### **Part (B)**

# **Determination of The Heat of Solution**

## **Introduction:**

The heat of solution of a solid or a liquid substance can be determined in practically the same manner as the employed for the determination of the heat of neutralization and the same apparatus can be employed. Since the heat which is evolved or absorbed on dissolving a substance depends on the amount of water or other solvent employed, the statement of the heat of solution has a definite meaning only when the concentration of the solution formed is given.

## **Experiment Method:**

1-Use the same Dewar's flask as in part A.

2-Place 100 ml distilled water heated to (36-40) °C in a Dewar's flask and record the temperature on the thermometer every minute for 10 minutes interval.

3-Add quickly a weighted quantity of ammonium chloride salt (8g) or any other salt and stir the solution with the continuous recording the temperature every half a minute for another five minutes.

**Calculation:**

1-Plot a graph between the temperatures as ordinate and the time as abscissa  $\Delta H$ .

2-Calculate the heat evolved or absorbed by dissolving this amount of salt using of equation:

$$X = \frac{W_1(T_2 - T_1)C_1}{1000} + C\Delta T \quad \dots\dots\dots 23$$

$W_1$ : Weight of dissolved salt.

$T_1$ : Laboratory temperature.

$T_2$ : Temperature of the heated water before the addition of the salt.

$C_1$ : Salt heat capacity (0.25).

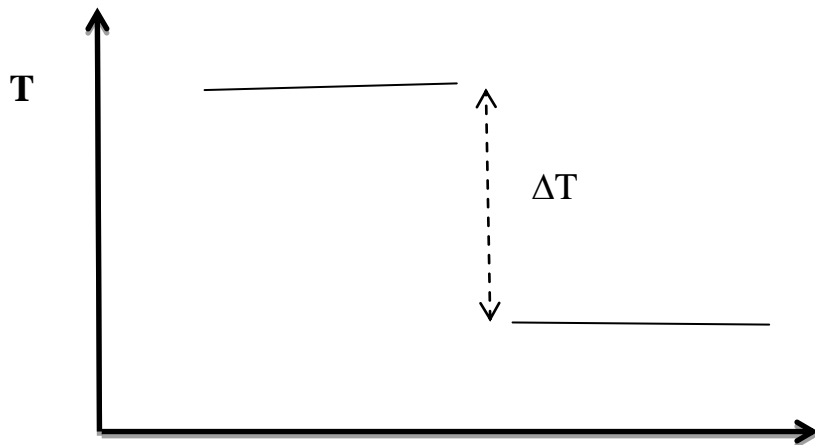
$H$ : heat evolved or absorbed.

$C$ : Calorimeter constant.

$$\Delta T = T_2 - T_1$$

3-Calculate the heat of solution that accompanying dissolving mal as:

$$\Delta H_{solubility} = \frac{X * M.wt_{salt}}{W_1} \quad \dots\dots\dots 24$$



**Fig. 14: a graph between the temperature as ordinate and the time as abscissa  $\Delta T$ .**

### **Question for discussion**

- Q1- Define the calorimetric constant and write the equation for calculating it. What is the Unit it?
- Q2- To which branch of chemistry is the determination of heat of solution, is linked?
- Q3- Define the endothermic and exothermic reaction.
- Q4- Write the mathematic equation for determining the heat of the solution. Define its Symbols. What is the unit?

## Experiment No. 7

# Equilibrium Constant

## Determination the Formula of the Complex Formed Between Copper (II) Ion and Ammonia

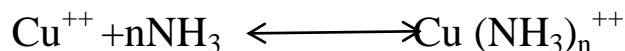
**The aim:** To Find the distribution coefficient (D) and calculate the stability constant  $K_s$ .

