AL-Mustansiriyah University College of Science Chemistry Department

Practical Physical Chemistry

Second stage Second course

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Second Course Experiments

1-Finding the molecular weight of an unknown solid by the method of decreasing the degree of freezing.

2- Findingthe molecular weight of an unknown solid by boiling point method.

3- Phase diagram of a binary group consisting of (solid - solid).

4- Mutual solubility between (phenol- water).

5-Determine the solubility of sodium sulfate and determine the transition point.

6-Solubility as a function of temperature.



Introduction

The effect of the solute on some properties of the solvent

The solvent has the most important properties :

1-*Vapor pressure:* It is a measure of a liquid's tendency to vaporize and it changes directly with temperature.

2-*Boiling point*: It is the temperature at which the vapor pressure of a liquid is equal to the pressure on it.

3-*Freezing point*: It is the temperature at which a liquid turns into a solid under atmospheric pressure.

-*It has been observed that any solution that contains a (non volatile solute) will exhibit the following bonding properties:

1-Decreased vapor pressure of the solvent.

- 2- High boiling point.
- 3- A decrease in the degree of freezing.
- 4- Osmosis and osmotic pressure of the solution.

Bonding properties: It is that property that depends only on the number of solute particles present in the solution and does not depend in any way on the chemical nature of these particles.

* Note : The present solute must not occur in any union or dissociation. If there is a union of solute particles, the actual number of particles added will become small and as a result, these properties will decrease. Similarly, if the solute particles dissociated, as in the case of the electrolytes, the number of particles becomes greater than the original number and the value of the bonding properties becomes higher. In these solutions in which the particles of the solute occur to unite or dissociate, there must be some basic modifications to the laws producing solutions in which the solute particles do not unite or dissociate While discussing these properties it should be assumed that solutions They are very dilute and ideal, that is, the unions between solute particles are small To the point of neglect. The study of these properties helped a lot in calculating the molecular weight of non-volatile solutes.

We will take the first associative property which is (no experiment only explanation)

1-The decrease in the vapor pressure of the solvent

When a non-volatile solute is added to the (liquid) solvent, the vapor pressure of the solvent decreases because the solute molecules impede the escape of the solvent molecules from the surface of the liquid. In the vapor pressure of the solvent, from this we conclude that the decrease in the vapor pressure of the solvent depends on the number of dissolved particles and not on the chemical nature of the solute, and this can be explain according to Raoult's law.

 $P = p^{o}. x_{1} \longrightarrow (1)$

X 1 = moL fraction of the solvent

 P^{o} =vapor pressure of the pure solvent

P= vapor pressure of a solvent when a substance is dissolved in it (above the solution)

Since X $_1$ Positive quantity less than one unit, then the vapor pressure of the solvent (P) is less than (p o)

The decrease in vapor pressure (ΔP) is given by the following equation :-

 $\Delta P = P^{\circ} - P \longrightarrow (2)$

Substituting (1) into (2), we get

$$\Delta P = p^{\circ} - (p^{\circ} \cdot x_{1})$$

$$\Delta P = p^{\circ} (1 - x_{1}) \longrightarrow (3)$$

$$X_{1} + x_{2} = 1$$

$$X_{2} = 1 - x_{1} \longrightarrow (4)$$

X 2 = mol fraction of the solute

Substituting (4) into (3), we get:

 $\Delta P = p^{\circ} x_2$

Equation (2) can be written as follows:

$$\frac{\Delta P}{p^{\circ}} = \frac{p^{\circ} - p}{p^{\circ}} = X_2$$

That :

p^o - p

 \mathbf{P}^{o}

-: It is the amount of decrease in vapor pressure and this indicates that the decrease the relative vapor pressure is a correlative property of being dependent on x_2 For the solute and nothing else.

The first experiment

Measurement of the molecular weight of a solid by the decrease in freezing point

2-Decrease in freezing point

The reason is that the presence of solute particles between the solvent molecules impedes the convergence of the solvent molecules until it freezes, for example, at the normal freezing point of water. The solute particles work to keep the water molecules apart, so the water does not freeze, and to bring the water molecules closer together, the temperature must be lowered to less than the normal freezing point.

