# PRACTICAL PHYSICAL CHEMISTRY

S. R. PALIT

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FOR B.Sc. AND ENGINEERING STUDENTS

*By*

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# PREFACE

In the present edition the book has been thoroughly revised and recast. The authors would welcome suggestion for improvement and would feel grateful to those who care to point out mistakes.

Thanks are due to Prof. B. Nayak, Dr. M. Biswas and Dr. S. K. Palit, all of I.I.T. Kharagpur for pointing out mistakes and making suggestions, and to Sri Sushanta Sengupta, M. Sc. for help in proof-reading. The authors appreciate the benign act of the publishers in keeping the low price of the book unchanged.

*June*, 1974.

S. R. PALIT
S. K. DE

## *FIRST EDITION*

This book has been written with a view to meet the need for a suitable guide-book on Practical Physical Chemistry for B.Sc., M.Sc., and Chemical Engineering students in India and neighbouring countries. The subject matter has been so presented that the students can perform the experiments on their own with little help from the instructors. All experiments have been arranged under the headings: Theory, Materials, Procedure, Results and Calculations. At the end of many experiments, suggestions for further work have been included. The appendix section at the end of the book consists of useful tables and conversion factors. The experiments have been arranged systematically, more or less subjectwise, and cover practically the whole domain of experimental physical chemistry. Some sophisticated experiments such as D.T.A., B.E.T. adsorption, and polarography have also been included. Some mistakes must have passed unnoticed and the authors would be grateful if these are brought to their notice. Suggestions for the improvement of the book will be thankfully received.

The authors wish to place on record their appreciation of all help they have received during the preparation of this book. In particular, they would like to thank Dr. Swapan K. Bose of the Calcutta University, Dr. S. K. Chakraborty of the North Bengal University, Dr. N. D. Ganguly and (Mrs.) Prajna P. De both of the I.I.T., Kharagpur, Dr. S. C. Rakhsit of the Burdwan University and Prof. J. N. Chatterjee of the Patna University. Thanks are also due to Dr. Dilip K. Sarkar of Presidency College, Calcutta and Prof. D. Sen, Head of the Chemistry Department, I.I.T., Kharagpur for their kind help.

*June* 5, 1971.

S.R.P.
S.K.D.

**Basic constants and conversion factors.**

1 Kilometer (Km) = 1,000 meters(m) = 0.621 mile
1 Meter = 100 centimeters(cm.) = 39.34 inches (in).
1 Centimeter = 10 millimeters(mm.) = 0.394 in.
1 Kilogram(kg.) = 1000 grams (g) = 2.20 pounds (lb.)
1 Gram = 1000 milligrams (mg.) = 0.0353 ounce (oz)
1 Litre (l) = 1000 millilitres (ml.)
1 Millilitres = 1.000028 Cubic Centimeter (c.c.).
1 atomic mass unit (a.m.u.) = $1.66 \times 10^{-24}$g.
1 angstrom (Å) = $1 \times 10^{-8}$cm.
1 Faraday = 96,500 coulombs
1 Electron Volt (ev.) = $1.60 \times 10^{-12}$ erg.
= 23.07 Kilocalories (K. cal.)/mole
1 erg = $2.39 \times 10^{-11}$ KCal.
1 K cal = 1000 calories (cal.)
1 Joule = $10^7$ ergs.
Velocity of light (c) = $2.9979 \times 10^{10}$ cm. $Sec^{-1}$
Avogadro number (N) = $6.0225 \times 10^{23}$
Gas constant (R) = 0.08205 liter. atm. $deg^{-1}$ $mole^{-1}$
= 8.31432 Joule $deg^{-1}mole^{-1}$
= 1.98717 cal. $deg^{-1}mole^{-1}$
Boltzmann constant ($k$) = $1.38057 \times 10^{-16}$ erg. $deg^{-1}$.
Planck's constant ($h$) = $6.6252 \times 10^{-27}$ erg. sec.
Electronic charge ($e$) = $1.60206 \times 10^{-19}$ coulomb.

"If a man will begin with certainties, he shall end in doubts; but if he will be content to begin with doubts, he shall end in certainties."

—FRANCIS BACON

# CONTENTS

## 6. *Partition (or Distribution) Coefficient*



## 7. *Surface Chemistry and Colloids*



## 8. *Thermochemistry*



## 9. *Colorimetry, Spectrophotometry, Refraction and Optical Rotation*



## 10. *Reaction Kinetics*

## 11. *Conductometry*



## 12, *Potentiometry* (*E.M.F. Studies*)

# INTRODUCTION

## 1. General Instructions to the students:

**Preparing for the experiment:**

In order to avoid unnecessary repetitions of experiments and loss of time, proper preparation before starting the experiment is essential.

(*i*) Read the theory and experimental procedure of the assigned experiment.

(*ii*) Make a rough estimate of the quantity of the chemicals, solutions, etc. to be required for the experiment.

(*iii*) Make a rough estimate of the number and type of flasks, pipettes, beakers, burettes and other apparatus.

(*iv*) Plan the programming of your experiment in such a way as to be completed within the alotted time.

(*v*) Plan the organisation of the data in your note book.

**Working in the Laboratory:**

Sense of discipline and cooperation among all members of the class are essential for smooth running of the laboratory.

(*i*) No chemicals or solutions should be taken from their place of storage to the working bench. Once the simple layout of the laboratory becomes known, the obtaining of chemicals and solutions seems to be an easy process.

(*ii*) Analytical balances are very expensive and delicate instruments. If you are in any doubt about the use of any type of balance, you should consult a demonstrator. Keep balances in a clean and tidy state after use.

(*iii*) While using other instruments like Beckmann thermometer, polarimeter, refractometer, spectrophotometer, potentiometer, etc., read instructions carefully, and if necessary consult a demonstrator.

(*iv*) Be sure that all glass apparatus, particularly volumetric apparatus is perfectly clean. Usually, a detergent solution is sufficient for cleaning, but for very dirty glassware use warm chromic acid solution prepared as follows:

**Preparation of chromic acid solution for cleaning:**

Make a saturated solution of potassium dichromate in warm water (about 500 gm. per liter) in a beaker and slowly add concentrated sulfuric acid until the solution becomes dark red and crystals of chromium trioxide begin to form. Stock the solution in a glass bottle.

Fill up the glassware to be cleaned with the chromic acid solution prepared as above and leave for a few hours, preferably under warm (not hot) condition. Next, wash the glassware thoroughly with tap

water and then with distilled water. If necessary, dry in a current of dust-free air after rinsing with pure acetone.

(*v*) Work in a pre-planned way. Repeat one set of the experiments in order to get an estimate of your precision.

(*vi*) If a pair of students is working, they should divide the work so that time can be saved.

(*vii*) Measure each quantity to the number of significant figures necessary to obtain the desired precision in the final results. Do not spend time and effort on unnecessary precision.

If the zero or zeros are just to the right of the decimal point, they merely serve to locate the decimal point. For example, in 0.0045 gm, the two zeros following the decimal point are not significant figures. However, in 0.450, the zero following five is a significant figure. In 450, the zero may or may not be significant. But if it were written as $4.50 \times 10^2$ the zero is significant.

**Reporting the results:**

Two laboratory note books are useful: one is laboratory 'diary' and the other is the final report book which must have stiff covers. Graph papers may be pasted preferably on the left side wherever necessary. As the experiment proceeds, all measurements and observations should be noted down on the diary. Preliminary calculations and plots done during the progress of the experiment should also be made on the diary. All the results and informations from the diary may finally be arranged in a logical sequence and discussed in the final report book. Write the final report as soon as possible after doing the experiment. It is easy to write the report while the procedure and results are still fresh in mind. Write the experimental procedure in past tense and passive mood. *Never note down the results on any loose sheet of paper.*

**The layout of the report should be as follows:**

---

*Date*.....
*Partner's name*.....
*and Roll No*.....

*Expt. No.*

*Title of the expt:*

(*i*) *Principle or theory:*

(*ii*) *Experimental procedure:* (Write briefly)

(*iii*) *Results and calculations:* (Arrange in tabular forms)

(*iv*) *Discussion and conclusions:* (Your experimental technique and results should be critically assessed. Precision of the results should be estimated. The results can be compared with those in the literature or those of other members of your Class.)

---

**Laboratory Safety:**

(*i*) Never work alone in the laboratory.

(*ii*) Never take any food while inside the laboratory.

(*iii*) Filling a pipette is an operation where caution is advisable. Acids, alkalis and many organic liquids are toxic. *Pipette bulb fillers and* or *appropriate traps should be used in such cases.*

(*iv*) All laboratories are provided with a number of basic safety devices. These include fire extinguishers, sand buckets and first aid equipment. All students should become familiar with the location of such things.

