where V_B is the volume of bromide added, and V_N is that of NH_3 added. Equation (4.10) can be written as:—

$$\frac{V_B}{V_N{}^x}=\text{constant} \qquad \ldots \quad (4.11)$$

∴ A plot of log V_B against log V_N should yield a straight line with a slope equal to x.

Materials:

1. 250 ml. KBr (0.005M); 2. 250 ml. $AgNO_3$ (0.01M); 3. 250 ml. NH_4OH (2M).

Procedure:

Fill up two burettes, one with 2M ammonia solution and the other with 0.005 M KBr solution. In five concial flasks, prepare solutions of the following compositions:—

Flask No.	NH_3 solution	$AgNO_3$ solution	Water
1	10 ml.	20 ml.	70 ml.
2	15	20	65
3	20	20	60
4	25	20	55
5	30	20	50

Titrate the solutions in each flask with KBr solution until a permanent cloudiness just appears. Note the titrant volume (T' ml.).

Repeat this series of experiments, but make the total volume to (100—T') ml. instead of 100 ml. Titrate again carefully with KBr solution until a permanent cloudiness just appears. The final solution volume at the end point should be 100±4ml. Let the second accurate titre be T ml.

Results and Calculations:

Flask No.	Vol. of NH_3 (V_N) ml.	Log V_N	T'ml	$T = V_B$ ml.	Log V_B

Plot log V_N *vs* log V_B and from the slope find the value of x.

EXPERIMENT NO. 5

DETERMINATION OF MOLECULAR WEIGHT

5.1 To determine the molecular weight of a given liquid by Victor Meyer Method:

Theory:

A known weight of a volatile material is made to displace its own volume of air which is then collected and measured under known conditions of temperature and pressure. If it is assumed that the material behaves as a perfect gas, then the molecular weight may be derived from the fact that 1 gram molecule of a gas occupies 22.4 litres at N.T.P.

Materials:

Experimental liquid. (Chloroform, acetone, carbon tetrachloride, etc. may be used as experimental liquid). Bulblets (Make yourself).

Procedure:

The Victor Meyer apparatus (Fig. 12) consists of a cylindrical vessel *B* having a long narrow neck with a side tube *C* and a rubber stopper at the upper end. The side tube is connected with a bent capillary tube *D*, the free end of which is attached to the top of a gas burette *E*. The gas burette is then connected to the reservoir *R* containing water, which can be lowered or raised to adjust the level of water. In making these connections, thick-walled rubber tubing should be employed.

The tube *B* is placed in a wider tube *A* — a cork being fixed at the upper end of *A*. The wider tube *A* contains a liquid the boiling point of which is at least 20-40°C above the boiling point of the experimental liquid. A small quantity of glass wool or asbestos is placed at the bottom of the inner tube *B* in order to avoid any fracture when the Victor Meyer bulblet is dropped in.

Weigh out accurately the dry Victor Meyer bulblet and then weigh into it about 0.1-0.2 gm. of liquid accurately. (The bulblet should not be filled more than 3/4 full). (In place of the bulblet, a small glass-stoppered bottle called Hoffmann bottle may be used). The bulblet is weighed first. Then the liquid is introduced by alternatively cooling and heating the bulb. When 3/4th of the bulb is filled in, the end of the capillary is sealed and the bulblet is weighed again.

The inner tube *B* is closed air-tight with a rubber stopper at the upper end. The side tube *C* is connected with the burette by a piece of thick-walled rubber tubing and the liquid in the jacket *A* is heated to brisk boiling. The three-way stop-cock *P* of the burette is kept open to air to allow the expanded air to escape. The heating is continued for about 10 minutes in order to make sure that the temperature in *B* has become constant (This is tested by turning the stop-cock and connecting the burette with the side tube *C* — the level of water should remain unchanged if the temperature in *B* is constant).

The pressure of air inside the burette is made equal to that of atomospheric pressure by equalising the two levels of water in the burette and the reservoir. The reading is noted (V_1).

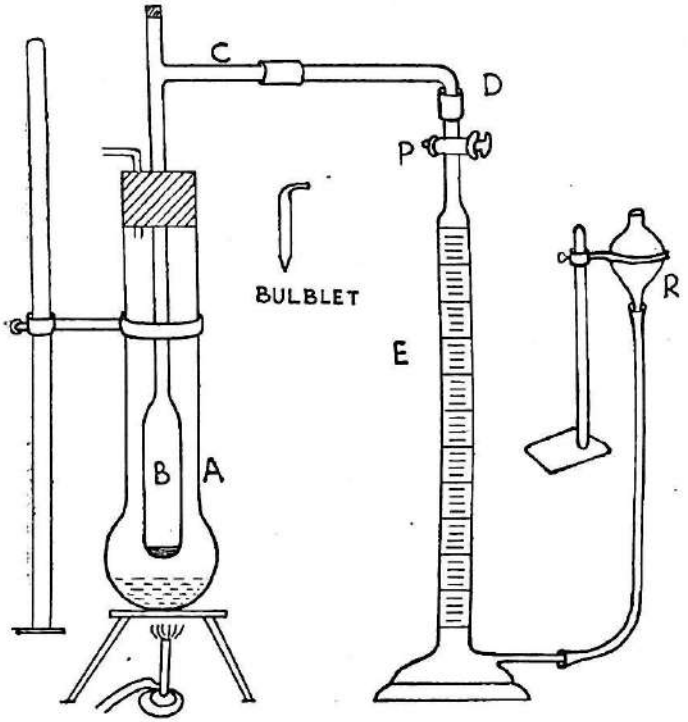


Fig. 12. Victor Meyer Apparatus

In case P is a simple two-way stopcock instead of a three-way one, the exerimental procedure will be somewhat different. Keep P open all the time and test the attainment of steady temperature inside B by closing the rubber cork (which of course should he kept open during the initial heating period) at the top of B. The water level in the gas burette should remain steady for the next few minutes. When steady conditions are found to be established, read the burette (V_1) and proceed with the experiment as described below.

The capillary end of the Victor Meyer bulblet is cut and it is quickly introduced into the tube *B* by removing the rubber cork; the rubber cork is replaced immediately. The liquid vaporises and the air is expelled into the burette, the volume of air expelled being equal to the volume of the liquid at that particular temperature. As the air passes over into the burette, the reservoir must be continuously lowered so that the level of water in the reservoir and the burette remains about the same. This diminishes the danger of leakage. When there is no more displacement of air, the tap *P* is closed. Remove the burner and open the rubber stopper at the top of *B*.

The burette is allowed to attain room temperature. Now the water level is again adjusted and the final reading on the burette is taken (V_2).

Results and Calculations:

Weight of empty bottle = W_1 gms.
Weight of bottle + liquid = W_2 gms.

$\therefore$ Weight of liquid = $(W_2 - W_1)$gm = W gms
Initial reading of burette = V_1 ml
Final reading of burette = = V_2 ml

$\therefore$ Volume of air collected = $(V_2 - V_1)$ml. = V ml.
Room temperature = t°C

Let V be the volume of the air expelled, measured in ml; t°C the temperature of the air; b the barometric pressure; f the vapor pressure of water at the temperature t°C; W the weight in grams of the substance taken. Then the molecular weight (M) may be calculated by using eqn. (5.1):

$$PV = nRT$$

$$PV = \frac{W}{M} RT$$

or $$M = \frac{WRT}{PV} \quad \ldots \quad \ldots \quad \ldots \quad (5.1)$$

Here $T = (273 + t)$ Abs.

$$P = \frac{b-f}{760} \text{ atm.}$$

$R = 82.1$ (when P is in atm. and V in ml.)

Modifications of Victor Meyer apparatus: There are quite a number of modifications or variations of the Victor Meyer apparatus of which the following are rather common.

(*i*) **Built-in bulblet introduction device:** In the form of the apparatus described above the rubber stopper is removed for introducing the bulblet and of course replaced as quickly as possible thereafter. In some modifications, the apparatus is provided with a side-tube-device to hold the bulblet near the top and to release it down the tube when desired.