Raoult found that the freezing point varies directly with the molality of the solution

Amount of decrease in freezing point α molality of the solution

 $\Delta t = Kf$ The molality of the solution

 $\Delta t = Kf \times number of moles of solute / weight of solvent (kg)$

Solute (M.wt/Wt) $x K_f = \Delta t$ Weight of solvent (kg)



Note: You must pay attention to the weight of the solvent converted by law directly to Kg

 $\mathbf{M.Wt} = \frac{K_{f} X \text{ solute } W_{1} X 1000}{\text{Solvent } W_{2} X \Delta t}$

Where K_f It is the constant of decrease in the degree of freezing (molality) and it is a constant specific to each solvent.

Kf : It is a constant specific to each solvent and is the amount of decrease that causes one mole of solute to dissolve in 1000 grams of the solvent.

The following table shows the values of (k) for some known solvents

solvent	K
water	1.86
Acetic acid	3.90
Benzen	4.9 - 5.10
Formic acid	2.8
Phenol	7.3
Camphor	40.0

Working method:

The simplified device consisting of two glass tubes, one inside the other is taken and placed inside a glass container containing ice and salt (ice bath). The solid substance and solvent are placed in the inner tube with a thermometer to measure the temperature. This device is called (Beckman device) and this method is called (Beckman method).

1- (10 ml) Benzene is weighed and the weight is recorded. Then it is placed in the inner tube with the thermometer while stirring, and the temperature is measured every (30 seconds) while recording the time until the solidification of the Benzene (solvent).

(Super Freezing phenomenon must be exceeded) In the event that it occurs, the tube is removed from the ice bath immediately.

2- The inner tube containing the pure solvent is taken out of the ice bath and held by hand to dissolve the Benzene

3-(0.5 g) of the unknown solid is weighed and placed in the inner tube with benzene, and the inner tube is placed inside the

second tube in the ice bath with stirring, and the temperature is measured every (30 seconds) with time recording until the mixture freezes and the freezing point recorded.



Beckman device

Calculations:

1 - Calculate the molecular weight from the law

M.Wt = $\frac{K_f X \text{ solute } W_1 X 1000}{M_1 W_1 W_2 W_2 W_2}$

Solvent $W_2 \mathbf{X} \Delta t$

M.Wt = Molecular weight of the solute (g/ mol)

=W 1 Solute weight (gm)

W₂ = Solvent Weight (Kg)

K_f =Freezing point decrease constant(5.19 K.Kg / mol)

 Δt =The difference in temperature between (freezing of a pure solvent and a solvent with an impurity)



2- We draw the graph between temperature and time

10

second experience

Measurement of the molecular weight of a solid by the height method boiling point

3 - High boiling point

As we studied previously, when adding a solute in a pure solvent will lead to a decrease in the freezing point of the solvent and at the same time lead to a rise in the boiling point and the reason is as we previously learned that the solute reduces the vapor pressure of the solvent and this needs heat more than the heat needed by the pure solvent until Their vapor pressures are equal, and thus the boiling point of the solvent rises in the presence of the solute when the pressure on it is constant. It was found that: The increase in the boiling point of the solvent varies directly with the molar concentration of the solution.

Amount of increase in boiling point α molality of the solution

- $\Delta t = K_b$ The molality of the solution
- $\Delta t = K_b \times \text{number of moles of solute / weight of solvent (kg)}$

Solute (M.wt /Wt)
Weight of solvent (kg)
$$x K_b = \Delta t$$



Note: You must pay attention to the weight of the solvent converted by law directly toKg

M.Wt = $\frac{K_b X \text{ solute } W_1 X 1000}{\text{Solvent } W_2 X \Delta t}$

Where kb :- is the boiling point constant, and it is a solvent-specific constant, and it varies with the change of the solvent.

The method of work:

1- Install the device for this experiment.