(*v*) Keep all bottles of flammable, poisonous and corrosive materials closed. *Use these materials in the fume hood and with proper traps.*

(*vi*) Use eye-shields or eye glasses whenever your experiment demands them.

**2. Treatment of Experimental Data:**

**Precision and accuracy:**

The random variations in conditions change the measured result by an unknowable, uncontrolled amount, and introduce an inherent uncertainty or random error whose magnitude depends on the method, the apparatus and the skill of the experimenter.

Because every measurement is associated with an unknown and unknowable random error the question naturally arises: What is the reliability of the measurement?

There are two expressions of reliability, *accuracy* and *precision.* Accuracy is the agreement of the experimental measurement with the 'true' or accepted value of the quantity. Precision is the degree of closeness among the experimental values, *i.e.* the reproducibility of a given technique. The less the "scatter" among the experimental values, the more is the precision. However, precision does not necessarily imply accuracy; for example, concordant results may not agree with the true value. On the other hand, an accurate measurement is always precise. In many cases of interest in physical chemistry the 'true' value is not known. Consequently, precision rather than accuracy is to be taken as an estimate of reliability.

**Calculation of precision indices:**

The usual procedure is to calculate the deviation (See next paragraph) of the particular measurement from the arithmetic mean and then to utilise this deviation in calculating the precision of interest in physical chemistry i.e., the average deviation and the standard deviation.

The average deviation, A.D., is the sum, *without regard to sign,* of the deviations of the individual data from the arithmetic mean (A.M.) divided by $n$, the number of experimental runs:

$$\therefore \quad \text{A.D.} = \frac{1}{n} \Sigma (\delta_i)$$

where $\delta_i = |x_i - \text{A.M}|$., $x_i$ being any particular data in a series of experimental values and $|\ldots|$ indicates the absolute value.

The standard deviation, $\sigma$, is the square root of the sum of the squares of the individual deviation of each datum, divided by the square root of $(n-1)$ where $n$ is the total number of data:

$$\sigma = \sqrt{\frac{\Sigma \delta_i^2}{n-1}}$$

The standard deviation is 1.25 times the average deviation and so it is more probable that the results will be within the range A.M. $\pm\sigma$ than within the range A.M. $\pm$A.D.

If the results of a few runs agree exactly with each other, the precision index should not be taken as zero, since this indicates no experimental error. Perhaps the apparatus was not sensitive enough to detect fluctuations. The student should however note that no statistical treatment can take care of a systematic error (for example, using a faulty balance or faulty weight box) and such error should be carefully guarded against.

The preciseness of a measurement can be expressed in terms of *relative precision*, which may be defined as the relative uncertainty of the measured magnitude. If a temperature is recorded as $25.26 \pm 0.01°$, the relative precision will be $\frac{0.01°}{25.26°} \times 100 = 0.033$ per cent.

**Treatment of doubtful values:**

In a set of data there may be one or two measurements which do not conform to the pattern indicated by the rest. If there is good experimental reason for the deviations, then these values may be rejected; even if no valid reason can be attributed, but if the set is large, many chemists would dismiss the 'discrepencies' as 'rogues'. Still the statistical method is helpful in sorting out the 'rogues'. One can reject a value if it differs from the mean by more than four times the average deviation.

**Confidence Limits :**

Precision is sometimes indicated by *confidence limits* instead of precision indices. A confidence limit is a range, on both sides of the arithmetic mean, within which one may have the specified confidence that the "true value" will be found. The "true value" is the arithmetic mean of an infinite number of repeated measurements.

A 90 per cent confidence means that there is a 90 per cent probability that the "true value" is within the range A.M. $\pm$ confidence limit.

It also implies that there is a 5 per cent chance that the "true value" is above the range and another 5 per cent chance that it is below the

range. In the absence of a constant error, the confidence limits are found by multiplying the standard deviation of the arithmetic mean by a factor $t$ which is selected from tables on the basis of the desired confidence and the number of runs. Some $t$ values are given in the following table.

**Table of t values**

| Desired confidence *per cent* | Two runs | Three runs | Four runs | Five runs |
|---|---|---|---|---|
| 99 | 63 | 9.9 | 5.8 | 4.6 |
| 95 | 13 | 4.3 | 3.2 | 2.8 |
| 90 | 6.3 | 2.9 | 2.4 | 2.1 |

**Drawing graphs from experimental data:**

Experimental data are plotted on graph paper, because the shape of the graph can quickly show trends of the data particularly minimum and maximum.

Put a caption on each graph. Use the ordinate for the dependent variable. The two axes must be labelled fully, with the quantity plotted and the scale values and units shown. Select a scale that places all the data on the graph, rather than a part of the data.

Draw circles around the individual points if there are uncertainties in the values of both ordinate and abscissa. Draw vertical lines *if* the uncertainty is only in the ordinate. The precision of the data (*i.e.*, the average deviation or the standard deviation of the mean if it is known) is indicated by the radius of the circle or the half height of the vertical line. If the precision is not known, indicate the value by a data point, such as + or ×.

When more than one curve is plotted on a single graph sheet for purposes of comparison, label each curve and use different shapes of the data points (for example, *open circles*, *filled circles*, *squares*, *triangles*, *inverted triangles*, × *signs*, + *signs* and *dagger signs*) for different curves. The size of each symbol, as indicated earlier, is always determined by the precision indices. If necessary, curves can also be distinguished by dotted lines, dashed lines etc.

Intermediate values can be obtained from a graph by **'interpolation'.** If a smooth curve is drawn through a series of data points, then the value of the dependent variable that corresponds to a particular unmeasured intermediate value of the independent variable can be read off the curve.

The value of a dependent variable at a point outside the limits of the data used to construct a curve on a graph may be obtained by **'extrapolation'.** The method is to extend the curve smoothly beyond

the limits of experimental data, provided that there is no reason for a deviation in the nature of the curve due to such extension.

Besides the regular cartesian coordinate graph paper, semilogarithmic paper, log-log paper, and triangular coordinate paper have been found to be useful and time-saving.

Semilogarithmic paper is useful for data like calculation of activation energy where the logarithm of rate constant is plotted against the reciprocal of the absolute temperature (*See* Expt. No. 10.4). The rate constant values can be plotted directly on the log-axis and the reciprocals of absolute temperatures on the regular coordinate axis.

The log-log paper is convenient for expressing the results of experiments like adsorption experiments (*See* relevant Expt.). According to the Freundlich isotherm, the plot of the logarithm of the amount of solute adsorbed per unit weight of adsorbent *versus* the logarithm of the concentration of solute in the solution is linear. In a log-log paper, these variables are plotted directly on the axes.

Triangular coordinate paper is used when three variables such as the percentages of the three components in the study of solubility relationships in a three-component system, are plotted simultaneously. An example of a three-component system is acetic acid-water-benzene.

**Fitting equations to experimental data:**

In experiments of physical chemistry it is very often necessary to find the equation that best fits the data. Straight line equations have been found to be simpler and easier for fitting than any other function. Therefore, various mathematical functions are tried in the hope of finding a linear function. Some of these functions together with linear forms and their respective linear coordinates, slopes and intercepts are given in the following table.

| Equation | Linear form | Linear coordinates | Slope | Intercept |
|---|---|---|---|---|
| $y = a\,e^{bx}$ | $\ln y = \ln a + bx$ | $\ln y$ vs. $x$ | $b$ | $\ln a$ |
| $y = ab^x$ | $\log y = \log a + x \log b$ | $\log y$ vs. $x$ | $\log b$ | $\log a$ |
| $y = ax^b$ | $\log y = \log a + b \log x$ | $\log y$ vs. $\log x$ | $b$ | $\log a$ |
| $y = ax + b$ | — | $y$ vs. $x$ | $a$ | $b$ |
| $y = a + bx^2$ | — | $y$ vs. $x^2$ | $b$ | $a$ |
| $y = a \log x + b$ | — | $y$ vs. $\log x$ | $a$ | $b$ |
| $y = a/(b+x)$ | $1/y = (b/a) + (x/a)$ | $1/y$ vs. $x$ | $1/a$ | $b/a$ |
| $y = ax/(1+bx)$ | $1/y = (1/ax) + (b/a)$ | $1/y$ vs. $1/x$ | $1/a$ | $b/a$ |
| $y =$ ,, | $1/x = (a/y) - b$ | $1/x$ vs. $1/y$ | $a$ | $-b$ |

**Straight line graphs:**

The two common methods commonly used to determine the slope and intercept of a straight line are (*i*) plotting by eye and (*ii*) the method of least squares.

The general equation for a straight line is $y = mx + b$ where $x$ is the independent variable, $m$ is the slope of the line and $b$ is the intercept of the line on the y-axis (i.e. at $x = 0$). The slope and intercept are easily estimated from the graph on which the line appears.