(*ii*) **Method of collecting displaced air:** Variation in the method of collecting the displaced air is also made. Instead of a gas burette as shown in Fig. 12, a very simple and common method is to keep the open end of the bent delivery tube immersed under water. A graduated tube full of water is kept inverted over this end so that all displaced air enters and collects in the graduated tube. Its volume under atmospheric pressure is then noted.

5.2 To determine the molecular weight of a given substance in benzene by the depression of freezing point method.

Theory:

The addition of a solute to a solvent decreases the tendency of the solvent molecules to escape into the gas phase, i.e., it lowers the vapour pressure of the solvent. When the solute is non-volatile, the total vapour pressure of the solution is also lowered and as a result the temperature of freezing is also lowered. The extent of freezing point depression depends on the concentration of the solute and the following quantitative relation holds good for *ideal dilute* solutions:

$$M_2 = 1000 \; K_f \frac{W_2}{\Delta T_f . \; W_1} \qquad \ldots \; (5.2)$$

where W_2 is the weight (gm.) of the solute of molecular weight M_2 dissolved in W_1 gm of solvent, ΔT_f is the observed depression of the freezing point and K_f is called the cryoscopic constant and corresponds to the depression per gm-molecule of the solute dissolved in 1000 gm. of the solvent (K_f for benzene is 5.12°C).

The theory is limited to dilute solutions of non-electrolytes. Solute that dissociates or associates gives abnormal values.

Materials:

(Camphor, urea, naphthalene, anthracene, etc. may be used as solutes).

(1) Experimental solute; (2) Benzene.

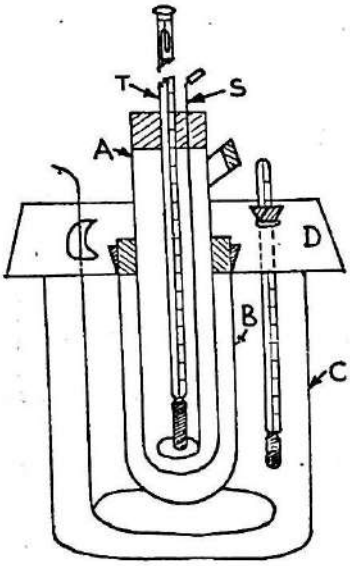


Fig. 13 Beckmann Freezing Point Apparatus

Procedure:

Apparatus: The freezing point apparatus consists basically of a tube (*A*) on the top of which rests a cork through which a Beckmann thermometer (*T*) and a stirrer (*S*) is inserted. The tube is supported in a wider tube, (*B*) so that an air jacket is provided between the liquid and the cooling bath (ice-salt or ice-water). On the top of the cooling bath (*C*) (made of glass or stone ware) rests a brass lid (*D*) through an opening of which passes a stirrer by means of which the temperature of the bath can be kept uniform; through another opening passes a thermometer to note the temperature of the bath. Through the larger opening at the middle of the lid passes the freezing point tube with the air jacket. The whole assembly

is shown in the figure (Fig. 13). The freezing point tube is provided with a side arm for insertion of the solute during the experiment.

Setting the Beckmann Thermometer:

Before using the Beckmann thermometer, it must be "*set*" *i.e.*, the amount of mercury in the bulb must be regulated so that at the temperature of the experiment, the end of the mercury thread is on the scale. The method of 'setting' is as follows:-

Hang the Beckmann thermometer along with another ordinary thermometer in a beaker of water the temperature of which is the same as the freezing point of the solvent. Now see whether or not the top of the mercury thread stands somewhere up on the scale. Suppose it does not; that is, there is too little mercury in the bulb. Under these conditions, place the thermometer in a beaker of warm water, the temperature of which is sufficiently high to cause the mercury to pass up to the top and to form a small drop at the end of the capillary. Now invert the thermometer and tap it *gently* so as to collect the mercury in the reservoir at the end of the capillary and to join with the mercury there.

The thermometer is now returned, without shaking, to the upright position and again placed in the first beaker or bath where the temperature is 2 to 3°C above the freezing point. The mercury in the bulb will contract and draw in more mercury from the reservoir. After several minutes, when the thermometer will have taken the temperature of the bath, *carefully* strike the upper end of the thermometer against the palm of the hand so as to cause the excess of mercury to break off from the end of the capillary.

Now see whether or not the amount of mercury has been properly regulated, by placing the thermometer in a bath (as in the preceding paragraph) and see whether the mercury thread stands on the scale. If it stands above the scale, too much mercury has been introduced and it must be transferred to the reservoir. This is achieved by warming the bulb of the thermometer with the palm and shaking off a few droplets formed at the capillary end. On the contrary if the mercury is found to stand too low on the scale, then more mercury must be introduced into the bulb in the manner described above. These operations are repeated until the proper amount of mercury has been introduced.

A small thermoflask ('*Thermos*' bottle) containing water at the required temperature can be very conveniently used in place of the beaker or bath mentioned in the foregoing paragraphs.

Once the Beckmann thermometer is *set*, it is ready for use.

Determination of freezing point:

Now introduce about 20 ml. of pure benzene into the dry freezing point tube; the weight of benzene must be known exactly—use a 100 *ml.* flask as a weighing bottle and find the weight of the charge by difference (Alternatively, pipette 25 *ml.* of benzene into the freezing point tube.

Caution: Benzene is poisonous; take proper precaution. The mass can be obtained by multiplying the volume by density). Then assemble the apparatus and adjust the temperature of the ice-bath (by varying the proportion of crushed ice, salt (*if necessary*) and water). The freezing point of benzene is then determined as follows.

In doing this, firstly the freezing point tube with benzene is placed directly in the cooling bath, so that the temperature falls comparatively rapidly. When solid benzene begins to separate, slightly warm the tube by the palm and quickly insert it into the jacket in the cooling bath. The stirrer is operated vigorously. Temperature is noted at various time intervals. Normally supercooling occurs, and the solid does not separate until the temperature is a few degree below the true freezing point. At some stage solid benzene starts separating and the mercury shoots up, as heat is evolved by the solidification. Finally the temperature rises to a steady stationary temperature (if the solvent is pure). In some cases, the supercooling has been known to continue for more than 10 mins. No fewer than three concordant readings should be taken (The readings should differ by less than 0.005°C.) The mean of the readings is taken as the freezing point of the solvent.

A weighed amount (about 0.2 gm.) of the unknown substance, compressed into a tablet form, is now introduced into the benzene through the side arm of the freezing point tube and allowed to get dissolved in benzene. The freezing point is again determined as described for the pure solvent. (If tablet making device is not available, experiments may be done with solutions of known concentrations prepared separately).

Make further additions of solute, so that the freezing point depression can be found at different concentrations of solute.

The molecular weight is calculated by applying equation (5.2).

Discuss the approximate concentration range over which these solutions appear to behave ideally.

Results and Calculations:

Weight of weighing bottle ... ... = ... gm.
Weight of weighing bottle + benzene ... ... gm
∴ Weight of benzene taken ... ... = ... gm.
Freezing point of benzene — (*i*) ...
(*ii*) ... *Mean*
(*iii*) ... ...

Weight of solute (gms.)	Freezing point *Beckmann Scale*	Depression of freezing point (°C)	Molecular weight [*Eqn.* 5.2]

Suggestions for further work:

1. The abnormal colligative properties of aqueous electrolytic solutions may be demonstrated.

2. Besides benzene, a number of other solvents can be employed for determining the molecular weight of organic compounds. A large freezing point constant is desirable in order to obtain a large depression. *Tert*-Butanol, cyclohexanol and phenol have large constants, but they are hygroscopic and require therefore special care to prevent absorption of water vapour.

5.3 To determine the molecular weight of the given substance by Rast's method.

Theory:

The basic theory of this experiment is the same as that of cryoscopic molecular weight determination (Expt. No. 5.2).

If W_2 gm. of a non-volatile non-electrolyte of molecular weight M_2 dissolved in W_1 gm. of solvent lowers the freezing point by $\Delta T_f°C$, then for dilute solutions,

$$\Delta T_f = K_f \times \frac{1000 W_2}{W_1 M_2} \quad \ldots \quad \ldots \quad \ldots \quad (5.2)$$

where K_f is a constant for a given solvent and is called the cryoscopic constant. In ordinary cryoscopic method benzene ($K_f = 5.12$) is the common solvent.

