1. Thermochemistry – Experiment 1.1.

WATER EQUIVALENT OF THE CALORIMETER

Aim: To determine the water equivalent of the given calorimeter.

Principle: A thermos flask of about 200 cm^3 capacity fitted with a thermometer and stirrer through the cap can serve as a good calorimeter for thermochemical experiments. When hot water of known temperature is mixed with cold water in the flask, heat lost by the hot water will be equal to the heat gained by cold water and the flask. Heat absorbed by the flask may be considered as equivalent to the heat absorbed by a certain mass of water for the same change in temperature, assuming the specific heat of water to be 1 calorie per gram. This calculated mass of water is called the water equivalent of the flask.

Procedure: Wash the flask with water and drain. Measure exactly 100 cm^3 of distilled water into the flask using a burette. Insert thermometer and stirrer and close the lid. Stir well and note the constant reading T_1 on the thermometer. (Do not remove this thermometer from the calorimeter).

Measure out exactly 100 cm^3 of distilled water into a clean 250 cm^3 beaker using the burette. Heat it to about 60 to 70°C (till vapours can be just seen above the surface). Remove the beaker from the flame and note the temperature T_2 of the hot water using a second thermometer while stirring. Transfer all of the hot water immediately into the flask, close lid and start stirring. Note the temperature every ten seconds for about two minutes. Draw a graph of temperature readings against time (in seconds) and obtain the maximum temperature T_3 attained.

Result: Water equivalent of the calorimeter = ________ grams.

Calculation:

Time in seconds	10	20	30	40	50	60	70	80	…
Temperature °C									

T_1 = ___ °C. T_2 = ___ °C. T_3 = ___ °C.

Heat lost by hot water = heat gained by (cold water + calorimeter)

$100\,(T_2 - T_3) = 100\,((T_3 - T_1)) + W\,(T_3 - T_1)$

$$\therefore\ W = \frac{100(T_2 - T_3) - 100(T_3 - T_1)}{(T_3 - T_1)} \quad = \text{\_\_\_\_ g.}$$

1. Thermochemistry – Experiment 1.2.

HEAT OF NEUTRALISATION OF STRONG ACID WITH STRONG BASE

Aim: To determine the heat of neutralization of HCl with NaOH.

Principle: Heat of neutralization is the heat liberated when 1 mole of an acid (or base) is completely neutralized using a base (or acid). In the case of strong acids and bases, the heat of neutralization is found to be a constant, namely 13.7 kcal mol^{-1} or 57.3 kJ mol^{-1}. This is equal to the heat of reaction between H^+ and OH^- to form H_2O.

Procedure: Prepare 250 cm^3 each of exactly 1N HCl and NaOH by quantitative dilution from standardized solutions of higher concentration.

Determine the water equivalent of the flask (as in experiment 1.1). Wash the flask with cold water and drain. Measure exactly 100 cm^3 of 1N HCl solution into the flask using a burette. Insert thermometer and stirrer and close the lid. Stir well and note the constant reading T_1 on the thermometer. (Do not remove this thermometer from the calorimeter).

Measure out exactly 100 cm^3 of 1N NaOH into a clean 250 cm^3 beaker using the burette. Note its temperature T_2 using a second thermometer. Then pour all of this alkali solution into the flask, close lid and start stirring. Note the temperature every ten seconds for about two minutes. Draw a graph of temperature readings against time (in seconds) and obtain the maximum temperature T_3 attained.

Result: Heat of neutralization of strong acid with strong base = ______ kJ mol^{-1}.

Calculation:

(Data, time-temperature plot and calculations for determining water equivalent are expected; see experiment 1.1)

Water equivalent of the calorimeter = _____ g.

Time in seconds	10	20	30	40	50	60	70	80	…
Temperature °C									

T_1 = ___ °C. T_2 = ___ °C. T_3 = ___ °C.

Heat liberated when 100 cm^3 of 1N acid is neutralized = $(100+W)(T_3-T_1)+100(T_3-T_2)$

$\therefore$ Heat liberated when 1000 cm^3 of 1N acid is neutralized

$$= (100+W)(T_3-T_1)+100(T_3-T_2)\times 10 = \_\_\_\_A\_\_ \text{ cal mol}^{-1}.$$

$$= A \times 4.186 = \_\_\_B\_\_\_ \text{ J mol}^{-1} = B/1000 = \_\_\_\_\_ \text{ kJ mol}^{-1}.$$

1. Thermochemistry – Experiment 1.3.

HEAT OF IONISATION OF A WEAK ACID

Aim: To determine the heat of ionisation of acetic acid.

Principle: Heat of neutralization of a weak acid like acetic acid with a strong base will be somewhat less than that for strong acid – strong base neutralization. While strong acids and bases are completely ionized in solution, some energy has to be used to ionize the weak acid before it can be neutralized. This energy is taken up from the heat of neutralization. The difference between the heats of neutralization for strong acid – strong base and that for weak acid – strong base gives the heat of ionisation of the weak acid.

Procedure: Determine the water equivalent of the flask and heat of neutralization for strong acid – strong base (as in experiments 1.1 and 1.2). Prepare 250 cm^3 of exactly 1N acetic acid by quantitative dilution from standardized solution of higher concentration. Determine the heat of neutralization of acetic acid using 100 cm^3 of 1N acetic acid solution and 100 cm^3 of 1N NaOH (as in experiment 1.2).

Result: Heat of ionisation of acetic acid = ______ kJ mol^{-1}.

Calculation:

(Data, time-temperature plot and calculations for determining water equivalent and both heats of neutralization are expected; see experiments 1.1 and 1.2)

Water equivalent of the calorimeter = _____ g.

Heat of neutralization for strong acid – strong base (H_1) = ______ kJ mol^{-1}.

Heat of neutralization for the given weak acid (H_2) = ______ kJ mol^{-1}.

$\therefore$ Heat of ionization of the weak acid = ($H_1 - H_2$) = ______ kJ mol^{-1}.

1. Thermochemistry – Experiment 1.4.

DETERMINATION OF THE NORMALITY OF THE GIVEN STRONG ACID

Aim: To determine the normality of the given HCl solution of unknown concentration.

Principle: Determine the heat of neutralization using (known) 1N HCl and 1N NaOH. Also determine the heat of neutralization using the given (unknown) acid using 1N NaOH. If the unknown concentration is 1N, then both determinations should give the same value. If the unknown concentration is less than 1N, the value will be less, such that:

$$\frac{\text{unknown normality}}{\text{known normality}} = \frac{\Delta H(\text{unknown})}{\Delta H(\text{known})}$$

Procedure: Determine the water equivalent of the flask and heat of neutralization for strong acid – strong base using 100 cm^3 each of exactly 1N HCl and 1N NaOH (as in experiments 1.1 and 1.2). Also determine the heat of neutralization using 100 cm^3 of the given (unknown) HCl solution and 1N NaOH.

Result: Normality of the given acid solution = ______ .

Calculation:

(Data, time-temperature plot and calculations for determining water equivalent and both heats of neutralization are expected; see experiments 1 and 2)

Water equivalent of the calorimeter = _____ g.

Heat of neutralization for strong acid – strong base using 1N HCl (H_1) = ______ kJ mol^{-1}.

Heat of neutralization for the given acid (H_2) = ______ kJ mol^{-1}.

$$\frac{\text{unknown normality}}{1} = \frac{H_2}{H_1}$$

∴ Unknown normality = ______.

2. Two component systems – Experiment 2.1.

PHASE DIAGRAM OF THE NAPHTHALENE – BIPHENYL SYSTEM

Aim: To draw the phase diagram of naphthalene – biphenyl system, which is a simple eutectic system, and to determine its eutectic composition and eutectic temperature.

Principle: Addition of a second component into a pure substance lowers its melting (or freezing) point. There is a particular composition of the mixture for which the freezing point is the lowest. The composition of this mixture is called the eutectic composition, and its freezing point is called the eutectic temperature.

Procedure: Take two clean dry boiling-tubes fitted with corks carrying a thermometer and ring-stirrer. About 5 grams of naphthalene is accurately weighed into one of the boiling-tubes. The tube is then placed in a water bath (use a 250 cm^3 beaker half full of water as the bath) and heated till it melts completely. The thermometer and stirrer are inserted into the melt. When completely melted, the tube is taken out of the water bath and placed in an air jacket (a small wide-mouthed bottle) and stirred continuously. The temperature is noted every 30 seconds till it solidifies completely, and then for two minutes more. A time-temperature graph is plotted. At the freezing point, the temperature remains steady for a few readings. This temperature is the freezing point. (If super cooling occurs, the temperature may rise up slightly before dropping again. This maximum is the freezing point.)