If fewer than five data points are obtained in the experiment, it is easiest to draw the 'best' straight line through them visually. The error in slope and intercept of this line may be estimated by constructing two other limiting lines. This method is clarified as follows:

In the adjacent figure (Fig. 1) the plot of $y$ vs. $x$ yields a straight line. The rectangle drawn about each point is an estimate of the 'blurriness' of the point resulting from the errors in the measurement. (Instead of rectangles, other data symbols can be used). The estimated error-spread measured by precision indices in the variable $y$ is the height of the rectangle and the estimated error-spread in the variable $x$ is the base of the rectangle. The solid line is the best straight line through the points, as judged by eye with the use of a transparent straight edge. Two limiting lines (dashed) with the least slope and the greatest slope can be drawn while still passing through the error rectangles of the points.

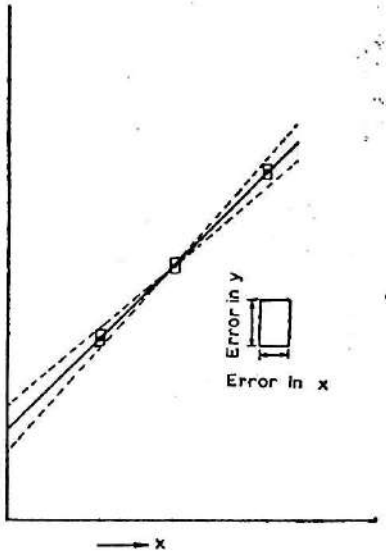



Fig. 1—Straight line graph

Now, calculate the slopes and intercepts of all the three lines. One-half the difference between the two limiting slopes is an estimate of the error in the 'best' slope. Similarly, one-half the difference between the two limiting intercepts is an estimate of the error in the 'best' intercept.

When a larger number of data points is available (say, more than five), it is then recommended to use the method of least squares to find the best line.

**Least Squares procedure:**

From a statistical point of view the best straight line is the one where the sum of the squares of the deviations of the experimental points is minimum.

It is assumed that the error lies solely in the dependent variable $y$, and that all data points are equally trustworthy.

*i.e.* $\Sigma\delta_i^2 = minimum$ where $\delta_i = x_i - \text{A.M.}$ (*vide* p. 4)

Suppose we have $n$ number of experimental values of $x$ and $y$. Then, according to this procedure, the slope ($m$) and intercept ($b$) for $n$ data points are as follows:

$$\text{Slope, } m = \frac{n\Sigma xy - \Sigma x \Sigma y}{n\Sigma x^2 - (\Sigma x)^2}$$

$$\text{Intercept, } b = \frac{\Sigma y \Sigma x^2 - \Sigma x \Sigma xy}{n\Sigma x^2 - (\Sigma x)^2}$$

To use the method of least squares, tabulate your data in the following way :—

| $x$ | $y$ | $xy$ | $x^2$ |
|---|---|---|---|
| ... | ... | ... | ... |
| ... | ... | ... | ... |
| ... | ... | ... | ... |
| ... | ... | ... | ... |
| ... | ... | ... | ... |
| ... | ... | ... | ... |
| $\Sigma x$ | $\Sigma y$ | $\Sigma xy$ | $\Sigma x^2$ |

Unlike the estimation of the best straight line by eye, the method of least squares does not involve personal judgement but depends only on the experimental data. But there is considerable amount of tedious arithmetic involved. In practical classes, you obtain generally small sets of data with which it becomes unjustified to use this method. In these circumstances the use of the best straight line by eye approach is admissible, but you must acquaint yourselves also with the other procedure.

## EXPERIMENT NO. 1

## DENSITY MEASUREMENT BY PYCNOMETER

**Theory:**

(*i*) The density of a liquid can be determined pycnometrically from the mass required to fill a container of known volume. It is given by the formula:

$$d_x^t = \frac{W_x}{V} = \frac{W_x . d_r}{W_r} \quad \ldots (1)$$

where $W_x$ = mass of test liquid
$V$ = volume of the pycnometer
$d_r$ = density of reference liquid
$W_r$ = mass of reference liquid
$d_x^t$ = density of test liquid at $t$°C

(*ii*) The density of a solid is determined pycnometrically from the volume of the reference liquid displaced by the submerged solid. If the following quantities are known, (*a*) the mass of the empty pycnometer, (*b*) the mass of the pycnometer filled with liquid, (*c*) the mass of the dry pycnometer containing about 1 gm. of solid and (*d*) the mass of the pyconometer containing the sample of solid and filled with liquid, the density of the solid $d_x$ is given by:

$$d_x = \frac{\text{Mass of solid}}{\text{Volume of solid}} = \frac{\text{Mass of solid}}{\text{Volume of displaced liquid}}$$

$$= \frac{(c) - (a)}{\text{Mass of displaced liquid/Density of liquid}}$$

$$= \frac{[(c) - (a)] \times \text{density of liquid}}{[(b) - (a)] - [(d) - (c)]} \quad \ldots (2)$$

**Materials:**

Pycnometer, constant temperature bath (or thermostat), filter paper, test liquid, acetone

**(A) Determination of liquid density:**

Two types of pycnometers are available: (*a*) *Ostwald-Sprengel* pycnometer (Fig. 2) and (*b*) *Weld* pycnometer (Fig. 3). Rubber or glass caps may be fitted over the ends of both types of pycnometers to prevent evaporation of volatile liquids. The Weld pycnometer is less accurate but easier to use.

Clean and dry the Ostwald-Sprengel pycnometer and weigh it ($W_1$). Fill the pycnometer with water, using either a hypodermic syringe or an aspirator. Otherwise, attach a rubber tube at the end $A$ of the

pycnometer, place the other end *B* in water and suck gently. *In case a volatile or poisonous liquid is used, interpose a vapour trap between the liquid and your mouth. (A drying tube filled with activated carbon*

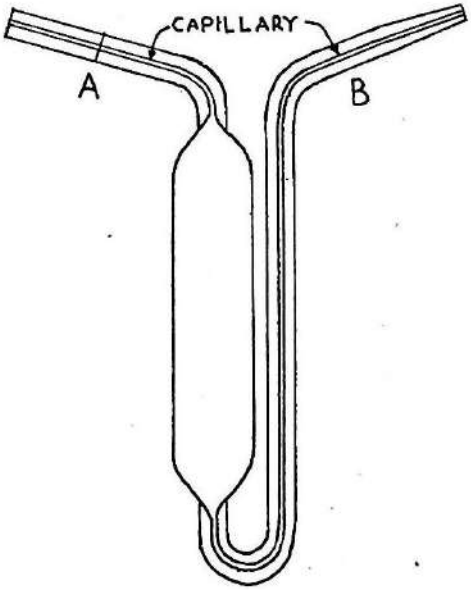



Fig. 2—Pycnometer (*Ostwald—Sprengel type*)

*is a convenient and effective trap*). If any air bubble is trapped, tilt the pycnometer so that the bubble is at the entrance to the outlet tube. Then suck more liquid into the pycnometer.

Place the pycnometer in the thermostat regulated at the temperature at which the density is required. After half an hour or so when the pycnometer has attained the temperature of the thermostat, observe whether water stands at mark *A*. This adjustment of water level can be most conveniently done by slightly tilting the pycnometer towards *B* and withdrawing the excess water by touching the *B*-end with a piece of filter paper. Add water, if necessary, with a pipette or medicine dropper drawn to a fine capillary. Remove the pycnometer, dry the outer side carefully and weigh it ($W_2$).

Wash the pycnometer with acetone and dry it. Repeat the above procedure with the test liquid instead of water. Let $W_3$ be the weight of pycnometer with the liquid.

**Results and Calculations**

Temperature = .....($t$°C)

$W_1$ = Weight of pycnometer

$W_2$ = Weight of pycnometer + water

$W_3$ = Weight of pycnometer + liquid
$(W_2 - W_1)$ = Weight of water at t°C = $W_r$
$(W_3 - W_1)$ = Weight of liquid at t°C = $W_x$

$$\text{Density of liquid} = \frac{W_x \cdot d_r}{W_r}$$

**(B) Determination of solid density:**

The Weld pycnometer is used for determination of solid density. This is essentially a specific gravity bottle with wide conically ground mouth into which is fitted leak-tight a ground capillary tube which serves as the ground glass stopper. A cap may also be put on this stopper. The quantities (*a*), (*b*), (*c*) and (*d*) are determined experimentally using the Weld pycnometer. Air bubbles trapped around the solid should be removed. This can be done by using an aspirator when the solid is covered with the liquid. Density is calculated using equation (2).