The fact that camphor has a large cryoscopic constant and therefore will produce a considerably larger depression in freezing point compared to ordinary solvents like benzene, is the basis of the method of Rast. The cryoscopic constant for camphor is about 40°C for 1 mole of solute in 1000 gm. of solvent (i.e., K_f is about 8 times that of benzene). Hence, the freezing point depression is large and can be measured by using an ordinary thermometer. In the present experiment the freezing point of pure camphor and that of the mixture of camphor and solute are determined. This is done by noting the temperature at which the samples in the melting-point capillary tubes are about to be completely melted; for, this is the point at which the liquid solution is in equilibrium with a small amount of solid solvent.

Because of its convenience and simplicity, the method has found wide application in organic chemistry. The method demands small amounts of the solute and the results are obtained fairly quickly.

The method is inapplicable if the unknown solute is insoluble in camphor, reacts with camphor, or decomposes when heated to the melting point of camphor. Moreover it is to be assumed that no eutectics of compounds separate out but that pure camphor crystallises out on cooling. Also it is assumed that solutions (Camphor+Solute) are ideal. The best way is to determine the depression as a function of concentration of solute and check whether the molecular weight determined for each concentration remains the same.

The chemical composition of camphor varies somewhat with its source; it is therefore necessary to determine K_f for the particular sample of camphor by carrying out a preliminary calibration experiment with a solute of known molecular weight, naphthalene or anthracene for example.

Materials: (1) Camphor; (2) Anthracene or naphthalene (3) Unknown solute; (4) Thermometer reading to tenth of a degree near M.P. of camphor.

Procedure:

(*a*) Preparation of solution

Take a pyrex glass tube (approximately 1 cm. diam). Pull out a capillary (about 1 mm. diam.) at one end and seal that end leaving about 5 cm. length of the capillary. Make a constriction at the other end (to be sealed later). Weigh about 10 mg. of the calibration solute and 100 mg. of camphor (solvent) into a mortar and mix them thoroughly with the pestle. Introduce this mixture into the aforementioned tube; seal the tube at the constriction. Immerse the tube in a bath (H_2SO_4; or paraffin oil, or silicone liquid). Raise the temperature of the bath to about 170°C until the content in the tube melts; then a portion is made to get into the capillary portion. Take out the tube and cool it; break the capillary portion off. Use this tube (tube A) for determination of melting point of camphor+solute.

(*b*) Determination of melting point

Take tube A and another melting-point-capillary tube containing powdered camphor. Attach the two tubes to the sides of the thermometer bulb by means of a rubber band cut from a rubber tubing. Clamp the thermometer so that the bulb with the sample (and not the rubber band) are just immersed in the heating bath (of paraffin oil or sulfuric acid or silicone liquid). Heat the bath and note the temperature where the crystals just melt into liquid. (Use magnifying glass). Do this both for the tube A and also for the other melting point tube containing camphor only. Also, after noting the melting point, note the temperature when crystals first appear on slow cooling. Repeat the measurements of melting point and freezing point until almost concordant results are obtained.

Now prepare the solution of camphor and the calibration solute at two other compositions (5% i.e. 5 mg. solute in 100 mg. camphor and 15% i.e. 15 mg. in 100 mg. camphor). Determine the freezing points in each case as described above. Calculate the freezing point depression at each of the three concentrations and from these values calculate the cryoscopic constant K_f. Take mean.

The whole procedure is now repeated using the unknown instead of the calibration substance.

Results and Calculations:

M. pt. of pure camphor	Solute	Concn. of Solute	M. pt. of Solutions °C	Depression in f. pt. °C	Kf (using eqn. 5.2)	M. Wt. of unknown (eqn. 5.2)
...	Known (for calibration)	5% 10% 15%			... ... (Mean value)	
	Unknown	5% 10% 15%				... ... (Mean Value)

5.4 To determine the molecular weight of a given solute in benzene by the boiling point elevation method.

(Urea, napthalene, etc. may be taken as solutes).

Theory:

When a non-volatile solute is dissolved in a solvent, the vapour pressure of the latter is decreased; as a result the boiling point of the solution is higher than that of the solvent. The extent of elevation depends on the concentration of the solute and the following relation holds for *ideal dilute* solutions—

$$M_2 = 1000K_b \times \frac{W_2}{\Delta T_b \times W_1} \quad \ldots \quad (5.3)$$

where ΔT_b is the elevation of boiling point for a solution containing W_2 gms. of solute of molecular weight M_2 in W_1 gms. of solvent of molal boiling point constant K_b.

The theory is limited to dilute solutions of non-electrolytes. Solute that dissociates or associates gives abnormal values.

Procedure:

Boiling point apparatus of the Cottrell type as shown in figure 14 is generally used.

Beckmann thermometer or ordinary thermometer graduated to 0.01° may be used. If Beckmann

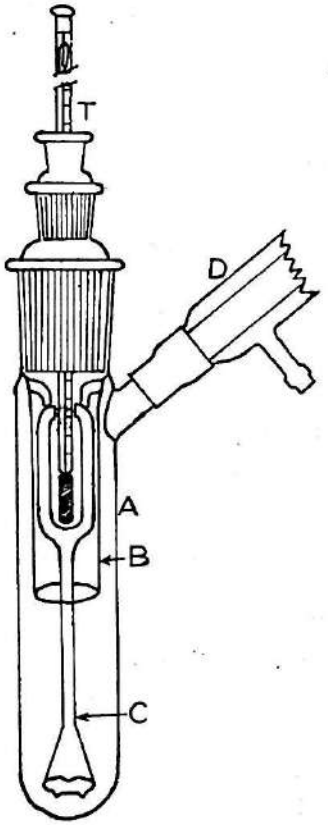


Fig. 14—Cottrell Boiling Point Apparatus

thermometer is to be used, it is to be *'set'* for the boiling point of the solvent as described in the previous experiment on P. 37.

A weighed quantity of the solvent sufficient to reach a centimeter or so below *B*, the shield for the thermometer bulb, is introduced into the boiling tube (*A*). The apparatus is clamped in a vertical position and heated with a small shielded gas flame. The purpose of the small inverted funnel, *C* which rests above the bottom on three small projections, is to catch the bubbles of vapor and to direct them through the center tube and the three (only two shown in Fig.) vertical tubes. As the bubbles discharge through these outlets, they direct three sprays of liquid and vapour against the thermometer; any superheated solution comes to full equilibrium with the vapour by the time it gets to the thermometer bulb. No fewer than three concordant readings should be taken. If the boiling point is not constant, it may be necessary to redistill the liquid. (If the liquid does not 'pump' vigorously over the thermometer bulb, the level of the liquid or the rate of heating is to be changed).

After the boiling point of the pure solvent has been determined, the gas burner is turned off and the liquid allowed to cool for sometime. The condenser is removed and a weighed quantity of the solute (sufficient to produce a 1 to 5 per cent solution) is introduced (the solute may be transformed into a 'pellet' by a pellet machine and then weighed and introduced).

The boiling point of the solution is then determined as described above.

Make further additions of solute, so that the boiling point elevation can be found at different concentrations of solute.

The molecular weight is calculated by applying equation (5.3).

Discuss the approximate concentration range over which these solutions appear to behave ideally.

The larger experimental errors are due to (1) fluctuations in atmospheric pressure; (2) appreciable loss of solvent in the vapour and condenser. The first difficulty may be met by using two sets of apparatus at the same time, one for solvent and the other for solution. The second difficulty may be met by analysing the solution after determination of the boiling point. A sample is withdrawn with a pipette and weighed in a weighing bottle. The solvent is then evaporated and the residue weighed.

Results and Calculations:

Weight of solvent taken	=		...	gms.
Boiling point of solvent	=	(*i*)	...	*Mean*
(*Beckmann Scale*)		(*ii*)	...	...
		(*iii*)	...	

Weight of solute in gms.	Boiling point (*Beckmann Scale*)	Elevation of Boiling pt. °C	Molecular Weight
	...		
	... ...		
	... (*Mean Value*)		

Suggestions for further work:

1. The association properties of some organic acids and hydroxy compounds in aprotic solvents (P. 45 & 49) can be studied. Also the abnormal properties of aqueous electrolytic solutions may be demonstrated.