### Introduction:

The distribution coefficient of ammonia between carbon tetrachloride and water is given by:

$$D = \frac{[\text{NH}_3]_{\text{org}}}{[\text{NH}_3]_{\text{aq}}}$$

Although in the presence of copper sulfate solution some of the ammonia is present as the complex copper ammonium ion,  $\text{Cu}(\text{NH}_3)_n^{++}$ , the relationship (1) still applies to the concentration of "free" ammonia. Thus, from a study of the distribution of the ammonia between water and chloroform and an aqueous solution of copper sulfate and chloroform, the formula of the complex ion can be determined, assuming that the equilibrium:



Is completely to the right.

### Experiment Method:

- 1-Prepare 25 ml of 0.1 M hydrochloric acid, and then from it prepare 25 ml of 0.01M for titration.
- 2-Mix (15ml) of carbon tetra chloride  $\text{CCl}_4$  with (15ml) of 1M ammonia solution in separating funnel for 20 minute. Leave it for 10 minute to separate into two layers.
- 3-Drop 5 ml of the organic layer by pipette in conical flask, then add 10 ml distilled water and 8 drops green bromogresol indicator.
- 4-Titrate against 0.01M HCl, shake well the green yellowish color is appear.
- 5-Leave the aqueous layer.
- 6-Mix (25ml) of carbon tetra chloride  $\text{CCl}_4$  with (8ml) of 1M ammonia solution and (8ml) of 0.1M copper sulfate in clean and dry separating funnel for 15 minute. Leave it for 10 minute to separate into two layers.
- 7-Drop 5 ml of the organic layer by pipette in conical flask, then add 10 ml distilled water and 8 drops green bromogresol indicator.

- 8-Titrate against 0.01M HCl, shake well the green yellowish color is appear.  
 9-Leave the aqueous layer.

**Calculation:**

**First separation funnel:**

- 1-Calculate the ammonia concentration at organic layer,  $[NH_3]_{org}$ .
- 2-Calculate the ammonia concentration at aqueous layer,  $[NH_3]_{aq}$  by abstract the ammonia primary concentration from  $[NH_3]_{org}$ .
- 3-Calculate the distribution coefficient D from the relationship:

$$D = \frac{[NH_3]_{org}}{[NH_3]_{aq}}$$

Where  $[NH_3]_{aq}$  = Ammonia primary concentration -  $[NH_3]_{org}$

**Second separation funnel:**

- 1-Calculate the ammonia concentration at organic layer,  $[NH_3]_{org}$ .
- 2-Calculate the moles number of ammonia at organic layer, X

$$X = \frac{[NH_3]_{org} * V_{organic}(25ml)}{1000}$$

- 3- Calculate the ammonia concentration  $[NH_3]_{aq}$  at aqueous layer, by this equation:

$$[NH_3]_{aq} = \frac{[NH_3]_{org}}{D}$$

- 4-Calculate the free moles number of ammonia at aqueous layer, Y

$$Y = \frac{[NH_3]_{aq} * V_{aqueous}(16ml)}{1000}$$

- 5- Calculate the total moles number of ammonia, Z

$$Z = \frac{primary\ concentration * V_{mixture}(8ml)}{1000}$$

- 6-Calculate the associated moles number of ammonia,  $\bar{Z}$ .

$$\bar{Z} = Z - (X + Y)$$

- 7-The moles number of copper =  $\frac{Conc.\ primary\ Cu * V(8ml)}{1000}$

$$8- \quad n = \frac{\text{the associated moles number of ammonia}}{\text{the moles number of copper}}$$

$$9- \quad K_s = \frac{[\text{complex}]}{[Cu][NH_3]^n} = \frac{1}{[NH_3]^n} = \frac{1}{Z} = \frac{1}{(Z \cdot 1000)/16}$$

### Question for discussion

- 1- Define the distribution coefficient and write the mathematic equation for calculating it.  
Define its symbols. What is the unit it?
- 2- Define the equilibrium constant for the complex copper ammonium ion. Write its Chemical equation.
- 3- Write the chemical equation for the titration.
- 4- Where is the concentration of ammonia is more, in organic layer or in aqueous layer. Why?
- 5- Calculate the number of moles of ammonia ions in 100ml and 1M concentration.