2-Weight (10 ml) of benzene and is placed in the beaker with two holes (one hole is placed in which a thermometer is placed and the other hole is connected to a condenser) and the boiling point of pure benzene is measured after we fix the temperature. 3-weigh (0.5 gm) of the unknown substance (solid) is placed on benzene and we measure its boiling point after we fix the temperature.



Calculations:

1-We calculate the molecular weight from the law:

M.Wt = $\frac{K_b X \text{ solute } W_1 X 1000}{\text{solvent} W_2 X \Delta t}$

M.Wt =Molecular weight of the solute (g/mol)

W₁ =Solute weight(gm)

 $W_2 =$ Solvent weight (Kg)

K b= Freezing point decrease constant (2.5 K.Kg / mol)

 Δt = The temperature difference between (pure solvent and solvent with impurity)

third experience The

Phase diagram of a binary group consisting of (solid (solid

The theoretical part:

The phase rule was developed by CBS: It expresses the conditions for the occurrence of a state of equilibrium in a heterogeneous system, regardless of the number of components or phases in that system.

F+P=C+2

C= Represent the number of components

P= represents the number of phases

F= Represents degrees of freedom

Phase: It is the homogeneous part that is physically distinguished and separated from the rest of the other parts of the system by separating boundaries.

Example (snow, liquid water and water vapor) Here each form is a separate phase

Solid system (homogeneous) where the phase is single, regardless of the number of components it contains



That mean, the two liquids are completely mixed and form one homogenous layer then it will be one phase

That mean, the two liquids are not mixed, then there are two separate phase, such as (benzene and water)

The gaseous system (homogeneous) means the gases are always mixed and form a homogeneous mixture that is always a single phase, regardless of the number of components Number of **components**: It is the smallest number of variable components by which the composition of each phase can be expressed either directly or indirectly or in the form of the chemical equation.

An example of a water system that is (ice, water, and water vapor) in equilibrium is considered a system with one component, which is water.

Degrees of Freedom: The number of variables such as temperature, pressure, or concentration that must be specified to define the system completely.

The phase base is affected by its equilibrium only by temperature, pressure, and concentration, and not by any other forces such as gravity, electricity and magnetism. Let's take some examples:

(One component system)

1- water (H₂O) system (ice and water and water vapor)

F+P=C+2 F+3=1+2 F=3-3=02-Acetone (liquid and vapor acetone F+P=C+2 F+2=1+2F=3-2=1

(G-S)(G-L)(LL)(SL)(SS) (Two-component system, twocomponent system)

(L-L) (SS) will be studied

In such systems experiments are conducted under atmospheric pressure, thus the pressure remains constant, and this will reduce the degree of freedom of the system by one degree, and the phase base becomes called (reduced phase rule). F+P=C+1

F=C-P+1

In our experiment, the container is a two-component system (P=1) and single phase (C=2)

The number of degrees of freedom according to the (reduced phase rule), then:

F+P=C+1

F=2-1+1

F=2

That is, it needs two variables to define the system, which are temperature and concentration.

As for the (normal phase rule), the following:

F+P=C+2

F=2-1+2

F=3

That is, it needs three variables to define the system: concentration, pressure and temperature. In such a case, it is difficult to draw in three dimensions on the graph, so one of the variables, which is pressure, is fixed, and the change in temperature and concentration is done for the purpose of defining the system.

Let's take a general case of concentrated systems, which are systems that do not have a two-component gas phase They contain two components, B and A, which mix well in the liquid state, and their solutions produce only pure A or pure B as solid phases. As shown in the chart below



% of one of two components

The figure shows the phase diagram

1- The components A and B mix completely in the liquid state and their solutions produce only pure A and pure B as solid phases.

2-(A,B) The points represent the two melting points (degrees of freezing) for pure A and pure B respectively

3- When a quantity of B is added to A, the degree of freezing of A decreases along the AC curve, and in the same way, when a quantity of A is added to B, the degree of freezing of B decreases along the curve BC.

4- The AC curve is a curve that represents the freezing point of component A and represents the composition of solutions saturated with solid A at temperatures between A and C, so we notice that the two phases are in equilibrium along AC (solid A and solution B are in A).