5.5 To determine the molecular weight of the given liquid by steam distillation.

Theory:

When a mixture of two immiscible liquids is heated, each exerts its own vapour pressure irrespective of the other. When the sum of the vapour pressures of the two liquids becomes equal to the atmospheric pressure, the two distil over together. The temperature of distillation is thus lower than the boiling point of either of the pure components. This temperature and the composition of the distillate remain constant until one of the liquids is entirely evaporated. In steam distillation one of the liquids is water.

The composition of the distillate is governed by the vapour pressures of the two liquids at the temperature of distillation, and by their molecular weights. The ratio of the two vapour pressures at the distillation temperature is equal to the ratio of the number of moles of the two substances in the vapour. For steam distillation:

$$\frac{P_x}{P_w} = \frac{n_x}{n_w} = \frac{W_x . M_w}{M_x . W_w} \quad \ldots \quad \ldots \quad \ldots \quad (5.4)$$

or, $$M_x = \frac{W_x}{W_w} M_w . \frac{P_w}{P_x} \quad \ldots \quad \ldots \quad \ldots \quad (5.5)$$

and $$P_x + P_w = \text{atmospheric pressure} \quad \ldots \quad \ldots \quad (5.6)$$

where M=molecular weight, n=number of moles, P=vapour pressure at the distillation temperature, W=mass of the distillate, and the subscripts x and w refer to the liquid and water respectively. The vapour pressure of water (P_w) at the distillation temperature may be obtained from tables (*vide* Appendix) and that of the liquid (P_x) may be obtained using equation (5.6). The relative weights of water and liquid (i.e., W_w and W_x) may be determined from their respective volumes in the distillate and their densities.

Steam distillation is very commonly employed in synthetic chemistry and in chemical technology for separating and purifying high-boiling liquids at temperatures considerably below their boiling points. Occasionally, the procedure is used to distil a substance which would decompose at higher temperatures, and highly inflammable materials are sometimes distilled with steam to avoid the fire hazard involved in ordinary distillation.

Materials

(1) Nitrobenzene; (2) Water.

Procedure

Fig. 15 represents the apparatus used for steam distillation. Steam is generated in flask *A*, provided with a safety tube which reaches to the bottom and extends about 40 cm. above the top. Steam is allowed to pass from flask *A* to flask *B* by tubes (t_1, t_2) connected by a rubber tube (r). *T* is a thermometer reading to tenths of a degree. *C* is the condenser and *D* is a measuring cylinder for collecting the distillate.

Take 50 ml. of water and 50 ml. of nitrobenzene in the flask *B*. Introduce steam from *A* with sufficient rapidity to keep the mixture thoroughly stirred. It will be necessary to heat both flasks at the beginning of the experiment until steam is passing freely through the

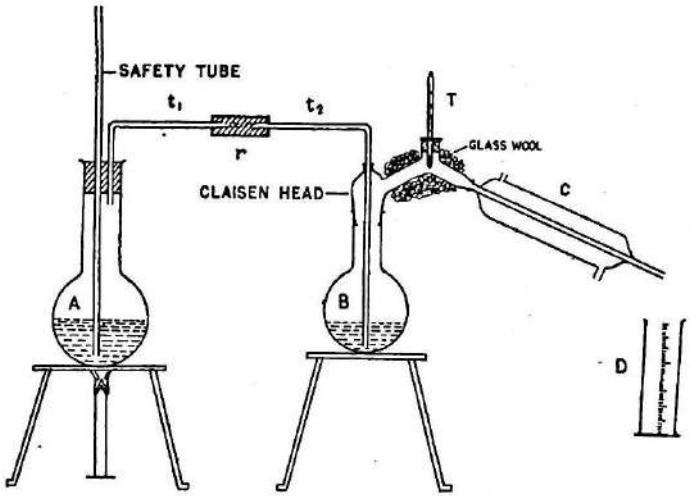


Fig. 15 Steam Distillation.

system, when the heating of *B* may be discontinued. Note that the flask *B* should be tilted if possible so that there is no possibility of liquid splashing up and passing over with the vapour. Estimate the mean temperature of distillation by noting the temperature at intervals during the process. Reject the first 10 ml. of the distillate and then collect 30 to 40 ml. of the distillate in the graduated cylinder.

Results and Calculations

Volume of liquid collected	=	...	ml
Volume of water collected	=	...	ml
Wt. of liquid collected	=	...	gm
	=	Wx	
and Wt. of water collected	=	...	gm.
	=	Ww	
Temperature of distillation	=	...	°C
Atomospheric pressure, P	=	...	mm Hg
Vapour pressure of water at distillation temperature (°C). P_w	=	...	mm Hg
	=	Pw	
Vapour pressure of liquid at distillation temperature (...°C), $P_x = P - P_w$ (equ. 5.6)	=	...	mm Hg
	=	Px	
Molecular weight of liquid X (Use equation 5.5)	=	...	
	=	Mx	

Suggestions for further work

Chlorobenzene, bromobenzene or toluene may be used instead of nitrobenzene.

5.6 Determination of the degree of association of benzoic acid in benzene

Theory:

According to equation (1) of experiment No. .....,

$$M_2 = K_f \frac{W_2.1000}{W_1.\Delta T_f} \qquad \ldots (1)$$

where W_2 is the weight (gm) of the solute of molecular weight M_2 dissolved in W_1 gm. of solvent, ΔT_f is the observed depression of the freezing point and K_f is the cryoscopic constant.

For benzene solutions of solutes like urea, the solute molecules exist as unassociated molecules (*monomers*), so that the molecular weight of solute (M_2) is given directly by the above equation. However, for solutions of benzoic acid in benzene, there is an appreciable degree of association (*dimerization*):

$$2C_6H_5.COOH \rightleftharpoons (C_6H_5COOH)_2$$

If α be the degree of association (*i.e.* fraction forming dimer) of the a moles of solid benzoic acid dissolved initially, then, at equilibrium, there will be $a(1-\alpha)$ moles of unassociated benzoic acid (*monomer*) of molecular weight M_2 (theoretical) (M_2 (Theoretical)=122 in this case) and $\frac{1}{2}a$ moles of the dimer. The total number of moles present are $[a(1-\alpha) + \frac{1}{2}\alpha\ a] = a(1-\frac{1}{2}\alpha)$

Since molecular weight is equal to weight in grams divided by number of moles, we have

$$M_2 = \frac{W_2}{a(1-\frac{1}{2}a)} = \frac{M_2(\text{Theory})}{(1-\frac{1}{2}a)}$$

$$\text{or} \quad a = 2(1-\frac{M_2(\text{Theory})}{M_2})$$

where M_2 is the observed molecular weight. $= 2(1-122/M_2)$ ... (2)

The object of the present experiment is to determine ΔT_f for solutions of different concentrations of benzoic acid and thereby to obtain M_2 and a in each case.

Materials:

Beckmann thermometer, benzoic acid, benzene.

Procedure:

See experiment No 5.2 .....

Results and Calculations:

Wei solute	Freezing point *Beckmann Scale*	Depression of freezing point	Molecular weight (M_2) by equation (1)	Degree of association (a) by equation (2)

Suggestions for further work:

Other aromatic acids and other solvents can be attempted.

EXPERIMENT NO. 6

PARTITION (OR DISTRIBUTION) COEFFICIENT

6.1. To determine the partition coefficient i.e. distribution coefficient of benzoic acid between water and benzene.

Theory:

When a solute is shaken with two immiscible solvents—if it is soluble in each of them—it will distribute itself between the two solvents in accordance with the distribution law. If the solute has normal molecular weight in both solvents (i.e. neither associated nor dissociated) the partition will take place according to the following equation (called Nernst Distribution Law)—

$$\text{Distribution coefficient, } K_D = \frac{C_1}{C_2} \quad \ldots \quad \ldots \quad 6.1$$

where C_1 and C_2 refer to the concentrations of the solute in the solvents 1 and 2 respectively; K_D is the partition coefficient (or distribution coefficient). The value of K_D is constant independent of the amount of solute provided the temperature is constant. (The constant K_D may be theoretically shown to be equal to the ratio of the solubilities of the solute in the two immiscible solvents).