The solid is again melted in the water bath and the thermometer and stirrer removed carefully, without losing any material. About 1 gram of biphenyl is accurately weighed into the same tube. Melt the mixture on the water bath and determine the freezing point of the mixture as before. The process is repeated, each time adding 1 gram of biphenyl, till a total of 5 grams is added.

Now, about 5 grams of biphenyl is accurately weighed into the second boiling-tube and the freezing point determined as before. Repeat five more times, each time adding about 1 gram (accurately weighed) of naphthalene into the tube.

Finally, calculate the percentage of naphthalene and biphenyl in each of the ten mixtures (both mass and mol %). Plot the freezing points against composition to get phase diagram of naphthalene – biphenyl system.

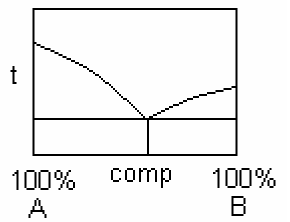
Result: Eutectic composition of naphthalene-biphenyl system = __ % naphthalene.(mass, mol)
Eutectic temperature of naphthalene-biphenyl system = __ °C.

Calculation:

Time in seconds	30	60	90	120	150	180	210	240	…
Temperature °C									

S.No.	Mass of naphthalene	Mass of biphenyl	Naphthalene mass%	mol%	Biphenyl mass%	mol%	Freezing point, °C
1.	---	---	100	100	0	0	---
2.	---	---					---
3.							

12.			0	0	100	100	

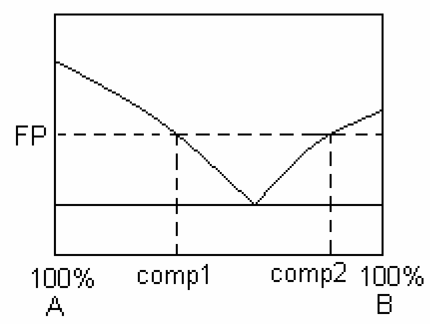


2. Two component systems – Experiment 2.2.

COMPOSITION OF THE GIVEN MIXTURE

Aim: To determine the percentage composition of the given mixture of naphthalene and biphenyl from the phase diagram of the simple eutectic system.

Principle: The composition of the given mixture of naphthalene and biphenyl can be determined by finding its freezing point and comparing it with the phase diagram for this system. There can be two possible compositions corresponding to a freezing point, on the two arms of the curve, except for the eutectic composition. The correct composition can then be determined by adding a small amount of either naphthalene or biphenyl, and checking whether the freezing point moves up or down in the phase diagram.



Procedure: Construct the phase diagram for the naphthalene-biphenyl system (as explained in experiment 2.1). Also determine the freezing point of the given mixture. Note the two possible compositions corresponding to this freezing point from the phase diagram. Now add about 0.5 gram of any one of the components to the given mixture, and again determine its freezing point. Note whether the new freezing point is higher or lower than the earlier one to decide which of the two is the correct composition.

Result: Composition of the given mixture = __ % naphthalene, __ % biphenyl. (mass%)
= __ % naphthalene, __ % biphenyl. (mol%)

Calculation:

(Data, cooling curves and phase diagram as in the earlier experiment are expected)

Time in seconds	30	60	90	120	150	180	210	240	…
Temperature °C									

S.No.	Mass of naphthalene	Mass of biphenyl	Naphthalene		Biphenyl		Freezing point, °C
			mass%	mol%	mass%	mol%	
1.	---	---	100	100	0	0	---
2.	---	---					---
3.							

12.			0	0	100	100	
Given	unknown	unknown	---	---	---	---	---
Given	unk + 0.5g	unknown	---	---	---	---	---

2. Two component systems – Experiment 2.3.

MOLAL DEPRESSION CONSTANT AND LATENT HEAT OF FUSION OF A SOLID SOLVENT

Aim: To determine the latent heats of fusion of naphthalene and biphenyl from the phase diagram.

Principle: The molal depression constant K_f is given by the equation $K_f = \frac{\Delta T_f M_2 w_1}{1000 w_2}$, where ΔT_f is the depression in freezing point, w_1 is the mass of solvent, w_2 is the mass of solute and M_2 is the molecular mass of the solute. Then latent heat of fusion L_f of the solvent is given by the equation $L_f = \frac{RT^2}{1000K_f}$, where R is the gas constant (8.314 $JK^{-1}mol^{-1}$) and T is the freezing point of the solvent in Kelvin.

Procedure: Construct the phase diagram for the naphthalene-biphenyl system (as explained in experiment 2.1). From the phase diagram, locate the freezing point corresponding to 5% (mass) of biphenyl and 95% naphthalene. This corresponds to a mixture of 5g (w_2) biphenyl in 95g (w_1) naphthalene. Calculate ΔT_f using the freezing point of pure naphthalene and that of this mixture. Use the data to calculate K_f and L_f of naphthalene.

Again, locate the freezing point corresponding to 5% (mass) of naphthalene and 95% biphenyl. This corresponds to a mixture of 5g (w_2) naphthalene in 95g (w_1) biphenyl. Then calculate K_f and L_f of biphenyl as above.

Results: Molal depression constant of naphthalene = ____ K mol^{-1}.
Molal depression constant of biphenyl = ____ K mol^{-1}.
Latent heat of fusion of naphthalene = ____ J.
Latent heat of fusion of biphenyl = ____ J.

Calculation:

(Data, cooling curves and phase diagram as in the earlier experiment are expected)

For naphthalene as solvent,
Freezing point of naphthalene, T = ___ °C.
Freezing point of naphthalene containing 5% biphenyl = ___ °C. Therefore ΔT_f = ___ °C.
Mass of naphthalene, w_1 = ___ g. Mass of biphenyl, w_2 = ___ g. Molar mass of biphenyl = ___g mol^{-1}.
$\therefore K_f =$
$L_f =$

For biphenyl as solvent,
Freezing point of biphenyl, T = ___ °C.
Freezing point of biphenyl containing 5% naphthalene = ___ °C. Therefore ΔT_f = ___ °C.
Mass of biphenyl, w_1 = ___ g. Mass of naphthalene, w_2 = ___ g. Molar mass of naphthalene = __g mol^{-1}.
$\therefore K_f =$
$L_f =$

3. Rast’s method – Experiment 3.1.

MOLAL DEPRESSION CONSTANT OF A SOLID SOLVENT

Aim: To determine the molal depression constant of a solid solvent like naphthalene, biphenyl, or diphenylamine.

Principle: The molal depression constant K_f is the depression in freezing point caused by a 1 molal solution. It is given by the equation $K_f = \frac{\Delta T_f M_2 w_1}{1000 w_2}$, where ΔT_f is the depression in freezing point, w_1 is the mass of solvent, w_2 is the mass of solute and M_2 is the molecular mass of the solute.

Procedure: Take a clean boiling tube fitted with a cork carrying a sensitive (110°C) thermometer and stirrer. Weigh about 10 g (w_1) of naphthalene accurately into it. Heat the tube in a water bath till the naphthalene melts, and fix the thermometer and stirrer such that the bulb of the thermometer is fully immersed in the melt. Heat to about 85°C and transfer the tube into an air jacket (a small wide-mouthed bottle) and stirred continuously. The temperature is noted every 30 seconds till the temperature falls below 75°C. A time-temperature graph is plotted. At the freezing point, the temperature remains steady for a few readings. This temperature is the freezing point (T_1). (If super cooling occurs, the temperature may rise up slightly before dropping again. This maximum is the freezing point.)

The solid is again melted in the water bath and the thermometer and stirrer removed carefully, without losing any material. About 0.2 gram (w_2) of biphenyl is accurately weighed into the same tube. Melt the mixture on the water bath and determine the freezing point of the mixture as before (T_2). A second addition of 0.2 gram of biphenyl is made and the freezing point is again noted as before to serve as a duplicate determination.

Results: Molal depression constant of naphthalene (K_f) = (1) ____ K mol^{-1}.
(2) ____ K mol^{-1}.

Calculation:

Time in seconds	30	60	90	120	150	180	210	240	…
Temperature °C									

S.No.	Mass of naphthalene	Mass of biphenyl	Freezing point, °C
1.	---	0	---
2.	---	---	---
3.	---	---	---

Freezing point of naphthalene, (T_1) = ___ °C.
Freezing point of naphthalene containing w_2 g biphenyl (T_2)= ___ °C. Therefore ΔT_f = ___ °C.
Mass of naphthalene, w_1 = ___ g. Mass of biphenyl, w_2 = ___ g.
Molar mass of biphenyl (M_2) = ___g mol^{-1}.

$$\therefore K_f = \frac{\Delta T_f M_2 w_1}{1000 w_2} = \_\_\_\_ \text{ K mol}^{-1}.$$

3. Rast’s method – Experiment 3.2.

MOLECULAR MASS OF THE GIVEN SOLUTE

Aim: To determine the molecular mass of the given solute from freezing point measurements.