If we apply the reduced phase rule, then:

F=C-P+1

F=2-2+1

F=1

5- Similarly, the curve BC is the freezing point curve of component B and represents the composition of solutions saturated with solid B at temperatures between B and C, so we notice that the two phases are in equilibrium along BC (solid B and solution A are in B).

If we apply the reduced phase rule, then:

F=C-P+1 F=2-2+1

F=1

6-The two curves intersect at point C where both solids A and B are in equilibrium with the liquid phase and since there are three phases in equilibrium at this point, the reduced phase rule is as follows at point c

F=C-P+1

$$F = 2 - 3 + 1$$

F=0

That is, at this point the temperature and composition of the solution are constant as long as the three phases are in equilibrium. If there is a change in one of these two variables, at least one of the phases will disappear

Point C is known as the eutectic point. It is the temperature at which the solids are in equilibrium with the liquid phase.

7- The area above the lines AC and BC is related as the field for the presence of the unsaturated solution or the molten liquid (the two components exist as a homogeneous liquid solution) and thus there is only one phase and the system is bivariate and according to the reduced phase rule F=C-P+1 F=2 - 1 + 1

F=2

That is, in order to define any point in this region, the temperature and composition must be specified.

Working method :

1- (11) test tubes are taken and the percentage set in the table for each of two substances is placed in them

(B- Naphthol - Acetamide). In our experiment (S-S), we will take two solid materials, which are (Bethanphthol) B and (Astamide) A. The sum of the total weight of the two materials = 6 gm in each tube

For example, if we take % A = 90 What is the percentage of B ? total sum of the two substances = 6gm

(A)



As for the percentage of substanceB

$$\% = \frac{0.6}{6} \times 100$$

A%	weight (A)	B weight	B %	tube
	acetamide	B-Naphthol		number
100%	6gm	0	0%	1
90%	5.4 gm	0.6 gm	10%	2
80%	4.8 gm	1.2 gm	20%	3
70%	4.2 gm	1.8 gm	30%	4
60%	3.6 g	2.4 gm	40%	5
50%	3 gm	3 gm	50%	6
40%	2.4 gm	3.6 g	60%	7
30%	1.8 gm	4.2 gm	70%	8
20%	1.2 gm	4.8 gm	80%	9
10%	0.6 gm	5.4 gm	90%	10
0%	0	6 gm	100%	11

Thus, the rest of the tubes are calculated in the same way

Each tube is placed in a hot water bath (except for tubes (1) and (11) and the beginning of melting and the end of melting are recorded and takes an average of two degrees. We take the average of the two readings.

As for the tube (1 and 11), it is placed on the (Hot Plate) directly because it contains the pure substance without adding the second substance to it, and the degrees are recorded in the same way mentioned above.

Calculations:

We draw the graphical relationship between the average of the temperature (Tem) and the percentage of one of the two components and calculate the eutectic point from the graph.



The percentage of one of the two components

Fourth experiment

Finding the mutual solubility of phenol and water The theoretical part

The critical temperature of dissolution is determined from the graph of the mutual dissolution between (H_2O , Phenol) and it was found experimentally that some liquids:

It is homogeneous (single phase) that mixes and dissolves with each other and in all proportions, such as (alcohol and water).

or be heterogeneous (two-phase) no They mix completely with each other, such as (ether and water), that is, they partially dissolve with each other, forming a heterogeneous solution. There is no excess ether in it, and the upper layer is the watersaturated ether layer.

It was found that the solubility of ether and water increases with increasing temperature until it reaches the temperature called: *the critical temperature* : It is the degree to which if you count the mixture, each of the two solutions becomes dissolved in the other for all proportions, forming a homogeneous solution with one phase. But if water is mixed with phenol, two layers are formed, and the ratio of the two substances in each layer depends on the temperature. If the two layers are heated, the amount of water in the phenolic solution and the phenol in the aqueous solution will increase until it reaches the critical temperature where the concentration of the two layers becomes equal and then the two liquids become completely miscible. And since there are liquids that have a higher critical temperature of dissolution, that is, the two liquids mix with each other with an increase in temperature, while other liquids have a lower critical temperature of dissolution, at which the two liquids mix with each other at a lower temperature. N(CH₃)₃ As shown below , the types of critical temperatures are:



Higher critical Temp. (water and phenol)



Lower critical Temp. (water and $N(\mbox{CH}_3)_3$)



Lower and higher critical Temp. (water and Nicotine)



Phase diagram of phenol and water

The method of work:

1- They are placed in the tubes and as shown in the table below, we will take two substances, phenol and water, bearing in mind that the total volume of the two substances is 10ml. If the percentage of phenol is 70%, how do we calculate the percentage of water? And the volume of phenol and the volume of water?



(Volume of phenol) 7 ml = Part

10 - 7 = 3 ml (volume of water)

%Water =
$$\frac{3}{10}$$
 x100

% water= 30%

water	water %	phenol	phenol%	tube
volume		volume		number
1	%10	9	%90	1
2	%20	8	%80	2
3	%30	7	%70	3
4	%40	6	%60	4
5	%50	5	%50	5
6	%60	4	%40	6
7	%70	3	%30	7
8	%80	2	%20	8
9	%90	1	%10	9

2- Each tube is placed in a hot water bath, and the temperature is calculated when the two liquids become completely mixed, and then the tube is cooled and the temperature is recorded when the two liquids become incompletely mixed (i.e. the solution becomes turbid). Then we take the average of two degrees for each tube.



Calculations:

We draw the graphic relationship between the average temperatures and the percentage of one of the two components for each tube and its color. The highest critical temperature for melting is determined from the graph



Fifth experience

Determine the solubility of sodium sulfate in water and find the transition point

The theoretical part

Solubility: It is the number of grams of solute in 1,000 grams of solvent. There is an equation called the Vant- Hoff equation .

It shows the change of solubility of a substance with temperature at constant pressure in order to calculate the solubility and temperature of the solution.

 $\frac{\partial \operatorname{Lin} S}{\partial t} = \frac{\Delta H}{RT}$

After integration for this equation and taking the logarithm of both sides, we get:

$$Log S = \frac{-\Delta H}{2.303 \text{ RT}}$$
whereas:

$$C = \text{proportionality constant}$$

$$S = \text{solubility}$$

R = general constant for gases

T = absolute temperature units (K)

 ΔH = heat of dissolution (solution) units (J/ mol) or (Cal / mol) Among the factors affecting solubility:

- 1-nature of solute
- 2-nature of solvent
- 3-temperature
- 4-Pressure

The solubility increases or decreases with the increase in temperature, and this depends on the type of reaction, whether it is emitting or endothermic. In both cases, the solubility curve is linear as long as the substance is in contact with the solution and without any change in its chemical composition. There will be a fracture or the so-called discontinuity and a change in direction.

In our experience this must know what is a saturated solution?

It is the solution in which the solvent does not absorb any additional amount of solute.

The unsaturated solution is the solution in which the solvent can dissolve quantities of solute (i.e. absorb additional quantities of solute) When the solid (the solute) is in contact with the liquid (the solvent) in which it is soluble, it diffuses in the solvent until the state of saturation occurs.

The temperature at which a substance changes from one crystalline form to another crystal form without any change in its composition is called a transition point.

Na $_2$ SO $_4$.10H $_2$ O \rightleftharpoons Na $_2$ SO $_4$ +10H $_2$ O

The solubility (S), it is calculated using the mathematical relationship:

Weight of solute Solubility (S)=100×

Weight of solution

The method of work:

1- We take six clean, dry sacks and number them according to the temperatures (55, 50, 45, 40, 35, 30) and weigh them empty and record the weight (six weights).

- 1- We take (40ml) of distilled water and put it in a beaker and heat it to a temperature of (60 °C), and then add sodium sulfate to the hot water until a saturated solution is prepared from it.
- 2- The solution is cooled to a temperature of (55 °C) and then withdrawn by a pipette (5ml) of the saturated solution and placed in the first beaker (55°C) and the same step is repeated in the remaining degrees.