If, however, in one solvent, the solute has the normal molecular weight, but in the second solvent *say* in solvent 2, is associated as follows:

$$n\,(\mathrm{HA}) \rightleftharpoons (\mathrm{HA})_n$$

then, at a given temperature, the ratio C_1/C_2 will no longer be constant. According to the law of mass action, the concentration of single molecules in the second solvent is proportional to the *nth* root of the total concentration. Therefore, the ratio $\frac{C_1}{\sqrt[n]{C_2}}$ should be constant.

In case of molecules like benzoic acid which generally exists as dimer in aprotic solvents, the value of n is expected to be 2.

Materials:

1. $N/10$ NaOH solution (also $N/50$ NaOH prepared from $N/10$ NaOH by exact ditution); 2. Phenolphthalein indicator; 3. Benzoic acid; 4. Benzene.

Procedure:

Place 1 gm., 1.5 gm., 2.0 gm., 3 gm. and 4 gm. of benzoic acid, respectively into five labelled stoppered 250 ml. bottles (or conical flasks).

Add 50 ml. CO_2-free water and 50 ml. of benzene into each bottle. Stopper the bottles properly and place them in a thermostat for about half an hour, and shake vigorously every 3 or 4 minutes for 1 hour.

Allow the mixture to separate into two clear layers—the upper layer is the organic layer and the lower layer is the aqueous layer.

Take two burettes, fill up one with $N/10$ NaOH and the other with $N/50$ NaOH.

Remove 10 ml. of the benzene layer by a pipette and deliver the sample into a conical flask containing about 30 ml. water. Titrate with N/10 alkali using phenolphthalein indicator—shake the solution vigorously during titration.

By using a separating funnel remove the lower water layer into a dry conical flask (or beaker); pipette out 10 ml. of this layer and run into a conical flask. Titrate with $N/50$ alkali as before.

Repeat the procedure for all bottles.

Results and Calculations:

Laboratory temperature = ...

Bottle No.	Vol. of $\frac{N}{50}$ NaOH for 10 ml. Aq. layer (ml.)	Concn. of acid in aq. layer in (N) gm. equiv./ lit. C_W	Vol. of $\frac{N}{10}$ NaOH for 10 ml. org. layer	Concn. of acid in org. layer in (N) gm. equiv./ lit. C_B	$\frac{C_W}{C_B}$	$\frac{C_W}{\sqrt{C_B}}$

See whether $\frac{C_{water}}{C_{benzene}}$ or $\frac{C_{water}}{\sqrt{C_{benzene}}}$ is constant and discuss the results accordingly.

Suggestions for further work:

The following distribution systems may be studied:

1. Hydrochloric acid between water and benzene.

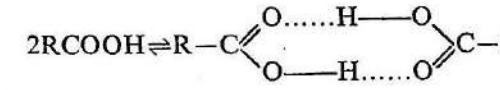
2. Salicylic acid or picric acid between water and benzene, and between water and chloroform as a function of the pH of the aqueous phase.

3. *Vide* Expt. No. 6.3 (Part I) for determination of distribution coefficient of iodine between CCl_4 and water.

6.2. Determination of the dimerisation constant of salicylic acid in benzene medium.

Theory:

Organic monocarboxylic acids tend to dimerize in non-polar solvents, such as benzene, on account of hydrogen bond formation:



$$2RCOOH \rightleftharpoons R-C\begin{matrix}O\cdots\cdots H-O\\ O-H\cdots\cdots O\end{matrix}C-R, \qquad \text{Acid} \overset{K_2}{\rightleftharpoons} \tfrac{1}{2}(\text{Acid})_2$$

The aim of the present experiment is to find out the dimerisation constant, K_2.

The partition of a monocarboxylic acid A between water and benzene may be represented as follows:

$$\begin{array}{ll} & A_{(B)} \overset{K_2}{\rightleftharpoons} \tfrac{1}{2}A_{2(B)} \quad \text{In benzene layer} \\ \cdots\cdots\cdots\cdots\cdots\cdots & \Big\downarrow K_1 \cdots\cdots\cdots\cdots\cdots\cdots \\ & A_{(W)} \quad \text{In water layer} \end{array}$$

Equilibrium constants for the two equilibria may be defined by—

$$K_1 = \frac{[A]_B}{[A]_W}, \quad K_2 = \frac{\sqrt{[A_2]^B}}{[A]_B} \qquad \ldots \qquad \ldots \quad (6.2)$$

where K_1 is the distribution coefficient and K_2 is the dimerisation constant.

If the total concentrations (expressed in terms of monomer) in aqueous and benzene solutions are represented as C_W and C_B respectively, then by the principle of mass balance, we get—

$$C_W = [A]_W \qquad \ldots \qquad \ldots \quad (6.3)$$

$$C_B = [A]_B + 2[A_2]_B \qquad \ldots \qquad \ldots \quad (6.4)$$

Dividing (6.4) by (6.3) :—

$$\frac{C_B}{C_W} = \frac{[A]_B}{[A]_W} + \frac{2[A_2]_B}{[A]_W}$$

$$= K_1 + 2.K_2^2 . \frac{[A]^2_B}{[A]_W} . \frac{[A]_W}{[A]_W} \qquad \ldots \qquad \ldots \quad 6.5$$

$$= K_1 + 2.K_2^2 . K_1^2 . C_W$$

Thus a plot of C_B/C_W *vs.* C_W should be a straight line of intercept K_1 and slope $2K_1^2 . K_2^2$, from which the constants K_1 and K_2 can be obtained.

Materials:

1. Salicylic acid; 2. Benzene; 3. 0.05 (*N*) NaOH; 4. 0.1 (*N*) succinic acid; 5. Phenolphthalein indicator.

Procedure:

Prepare a standard solution of succinic acid (or oxalic acid) and titrate this with alkali. Find out the exact normality of alkali.

Prepare a saturated solution of salicylic acid in benzene. In four stoppered bottles, prepare solutions of the following compositions:—

Bottle No.	Saturated Solution of acid	Water	Benzene
I	50 ml.	20 ml.	0 ml.
II	40	20	10
III	30	20	20
IV	20	20	30

Bring these bottles to partition equilibrium at 25°C by placing them in a thermostat—withdrawing frequently for vigorous shaking —for a period of about ½ hour. Allow to stand for 10 minutes and titrate the acid in the water as well as in the benzene layer with standard alkali using phenolphthalein indicator. (Add about 25 ml. of water to the benzene solutions before titration and shake vigorously). Find out C_W and C_B (in terms of moles per liter) for the four bottles. If the room temperature is higher than 25°C, set the thermostat a few degrees higher than the room temperature and carry out the experiment as above.

Results and Calculations: Temperature = ...°C

Bottle No.	Vol. of acid in water layer taken, ml.	Vol. of alkali required for acid, ml.	Concn. of acid in water, C_W (moles/lit.)	Vol. of acid in benzene layer taken, ml.	Vol. of alkali required for acid ml.	Concn. of acid in benzene, C_B (moles/lit.)	$\frac{C_B}{C_W}$

Plot C_B/C_W vs. C_W. Find out the slope and intercept. Intercept = K_1=.....
Slope = $2K_1^2K_2^2$ =...; ∴ K_2 = ... (at ...°C)

Suggestions for further work:

1. Benzoic acid, chlorobenzoic acid, or phthalic acid may be tried. Toluene, chloroform or carbon tetrachloride may be used as solvents instead of benzene. Note that the value of K_2 for salicylic acid is smaller due to intra-molcular hydrogen bond formation.

2. In a particular solvent system for one acid, the dimerisation constant can be determined at different temperature. Hence, the enthalpy change and other thermodynamic parameters can be estimated.

6.3. (i) To determine the partition (or distribution) coefficient of iodine between water and carbon tetrachloride, and (ii) to determine the equilibrium constant for tri-iodide formation:

$$I_2 + I^- \rightleftharpoons I_3^-$$

Theory:

The simple distribution (or partition) law is obeyed quite well for the distribution of iodine between carbon tetrachloride and water. At constant temperature, the partition (or distribution) coefficient is given by

$$K_D = \frac{C_{organic}}{C_{aqueous}}$$

when $C_{organic}$ and $C_{aqueous}$ represent the concentrations of iodine in the carbon tetrachloride and water layer respectively. This law does not hold good in the distribution of iodine between the organic layer and an aqueous solution of potassium iodide because in the aqueous layer the complex KI_3 (i.e. the ion I_3^-) is formed ($I_2 + KI = KI_3$). This failure of the distribution law is only apparent and it is expected to hold good provided the concentration of "free" iodine in the aqueous layer is taken into consideration.