## Experiment No. 8:

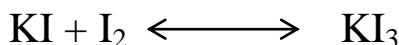
# Properties of Dilute Solution

## Distribution of a solute between immiscible solvents

**The aim:** To Find the distribution coefficient and calculate the equilibrium constant  $K_C$ .

### Introduction:

The reversible reaction:



Occurs in aqueous solution and according to the law of mass action the equilibrium constant  $K_C$  is given by:

$$K_C = \frac{[\text{KI}_3]}{[\text{KI}][\text{I}_2]}$$

The equilibrium may be investigated by studying the distribution of iodine between an organic solvent and water, followed by a similar study for the distribution of iodine between the same organic solvent and an aqueous solution of potassium iodide. The first study enables the distribution coefficient  $D$  to be calculated from the relationship:

$$D = \frac{C_{org}}{C_{aq}}$$

Where  $C$  is the concentration of the iodine (determined by titration).

Since the distribution law only applied to the species common to both layers, the concentration of free iodine in the aqueous potassium iodide layer  $C_{\text{KI,aq}}$  can be determined from the relationship:

$$C_{\text{KI,aq}} = \frac{C_{org}}{D}$$

The iodine combined with potassium iodide to form may be determined since the total iodine in the aqueous potassium iodide layer may be obtained by titration.

The amount of iodide which has combined with the iodine can then be found and as the original concentration of iodide is known the amount of uncombined iodide may be obtained by difference, hence  $K_C$  may be calculated.

### **Experiment Method:**

#### **First separation funnel:**

- 1- 5 ml of saturated solution iodine in carbon tetra chloride is shaken with 50 ml of distilled water in cleaned and dried glass Stoppard for 15 minutes.
- 2-Leave the solution to separate into two layers at least 15 minutes.
- 3-Use a pipette to take 20 ml of aqueous layer, and then titrate with 0.025 M sodium thiosulphate by using starch solution as an indicator.
- 4-Use a pipette to take 1 ml of organic layer, add 10 ml of distilled water then titrate with 0.025 M of sodium thiosulphate by using starch solution as an indicator.

#### **Second separation funnel:**

- 1- 5 ml of saturated solution iodine in carbon tetra chloride is shaken with 50 ml of aqueous solution of potassium iodide KI (0.1 M) in cleaned and dried glass Stoppard bottles for 15 minutes.
- 2 -Repeat steps (2, 3, and 4) of first funnel.

#### **Calculation:**

- 1-Calculate the distribution coefficient H from the following equation:

$$D = \frac{[I_2]_{org}}{[I_2]_{aq}}$$

- 2-Calculate equilibrium constant  $K_C$  from equation No. (27) by calculate each concentration:

$$\text{Uncombined } [I_2]_{aq} = \frac{[I_2]_{org}}{[D]}$$

$$\text{Combined } [I_2] = \text{total } [I_2] - \text{uncombined } [I_2]$$

$$\text{Combined } [I_2] = \text{combined } [KI] = \text{formed } [KI_3]$$

- 3- Remaining  $[KI] = \text{total } [KI] - \text{combined } [KI]$

$$K_C = \frac{\text{formed } [KI_3]_{org}}{\text{remaining } [KI] * \text{uncombined } [I_2]}$$

### **Question for discussion**

- 1-Define the distribution coefficient and write the mathematic equation of it. Define its symbols. What is the unit it?
- 2-Write the chemical equation for the titration.
- 3- Define the equilibrium constant for the complex. Write its chemical and mathematic equations. What is the unit it?
- 4- Where is the concentration of  $I_2$  is more, in organic layer or in aqueous layer. Why?
- 5-Write the benefits of the distribution law.