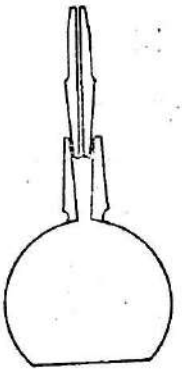


Fig. 3—Pycnometer (*Weld type*)

## EXPERIMENT NO. 2

## VISCOSITY DETERMINATION

### (A) Determination of liquid viscosity using Ostwald Viscometer:

**Theory:**

When a liquid flows, each portion of the liquid experiences a resistance to flow when flowing past another portion. The coefficient of viscosity is a measure of this internal friction or resistance to flow. It is numerically equal to the tangential force per unit area required to maintain unit difference of velocity of displacement of two parallel planes at unit distance apart, the space between the planes being filled with the viscous liquid. That is,

$$\text{Coefficient of viscosity} = \eta = \frac{\text{Tangential force}}{\text{Area} \times \text{Velocity gradient}}$$

The unit of $\eta$ is thus dyne-second per square cm. This unit is called a poise, after the name of Poiseuille, who first made a systematic study of liquid flow through capillaies.

According to Poiseuille's formula for the flow of a homogenous liquid through a capillary tube,

$$\eta = \frac{\pi p r^4 t}{8Vl} \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

where $p$ is the driving force, $r$ is the radius of the tube, $t$ is the time required for the volume $V$ of liquid to flow through the tube of length $l$.

The experimental determination of the absolute viscosity of a liquid is a difficult task, but the measurement of relative viscosity, the ratio of the viscosity of a liquid to that of some standard liquid such as water, is simple and adequate for many purposes. If necessary, the absolute viscosity can be calculated from a knowledge of the absolute viscosity of the reference liquid.

In simple viscometer (Ostwald modification of the Poiseuile's apparatus, as shown in Fig. 4), the force driving a liquid of viscosity $\eta_1$ through the capillary depends on the difference in liquid level $h$, the density $d_1$, and the accceleration due to gravity, $g$, and is given by the expression $hgd_1$. If exactly the same volume of a liquid of viscosity $\eta_2$ is introduced into the same tube, the driving force is equal to $hgd_2$, where $d_2$ is the density of this liquid.

By eqn. (1), Viscosity, $\eta$, is equal to $\frac{\pi r^4}{8Vl} . pt$. Therefore for a given apparatus and the same volume $V$ of liquid, $\eta$ is proportional to the driving force and to the time of outflow. Hence,

$$\frac{\eta_2}{\eta_1} = \frac{hd_2g}{hd_1g} \cdot \frac{t_2}{t_1} = \frac{d_2t_2}{d_1t_1} \quad \ldots (2)$$

This expression gives the viscosity of the second liquid relative to that of the first. In order to obtain the coefficient of viscosity of the second liquid in absolute units, it is just necessary to put the value of coefficient of viscosity of the reference liquid ($\eta_1$) in absolute units in the above equation (*See* Appendix, table IV).

**Materials:**

Ostwald viscometer, rubber tubing, clamps, stop watch, constant temperature bath (thermostat), test liquid, acetone.

**Procedure:**

The Ostwald viscometer is shown in Fig. 4

Thoroughly clean the viscometer with warm chromic acid and rinse several times with distilled water. Fix a rubber tubing onto the viscometer at end *A*. While putting the rubber tubing, hold the end to which the tubing is being attached. *Even a small torque may break the viscometer.* Clamp the viscometer vertically in a thermostat maintained at constant temperature, say, 25°C. Introduce a known volume of water (*use pipette*) into the larger bulb *E* through the end *F*. The quantity of water will be such that it more than fills the bulb say, 10 *ml*. By blowing through *F* force up the water until its level rises above the mark *c*. (If the liquid is raised by sucking at *A*, liquid often gets into the rubber tubing contaminating the system). Then allow the liquid to flow through the capillary and start the stop watch when the meniscus passes the upper mark *c* and stop the watch when it passes the lower mark *d*. Determine the flow time at least twice more.

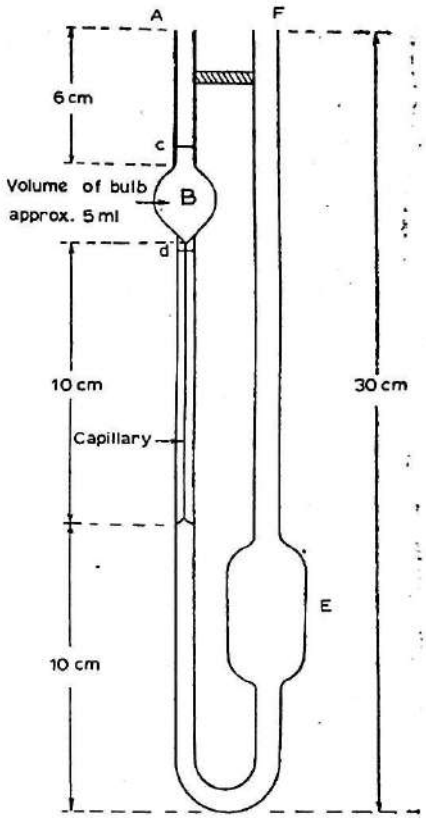



Fig. 4—Ostwald Viscometer

Drain the water from the viscometer, rinse twice with acetone and dry by blowing air.

Introduce *same volume* of the given liquid as was used in the measurement with water. Allow sufficient time until the viscometer attains the temperature of the thermostat. Determine the flow time between *c* and *d* as before.

**Results and calculations;**

Temperature = °C ; $\eta_1$=...poise

| Serial no. of obser-vations | Time of flow in seconds: for water ($t_1$) | Mean $t_1$ | for second liquid ($t_2$) | Mean $t$ | Relative viscosity $= \eta_2/\eta_1$ $= (d_2t_2)/(d_1t_1)$ | Coeff. of Viscosity $= \eta_2$ $= \eta_1 \times \frac{d_2t_2}{d_1t_1}$ (Poise) |
|---|---|---|---|---|---|---|
| | ... | | ... | | | |
| | ... | ... | ... | ... | | |
| | ... | | ... | | | |

**(B) Determination of the molecular weight of polystyrene by viscometry:**

**Theory:** With polymers the viscosity of the solution depends on the concentration of the solute, its molecular weight, and the shape of the solute molecule. The relative increase in viscosity due to the presence of the solute is called the specific viscosity, defined by

$$\eta_{sp} = \frac{\eta_{solution} - \eta_{solvent}}{\eta_{solvent}} \quad \ldots (3)$$

The value of specific viscosity extrapolated to infinite dilution is called intrinsic viscosity, *i. e.*

$$\lim_{c \longrightarrow 0} \frac{\eta_{sp}}{c} = [\eta] \quad \ldots (4)$$

where $[\eta]$ is the intrinsic viscosity.

For solutions of polymers of molecular weight above 10,000 the intrinsic viscosity $[\eta]$ is related to the average molecular weight M of a polymer sample by the following equation:

$$[\eta] = KM^{a} \quad \ldots (5)$$

where $K$ and $a$ are constants characteristic of the solvent-solute system. For benzene-polystyrene system, $K = 0.952 \times 10^{-2}$ and $a = 0.744$.

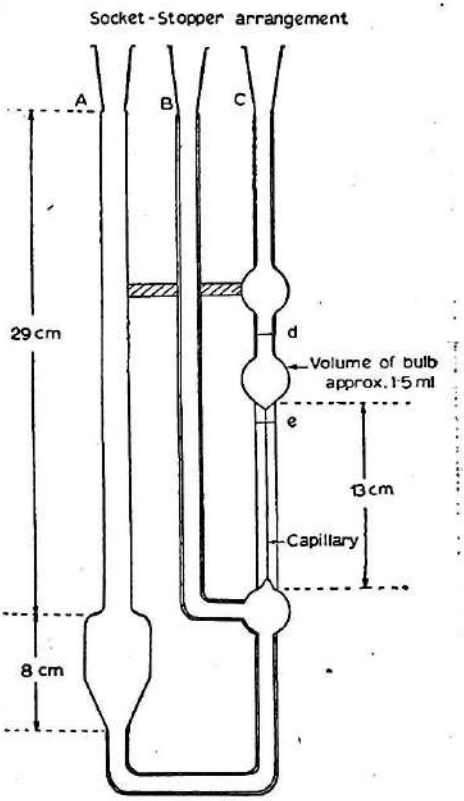
**Materials:**

Ubbelohde viscometer, pipettes, stop watch, beakers, measuring flasks, polystyrene, benzene.

**Procedure:**

Thoroughly clean the Ubbelohde dilution viscometer (Fig. 5) and dry it.

Weigh out accurately about 1 gm of polystyrene in the beaker and add 50 ml. of benzene to it. Allow to stand for 24 hours when dissolution of the polystyrene is complete. Transfer the solution quantitatively into a 100 ml measuring flask and make up the mark with benzene.