If iodine is distributed between CCl_4 and aqueous KI solution, the total concentration of iodine in the aqueous layer is given by $C_{I_2}(free) + C_{I_3^-}$, which can be determined by titration with standard sodium thiosulfate solution. Now the concentration of iodine in the organic layer can also be determined by titration with $Na_2S_2O_3$; therefore the concentration of "free' iodine in the aqueous layer can be determined by dividing the concentration in organic layer by partition coefficient. It is then possible to calculate the value of $C_{I_3^-}$ and C_{I^-} if the initial concentration of KI is known. If $C_{I_8^-}$, C_{I_2} and C_{I^-} are all known, the required equilibrium constant can be calculated.

$$K = \frac{C_{I_3^-}}{C_{I_2} \times C_{I^-}} \quad \ldots \ 6.6$$

Let the concentration of iodine in organic layer $= C_1$ moles/lit., concentration of iodine in aqueous KI layer $= C_2$ moles/lit., and K_D = Partition coefficient of iodine between organic and water layer.

$\therefore$ Concentration of "free" iodine in aqueous layer $= \frac{C_1}{K_D}$ moles/lit.

$\therefore$ Concentration of I_3^- = Total iodine concentration in aqueous layer − "free" iodine concentration $= \left(C_2 - \frac{C_1}{K_D} \right)$ moles/lit.

Let initial concentration of $I^- = C_3$ moles/lit. Since 1 mole of I_3^- is formed out of 1 mole of I^- therefore, concentration of free KI at

$$\text{equilibrium} = C_3 - \left(C_2 - \frac{C_1}{K_D}\right) \text{moles/lit.}$$

$$K = \frac{\left(C_2 - \frac{C_1}{K_D}\right)}{\frac{C_1}{K_D} \times \left\{C_3 - \left(C_2 - \frac{C_1}{K_D}\right)\right\}} \text{mole}^{-1} \text{ lit.} \quad \ldots \quad 6.7$$

Materials:

1. $N/10$ $Na_2S_2O_3$ solution; 2. $N/100$ $Na_2S_2O_3$ solution (prepared from $N/10$ solution by exact dilution); 3. Saturated solution of iodine in carbon tetrachloride; 4. $N/10$ KI (aqueous) solution; 5. Starch solution; 6. Approx. 10% KI solution in water.

Procedure:

Part I: Determination of the distribution coefficient for iodine between CCl_4 and water

Take 3 stoppered bottles of approx. 500 ml. capacity. Number the bottles and make up the following mixtures from them.

Bottle No.	Vol. of saturated I_2 solution in CCl_4 (ml.)	Vol. of CCl_4 (ml.)	Vol. of water (ml.)
1	20	0	200
2	15	5	200
3	10	10	200

Stopper the bottles carefully and shake them vigorously. Then fasten them in a thermostat, so that they are immersed up to their neck in the thermostat water. Allow them to remain in the thermostat for 1 to 2 hours. At frequent intervals, remove the bottles one at a time, shake them vigorously for 1 or 2 minutes and then return them to the thermostat. Before removing the samples for titration, let each of the bottles remain in the thermostat for at least 20 minutes after its last shaking in order to allow the liquid layers to separate completely.

Pipette a 50 ml. sample from the aqueous layer into a glass-stoppered 250 ml. conical flask containing 10 ml. of $N/10$ KI solution and 1 ml. of starch solution. (It is important to avoid contamination of the aqueous layer by the CCl_4 layer, since I_2 is so much more concentrated in the non-aqueous layer that even a drop of the CCl_4 solution would produce an appreciable error in the estimation of the aqueous phase). Titrate against $N/100$ $Na_2S_2O_3$ solution.

Similarly pipette 5 ml. of the CCl_4 solution into a conical flask containing 10 ml. of $N/10$ KI solution and 1 ml. of starch solution. Titrate with $N/10$ $Na_2S_2O_3$ solution.

Repeat the process for all the bottles.

Results and Calculationss

Temperature = ...

Bottle No.	Volume of $\frac{N}{100}$ $S_2O_3^=$ for 50ml. aqueous layer (ml.)	Concentration of I_2 in Aqueous layer, (Normality) $C_{aqueous}$	Volume of $\frac{N}{10}$ $S_2O_3^=$ for 5ml. of organic layer (ml.)	Concentration of I_2 in organic layer, (Normality) $C_{organic}$	$K_D = \frac{C_{org.}}{C_{aq.}}$
1					
2					
3					

Mean Partition coefficient, K_D = ...

Part II: Determination of the equilibrium constant for $KI+I_2 \rightleftharpoons KI_3$ (*i.e.* $I^- + I_2 \rightleftharpoons I_3^-$)

Carry out similar experiments with $\frac{M}{10}$, $\frac{M}{15}$ and $\frac{M}{20}$ KI solutions in place of water. The different bottles will have the following compositions:

Bottle No.	Volume of Saturated Solution of I_2 in CCl_4 (ml.)	Volume of CCl_4 (ml.)	Volume of KI Solution (ml.)	
4	20	0	200 ml. $\frac{M}{10}$	
5	15	5	200 ml. $\frac{M}{15}$	(or, 133.3 ml. N/10 KI soln. +66.7 ml. water)
6	10	10	20 ml. $\frac{M}{20}$	(or 100 ml. M/10 KI Solution + 100 ml. water)

The rest of the procedure is similar to as in Part I. Use $\frac{N}{10}$ $Na_2S_2O_3$ for titrating the aqueous phase and $\frac{N}{100}$ $Na_2S_2O_3$ for the organic phase. Let X and Y be the titre for the organic and the aqueous phase respectively.

Results and Calculations :

Let the strength of $Na_2S_2O_3$ $= f' \frac{N}{10}$

$$2\ Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$$

$\therefore$ 1 mole $S_2O_3^=$ = $\frac{1}{2}$ mole of Iodine

$\therefore$ 1000 c.c. (N) $S_2O_3^=$ = 0.5 mole Iodine

$\therefore$ 1 cc. (N) $S_2O_3^=$ = 0.5×10^{-3} mole Iodine

$\therefore$ 1 cc. $\frac{N}{10} S_2O_3^=$ = 0.5×10^{-4} mole Iodine

$\therefore$ Ycc $f' \frac{N}{10} S_2O_3^=$ = $f' \times Y \times 0.5 \times 10^{-4}$ mole Iodine

Similarly, X cc. $\frac{N}{100}S_2O_3^{=} = f' \times X \times 0.5 \times 10^{-5}$ mole Iodine

Let A ml. of organic layer be pipetted for titration.

A ml. contains $f' \times X \times 0.5 \times 10^{-5}$ moles of I_2

1000 ml..... $\frac{f' \times X \times 0.5 \times 10^{-5}}{A} \times 1000 = C_1$

[Value of A is 5 in the present case]

Similarly, say, B ml. of aqueous layer was pipetted for titration.

$\therefore$ B ml. contains $f' \times Y \times 0.5 \times 10^{-4}$ moles of iodine

1000 ml. ... ... $\frac{f' \times Y \times 0.5}{B} \times 10^{-4} \times 1000$ moles/lit.

$$= \frac{f' \times Y \times 0.5 \times 10^{-1}}{B} \text{ moles/lit.} = C_2$$

[B is 50 in the present case]

Bottle No.	Volume of $\frac{N}{10}S_2O_3^{=}$ for 50 ml. aqueous layer (ml.)	Concentration of Iodine (total) in the aqueous layer, (moles/lit). (C_2)	Volume of $\frac{N}{100}S_2O_3^{=}$ for 5ml. organic layer (ml.)	Concentration of Iodine in organic layer, (mole/lit.) (C_1)	Concentration of free iodine aqueous layer (C_1/K_D)

Bottle No.	Concentration of KI_3 formed ($C_2 - C_1/K_D$) (moles/lit.)	Concentration of KI initially (C_2) (moles/lit.)	Concentration of KI in equilibrium $C_2-(C_2-C_1/K_D)$ (moles/lit.)	Equilibrium constant, K (mol^{-1} lit.) (use eqn. 6.7)
1				
2				
3				

Mean Equilibrium constant.=.....