Principle: The molal depression constant K_f is the depression in freezing point caused by a 1 molal solution. Using known masses of solute and solvent, the molality of the solution can be calculated. From the molality, molecular mass can be obtained.

Procedure: Determine freezing point (T_1) of the solvent (naphthalene) as in experiment 3.1.

The solid is again melted in the water bath and the thermometer and stirrer removed carefully, without losing any material. About 0.2 gram (w_2) of the given solute is accurately weighed into the same tube. Melt the mixture on the water bath and determine the freezing point of the mixture as before (T_2). A second addition of 0.2 gram of solute is made and the freezing point is again noted as before to serve as a duplicate determination.

Using the K_f of naphthalene determined in experiment 3.1, calculate molecular mass of the given solute using the formula $M_2 = \frac{K_f.1000.w_2}{\Delta T_f w_1}$.

Results: Molar mass of the given solute = (1) ____ g mol^{-1}.
(2) ____ g mol^{-1}.

Calculation:

Time in seconds	30	60	90	120	150	180	210	240	…
Temperature °C									

S.No.	Mass of naphthalene	Mass of solute	Freezing point, °C
1.	---	0	---
2.	---	---	---
3.	---	---	---

Freezing point of naphthalene, (T_1) = ___ °C.
Freezing point of naphthalene containing w_2 g biphenyl (T_2) = ___ °C. Therefore ΔT_f = ___ °C.
Mass of naphthalene, w_1 = ___ g. Mass of biphenyl, w_2 = ___ g.
Molar mass of biphenyl (M_2) = ___g mol^{-1}.

$$\therefore\ M_2 = \frac{K_f.1000.w_2}{\Delta T_f w_1} = \_\_\_\_ \text{ g mol}^{-1}.$$

3. Rast's method – Experiment 3.3.

MOLAL DEPRESSION CONSTANT OF A SOLID SOLVENT
(GRAPHICAL METHOD)

Aim: To determine the molal depression constant of a solid solvent like naphthalene, biphenyl, or diphenylamine using graphical method.

Principle: The molal depression constant K_f is the depression in freezing point caused by a 1 molal solution. The depression in freezing point is directly proportional to the molality of the solution, where K_f is the proportionality constant. $\Delta T_f = K_f \cdot molality$. This equation is of the form $y = mx + c$, where 'c' = 0. Therefore, a plot of ΔT_f against molality must give a straight line with slope = K_f and passing through the origin.

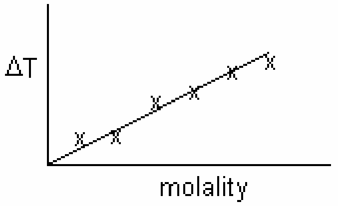
Procedure: Determine freezing point (T_1) of the solvent (naphthalene) as in experiment 3.1.

The solid is again melted in the water bath and the thermometer and stirrer removed carefully, without losing any material. About 0.2 gram (w_2) of a known solute (biphenyl, M = 154) is accurately weighed into the same tube. Melt the mixture on the water bath and determine the freezing point of the mixture as before (T_2). A second addition of 0.2 gram of solute is made and the freezing point is again noted as before. This is repeated three more times to obtain a total of five different values for w_2 and T_2. The molality of the solution and ΔT_f in each case is calculated and plotted on a graph paper. The slope of the line gives K_f.

Result: Molal depression constant of naphthalene (K_f) = (1) ____ K mol^{-1}.

Calculation:

S.No.	Mass of naphthalene w_1	Mass of solute w_2	Freezing point, °C	Molality = $\frac{1000.w_2}{M_2 w_1}$	ΔT_f
1.	---	0	---	0	
2.	---	---	---	---	---
3.	---	---	---	---	---
4.					
5.					
6.					



K_f = slope =

3. Rast’s method – Experiment 3.4.

MASS OF THE GIVEN SOLID SOLVENT – GRAPHICAL METHOD

Aim: To determine the mass of the given solid solvent like naphthalene, biphenyl, or diphenylamine using graphical method.

Principle: The depression in freezing point is directly proportional to the molality of the solution, where K_f is the proportionality constant. $\Delta T_f = K_f \, . \, molality$. This equation is of the form $y = mx + c$, where ‘c’ = 0. Therefore, a plot of ΔT_f against molality must give a straight line with slope = K_f and passing through the origin. Instead of molality, mole fraction of solute may be used on the X-axis. By determining ΔT_f for any given mixture, its mole fraction can be obtained from the graph. Knowing the molar mass of solvent and solute, the mass of solvent can be calculated.

Procedure: Determine freezing point (T_1) of the solvent (naphthalene, M = 130) as in experiment 3.1.

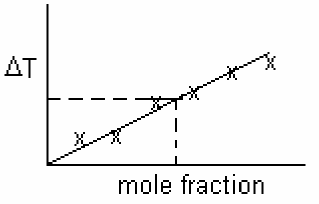
Determine freezing points for five different additions of a known solute (biphenyl, M = 154) as explained in experiment 3.3. The mole fraction of solute and ΔT_f in each case is calculated and plotted on a graph paper.

To the given solid solvent (which is the same as that used to construct the graph), add a known mass (between 0.3 to 0.8 g) of solute and determine its freezing point. Calculate ΔT_f. Obtain mole fraction corresponding to this value from the graph and calculate mass of solvent.

Result: Mass of the given solid solvent = ____ g.

Calculation:

S.No.	Mass of naphthalene w_1	Mass of solute w_2	Freezing point, °C	Mole fraction = $\frac{M_1.w_2}{M_2 w_1}$	ΔT_f
1.	---		---		
2.	---	---	---	---	---
3.	---	---	---	---	---
4.					
5.					
6.					
7.	unknown				



Mole fraction of solute obtained from graph = ____

But mole fraction (χ) = $\frac{M_1.w_2}{M_2 w_1}$

$\therefore$ Mass of the solvent = $w_1 = \frac{M_1.w_2}{M_2 \times \chi}$ = ___ g.

3. Rast’s method – Experiment 3.5.

MOLAL DEPRESSION CONSTANT OF A SALT HYDRATE

Aim: To determine the molal depression constant of a salt hydrate like sodium thiosulphate pentahydrate or sodium acetate trihydrate.

Principle: The molal depression constant K_f is the depression in freezing point caused by a 1 molal solution. A water soluble solute such as glucose or urea is used in the case of a salt hydrate.

Procedure: Take a clean boiling tube fitted with a cork carrying a sensitive (110°C) thermometer and stirrer. Weigh about 10 g (w_1) of crystalline $Na_2S_2O_3.5H_2O$ accurately into it. Heat the tube in a water bath till the salt melts, and fix the thermometer and stirrer such that the bulb of the thermometer is fully immersed in the melt. Heat to about 55°C and transfer the tube into an air jacket (a small wide-mouthed bottle) and stirred continuously. The temperature is noted every 30 seconds till the temperature falls below 40°C. A time-temperature graph is plotted. At the freezing point, the temperature remains steady for a few readings. This temperature is the freezing point (T_1). (If super cooling occurs, the temperature may rise up slightly before dropping again. This maximum is the freezing point.)

The salt hydrate is again melted in the water bath and the thermometer and stirrer removed carefully, without losing any material. About 0.2 gram (w_2) of glucose is accurately weighed into the same tube. Melt the mixture on the water bath and determine the freezing point of the mixture as before (T_2). A second addition of 0.2 gram of glucose is made and the freezing point is again noted as before to serve as a duplicate determination.

Results: Molal depression constant of sodium thiosulphate pentahydrate (K_f)
= (1) ____ K mol^{-1}.
(2) ____ K mol^{-1}.

Calculation:

Time in seconds	30	60	90	120	150	180	210	240	…
Temperature °C									

S.No.	Mass of $Na_2S_2O_3.5H_2O$	Mass of glucose	Freezing point, °C
1.	---		---
2.	---	---	---
3.	---	---	---

Freezing point of sodium thiosulphate pentahydrate, (T_1) = ___ °C.
Freezing point of sodium thiosulphate containing w_2 g glucose (T_2)= ___ °C. Therefore ΔT_f = ___ °C.
Mass of sodium thiosulphate pentahydrate, w_1 = ___ g. Mass of glucose, w_2 = ___ g.
Molar mass of glucose (M_2) = ___g mol^{-1}.

$$\therefore\ K_f = \frac{\Delta T_f M_2 w_1}{1000 w_2} = \_\_\_\_ \text{ K mol}^{-1}.$$

4. CST – Experiment 4.1.

CRITICAL SOLUTION TEMPERATURE OF PHENOL-WATER SYSTEM

Aim: To determine the CST or upper consolute point of phenol-water system.