Fig, 5—Ubbelohde Viscometer

Rinse the pipette (10 ml) and the viscometer with benzene. Drain the benzene out of the viscomter and dry it preferably by blowing clean dust-free air through it. Next pipette 10 ml. of benzene into the large bulb of the viscometer *via* end *A* (Fig. 5). Lightly stopper the three limbs of the viscometer. Place it in a thermostat maintained at 25°C in vertical condition. Allow 15 minutes for thermal equilibrium.

Remove stoppers from limbs *A* and *C*. By blowing apply air pressure to limb *A* to force the benzene up until its level rises above the mark *d* in limb *C*.

Remove the stopper from limb *B* and allow the liquid to flow through the capillary. Determine the flow time for the meniscus to pass between *d* and *e*. Repeat the procedure at least twice more.

Drain the viscometer and dry it by blowing air. Rinse the 5 ml. pipette with polystyrene solution and then pipette 5 ml. of the solution into the viscometer. As previously. determine at least thrice the flow time for the passage of the meniscus between the two marks.

Pipette 2 ml. of benzene into the viscometer and mix its contents by blowing air into limb *B*. By blowing at *A* force the solution into limb *C* a few times in order to complete the mixing process. Determine the flow time as before.

Repeat the measurements after consecutive additions of 3, 5, and

5 ml of benzene. Note that the driving force in this viscometer unlike in Ostwald's is independent of the volume of liquid inside the viscometer.

**Results and Calculations;**

Since the densities of the various solutions can be taken as approximately the same as the density of the solvent, it may be assumed that viscosity of each solution is proportional to its flow time. Therefore, equation (2) becomes-

$$\eta_{sp} = \frac{t_2 - t_1}{t_1} \quad \ldots \quad \ldots \quad (6)$$

where $t_1$ and $t_2$ are flow times for benzene and polymer solutions respectively.

| Concentration (c) gm/100 cc | Time of flow in seconds | Mean of Time flow in seconds ($t_2$) | $\eta_{sp} = \frac{t_2 - t_1}{t_1}$ | $\frac{\eta_{sp}}{c}$ |
|---|---|---|---|---|
| 0 | ... | | | |
| | ... | ($t_1$) | ... | |
| | ... | | | |
| | ... | | | |
| ... | ... | ... | ... | |
| | ... | | | |
| | ... | | | |
| ... | ... | ... | ... | |
| | ... | | | |
| | ... | | | |
| ... | ... | ... | ... | |
| | ... | | | |

Plot a graph of $\eta_{sp}/c$ versus $c$ and extrapolate to $c = 0$ in order to obtain the value of $[\eta]$ in decilitre $gm^{-1}$. Next calculate the average molecular weight by equation (5).

## EXPERIMENT NO. 3

## DETERMINATION OF SURFACE TENSION OF LIQUIDS

### (A) Surface tension determination by Stalagmometer methods:

**Theory:** A molecule lying inside the body of a liquid is equally attracted in all directions, but a molecule in the surface layer is subject to an unbalanced force acting inwards at right angles to the surface. This force, acting perpendicularly to any imaginary line, 1 cm. long, drawn on the surface and acting along the surface is called the surface tension. Its unit is thus *dyne/cm.*

The measurement of surface tension by Stalagmometer method is a modification of the drop weight method. The measurement consists of counting the number of drops formed when a definite volume of liquid is allowed to flow slowly out of a capillary orifice. The ratio of the weight, ($W_1$) of a drop of the liquid to that of a reference substance ($W_2$) falling out of the same capillary orifice is equal to the ratio of their surface tensions provided the volumes of the drops are not very different. If $\gamma_1$ and $\gamma_2$ are the surface tensions of the liquid and the reference substance respectively, then we have,

$$\frac{W_1}{W_2} = \frac{\gamma_1}{\gamma_2} \qquad \ldots \quad (3.1)$$

If $V$ is the volume of the liquid delivered by the stalagmometer, $d_1$ its density and $n_1$ the number of drops, then the weight, $W_1$ of a single drop is

$$W_1 = \frac{Vd_1}{n_1}$$

Similarly, for the same volume of reference substance of density $d_2$, the weight $W_2$ of a single drop is

$$W_2 = \frac{Vd_2}{n_2}$$

where $d_2$ is the density of the reference substance and $n_2$ the number of drops.

Hence, $$\frac{\gamma_1}{\gamma_2} = \frac{Vd_1}{n_1} \cdot \frac{n_2}{Vd_2} = \frac{d_1}{d_2} \cdot \frac{n_2}{n_1}$$

$$\therefore \quad \gamma_1 = \frac{d_1}{d_2} \cdot \frac{n_2}{n_1} \cdot \gamma_2 \qquad \ldots \quad (3.2)$$

Water is generally used as the reference substance. For a fair degree of accuracy the tip of the tube, where drops form, should be sharply ground and the drops must form slowly.

**Materials:**

Stalagmometer, test liquid, acetone.

**Procedure:**

The Stalagmometer is shown in Fig. 6. Clean the Stalagmometer with warm chromic acid (page 1) and rinse thoroughly with distilled water. Note that cleanliness is very important for all measurements of surface properties.

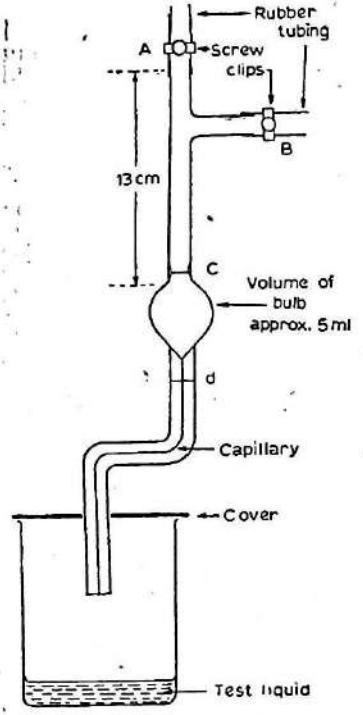



Fig. 6—Stalagmometer

Arrange the apparatus as shown in Fig. 6. Close clip *B*, suck up to above level *C* and close clip *A*. Adjust clip *B* so that water drops fall at the rate of 10—15 per minute. Count the number of drops as the meniscus passes between the marks *C* and *d*. Repeat the measurement at least twice.

Rinse the stalagmometer with acetone and blow air through it until thoroughly dry. Repeat the measurements with the given liquid.

**Results and Calculations:**

Laboratory temperature =...°C
Surface tension of water =...dyne/cm.
Density of water =...gm/c.c.
Density of liquid =...gm/c.c.

| Serial No. of observations | No. of drops | | | | Surface tension of liquid $\gamma_1$ dyne/cm. [as per eqn. (3.2)] |
|---|---|---|---|---|---|
| | Water ($n_2$) | Mean $n_2$ | liquid ($n_1$) | Mean $n_1$ | |
| | ... | | ... | | |
| | ... | | ... | | |
| | ... | ... | ... | ... | |
| | ... | | ... | | |
| | ... | | ... | | |

**(B) Surface tension determination by capillary-rise method:**

**Theory:**

If one end of a glass capillary is placed below the surface of water or any other liquid that wets the glass, the liquid rises in the capillary owing to its surface tension (Fig. 7). The circular boundary line above the meniscus has a length $2\pi r$ where $r$ is the inside radius. Let the surface tension of the liquid be $\gamma$; therefore the total force $f$ acting in the plane of the surface and perpendicular to the boundary is $2\pi r\gamma$. However, at equilibrium downward force prevents the liquid from rising higher in the capillary. This downward force is $\pi r^2hdg$. The vertical component of the upward force is $f\cos\theta = 2\pi r\gamma \cos\theta$ where $\theta$ is the contact angle of the liquid with the vertical side wall of the capillary. If the liquid wets the glass wall perfectly, the contact angle $\theta$ is zero. For common liquids $\theta$ is zero. The two forces being equal at equilibrium

$$2\pi r\gamma = \pi r^2hdg$$

$$\gamma = 1/2 \ (hdgr) \quad \ldots \quad \ldots \ (3.3)$$

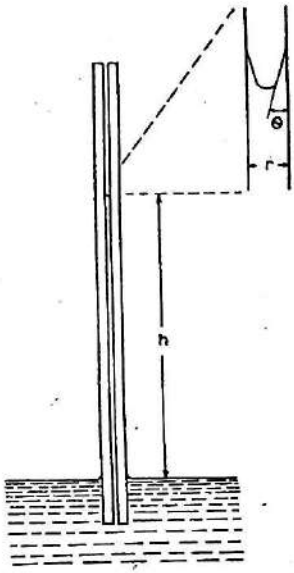



Fig. 7—Capillary rise (*Theory*)

In order to use this formula in the calculation of surface tension, it is necessary to measure the height $h$ to which a liquid of density $d$ rises in a capillary of radius $r$.