Suggestions for further work:

(1) Equilibrium Constants for the following equilibria may be similarly determined:—

1. $Br^- + Br_2 \rightleftharpoons Br_3^-$
2. $I^- + Br_2 \rightleftharpoons IBr_2^-$, *etc.*

(2) Benzene, chloroform, etc. may be used for carbon tetrachloride in the above experiments. (CS_2 is unsuitable)

6·4 To determine the formula of the Cuprammonium ion.

Theory:

When an excess of ammonia is added to a solution of a cupric salt a deep blue colour results due to the formation of the cuprammonium ion according to the following equilibrium—

$$Cu^{2+} + xNH_3 \rightleftharpoons Cu(NH_3)_x^{++}$$

The aim of the present experiment is to determine the value of x. While a part of the ammonia has been consumed for complex formation, the balance will remain as "free" ammonia. The value of x can be calculated provided we know the concentration of "complexed" ammonia as well as that of "free" ammonia in the system.

However, we can not determine the concentration of "free" and "complexed" ammonia in the system by simple titration, because as the ammonia is removed during titration, the above equilibrium is shifted from right to left. Such difficulty can be overcome if an immiscible solvent is used in which one of the species (free ammonia in the present case) is soluble, but not the others, for it is then possible to determine the concentration of this species in the solvent without disturbing the equilibrium between complexed and uncomplexed entities with the help of its distribution coefficient between the two immiscible liquids (*cf.* expt. No. 6·3).

In the present experiment an aqueous solution of known concentration of copper sulfate which has been treated with ammonia is mixed with chloroform, the immiscible solvent. The total ammonia, complexed and uncomplexed, is determined by titration of the aqueous solution. The concentration of ammonia in the chloroform layer is also determined. Therefore, from a knowledge of the distribution coefficient, K_D of ammonia between water and chloroform, the concentration of free ammonia in the aqueous layer can be found out. The distribution coefficient is related to the concentrations of ammonia in the water layer and in the chloroform layer by—

$$K_D = \frac{[NH_3]_{aqueous}}{[NH_3]_{chloroform}}$$

The concentration of complexed ammonia $Cu(NH_3)_x^{++}$ is then obtained from the difference between the total ammonia [both NH_3 and $Cu(NH_3)_x^{++}$] and the "free" ammonia concentrations. From a knowledge of the initial cupric ion concentration, the value of x can be determined.

Materials:

1. $\frac{M}{2}$ copper sulphate; 2. $1.2N$ NH_4OH; 3. $\frac{N}{2}$ HCl;
4. Methyl orange indicator; 5. Chloroform.

Procedure:

Part I. Determination of the distribution coefficient of ammonia between water and chloroform.

By accurate dilution of the *N*/2 HCl, prepare a solution of *N*/20 HCl (one litre).

Mix in a stoppered bottle 50 ml. of the ammonia solution and an equal volume of the chloroform, shake well (about ten minutes) and allow the layers to separate (five minutes). Pipette out 10 ml. from the upper layer (aqueous) and deliver the sample into a conical flask containing 100 ml. water and titrate with *N*/2 HCl, using methyl orange as indicator. Insert a 25 ml. pipette into the lower layer (chloroform) carefully so that inclusion of any upper aqueous layer is avoided; deliver the sample into a stoppered bottle (or flask) containing about 100 ml. water and titrate with *N*/20 HCl until the indicator colour change is permanent on shaking.

After the titration is over, the solution in the titration bottle contains water and ammonia-free chloroform. Remove water (using a separating funnel) and use this chloroform for another determination of the distribution coefficient at a lower concentration of ammonia (for example, this time mix 25 ml. chloroform, 10 ml. water and 15 ml. ammonia solution). In this way, after the second titration, 25 ml. of chloroform again may be transferred to the partition bottle without the addition of fresh chloroform and a number of measurements can be made at varying concentrations of ammonia with a limited quantity of solvent. The readings should be taken at least three concentrations of ammonia.

Part II. Determination of the formula of the cuprammonium ion.

Take 40 ml. of the 1.2*N* ammonia solution in a graduated 100 ml. cylinder and add by pipette 5 ml. of the *M*/2 copper sulfate solution. Stir with a glass rod until all the precipitate dissolves and add ammonia solution until the volume is 50 ml. (Note that the resulting dark blue solution is now *M*/20 in cupric ion).

Pour the solution into a separating funnel together with 50 ml. of chloroform, shake the liquids together (about ten minutes) and allow to separate (five minutes). 10 ml. of the upper blue layer is taken out and delivered into a conical flask containing 100 ml. distilled water. Titrate this solution with *N*/2 HCl using methyl orrange indicator. The blue colour which initially masks the colour of the methyl orange indicator will fade before the end point is reached.

The whole of the lower chloroform layer in the separating funnel is run into a stoppered bottle containing 100 ml. of water. (Great care must be taken to observe that none of the blue aqueous layer enters the bottle. Also a cork should be fitted on the stem of the funnel to rest on the top of the unstoppered bottle so as to reduce the loss of

ammonia by evaporation). The chloroform layer is now titrated with $N/20$ HCl using the same indicator as before. After the titration is over, the contents of the titration bottle are poured into the separating funnel, which had previously been emptied and washed. This chloroform, now free from ammonia, can be separated from water and may be used in the next experiment.

The procedure is now repeated with a lower concentration of ammonia. Place 35 ml. of ammonia solution and 5 ml. of copper sulphate solution in the 100 ml. graduated cylinder and make up to 50 ml. with distilled water. Chloroform is run in from the separating funnel (adding, if necessary a further small quantity of fresh chloroform) to bring the total volume of the liquids to 100 ml. Wash the separating funnel and make it empty. Now pour the contents of the cylinder into the separating funnel and shake for ten minutes as before. The titrations of 10 ml. portions of the upper layer (water) and the whole of the lower layer (chloroform) are repeated, as in the first determination.

A third set of measurements is then made, using the proportions 25 ml. ammonia solution, 5 ml. copper sulphate made up to a total of 50 ml. with water.

Results and calculations:

In each of the 3 determinations the 1/2 molar copper sulphate solution has been diluted ten times, so that the concentration of cupric ion required in the calculation of x is 1/20 gm. ion/lit.

Table I

Partition coefficient of NH_3 between water and chloroform

Expt.	Vol. of $N/2$ HCl needed for 10 ml. aq. layer	Vol. of $N/20$ HCl for 25 ml. chloroform layer	Concentration of NH_3 in aq. layer (C_1) in Normality	Concentration of NH_3 in chloroform layer (C_2) in Normality	$K_D = \frac{C_1}{C_2}$	Mean K_D
I						
II						
III						
IV						

Table II

The value of x

Expt.	Vol. of $N/2$ HCl needed for 10 ml. aq. layer (V_a ml.)	Vol. of $N/20$ HCl needed for 50ml. chloroform layer (V_o ml.)	Concentration of NH_3 (combined + free) $= V_a/20$ mole/lit. (X)	Concentration of NH_3 in chloroform layer $= V_o/1000$ mole/lit.	Concentration of free NH_3 in aqueous layer $= (K_D V_o/1000)$ mole/lit. (Y)
I					
II					
III					

Experiment	Concentration of combined NH_3 (mole/lit.) $(X-Y)$	Concentration Cu^{2+} (g. ion/lit.)	$x = \frac{[\text{Combined } NH_3]}{Cu^{2+}} = 20 \times (X-Y)$.
I		1/20	
II		1/20	
III		1/20	

$\therefore$ $x =$ ..... (*mean value*)

EXPERIMENT NO. 7

SURFACE CHEMISTRY AND COLLOIDS

7.1 Studies on adsorption of acetic acid on charcoal.

Theory:

When a solid (i.e. charcoal) with a large surface area per unit weight is added to a solution (*say*, of acetic acid or oxalic acid), it happens that a fraction of the solute is taken out of the solution on to the surface of the solid. This is called adsorption. In a similar fashion, gases can be adsorbed on to a solid surface.