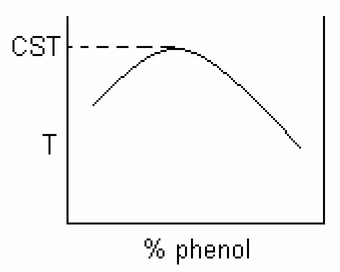
Principle: Two partially miscible liquids may become completely miscible at a higher temperature since solubility increases with temperature generally. This miscibility temperature is different for different compositions of the mixture. The highest miscibility temperature is called the critical solution temperature or CST. Above this temperature, all compositions of this mixture are completely miscible.

Procedure: Take a clean boiling tube fitted with a cork carrying a sensitive (110°C) thermometer and stirrer. Measure 5 mL of phenol into the boiling tube. Fill a burette with water and add 2 mL water into the boiling tube containing phenol. Fix the thermometer and stirrer and heat slowly on a water bath, stirring continuously. Note the temperature at which turbidity just disappears. Take out from the water bath and allow the tube to cool slowly while stirring. Note the temperature at which turbidity reappears. Then add 2 mL more of water into the same boiling tube and repeat the experiment. Continue like this till a total of 30 mL water is added. Plot the average miscibility temperatures against percentage of phenol on a graph paper. The maximum point in the curve is the CST of phenol-water system.

Results: CST of phenol-water system = ____ °C.
Critical composition = ____ % phenol, ____ % water.

Calculation:

Vol. of phenol mL	Vol. of water mL	% of phenol	Miscibility temperature		
			Disappear	Appear	Average
5	2				
5	4				
…	…				



4. CST – Experiment 4.2.

EFFECT OF ADDING NaCl ON THE CST OF PHENOL-WATER SYSTEM AND DETERMINATION OF UNKNOWN CONCENTRATION

Aim: To study the effect of adding NaCl on the CST of phenol-water system and thus determine the concentration of the given NaCl solution.

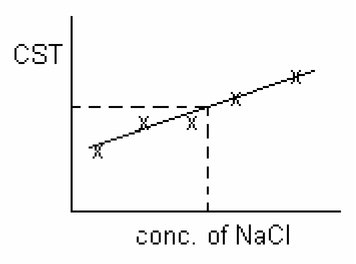
Principle: The CST of a system is usually increased when a solute soluble in only one of the component liquids is added. Thus when NaCl or KCl, which are soluble only in water and not in phenol, is added, the CST of phenol-water system is found to increase with concentration.

Procedure: Prepare 250 cm^3 of 0.2 molar NaCl solution. Transfer 10, 20, 30, 40 and 50 cm^3 of this solution into five different 100 cm^3 volumetric flasks and make up with distilled water to get 0.02, 0.04, 0.06, 0.08 and 0.10 molar solutions of NaCl respectively. Determine the CST of phenol-water system using each of these solutions in the place of water (as explained in experiment 4.1). Also determine the CST using the given solution of unknown concentration.

Result: Concentration of the given NaCl solution = ____ M.

Calculation:

(Tables and plots for the determination of CST in all six cases are expected. See experiment 4.1)



4. CST – Experiment 4.3.

EFFECT OF ADDING SUCCINIC ACID ON THE CST OF PHENOL-WATER SYSTEM AND DETERMINATION OF UNKNOWN CONCENTRATION

Aim: To study the effect of adding succinic acid on the CST of phenol-water system and thus determine the concentration of the given succinic acid solution.

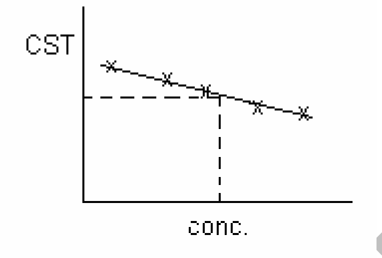
Principle: The CST of a system usually decreases when a solute soluble in both the component liquids is added. Thus when succinic acid, which is soluble both in water and phenol, is added, the CST of phenol-water system is found to decrease with concentration.

Procedure: Prepare 250 cm^{3} of 0.2 molar succinic acid solution. Transfer 10, 20, 30, 40 and 50 cm^{3} of this solution into five different 100 cm^{3} volumetric flasks and make up with distilled water to get 0.02, 0.04, 0.06, 0.08 and 0.10 molar solutions of succinic acid respectively. Determine the CST of phenol-water system using each of these solutions in the place of water (as explained in experiment 4.1). Also determine the CST using the given solution of unknown concentration.

Result: Concentration of the given succinic acid solution = ____ M.

Calculation:

(Tables and plots for the determination of CST in all six cases are expected. See experiment 4.1)



4. CST – Experiment 4.4.

EFFECT OF ADDING KCl ON THE MISCIBILITY OF PHENOL AND WATER AND DETERMINATION OF UNKNOWN CONCENTRATION

Aim: To study the effect of adding KCl on the miscibility of phenol and water and thus determine the concentration of the given KCl solution.

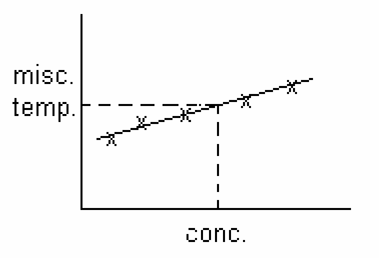
Principle: The miscibility temperature of phenol-water system is usually increased when a solute soluble in only one of the component liquids is added. Thus when NaCl or KCl, which are soluble only in water and not in phenol, is added, the miscibility temperature of phenol-water system is found to increase with concentration.

Procedure: Prepare 250 cm^3 of 0.2 molar KCl solution. Transfer 10, 20, 30, 40 and 50 cm^3 of this solution into five different 100 cm^3 volumetric flasks and make up with distilled water to get 0.02, 0.04, 0.06, 0.08 and 0.10 molar solutions of KCl respectively. Determine the miscibility temperature using 5 cm^3 of phenol and 5 cm^3 of 0.02 molar KCl solution. Similarly repeat the determination using 5 cm^3 of fresh phenol and 5 cm^3 of each of the other concentrations, and also using the unknown solution.

Result: Concentration of the given KCl solution = ____ M.

Calculation:

Conc.	0.02	0.04	0.06	0.08	0.10	unknown
Misc. temp.						



4. CST – Experiment 4.5.

EFFECT OF ADDING SUCCINIC ACID ON THE MISCIBILITY OF PHENOL AND WATER AND DETERMINATION OF UNKNOWN CONCENTRATION

Aim: To study the effect of adding succinic acid on the miscibility of phenol and water and thus determine the concentration of the given succinic acid solution.

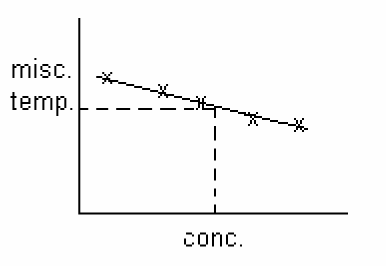
Principle: The miscibility temperature of phenol-water system is usually decreased when a solute soluble in both the component liquids is added. Thus when succinic acid, which is soluble in both water and phenol, is added, the miscibility temperature of phenol-water system is found to decrease with concentration.

Procedure: Prepare 250 cm^3 of 0.2 molar succinic acid solution. Transfer 10, 20, 30, 40 and 50 cm^3 of this solution into five different 100 cm^3 volumetric flasks and make up with distilled water to get 0.02, 0.04, 0.06, 0.08 and 0.10 molar solutions of succinic acid respectively. Determine the miscibility temperature using 5 cm^3 of phenol and 5 cm^3 of 0.02 molar succinic acid solution. Similarly repeat the determination using 5 cm^3 of fresh phenol and 5 cm^3 of each of the other concentrations, and also using the unknown solution.

Result: Concentration of the given succinic acid solution = ____ M.

Calculation:

Conc.	0.02	0.04	0.06	0.08	0.10	unknown
Misc. temp.						



5. Three component systems – Experiment 5.1.

PHASE DIAGRAM OF A THREE-COMPONENT SYSTEM

Aim: To construct the phase diagram of nitrobenzene-acetic acid-water system.

Principle: For a three-component system, four degrees of freedom are possible ($F = C-P+2 = 3-1+2 = 4$). These are the pressure, temperature and concentration of any two components. In order to simplify the graphical representation, pressure and temperature are kept constant, while the two concentration terms can be represented on a planar diagram. Triangular diagrams are most commonly used. The pure components are represented by the corners of an equilateral triangle. Since the sum of the distances from a point inside the triangle drawn parallel to the sides is always the same (and equal to one side), the composition of a mixture of three liquids can be represented by any point inside the triangle, taking the side as 100% (percentage composition by mass) or as 1 (mole fraction). Any side will then represent two components and the apex, one component. A known mixture of any two miscible liquids are taken and titrated against the third from a burette, till turbidity just appears, to determine the full-miscibility range.