**Materials:**

Capillary-rise apparatus, constant temperature bath, test liquid, acetone.

**Procedure:**

The capillary-rise apparatus is shown in Fig. 8. The capillary tube is engraved in millimeter graduations.

Clean the capillary with warm cleaning solution (page 1), rinse thoroughly with distilled water and then with acetone. Next place it in an oven at about 100°C until perfectly dry. The test tube also must be cleaned in the same manner.

Put the test tube with the capillary in a thermostat maintained at constant temperature, say 25°C. Pour a few ml of the liquid in the test tube after temporarily removing the cork. Fit a dust-free rubber tubing in the side arm. After about 15 minutes when thermal equilibrium has been attained, raise the liquid in the capillary by gently

blowing through the rubber tube. Then allow the level to fall back to its equilibrium position. Next depress the level slightly by applying suction and allow to come to equilibrium. The equilibrium position should be same after raising the level as after depressing it. If this is not so, the capillary is not clean.

Read the bottom of the meniscus and note the difference in the level of the liquid in the capillary tube and in the test tube. Make five measurements.

In order to find out radius of the capillary tube, repeat this procedure with pure water. The surface tension of water at 25°C is given as 71.8 dynes/cm.

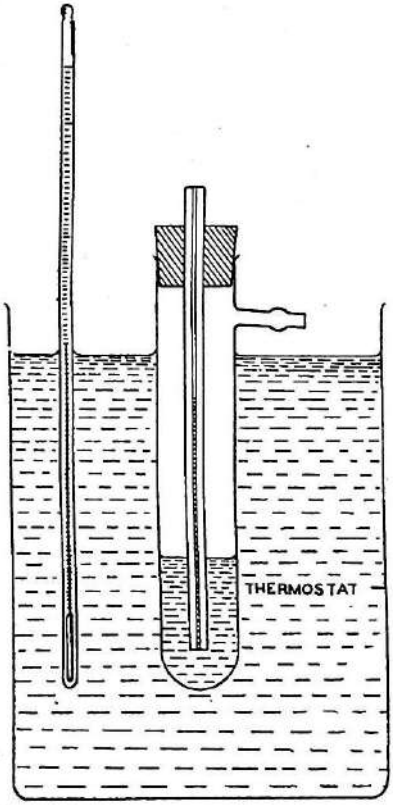



Fig. 8—Capillary Rise Method

**Suggestions for further work**[7]

(*i*) Measure surface tension versus concentration of any soap solution and thus verify how a trace of soap lowers the surface tension considerably. That is why detergents are sometimes called surface active or capillary active substances.

**Results and Calculations:**

*Results with water:* $\gamma = 71.8$ dynes/cm. (25°C)

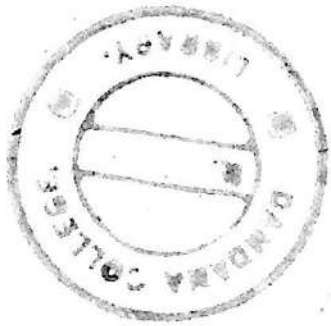
| No. of observations | $h$ (cm.) | Mean $h$ (cm.) | $r = \frac{2\gamma}{hdg}$ |
|---|---|---|---|
| | ... | | |
| | ... | | |
| | ... | ... | ... |
| | ... | | |
| | ... | | |

*Results with test liquid:*

| No. of observations | $h$ (cm.) | Mean $h$ (cm.) | $\gamma = 1/2\ (hrdg)$ |
|---|---|---|---|
| | ... | | |
| | ... | | |
| | ... | ... | ... |
| | ... | | |
| | ... | | |

The value of $d$ should be either already known or has to be determined with a pyknometer or specific gravity bottle (Expt. No. 1)

(*ii*) Measure the variation of surface tension and density of any organic liquid with temperature and from the data (*i*) check Eotvos equation and (*ii*) calculate the parachor value of the liquid and check how this value agrees with the expected value (sum of the component parachors).



## EXPERIMENT NO. 4

## SOLUBILITY MEASUREMENTS

### (A) Determination of Solubility Curve

**Theory:**

The solubility of a substance in a given solvent at a given temperature is the concentration of the solution which is in equilibrium with the solid phase. There are three common units of concentration: molality, molarity and mole fraction.

Fig. 9—Solubility Tube

**Molality** is the number of moles of solute per 1000 gm. of solvent.

**Molarity** is the number of moles of solute per litre of solution.

**Mole fraction** is the number of moles of solute divided by the total number of moles of solute and solvent.

It may be noted that the molality and mole fraction units are independent of temperature. In some instances solubility is defined as the number of grams of substance which saturates 100 gm. of the given solvent at a given temperature. However, this definition of solubility can be converted into molal or mole fraction units.

The solubility of a substance varies with temperature. Depending on the heat of solution, solubility increases or decreases or remains constant with increase of temperature. Solubility values at different temperatures when plotted against temperature constitute what is known as the solubility curve.

**Materials:**

One boiling tube fitted with a thermometer (0—110°C) and a stirrer (Fig. 9), test substance (say, potassium nitrate).

**Procedure:**

Clean, dry and weigh the boiling tube. Add about 18 mg of potassium nitrate and reweigh. Add 10 ml of water. Warm until the salt has dissolved. Continue stirring and allow the solution to cool. Note the temperature when crystals first appear. Add a further 2 ml of water and repeat the procedure. Continue 2 ml additions of water and determination of crystallization temperature after each addition, until the solute no longer crystallizes when cooled to room temperature.

**Results and Calculations**

Tabulate your results in the following manner:

| Weight of potassium nitrate (gm) | Volume of water added (ml) | Crystallization temperature (°C) | Weight of solute that would be dissolved in 100 gm of water to make saturated solution |
|---|---|---|---|
| | ... | ... | ... |
| | ... | ... | ... |
| | ... | ... | ... |
| | ... | ... | ... |
| | ... | ... | ... |

Plot solubility (Column 4 in the table) against crystallization temperature.

**Suggestions for further work:**

Other salts can be used. For example, with lead nitrate take 12 gm. of salt and 12 ml. of water. Make 0.5 ml. additions of water.

**(B) Determination of transition temperature of sodium sulfate and the heats of solution of the hydrate and of the anhydrous salt by solubility method.**

**Theory:**

The solubility(S) of a salt at a given temperature is defined as the weight of the salt in gram per 1000 gm. of solvent in order to make a saturated solution. If the given salt exists in 2 forms, the plot of solubility versus temperature exhibits a sharp break at the temperature of transition between the two forms.

The object of the present experiment is to determine the solubility of sodium sulfate in water at a number of temperatures and hence to determine the temperature of transition:

$$Na_2SO_4.10H_2O \rightleftharpoons Na_2SO_4 + 10H_2O$$

The heats of solution of the hydrate and of the anhydrous salt can be determined according to the following equation:

$$\log S = -\frac{\triangle H}{2.303\ RT} + \text{constant} \quad \ldots\ (4.1)$$

where $R = 1.987$ cal mole$^{-1}$deg$^{-1}$, and

$\triangle H$ (Cal mole$^{-1}$) is the heat of solution.

**Materials:**

Salt, suitable constant temperature bath.

**Procedure:**

Take about 150 ml. water in a 250 ml. beaker or conical flask and prepare a saturated solution of the salt at higher temperature (say, 48°C). Maintain the saturated solution at the given temperature for about 3 minutes with stirring and then pipette out (use dry pipette) tipped with cotton glass wool plug 5 ml. of clear solution in a previously weighed evaporating dish. Weigh the dish again. Evaporate the solution to dryness on a sand bath or water bath; and dry in an oven at about 100°C, cool in a desiccator and weigh again. Calculate the solubility at the temperature *say*, 48°C. (*See* Expt. No. 4A for calculation of solubility).

Allow the temperature of the solution in the beaker to fall to, say, 44°C. Again pipette out 5 ml. of solution at this temperature and determine the solubility as above.

Repeat the procedure at lower temperatures (say, 40°, 37°, 35°, 33°, 31°, 29°, 25°, 20°C). A convenient device to maintain constant temperature for short periods is to use a wide-mouth thermoflask containing water at the desired temperature. Proper arrangement should be made to keep the beaker almost wholly immersed in water.

**Results and Calculations:**

| Temp. °C | Wt. of empty dish $W_1$ gm | Wt. of dish + 5 ml. solution $W_2$ gm | Wt. of dish + solute $W_3$ gm | Wt. of solute $(W_3-W_1)$ gm | Wt. of solvent $(W_2-W_3)$ gm | Solubility $= \frac{(W_3-W_1)}{(W_2-W_3)} \times 1000$ gm/1000 gm |
|---|---|---|---|---|---|---|
| | | | | | | |

Plot solubility vs. temperature and from the point of intersection of the two solubility curves find out the transition temperature.