## Experiment No. 9

# Relative Molecular Mass

### Determine the relative molecular mass of polymer from viscosity measurements

**The aim:** Find the value  $|\eta|$  then find the relative molecular mass of polymer.

#### Introduction:

The viscosity of polymer solution is related to the relative molecular mass,  $M_r$  of the polymer by equation:

$$\frac{\eta_{sp}}{c} = \frac{\eta - \eta_0}{c} = KM_r^\alpha \dots\dots\dots 25$$

Where  $\eta_{sp}$  is the specific viscosity of the solution,  $\eta_0$  and  $\eta$  the viscosities of solvent and solution respectively, g/l the weight of polymer in 100 cm<sup>3</sup> of solution and K and  $\alpha$  constants. This equation is only valid for low concentrations (<0.5 to 1%) of  $\eta$  linear polymer, dissolved in a solvent in which there is no association. It is thus necessary to extrapolate the curve of C against  $\eta_{sp}/c$  to  $c=0$ ; the intercept is the intrinsic viscosity  $|\eta|$ . Thus, in the limit, equation (1) becomes:

$$|\eta| = KM_r^\alpha \dots\dots\dots 26$$

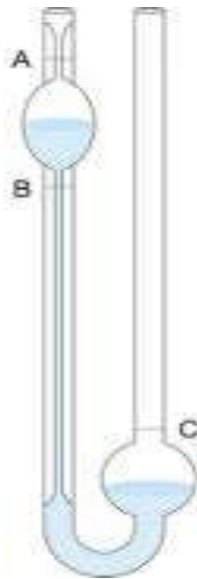
In general, the value of K depends on the type of polymer, the solvent and the temperature, while  $\alpha$  is  $\eta$  function of the geometry of the molecule. The isometric method of determining relative molecular masses is very convenient and gives accurate results K and  $\alpha$  is known. These are obtained from samples of polymer of known  $M_r$  determined by alternative methods.

To calculate the relative viscosity for the solution, use equation (3).

$$\frac{\eta}{\eta_0} = \frac{\rho t}{\rho_0 t_0}$$

### Experiment Method:

- 1-Weight the five empty cleaned and dried (25ml) volumetric flask with its cover.
- 2-Prepare four polymer solutions (2, 4, 6 and 10 g/l).
- 3-Weight them again after fill one of them with distilled water and the others with polymer solutions above to calculate the density.
- 4-Cleaned and dried the viscometer then clamped it vertically.
- 5-Distilled water (10 ml) is introduced in the wide tube of the viscometer.
- 6-The water in the viscometer is forced up through the capillary tube by suction through a rubber tube attached to the end (a) the volume of the water introduced must be sufficient to fill the bulb (c), otherwise, air bubbles will form in the capillary and affect the time of flow (t), repeat that twice to get the correct time.
- 7-Allowed the water to flow down the capillary tub. The time required for the liquid to pass from the upper mark (a) to lower mark (b) is noted  $t_0$
- 8-Repeat the above steps on using different concentration of polymer using exactly the same volume (10 ml) to calculate  $\eta$  in different concentration.



### Calculation:

- 1-Let the time of flow of the polymer be  $t$ , its density  $\rho$ , and its viscosity  $\eta$ . The time of flow of water be  $t_0$ , its density  $\rho_0$ , and its absolute viscosity  $\eta_0$ . Then:

$$\frac{\eta}{\eta_0} = \frac{t \rho}{t_0 \rho_0}$$

Poise= dynes /cm<sup>3</sup>/ unit viscosity gradient.

Take the viscosity of water at laboratory temperature from the table.