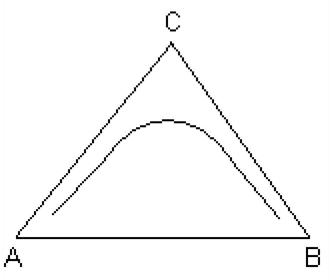
Procedure: Three burettes are washed with water and all water drained off. They are then rinsed twice with small amounts of acetone and allowed to dry. Fill pure nitrobenzene, acetic acid and water respectively in the burettes and clamp them vertically. Take a clean, dry 100 cm^3 conical flask and weigh accurately. Measure 20 cm^3 of nitrobenzene into it from the burette and again weigh. Calculate density of nitrobenzene from these measurements. Similarly calculate densities of glacial acetic acid and water also. After weighing, pour the liquids back into their respective burettes.

Take nine clean, dry 100 cm^3 conical flasks and label them. Measure 9 cm^3 of nitrobenzene and 1 cm^3 of acetic acid into flask 1, 8 cm^3 of nitrobenzene and 2 cm^3 of acetic acid into flask 2, 7 cm^3 of nitrobenzene and 3 cm^3 of acetic acid into flask 3, etc. Titrate each of them carefully using water till a faint turbidity appears, and note the volumes of water used in each case.

Clean and dry the labeled conical flasks. Measure 9 cm^3 of water and 1 cm^3 of acetic acid into flask 1, 8 cm^3 of water and 2 cm^3 of acetic acid into flask 2, 7 cm^3 of water and 3 cm^3 of acetic acid into flask 3, etc. Titrate each of them carefully using nitrobenzene till a faint turbidity appears, and note the volumes of nitrobenzene used in each case.

Calculate the mass % of nitrobenzene, acetic acid and water in each case and tabulate them. Plot the values on a triangular graph (nitrobenzene and water on the base and acetic acid on the apex) to obtain the phase diagram of the system.

Result: Phase diagram of nitrobenzene-acetic acid-water system was constructed.



Calculation:

Mass of 20 cm^3 of nitrobenzene = ___ g. ∴ Density of nitrobenzene =
Mass of 20 cm^3 of acetic acid = ___ g. ∴ Density of acetic acid =
Mass of 20 cm^3 of water = ___ g. ∴ Density of water =

Ser No.	Volume (mL)			Mass (g) (V × d)			Mass %		
	$PhNO_2$	HOAc	H_2O	$PhNO_2$	HOAc	H_2O	$PhNO_2$	HOAc	H_2O
1	9	1	---						
2	8	2	---						
3	7	3	---						
4	6	4	---						
5	5	5	---						
6	4	6	---						
7	3	7	---						
8	2	8	---						
9	1	9	---						
1	---	1	9						
2	---	2	8						
3	---	3	7						
4	---	4	6						
5	---	5	5						
6	---	6	4						
7	---	7	3						
8	---	8	2						
9	---	9	1						

5. Three component systems – Experiment 5.2.

DRAWING A TIE-LINE ON THE PHASE DIAGRAM OF A THREE-COMPONENT SYSTEM

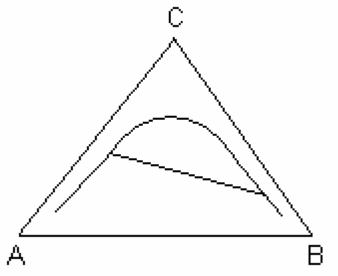
Aim: To draw a tie-line on the phase diagram of nitrobenzene-acetic acid-water system.

Principle: Any mixture represented by a point within the miscibility curve of a three-component system will separate into two layers. One layer is a solution of C in A and the other is a solution of C in B. The compositions of these two layers will be points on the binodal curve of the system. The line joining these two points is called the tie-line. It is expected to pass through the point representing the original mixture taken.

Procedure: Prepare and standardize 250 cm^3 of 0.5 N NaOH solution. Get about 60 cm^3 of a mixture of the three components from the instructor. Mix it well and pour into a small separating funnel. Allow the layers to separate. The bottom layer is a solution of acetic acid in nitrobenzene and the top layer is a solution of acetic acid in water.

Collect the layers separately into two clean, dry 100 cm^3 beakers. Take two clean, dry 250 cm^3 conical flasks and weigh them accurately. Pipette out exactly 2 cm^3 of nitrobenzene layer into one flask and 2 cm^3 of aqueous layer into the other. Weigh again and calculate the mass of each layer. Add 20 cm^3 of water and a drop of phenolphthalein indicator into each and titrate against standard 0.5 N NaOH solution from the burette. Calculate the mass % of acetic acid in each layer.

Mark the points corresponding to the percentages of acetic acid on the binodal curve obtained for nitrobenzene-water system earlier. Draw the tie-line connecting these two points. The line should, theoretically, pass through the point representing the composition of the original mixture given to you.



Result: Mass % of acetic acid in the organic layer = ___
Mass % of acetic acid in the aqueous layer = ___
Tie-line passes through the point representing the composition of the given mixture.

Calculation:

Nitrobenzene layer:
Mass of conical flask = ___ g. Mass of flask + 2 cm^3 organic layer = ___ g.
$\therefore$ Mass of 2 cm^3 organic layer (W_1) = ___ g.
Volume of NaOH solution used (V_1) = ___ cm^3. Normality of NaOH (N) = ___.
Normality of organic layer (N_1)= (V_1N)/2 = ___. Mass of acetic acid per litre = $N_1 \times 60$.
Mass of acetic acid in 2 cm^3 organic layer (W_2) = ($N_1 \times 60$) × (2/1000) = ___ g.
$\therefore$ Mass % of acetic acid in the organic layer = $(W_2/W_1)\times100$ = ___

Aqueous layer:
Mass of conical flask = ___ g. Mass of flask + 2 cm^3 aqueous layer = ___ g.
$\therefore$ Mass of 2 cm^3 aqueous layer (W_3) = ___ g.
Volume of NaOH solution used (V_2) = ___ cm^3. Normality of NaOH (N) = ___.
Normality of aqueous layer (N_2)= (V_2N)/2 = ___. Mass of acetic acid per litre = $N_2 \times 60$.
Mass of acetic acid in 5 cm^3 aqueous layer (W_4) = ($N_2 \times 60$) × (2/1000) = ___ g.
$\therefore$ Mass % of acetic acid in the aqueous layer = $(W_4/W_3)\times100$ = ___

5. Three component systems – Experiment 5.3.

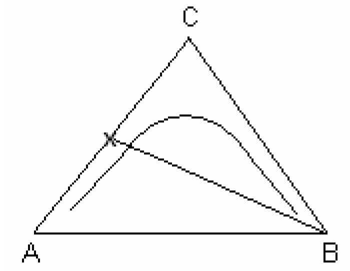
COMPOSITION OF THE GIVEN MIXTURE

Aim: To find out the mass percentage of acetic acid and water in the given mixture.

Principle: Any mixture of acetic acid and water will fall on the edge joining acetic acid and water on the triangular graph of the three-component system. Adding just enough nitrobenzene to form a separate layer will bring the composition inward so as to be represented by a point on the bimodal curve.

Procedure: Phase diagram for nitrobenzene-water-acetic acid is constructed as explained in experiment 5.1.

The unknown mixture of acetic acid and water is collected from the instructor in a dry, previously weighed 100 cm^3 conical flask. Weigh again and calculate the mass of the given mixture. It is titrated using nitrobenzene from the burette till a faint turbidity appears. Calculate the mass of nitrobenzene used from its volume and density. Calculate the mass percent of nitrobenzene in the mixture. Mark this point on the binodal curve. Draw a line from the corner representing 100% nitrobenzene to this point on the bimodal curve, and extend it to meet the opposite edge. The point where it meets the edge gives the mass percentage of acetic acid and water.



Result: Mass percent of acetic acid in the given mixture = ___ .

Calculation:

Mass of conical flask = ___ g. Mass of flask + mixture = ___ g.
∴Mass of mixture = ___ g.
Volume of nitrobenzene used = ___ cm^3. Density of nitrobenzene = ___.
∴Mass of nitrobenzene = ___ g.
Total mass = ___ g.
Mass % of nitrobenzene = ___.
Mass % of acetic acid (from graph) = ___.

6. Partition – Experiment 6.1.

PARTITION COEFFICIENT FOR THE DISTRIBUTION OF IODINE BETWEEN CARBON TETRACHLORIDE AND WATER

Aim: To determine the partition coefficient for distribution of iodine between CCl_4 and water.