Applying equation (1) Calculate the heats of solution of the hydrate and of the anhydrous salt.

**Suggestions for further work:**

(1) Other salt hydrates can be used. A few salt hydrates having convenient transition temperature are listed below:

| | |
|---|---|
| $Na_2CrO_4, 10H_2O \rightleftharpoons Na_2CrO_4, 6H_2O$ | 19.71°C |
| $Na_2CO_3, 10H_2O \rightleftharpoons Na_2CO_3, 7H_2O$ | 32.31°C |
| $NaBr, 2H_2O \rightleftharpoons NaBr$ | 50.78°C |
| $MnCl_2, 4H_2O \rightleftharpoons MnCl_2, 2H_2O$ | 58.33°C |
| $SrCl_2, 6H_2O \rightleftharpoons SrCl_2, 2H_2O$ | 61.34°C |

(2) The transition temperature of sulphur may be obtained by determining the solubility curves of monoclinic and rhombic sulphur in nitrobenzene between 80° and 120°C.

**(C) Determination of critical solution temperature of the phenol—water system**

**Theory:**

If two liquids not reacting chemically are mixed, three types of miscibility behaviour are possible:

(*a*) the liquids may be immiscible (for example, mercury and water).

(*b*) the liquids may be miscible in all proportions (for example, ethanol and water).

(*c*) the liquids may be partially miscible (for example, phenol and water).

In case (*c*), solubility varies with temperature and solubility (or miscibility) curve can be constructed. Above a certain temperature,

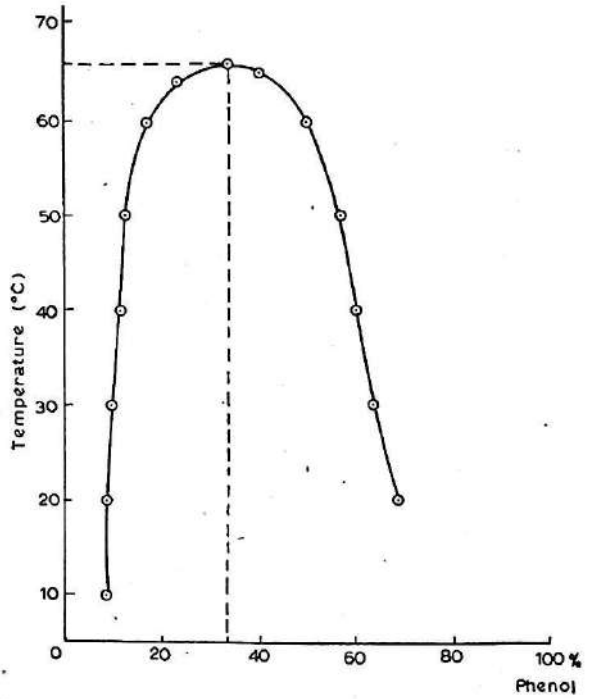



Fig. 10 Mulual Solubility Curve (Phenol-Water)

however, the two components become completely miscible in all proportions. This temperature is called the critical solution tempera-

ture or consolute temperature. For the phenol-water system the critical solution temperature is 65.85°C, the composition at this critical temperature is 34.5 per cent by weight of phenol (Fig. 10). Critical solution temperatures are very sensitive to the presence of impurities. Commercial phenol gives a higher value than a sample of purified phenol.

**Materials:**

Phenol, distilled water, ice.

**Procedure:**

Weigh 8 gm. of phenol in a tall beaker (100 ml.) (**CAUTION:** Phenol is corrosive). Place the beaker on a tripod and fix a burette containing distilled water. Add 2 ml. of water to the phenol. Stir the mixture and heat *slowly*. Note down the temperature at which the system becomes homogeneous (*clear solution*). Allow the beaker to cool down and note the temperature at which the mixture becomes opalescent (*milky-white*) due to the separation of two liquid layers. The mean of these two temperatures is the miscibility temperature of the particular mixture used.

Repeat the procedure with further additions of water (2ml in the initial stages to be followed by 3 ml and 5 ml of water in each addition).

If the miscibility temperature goes down below room temperature, use ice-water mixture to cool down the temperature of the beaker.

**Results and Calculations**

Density of water = 1 gm./ml.
Weight of Phenol = 8 gms (say)

| Serial no. of observations | Wt. of water ($x$ gm). | percentage by wt. phenol $\frac{8}{8+x} \times 100$ | Miscibility temperature | | |
|---|---|---|---|---|---|
| | | | Opalescence disappears °C | Opalescence reappears °C | Average °C |
| | | | | | |

Plot the miscibility temperature-percentage composition curve and find out the critical solution temperature.

**Suggestion for further work:**

Instead of water, sodium chloride solution (about 1%) in water may be used and the experiment repeated to study any effect of impurity on the critical solution temperature of phenol and water. (Sodium chloride is soluble in water only).

You can also use 2% Succinic acid Solution (Succinic acid is soluble in both phenol and water).

Also 0.1 gm of naphthalene in phenol will demonstrate the effect of additive on critical solution temperature (naphthalene is soluble in phenol only).

**(D) Determination of solubility diagram for a three-component liquid system:**

According to the phase rule ($F = C-P+2$) there are at most four degrees of freedom, for a system containing three liquid components. If the pressure and temperature be kept constant, it follows that the concentrations of only two of the three components can be *independently* varied. When only two of the three parameters are independently variable, all three parameters can be represented in one plane by means of the traingular diagram shown in Fig. 11.

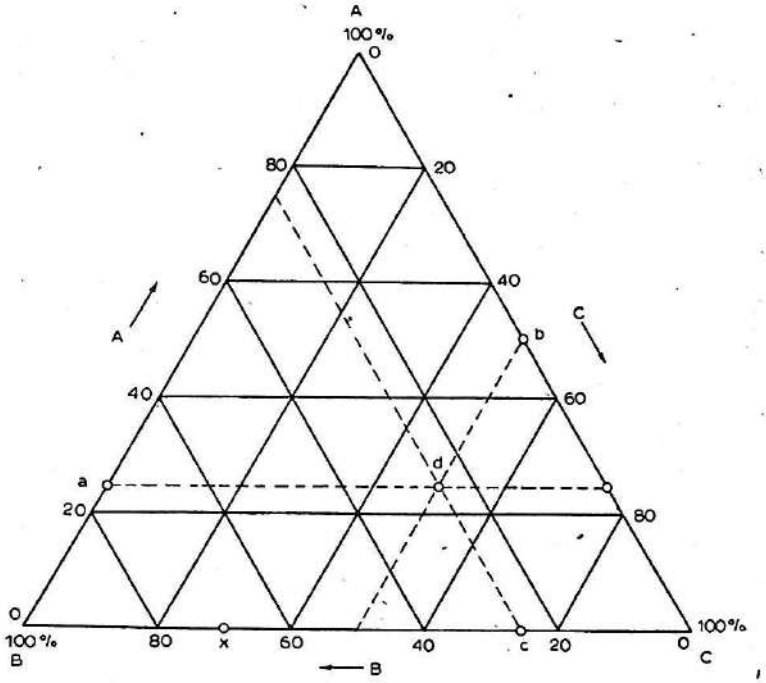



Fig. 11 Three component Solubility Diagram

Each side of the equilateral triangle represents 100 per cent of one of the components. Let us fix the point that represents a mixture containing 25 per cent of A, 25 per cent of B, and 50 per cent of C. Let us mark the point *a* on side AB, which represents 25 per cent of A. Now draw a dotted line from *a* to the opposite side (AC), parallel to the side BC. All mixtures containing 25 per cent of A will fall on this

dotted line. Similarly, the point *b* on the side AC represents 50 per cent of C. Draw a dotted line from *b* parallel to AB to the opposite side of the traingle. The point *c* on BC represents 25 per cent of B and draw the proper dotted line from *c* parallel to AC. The three dotted lines intersect at point *d*, which represents the composition of the mixture.

It may be noted that only two of the three dotted lines are required to find out *d*. Any mixture of only two components can be represented on one side of the traingle. For instance, the point *x* represents the composition of a mixture containing 30 per cent of C and 70 per cent of B.

**Materials:**

Glacial actic acid, chloroform, water, acetone.

**Procedure:**

Set up three burettes containing acetic acid, chloroform and water. **(Caution:** Glacial acetic acid is corrosive. Burettes for chloroform and acetic acid should be previously washed and dried with acetone).

Make up 7 mixtures of chloroform and acetic acid in clean, dry, glass-stoppered bottles (or conical flasks) as shown in the following table The total volume of each mixture is 20 ml.

Add water into each mixture, shaking well after each addition, until the clear solution becomes permanently turbid. Note the volumes of water added in each case.