The Freundlich adsorption isotherm is usually applied to adsorption of a substance from solution—

$$\left(\frac{X}{m}\right) = kC_e^n$$

$$\text{or} \quad \log\left(\frac{X}{m}\right) = \text{constant} + n \log C_e \qquad \ldots (7.1)$$

where X is the number of moles of acetic acid adsorbed by m gms. of charcoal and C_e is the equilibrium concentration of the acid, k and n are constants. According to equation (7.1), $\log\left(\frac{X}{m}\right)$ is linear with $\log C_e$

Materials:

1. Powdered animal charcoal; 2. $\frac{N}{2}$ acetic acid; 3. $\frac{N}{10}$ NaOH;
4. Phenolphthalein indicator.

Procedure:

Into each of the six stoppered concial flasks (or bottles) labelled 1 to 6, place 2 gms. of well powdered animal charcoal (weighed out on paper to 0.01 gm.). Now into the six flasks containing charcoal, add the following:—

Flask No.	$\frac{N}{2}$ Acetic acid	Water
1	50 ml.	0 ml.
2	40 ml.	10 ml.
3	30 ml.	20 ml.
4	20 ml.	30 ml.
5	15 ml.	35 ml.
6	10 ml.	40 ml.

Shake each sample from time to time during a period of, say, 20 minutes. Allow to stand (5 minutes) and filter each solution through a small filter paper and collect the filtrate in properly labelled.

flasks. (For filtration small filter paper should be used so that error due to any adsorption of the acid by the filter paper is minimised. Also the first 5 ml. of the filtrate should be rejected).

Take 10 ml. samples of each filtrate and titrate with $\frac{N}{10}$ caustic soda using phenolphthalein as indicator.

Also titrate 10 ml. of stock $\left(\frac{N}{2}\right)$ acetic acid with the same alkali.

Results and Calculations

10 ml. of stock acetic acid solution $= x$ ml. of $\frac{N}{10}$ NaOH.

Flask	Amount of charcoal taken, (m)gm.	Initial concn. of acid before adsorption, C (in ml. NaOH)	Equilibrium concn. after adsorption C_e (in ml. NaOH)	Amount of acid adsorbed, $C - C_e = X$ (in ml. NaOH)	$\frac{X}{m}$	$\log\frac{X}{m}$	$\log C_e$
1		x					
2		$\frac{4}{5}x$					
3		$\frac{3}{5}x$					
4		$\frac{2}{5}x$					
5		$\frac{1}{10}x$					
6		$\frac{1}{5}x$					

Plot $\log\frac{X}{m}$ vs. $\log C_e$; check if Freundlich isotherm is obeyed.

Suggestions for further work:

1. The effect of temperature on adsorption can be obtained by performing the adsorption experiment in a thermostat maintained at a higher temperature.

2. The adsorption isotherm can also be tested with dyes adsorbed on charcoal, the initial and the final concentrations of dye in solution being obtained by measuring the optical density at the $\lambda max.$ of the dye with the help of a colorimeter (or spectrophotometer) [*vide* expt. No. 9.1]. The difference between the two O.D. readings (initial —final) gives a measure of the quantity of dye adsorbed by the charcoal. Methyl violet and malachite green may be used as suitable dyes.

(7.2) Determination of the flocculation value (also called coagulation value or precipitation value) for arsenious sulphide (As_2S_3) sol. (negative) using electrolytes having cations of different valence.

(a) To test the validity of the Schulze-Hardy rule.

(b) To test Freundlich adsorption isotherm.

Theory:

The flocculation value of a suspensoid sol is the minimum concentration (in *millimoles per liter*) necessary to precipitate the sol completely after a stated interval of time. The values obtained for the negative As_2S_3 sol, according to Schulze-Hardy rule, should decrease in a regular order with salts having mono-, di-, and tri-valent cations (that is, the coagulating power increases with increasing valence of the ion).

It is generally supposed that ions of opposite charge get adsorbed on colloidal particles to bring down its zeta potential below a critical value. Since zeta potential is responsible for the stability of colloids, such lowering of the zeta potential makes the colloid unstable and ultimately causes precipitation. Therefore electrically equivalent amounts of ions of different valences should be adsorbed; that is, the quantities of uni-, bi-, and ter-valent ions adsorbed should be in the ratio 3.0 to 1.5 to 1.0. Since adsorption often satisfies Freundlich's equation, $X=k.C^n$[*vide* expt No. 7.1], it is clear that these numbers should be proportional to X; C, of course, represents the flocculation values. Therefore, a plot of log (these numbers) vs. log C should be a straight line.

Materials:

(1) CO_2 generator (or H_2 generator); (2) H_2S generator; (3) 0.2 *M* NaCl (11.7 g./lit); (4) 0.005*M* $BaCl_2$ (1.22 g. $BaCl_2.2H_2O$ per liter); (5) 0.0005 *M* Potash alum (0.237 gm. $KAl(SO_4)_2$, 12 H_2O per lit) (6) Arsenious oxide, As_2O_3.

Procedure:

Boil about 2.5 gm of As_2O_3 for 10 minutes with 100 ml. of distilled water, filter the hot solution into a l-litre Erlenmeyer flask and dilute the filtrate to 500 ml. Pass a stream of H_2S (previously washed by bubbling through water) into the solution until the opalescent liquid becomes turbid. Remove the excess of H_2S by bubbling a stream of CO_2 (or H_2) through tne sol. Filter the sol. Collect the bright yellow filtrate (As_2S_3 sol) in a corked dry conical flask.

Take 10 test tubes (clean and dry). Number them 1 to 10 and arrange in a test tube rack. From two burettes containing distilled

water, and the stock solution of NaCl, run into the test tubes the following volumes of water and NaCl solution.

Test tube No.	Ml. 0.2 M NaCl	Ml. of water	Final observation*
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	
10	10	0	

*Note in this column whether a clear supernatant liquid is obtained after the experiment.

Add to each test tube 10 ml. of As_2S_3 Sol. Mix the electrolyte and the sol in each case in exactly the same manner by inverting the stoppered tubes twice, without vigorus shaking. After 30 minutes standing (for more accurate work 2 hours) each tube is once more inverted. After another 30 minutes the tubes are examined against a dark background. The lowest concentration at which clear solution appears above the settling precipitate may be taken as the flocculation value (*C*). Record your observation in the last column of the above Table.

Follow the same procedure for the other two electrolytes and find their flocculation values. Compare the values with those given in Appendix, Table XX.

[Calculate the concentration of NaCl in each tube as follows:—1 ml. of stock NaCl solution contains 0.2 millimole and this amount is then diluted to 20 ml. Therefore, 1000 ml. of such solution contains $2/20 \times 1000 = 10$ millimoles. Similarly the concentration of NaCl in other test tubes will be 20, 30, 40, 50, 60, 70, 80, 90, 100 millimoles per liter].

Dilute the original sol 2 times. Repeat the procedure and find out the precipitation values for a sol having half of the previous concentration.

Results and calculations:

Room temperature = ...

Experiment (1)				Experiment (2)*			
Electrolyte	C	log C	log X	Electrolyte	C	log C	log X
NaCl			log 3	NaCl			log 3
$BaCl_2$			log 1.5	$BaCl_2$			log 1.5
Alum (Al^{3+})			log 1	Alum (Al^{3+})			log 1

*The Sol concentrations is $\frac{1}{2}$ of that in expt. (1)

Show that values of C in expt (1) and (2) agree closely.

Plot log X vs log C. (The plot should be linear, as predicted by Freundlich).

Suggestions for further work:

Similar experiments can be done with ferric hydroxide sol (positive) by using chloride, sulfate, phosphate and ferrocyanide ions.

Preparation of ferric hydroxide sol: To vigorously boiling distilled water, is added drop by drop, a freshly prepared saturated solution of ferric chloride. As each drop falls in the boiling water, the $FeCl_3$ suffers hydrolysis forming a deep red sol. The sol obtained is rapidly dialysed in a parchment bag against warm water to free it from the HCl and undecomposed $FeCl_3$. For best results 12 ml. of 32% $FeCl_3$ is poured into 750 ml. of boiling water.