Principle: When a solute is distributed between two solvents which are immiscible so as to form two separate layers in contact with each other, the ratio of the equilibrium concentrations of the solute in the two solvents $\left(\frac{C_1}{C_2}\right)$ will be a constant at a given temperature. This constant is called the partition coefficient for that system.

Procedure: Take two stoppered 250 cm^3 iodine flasks A and B. Fill burette with a saturated solution of iodine in CCl_4 and transfer 30 cm^3 iodine solution into flask A and 25 cm^3 iodine solution into flask B. Add 5 cm^3 of pure CCl_4 into flask B only to make the volumes same. Then pour 150 cm^3 of water each into the two flasks. Put the stoppers and shake the flasks on a mechanized shaker for 5 minutes. Then let the bottles rest for 15 minutes so that the layers separate. While waiting, fill one burette with 0.1N thiosulphate solution. From this, transfer 10 cm^3 into the volumetric flask and make up to 100 cm^3 to get 0.01N thiosulphate solution. Fill the second burette with this solution.

From iodine flask A, pipette out 5 cm^3 of organic layer into a conical flask (organic layer should not be contaminated by the aqueous layer; close the upper tip of the pipette with your finger while inserting the bottom tip to the very bottom of the organic layer and only then remove your finger). Add 5 cm^3 of 10% KI solution and titrate against 0.1N thiosulphate solution, without indicator till the colour becomes yellow, and continue using starch indicator till the blue colour just disappears. Pipette out 40 cm^3 of aqueous layer from the same bottle into the conical flask, (adding starch at the beginning itself since the colour is light) and titrate against 0.01N thiosulphate solution.

Repeat the two titrations for iodine flask B also as a duplicate. Calculate partition coefficient for each flask.

Result: Partition coefficient of iodine between CCl_4 and water = (1) _____ (2) _____

Calculation:

Flask No.	Volume of 0.1N thio (V_1)	Volume of 0.01N thio (V_2)	Partition Coefficient K
A			
B			

Concentrations are proportional to volumes of thio used. Since this is a ratio, volumes may be used directly.
Volume of 0.01N thio $\equiv$ iodine in 40 cm^3 CCl_4 = $V_1 \times 10 \times 8$ cm^3
Volume of 0.01N thio $\equiv$ iodine in 40 cm^3 water = V_2 cm^3

$$K = \frac{V_1 \times 10 \times 8}{V_2} = \_\_\_\_\_\_\_\_ .$$

6. Partition – Experiment 6.2.

EQUILIBRIUM CONSTANT OF THE REACTION
$KI + I_2 \leftrightarrow KI_3$

Aim: To determine the equilibrium constant for the reaction $KI + I_2 \leftrightarrow KI_3$ using partition method.

Principle: When iodine is distributed between CCl_4 and aqueous KI solution, the equilibrium $KI + I_2 \leftrightarrow KI_3$ exists in the aqueous solution. Partition law applies only to the molecular iodine present in the aqueous layer since KI and KI_3 are insoluble in CCl_4. This property can be used to determine the concentrations of the three species present in the aqueous layer. Equilibrium constant $= \frac{[KI_3]}{[KI][I_2]}$.

Procedure: Prepare 100 cm^3 of standard 0.1N potassium dichromate solution. Standardise the 0.1 N thiosulphate against acidified dichromate solution and KI (refer B.Sc. iodometry). Determine the partition coefficient for distribution of iodine between CCl_4 and water as explained in experiment 6.1.

Prepare 500 cm^3 of 0.1M KI solution (of exactly known concentration) by weighing KI and making up to the required volume. Take two stoppered 250 cm^3 iodine flasks C and D. Fill burette with a saturated solution of iodine in CCl_4 and transfer 30 cm^3 iodine solution into flask C and 25 cm^3 iodine solution into flask D. Add 5 cm^3 of pure CCl_4 into flask B only to make the volumes same. Then pour 150 cm^3 of the 0.1M KI solution into each into the two flasks. Put the stoppers and shake the flasks on a mechanized shaker for 5 minutes. Then let the bottles rest for 15 minutes so that the layers separate.

Titrate 5 cm^3 of organic layer (after adding KI solution as in experiment 6.1) and 40 cm^3 of the aqueous layer from each flask, both using 0.1N thiosulphate solution, using starch towards the end.

$[I_2]$ in the aqueous layer can be calculated using the concentration in the organic layer and partition coefficient. From titre of the aqueous layer, calculate the concentration of $(I_2 + KI_3)$ in that layer. $[KI_3]$ can be obtained by subtracting $[I_2]$ from total concentration of $(I_2 + KI_3)$. Equilibrium concentration of [KI] can be obtained by subtracting $[KI_3]$ from the concentration of the original KI solution used.

Result: Equilibrium constant for the reaction $KI + I_2 \leftrightarrow KI_3$ = (1) _____ (2) _____

Calculation: [Table and calculation as in experiment 6.1 expected. Add flasks C & D to the tables]

Let N be the normality of thiosulphate, V_1 the titre of CCl_4 layer and V_2 the titre of aqueous layer.
Let K be the partition coefficient. Normality of solutions ≡ concentration of iodine.

Normality of iodine in CCl_4 layer $(N_1) = \frac{V_1 N}{5}$ $\therefore$ Normality of I_2 in aqueous layer $(N_2) = \frac{N_1}{K}$

Normality of $(I_2 + KI_3)$ in aqueous layer $(N_3) = \frac{V_2 N}{40}$ $\therefore$ Normality of KI_3 in aqueous layer $(N_4) = (N_3 - N_2)$

$\therefore$ Normality of KI in aqueous layer (N_5) = original conc. – N_4. Eq. constant $K_{eq} = \frac{N_4}{N_5 \times N_2}$

6. Partition – Experiment 6.3.

DETERMINING THE CONCENTRATION OF THE GIVEN KI SOLUTION

Aim: To determine the concentration of the given KI solution using partition method.

Principle: Equilibrium constant = $\frac{[KI_3]}{[KI][I_2]}$. Knowing the value of the equilibrium constant, the equilibrium concentration [KI] can be calculated if $[KI_3]$ and $[I_2]$ are known. These can be obtained by titration of the organic layer and aqueous layer as in experiment 6.2. Since [KI] = original concentration of KI – $[KI_3]$, the original concentration can be calculated.

Procedure: Take two stoppered 250 cm^3 iodine flasks E and F. Repeat the experiment exactly as in experiment 6.2, but using the given KI solution instead of the solution of known concentration.

Result: Concentration of the given KI solution = (1) _____ (2) _____

Calculation: [Table and calculations as in experiment 6.1 and 6.2 are expected. Add E & F to the table]

Flask No.	Volume of 0.1N thio (V_1)	Volume of 0.01N thio (V_2)	Partition Coefficient K
A B			

Flask No.	Volume of 0.1N thio (V_1)
C D	
E F	

Let N be the normality of thiosulphate, V_1 the titre of CCl_4 layer and V_2 the titre of aqueous layer.
Let K be the partition coefficient and K_{eq} be the equilibrium constant.

Normality of iodine in CCl_4 layer (N_1) = $\frac{V_1 N}{5}$ $\therefore$ Normality of I_2 in aqueous layer (N_2) = $\frac{N_1}{K}$

Normality of ($I_2 + KI_3$) in aqueous layer (N_3) = $\frac{V_2 N}{40}$ $\therefore$ Normality of KI_3 in aqueous layer (N_4) = ($N_3 – N_2$)

But $\frac{[KI_3]}{[KI][I_2]} = K_{eq}$. $\therefore$ [KI] = $\frac{[KI_3]}{K_{eq}[I_2]}$ But [KI] = Original concentration – $[KI_3]$

$\therefore$ Original concentration of KI = [KI] + $[KI_3]$

7. Viscosity – Experiment 7.1.

DETERMINING THE COEFFICIENT OF VISCOSITIES OF DIFFERENT LIQUIDS

Aim: To determine the coefficient of viscosities of various liquids like benzene, nitrobenzene and acetic acid.

Principle: Resistance to flow of a liquid is known as viscosity. The retarding force is proportional to the area of contact and the velocity gradient. The proportionality constant 'η' is the coefficient of viscosity, and is characteristic of a liquid. When a liquid flows through a capillary tube, $\eta = \frac{\pi P r^4 t}{8lV}$, where 'P' is the pressure head, 'r' is the radius of the tube, 't' is the time of flow, 'l' is the length of the tube and V is the volume of liquid. This is called absolute viscosity determination. But if the same volumes of two liquids are allowed to flow through the same tube, then we have the relation $\frac{\eta_1}{\eta_2} = \frac{\rho_1 t_1}{\rho_2 t_2}$, where 'ρ' is the density of the liquid. If the viscosity of one liquid is known, then the other can be calculated. An Ostwald's viscometer is used to determine relative viscosity of liquids.