**Results and Calculations:**

Tabulate your results as follows:

| Volume of chloroform (ml) | Volume of acetic acid (ml) | Volume of water (ml) | % by weight chloroform | % by weight acetic acid | % by weight water |
|---|---|---|---|---|---|
| 1.5 | 18.5 | | | | |
| 2.0 | 18.0 | | | | |
| 3.5 | 16.5 | | | | |
| 6.5 | 13.5 | | | | |
| 10.0 | 10.0 | | | | |
| 12.5 | 7.5 | | | | |
| 16.0 | 4.0 | | | | |
| 16.0 | 4.0 | | | | |
| — | | — | 99.0 | | 1.0 |
| — | | — | 0.8 | | 99.2 |

Draw the solubility diagram according to the method discussed in theory. The last two points in the table indicate that at room temperature a saturated solution of chloroform in water contains 0.8 per cent chloroform and a saturated solution of water in chloroform contains 99.0 per cent chloroform.

**(E) Determination of the solubility product of a sparingly soluble electrolyte and to investigate the effect of common ions on its solubility**

**(*a*) Silver bromate:**

**Theory:**

Silver bromate is sparingly soluble in water. It ionises as follows:

$$AgBrO_3(\text{solid}) \rightleftharpoons Ag^+ + BrO_3^-$$

Since the dissolved portion is a strong electrolyte in dilute solution, it is practically completely ionised, and so applying mass law to the above equilibrium, we get

$$S = C_{Ag^+} \times C_{BrO_3^-} = x^2 \qquad \ldots \quad (4.2)$$

where $x$ is the solubility and $S$ is the solubility product constant; $C_{Ag^+}$ and $C_{BrO_3^-}$ are the ionic concentrations of $Ag^+$ and $BrO_3^-$ respectively in a saturated solution i.e. $x = C_{Ag^+} = C_{BrO_3^-}$.

**Effect of common ion:**

*Case I.* When a saturated solution of silver bromate is prepared in the presence of an electrolyte which produces a common silver ion, the solubility is lowered in accordance with the following mass law equation:

$$S = (X_1 + C_{Ag^+})X_1 \qquad \ldots \quad (4.3)$$

where $C_{Ag^+}$ is the concentration of silver ion originating from dissociation of the added electrolyte; and $X_1$ is that originating from the dissolved silver bromate.

*Case II.* Similarly, the solubility of silver bromate in the presence of sodium bromate is given as—

$$S = (X_2 + C_{BrO_3^-})X_2 \qquad \ldots \quad (4.4)$$

where $C_{BrO_3^-}$ is the concentration of bromate ion originating from the added sodium bromate; $X_2$ is that originating from the dissolved silver bromate.

**Materials:**

(1) Silver bromate; (2) 0.01*N* sodium bromate; (3) 0.05*N* KCNS; (4) Saturated ferric ammonium sulfate solution; (5) Conc. nitric acid; (6) 0.01 *N* Silver Nitrate.

**Procedure:**

Take three stoppered bottles. Place 1 gm. of silver bromate (weighed approximately) in each. Then make the following additions as follows:

75 ml. distilled water to Bottle No. 1
75 ml. 0.01 *N* $AgNO_3$ to Bottle No. 2
75 ml. 0.01 *N* $NaBrO_3$ to Bottle No. 3.

Stopper the bottles carefully and label them. Shake each of the bottles for 15 minutes and then keep them in a thermostat for about six hours (during this period the bottles should be occasionally stirred).

Standardise the KCNS solution against the 0.01*N* $AgNO_3$, as follows; Pipette out 50 ml. of silver nitrate into a conical flask containing 25 ml. distilled water. Add 5 ml. of ferric ammonium sulfate solution and 5 drops of nitric acid; titrate to a faint permanent pink.

Analyze the solution in each of the three bottles in the same manner. While pipetting out the samples from the bottles, put cotton/glass wool in the tip of the pipette.

**Results and Calculations:**

Analysis of bottle No. 1 will give $S$, the solubility product of silver bromate (use equation (4.2).

Analysis of bottle No. 2 and bottle No. 3 will give the value of $X_1$ and $X_2$ respectively (*vide*, equations (4.3) & (4.4). Discuss how the common ion effect reduces the solubility of silver bromate (*i.e.*, values of $X_1$ and $X_2$ will be lower than $X$).

**Suggestions for further work:**

Similar experiments with silver iodate (solubility, 0.005 gm./100 ml. water at 25°C) may be performed. In this case the solubility product may be easily determined by estimating the iodate ion concentration in a known volume of the saturated solution. The method is as follows:

Pipette out 50 ml. of the saturated solution in a 250 ml. conical flask. Add 1 gm. of solid potassium iodide and 10 ml. of 4*N* sulfuric acid. (Note that silver iodide will be precipitated). Add about 1 ml. of starch solution and titrate the liberated iodine with 0.005 *N* sodium thiosulfate until the blue starch-iodine colour just disappears.

**(*b*) Calcium hydroxide:**

The solubility product of calcium hydroxide and the effect of hydroxyl ion on its solubility can be determined as follows:

Prepare a saturated solution of calcium hydroxide in distilled water and in N/20 sodium hydroxide solution. Pipette out 25 ml samples of the clear liquid (*Take care not to disturb the layer of the settled calcium hydroxide; put cotton or glass wool in the tip of the pipette*). Titrate the sample with N/10 HCl.

**Results with distilled water:**

Let normality of saturated solution $= x$

$\therefore$ $[OH^-] = x$ gm-ion/lit.

$[Ca^{2+}] = 1/2\ [OH^-] = x/2$ gm-ion/lit.

$\therefore$ $S = [Ca^{2+}]\ [OH^-]^2 = x/2 \times x^2 = x^3/2$

**Results with N/20 NaOH solution:**

Let normality of saturated solution $= y$

$\therefore$ Total $[OH^-] = y$ gm-ion/lit.

$[OH^-]$ from NaOH $= 0.05$ gm-ion/lit.

$\therefore$ $[OH^-]$ due to $Ca(OH)_2 = (y-0.05)$ gm-ion/lit.

$[Ca^{2+}] = (y-0.05)/2$ gm-ion/lit.

$\therefore$ $S = \left(\frac{y-0.05}{2}\right)y^2$

**(F) Determination of the formula of the Silver-ammonia complex ion**

**Theory:**

Many silver salts which are only sparingly soluble in water, are found to be readily soluble in the presence of ammonia. This is due to the formation of a complex ion

$$Ag^+ + x\,NH_3 \rightleftharpoons Ag(NH_3)_x^+ \quad \ldots \quad (4.5)$$

Using the solubility product of sparingly soluble silver bromide, it is possible to find out $x$, that is, the number of molecules of ammonia associated with each silver ion.

The equilibrium constant ($K$) is given by

$$K = \frac{[Ag(NH_3)_x]^+}{[Ag^+]\,[NH_3]^x} \quad \ldots \quad (4.6)$$

The aim of the present experiment is to find out the value of $x$. This can not be done by ordinary titrations because as the ammonia is removed during tiration, the equilibrium is shifted from right to left. Therefore, the concentrations of "free' and 'complexed' ammonia at equilibrium can not be determined. However, this difficulty can be overcome in an indirect way which is as follows—

When a solution containing bromide ion (say, KBr) is added to a solution containing silver ion (say, $AgNO_3$), silver bromide will get precipitated when the quantity $[Ag^+[\,[Br^-]$ exceeds the solubility product, $K_s$, which is defined as

$$K_s = [Ag^+]\;[Br^-] \quad \ldots \quad (4.7)$$

If ammonia is added to this sytem, a stable complex between $Ag^+$ and the ammonia is formed, leading to a fall of $[Ag^+]$. Therefore, relatively large concentrations of bromide ions are to be added to ammoniacal silver nitrate in order to precipitate AgBr (*vide* eqn. (4.7)]. Thus it appears that when precipitation occurs, the concentration of uncomplexed silver ions in the solution is inversely proportional to the concentration of bromide ion added, i.e.

$$[Ag^+] = K_s/[Br^-] \quad \ldots \quad (4.8)$$

When AgBr is precipitated from ammoniacal silver nitrate, we get from relationship (4.6) and (4.8)—

$$K = \frac{[Ag(NH_3)_x]^+[Br^-]}{K_s\;[NH_3]^x} \quad \ldots \quad (4.9)$$

By maintaining proper experimental conditions i.e. a large excess of ammonia, so that the concentration of the complex ion is effectively constant for a set of experiments, the relationship (4.9) can be written as

$$K = \text{a constant} \times \frac{[Br^-]}{[NH_3]^x}$$

$$= \text{a constant} \times \frac{V_B}{V_N^x} \quad \ldots \quad (4.10)$$