2 -Put the results as in the following tables:

C g/l	ρ (g/cm <sup>3</sup> )	t (sec)	$\frac{\eta}{\eta_0}$	$\frac{\eta}{\eta_0} - 1$ ( $\eta_{sp}$ )	$\frac{\eta_{sp}}{C}$

3-Plot  $\eta$  curve between ( $\eta_{sp}/c$ ) against C from the equation:

$$\frac{\eta_{sp}}{C} = \frac{\eta - \eta_0}{C} = KM_r^\alpha \dots\dots\dots(1)$$

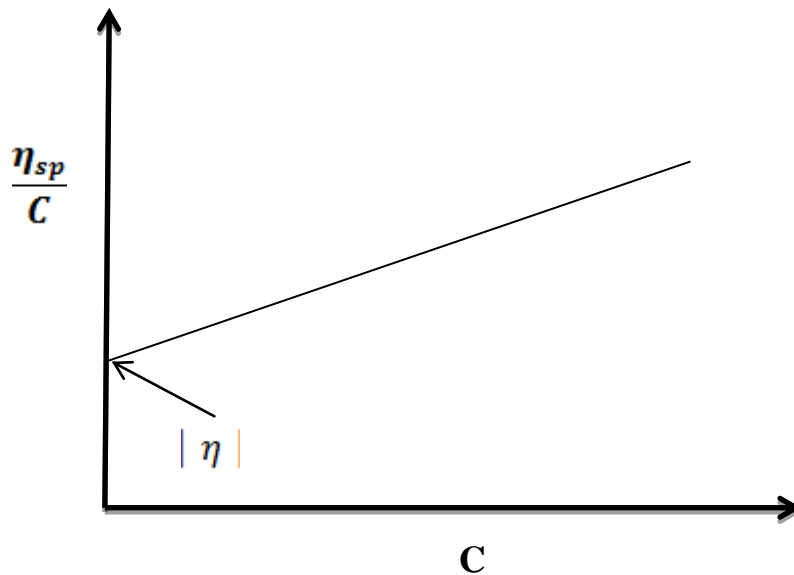


Fig 15: curve between ( $\eta_{sp}/c$ ) against C

2-Find the value  $|\eta|$  from the intercept, then find the relative molecular mass of polymer (M) from the equation (2),  $\alpha = 0.76$  and  $K = 2 \cdot 10^{-4}$ .

$$|\eta| = KM_r^\alpha \dots\dots\dots (2)$$

**Question for discussion**

- 1: Define the viscosity. What is the unit of it?
- 2: What is van Hunk'η equation? Define its symbols.
- 3: Write the linear equation for your experiment. Define the slope, intercept, and the symbols.
- 4: What are the affective factors determine the relative molecular mass of η polymer from η viscosity measurement?
- 5: What is the relative viscosity of a solution? Write the mathematic equations of it. Define the symbols.

## Experiment No. 10

# A Three Component Liquid System

## The Triple System

### **The aim :**

3-Plot the triangular diagram.

4-Find the number of phases on the triangular diagram, above it and under it.

### **Introduction:**

In many cases, the addition of a third component to a pair of almost immiscible liquids does not appreciably increase their solubility in each other. However, the addition of a third liquid intermediate in polarity may have a large effect, and such a case is illustrated in this experiment.

To depict the phase behavior of three component system on a two-dimensional diagram, it is necessary to consider both the pressure and the temperature as fixed. The phase of the system as a function of the composition can then be shown Fig 16. The relative amount of the three components, usually presented as percent by weight, can be shown on a triangular plot, as indicated in Fig below. The corners of the triangle labeled A, B, and C correspond to the pure component A, B, and C the side of the triangle opposite the corner labeled A, for example implies the absence of A. Thus the horizontal lines across the triangle show increase the percentage of A from zero at base to 100 percent at the apex. In similar way the percentage of B and C are given by the distance from the other two types to the remaining two apices. From the three composition scales of the diagram the composition corresponding to any point can be read off. This procedure for handling the composition of the three-component system is possible, and the total composition is always 100 percent. Necessary part of the diagram is the tie lines through the two phase region joining the composition of the two phases that are in equilibrium

This principle is applied in constructing the solubility curves. Mixtures of liquids A and C of various proportions are prepared corresponding to the points marked Component B is added until the solubility curve is intersected, whereupon a second conjugate ternary solution appears, its composition being given by the tie line. Necessary part of the diagram is the tie lines through the two phase region joining the composition of the two phases that are in equilibrium