Procedure: An Ostwald viscometer is cleaned by rinsing three times with small volumes of acetone and dried. The lower bulb is filled with distilled water and clamped vertically. A rubber bulb is attached to the tip of the narrow limb and the liquid drawn up to a level much above the upper mark. The rubber bulb is removed and the liquid allowed to flow down freely. A stop watch is started just as the liquid meniscus passes the upper mark and stopped when it passes the lower mark. The time of flow 't_1' is noted. Density of water is 0.997 kg m^{-3} and 'η_1' for water is 8.00×10^{-4} kg $m^{-1}s^{-1}$ (8.00 millipoise) at 28°C.

The viscometer is again cleaned and dried as before. It is then filled with the experimental liquid (benzene, nitrobenzene or glacial acetic acid as the case may be). Time of flow 't_2' is determined as in the case of water. The densities of the liquids may either be determined or taken from literature. The coefficient of viscosity 'η_2' of the liquid can be calculated.

Result: Coefficient of viscosity of benzene = ___ kg $m^{-1}s^{-1}$
Coefficient of viscosity of nitrobenzene = ___ kg $m^{-1}s^{-1}$
Coefficient of viscosity of acetic acid = ___ kg $m^{-1}s^{-1}$

Calculation:

Liquid	Density (kg m^{-3})	Time of flow (s)	Viscosity coefft.
1. Water 2. Benzene 3. Nitrobenzene 4. Acetic acid			

$$\eta_2 = \frac{\eta_1 \rho_2 t_2}{\rho_1 t_1} =$$

7. Viscosity – Experiment 7.2.

DETERMINING THE COMPOSITION OF THE GIVEN MIXTURE

Aim: To determine the composition of the given mixture of benzene and nitrobenzene.

Principle: The viscosities of various mixtures of two non-interacting liquids will lie between those of the pure components. Since time of flow in the Ostwald viscometer varies linearly with viscosity (and hence with composition), the unknown composition can be obtained from the graph by measuring the time of flow.

Procedure: Take five clean, dry stoppered bottles and label them 1 to 5. Take 4 cm^3 of benzene and 16 cm^3 of nitrobenzene (= 20% benzene v/v) in bottle 1, 8 cm^3 of benzene and 12 cm^3 of nitrobenzene (= 40% benzene v/v) in bottle 2, 12 cm^3 of benzene and 8 cm^3 of nitrobenzene (= 60% benzene v/v) in bottle 3, 16 cm^3 of benzene and 4 cm^3 of nitrobenzene (= 80% benzene v/v) in bottle 4. Get the unknown mixture from the instructor in bottle 5. Mix the contents of each bottle well by gently swirling the contents.

Measure the time of flow for each mixture using the Ostwald viscometer as explained in experiment 7.1. Also determine the times of flow for pure benzene and nitrobenzene.

Plot the times of flow against volume percentage of benzene on a graph paper (if weight percentages are required, they can be calculated knowing the densities of pure benzene and nitrobenzene). Get the composition corresponding to the time of flow of the unknown mixture from the graph.

Result: The composition of the given mixture = ____ % benzene, ____ % nitrobenzene.

Calculation:

Composition	Time of flow (s)
Pure nitrobenzene	
20% benzene	
40% benzene	
60% benzene	
80% benzene	
Pure benzene	
Unknown	

7. Viscosity – Experiment 7.3.

TO VERIFY KENDALL’S EQUATION

Aim: To verify Kendall’s equation by showing that a plot of log(*fluidity*) of the mixture against mole fraction is a straight line, and to calculate the viscosities of the pure components.

Principle: For mixtures of two non-associated non-polar liquids like benzene and nitrobenzene, Kendall suggested the equation $\log \phi = x_1 \log \phi_1 + x_2 \log \phi_2$, where x_1 and x_2 represents the mole fractions of the two liquids and ϕ, ϕ_1 and ϕ_2 represent fluidities of the mixture and pure liquids respectively (fluidity is the inverse of viscosity). Since $x_2 = (1 - x_1)$, the equation may be rewritten as $\log \phi = x_1 (\log \phi_1 - \log \phi_2) + \log \phi_2$. Therefore a plot of $\log \phi$ against x_1 will give a straight line with slope = $(\log \phi_1 - \log \phi_2)$ and y-intercept = $\log \phi_2$.

Procedure: Prepare four mixtures of benzene and nitrobenzene as in experiment 7.2. Find the density of each mixture by weighing a known volume, or calculate densities using the densities of the pure liquids. Calculate mole fraction of benzene in each mixture. Set up the viscometer and measure the times of flow of the mixtures and that of pure water. Calculate the viscosity of each mixture relative to water as explained in experiment 7.1. The inverse of each viscosity gives the fluidity ϕ. Plot $\log \phi$ against mole fraction of benzene, and extend the line to cut the y-axis. From the y-intercept, calculate fluidity of nitrobenzene. From the slope, calculate fluidity of benzene. From the fluidities, calculate the viscosities of benzene and nitrobenzene.

Result: (1) Plot of $\log \phi$ against mole fraction of benzene gives a straight line, thus verifying
Kendall’s equation.
(2) Viscosity of benzene calculated from graph =
(3) Viscosity of nitrobenzene calculated from graph =

Calculation: (All calculations as in experiment 7.1 necessary for each mixture)

Liquid	Density (kg m^{-3})	Mole fraction of benzene, x_1	Time of flow (s)	Viscosity coefft. η	Fluidity, $\phi = 1/\eta$	$\log \phi$
Water						
20% benzene						
40% benzene						
60% benzene						
80% benzene						

8. Solubility – Experiment 8.1.

TO DETERMINE THE SOLUBILITY OF AMMONIUM OXALATE IN WATER

Aim: To determine the solubility of crystalline ammonium oxalate [$(NH_4)_2C_2O_4.H_2O$] in water at room temperature using analytical method.

Principle: Solubility of a salt is the amount of salt present in a known volume of saturated solution of the salt in a specified solvent at a given temperature. It may be expressed in grams per 100 cm^3 of solution, or in grams per 1000 cm^3 of solution. Ammonium oxalate in solution can be estimated by titrating a known volume against standard acidified potassium permanganate solution.

Procedure: Prepare 250 cm^3 of approximately 0.1N potassium permanganate solution and standardize it against hot standard oxalic acid solution after acidifying with 6N sulfuric acid.

Take about 100 cm^3 of distilled water in a 250 cm^3 beaker. Add small quantities of crystalline ammonium oxalate and stir well till some salt remains undissolved even on prolonged stirring. Keep aside for about 30 minutes to make sure that no more salt dissolves. Note the temperature of the solution. Close the tip of a 10 cm^3 pipette with a short rubber tube plugged with cotton (to prevent the entry of any small crystals) and pipette out 10 cm^3 of solution into a 100 cm^3 volumetric flask and make up to the mark with distilled water.

Titrate 20 cm^3 of the made up solution against the standard 0.1N permanganate solution after adding an equal volume of 6N sulphuric acid solution and warming to 60-70°C. Repeat titration to get concordant values. Calculate the mass of crystalline ammonium oxalate present in 100 cm^3 solution. This was originally present in 10 cm^3 of solution. Therefore calculate the mass of crystalline ammonium oxalate present in 1000 cm^3 of original solution.

Result: Solubility of crystalline ammonium oxalate in water = ___ g per litre at ___ °C

Calculation:

Temperature of the solution = __ °C.

[Give details of standardization of permanganate solution].

Normality of permanganate solution (N) = ___
Volume of ammonium oxalate solution titrated (V_1) = 20 cm^3.
Volume of permanganate used (V_2) = ___ cm^3.

∴ Normality of ammonium oxalate solution (N_1) = $\frac{V_2 N}{V_1}$ = ___

Equivalent mass of $(NH_4)_2C_2O_4.H_2O$ = (molar mass) / 2 = 71

∴ Mass of crystalline ammonium oxalate in 100 cm^3 solution = $\frac{N_1 \times 71}{10}$ g

But this was present in 10 cm^3 of original solution.

∴ Mass of crystalline ammonium oxalate in 1000 cm^3 of original solution = $\frac{N_1 \times 71 \times 100}{10}$ = ___ g.

8. Solubility – Experiment 8.2.

TO DETERMINE THE HEAT OF SOLUTION OF A SALT AT INFINITE DILUTION

Aim: To determine the heat of solution of a salt like KNO_3 at infinite dilution using graphical method.