4- Weigh the six beakers with the solution to get (six weights), then leave them in the oven until the next day :Weight of the beaker with the solution - the weight of the beaker when it is empty = weight of the solution

5 -On the second day, the beakers are weighed with the solute (the precipitate) and the weight (six weights) is recorded.

Weight of beaker with solute - weight of beaker when empty = weight of solute

Calculations:

A-We calculate the solubility (${\bf S}$) of the six beakers

Solubility(S) = 100 ×-

Weight of solute

Weight of solution

tc °	Т (К)	1/T	weight of	solute weight	S	LogS
			solution			
55	(55+273)		4 4	р 5		
50			e ste iber	e ste ber		
45			n the	ո the ոսm		
40			rom	rom		
35				LL.		
30						

B - We draw the graph between Log S and 1/T to calculate the heat of dissolution (solution):

It is the heat resulting from dissolving sodium sulfate in 40 ml of distilled water.

After that, we calculate the transition point, that is, the temperature at which a change in the crystalline form of sodium sulfate occurs.



The transition point will be 1/T, we take its reciprocal, we get (K) T, subtract from it (-237), we get ($t^{o}c$), which is the transition point.

R: value can be used

R = 0.082 Lit. atm .mol⁻¹. K⁻¹

 $R = 8.314 \text{ J. mol}^{-1} \text{ K}^{-1}$

R = 1.987 Cal. atm .mol⁻¹. K⁻¹

Sixth experiment

Solubility as a function of temperature

The theoretical part:

Similar to the theoretical part of the fifth experiment

The method of work



1- Prepare three saturated solutions of oxalic acid at different temperatures (ice) (water with ice) (water)

2- Leave the three solutions for 5 minutes to take the temperature of the bath in which they were placed.

3- Take three clean, dry conical flasks and weigh them while they are empty

4- (10) of the clear solution is withdrawn from each solution by the pipette and placed in a clean, dry conical flask, weighed and recorded (the weight of the flask with the solution). 5- The solution is diluted with (10) of distilled water and two drops of phenophthalein are added to it and then it is titrated with NaOH (1N) and the volume of the three solutions is recorded.

Calculations:

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the method of work according to steps 3 and 2 From

The weight of the beaker when empty = known

The weight of the beaker with the solution (10ml)= known three times

1- Calculate the standard of oxalic acid according to step No. (5) for each solution according to the law

$$\left(\begin{array}{c} (N_{1} \times V_{1})_{NaOH} = (N_{2} \times V_{2})_{H2C2O4} \\ (1N \times \text{ from burette})_{NaOH} = (N 2 \times 10 \text{ ml})_{H2C2O4} \end{array} \right)$$
Three times for three solutions
2- Calculate the number of grams of oxalic acid for each solution, i.e. (the weight of the solute)

$$\begin{bmatrix} N_{1} = \frac{Wt_{1}}{eq.wt} & \frac{1000}{Vml} \\ Wt_{1} = ? \end{bmatrix}$$
Three times for three solutions

$V = 10 \text{ ml} = \text{acid size}$ $eq.wt = \frac{90}{2} = H_2 C_2 O_{4 \text{ of oxalic acid}}$	
3- We calculate the number of grams of solution for each solution (ie (the weight of the solution)	
<pre>Weight of solution = Weight of beaker with solution - Weight of beaker empty Weight of solution =?</pre>	Three times for three solutions
3- Calculate the number of grams of solvent (water) for each solution (the weight of the solvent)	
The number of grams of solvent = weight of the solution - weight of the acid Grams of solvent =?	Three times for three solution
5-We calculate the number of grams of acid (weight) in (1000)

gm) of solvent for each solution (molality of acid).

Three times for three solutions	Weight of acid solute	Weight of solvent water
(molality)	W 1	W 1
	l m	1000

6-work schedule

m	Logm	Т	1/T

7-We draw the graphic relationship between Logm and 1/T and then calculate the heat of the solution ΔH



 $R = 8.314 \text{ J. mol}^{-1} \text{ K}^{-1}$

 $(\Delta H = J/mol$