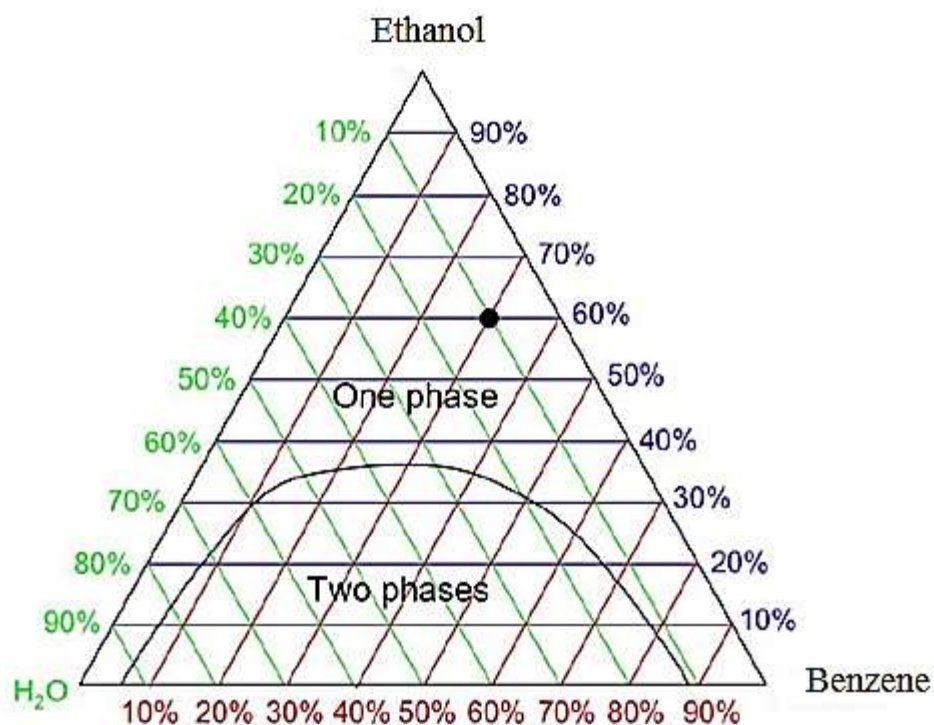


Fig. 16: triangular diagram for Three Component Liquid System

1-Put in five clean, dry round bottle flask benzene and ethanol as shown in the table to get a clear mixture:

No. of flask	Benzene/ ml	Ethyl alcohol/ml
1	8	3.8
2	5.7	6.4
3	3.7	8.9
4	1.2	10.9
5	0.5	12.0

2-Fill the burette with water.

3-Add to each flask the water drop after drop until get turbid mixture, then record the volume of water.

### **Calculation:**

- 1-The density of Ethanol is 0.789 gm/ml, water is 0.996 gm/ml and benzene is 0.87 gm/ml.
- 2-Calculate weight percentage for each substance in the mixture, then fill the table:

<b>Flask number</b>	<b>Weight % of benzene</b>	<b>Weight % of ethanol</b>	<b>Weight % of water</b>	<b>Total Weight %</b>
<b>1</b>				
<b>2</b>				
<b>3</b>				
<b>4</b>				
<b>5</b>				

- 3-Plot the triangular diagram.
- 4-Find the number of phases on the triangular diagram, above it and under it.

### **Question for discussion**

- 1- What is the benefit from studying the triple phase system? What are the affective factors  
Depend on?
- 2- Define the phase of a triangular diagram.
- 3- Why is Benzene and Ethanol mixture turbid on adding water?
- 4- Find the number of phases in the triangular diagram, (above and under the curve).
- 5- Calculate the percentage of a mixture with three component, (Benzene, Ethanol and Water) knowing that the weight of the three components is 0.1, 0.2 and 0.4 gm Respectively.