Principle: Heat of solution of a salt is defined as the heat change produced when one formula mass (mole) of the salt is dissolved in a suitable solvent, usually water, to get a solution of specified concentration. Depending on the method used, integral and differential heats of solution are defined. Heat of solution at infinite dilution is defined as the heat change produced when the solute is dissolved in such a large excess of water so that any further dilution does not produce any heat change. This is difficult to determine practically. Therefore for the purpose of this experiment, heat of solution at infinite dilution is taken as the heat change when the molar ratio of water to salt (n_w/n_s) is 200. The value may be positive for some salts, while it may be negative for others (dissolution may be exothermic or endothermic).

Procedure: Take a vacuum flask of 250 cm^3 capacity fitted with a stopper carrying a thermometer and stirrer for use as a calorimeter. Determine the water equivalent of the calorimeter (as explained in experiment 1.1).

Take exactly 200 cm^3 of water in the calorimeter and measure its initial temperature. Add an exactly weighed amount (about 5 g) of potassium nitrate rapidly into the flask, immediately stopper and stir rapidly. Note the temperature every 10 seconds till the temperature remains steady for three or four readings. Plot a graph of temperature against time, starting with the initial temperature at zero time, and get ΔT. Assuming density of water to be 1, calculate number of moles of water and number of moles of potassium nitrate used.

Repeat the experiment using 10, 15, 20 and 25 grams of potassium nitrate, and determine ΔT in each case. Plot ΔT against (n_w/n_s) and extrapolate to obtain ΔT corresponding to (n_w/n_s) = 200.

Calculate heat change for one mole of solute using ΔT and n_s corresponding to (n_w/n_s) = 200.

Result: Heat of solution at infinite dilution for potassium nitrate = ___ kJ mol^{-1}

Calculation:

mass of KNO_3	mass of H_2O	n_s	n_w	n_w/n_s	ΔT
…	200g	…	11.11	…	…
…	200g	…	11.11	…	…
…	200g	…	11.11	…	…
…	200g	…	11.11	…	…
…	200g	…	11.11	…	…
				200	…

Calculations for water equivalent of calorimeter (W)
Formula mass of KNO_3 = 101
Mass of KNO_3 corresponding to (n_w/n_s = 200) = w_s = ___ g

Heat of solution of KNO_3 for (n_w/n_s = 200) = $\frac{(200+W)\Delta T \times 101}{w_S} \times \frac{4.18}{1000}$ = ___ kJ mol^{-1}

9. Adsorption – Experiment 9.1.

VERIFICATION OF LANGMUIR ADSORPTION ISOTHERM

Aim: To determine the adsorption of oxalic acid from solutions of various concentrations using activated carbon and show that the data fits the Langmuir adsorption isotherm. Also to calculate the Langmuir parameters ‘*a*’ and ‘*b*’.

Principle: The mass of a solute adsorbed per unit mass of an adsorbent (x/m) from solution at equilibrium is usually proportional to the equilibrium concentration of the solution at constant temperature. According to Langmuir adsorption isotherm, $\frac{x}{m} = \frac{ac}{1+bc}$ where ‘*a*’ and ‘*b*’ are Langmuir constants, and ‘c’ is the concentration of the solution. The equation can be rewritten in the form $\frac{c}{x/m} = \frac{b}{a}c + \frac{1}{a}$ which is of the form y = mx + c. Therefore, a plot of $\frac{c}{x/m}$ against c should give a straight line, with y-intercept = $1/a$ and slope = b/a. From these values, ‘*a*’ and ‘*b*’ can be calculated.

Procedure: Prepare 250 cm^3 of 1N oxalic acid solution by weighing out 15.7500 g of crystalline oxalic acid into a volumetric flask and making up to the mark using distilled water. Using a burette, transfer 10, 20, 30, 40 and 50 cm^3 of this solution into separate (labeled 1 to 5) 100 cm^3 volumetric flasks and make up to get 0.1, 0.2, 0.3, 0.4 and 0.5 N solutions respectively.

Prepare another 100 cm^3 of standard oxalic acid solution. Prepare 500 cm^3 of approximately 0.1N NaOH solution and standardize using standard oxalic acid solution and phenolphthalein indicator.

Take five labeled 250 cm^3 conical flasks and weigh out exactly 2 g of activated charcoal into each flask. Using a burette, pour exactly 50 cm^3 each of oxalic acid solutions of the different concentrations into the flasks respectively. Stopper and shake the flasks for 30 minutes on a rotary shaker at low speed. Filter each solution (using different funnels and filter papers) into separate vessels. Titrate 20 cm^3 of solution 1, 10 cm^3 of solution 2 and 5 cm^3 of solutions 3, 4 and 5 respectively (V cm^3) against the NaOH solution using phenolphthalein indicator. Calculate the equilibrium concentration of oxalic acid C_e in each case. Also calculate the mass of oxalic acid (x) adsorbed by the charcoal from the solution in each case and hence x/m and $\frac{C_e}{x/m}$.

Result: Plot of $\frac{C_e}{x/m}$ against C_e gives a straight line. Hence Langmuir isotherm is verified.

Langmuir parameter ‘a’ = ____ and ‘b’ = ____.

Calculation:

Flask	Initial conc. (C)	Initial Mass of oxalic acid in 50 cm^3	Final conc. (C_e)	Final Mass of oxalic acid in 50 cm^3	Mass adsorbed (x)	x/m	$\frac{C_e}{x/m}$
1	0.1 N	0.3150 g					
2	0.2 N	0.6300 g					
3	0.3 N	0.9450 g					
4	0.4 N	1.2600 g					
5	0.5 N	1.5750 g					

(Calculate for all five flasks separately):

Normality of NaOH (N_1) = ____
Volume of NaOH used (V_1) = ____
Volume of oxalic acid solution pipetted (V_2) = ____

$\therefore$ Normality of oxalic acid after adsorption (C_e) = $\frac{V_1 N_1}{V_2}$ = ____

$\therefore$ Mass of oxalic acid in 50 cm^3 after adsorption = $\frac{C_e \times 63g \times 50}{1000}$ = ____ g.

Mass of oxalic acid adsorbed (x) = (mass before adsorption) – (mass after adsorption).

Plot $\frac{C_e}{x/m}$ against C_e and check whether points fall on a straight line. y-intercept = $1/a$ and slope = b/a.

9. Adsorption – Experiment 9.2.

DETERMINING THE CONCENTRATION OF THE GIVEN OXALIC ACID SOLUTION

Aim: To determine the unknown concentration of the given oxalic acid solution by studying the adsorption of oxalic acid from solutions of various concentrations using activated carbon and calculating the Langmuir parameters '*a*' and '*b*'.

Principle: The equilibrium concentration C_e after adsorption for the given solution can be determined, and the corresponding $\frac{C_e}{x/m}$ value can be obtained from the Langmuir adsorption isotherm. Then the amount adsorbed can be calculated using the equation $\frac{C_e}{x/m} = \frac{b}{a}C_e + \frac{1}{a}$ where '*a*' and '*b*' are Langmuir constants. Using this information, the original concentration can be arrived at.

Procedure: Repeat experiment 9.1 using 50 cm^3 oxalic acid solutions of five different known concentrations and also the solution of unknown concentration in exactly the same manner. Titrate 10 cm^3 of the unknown solution after adsorption against standard NaOH solution. Construct the Langmuir adsorption isotherm using data from solutions of known concentrations, and determine the Langmuir parameters '*a*' and '*b*'. Calculate C_e for the unknown solution, and read the corresponding $\frac{C_e}{x/m}$ value from the graph. Calculate x/m for the unknown solution using the equation $\frac{C_e}{x/m} = \frac{b}{a}C_e + \frac{1}{a}$. Calculate the amount of oxalic acid adsorbed, x g.

Calculation:

Flask	Initial conc. (C)	Initial Mass of oxalic acid in 50 cm^3	Final conc. (C_e)	Final Mass of oxalic acid in 50 cm^3	Mass adsorbed (x)	x/m	$\frac{C_e}{x/m}$
1	0.1 N	0.3150 g					
2	0.2 N	0.6300 g					
3	0.3 N	0.9450 g					
4	0.4 N	1.2600 g					
5	0.5 N	1.5750 g					
6	unknown						

(Calculate for all six flasks separately as in experiment 9.1 and construct the adsorption isotherm)

Unknown:

C_e = ____; x = ____.

Mass of oxalic acid in 50 cm^3 after adsorption = $\frac{C_e \times 63g \times 50}{1000}$ = ____ g.

But mass of oxalic acid adsorbed (x) = (mass before adsorption) – (mass after adsorption).

$\therefore$ Mass of oxalic acid in 50 cm^3 before adsorption (M) = x + (mass after adsorption)

$\therefore$ Initial normality = $\frac{\text{mass per litre}}{\text{equivalent mass}} = \frac{M \times 1000}{50 \times 63}$ = ____.