EXPERIMENT NO. 8

THEROMOCHEMISTRY

(8.1) To determine the heat of neutralisation af hydrochloric acid by sodium hydroxide..

Theory:

The heat of reaction is defined as the heat evolved when gram-

$$HCl + NaOH = NaCl + H_2O$$

molecular quantities of the reactants as shown in the chemical equation react. When the two reactants are mixed, a rise in temperature accompanies the neutralisation process. From a measurement of the rise in temperature, the heat evolved can be calculated, account being taken of the heat capacities of the product and the calorimeter.

Reagents:

1. 250 ml. hydrochloric acid solution of known normality (about 0.25 *N*); 2. A solution of sodium hydroxide having the same concentration as that of the acid.; 3. Phenolphthalein indicator.

Procedure:

The calorimeter is generally cylindrical in shape and is usually made of copper, nickel or silver. The calorimeter is provided with a cardboard or ebonite cover through which passes the thermometer (graduated to 0.1°C) and stirrer. Weigh the calorimeter and stirrer separately. The calorimeter vessel is surrounded by three other cylindrical vessels and the annular space between the two outer cylinders is filled with water in order to diminish the loss or gain of heat by radiation. *A simple calorimeter can be made by standing a* 600 *ml. beaker on a cork in a* 1000 *ml. beaker and placing the stirrer in the smaller beaker* (*Fig.* 16)]

Take 250 ml. of the alkali solution in the previously weighed calorimeter while 250 ml. of the acid solution are taken in a conical flask surrounded by insulators to minimize changes of temperature by radiation.

Place two thermometers in the acid and the alkali solution respectively. Read the temperature in both solutions, say every minute, for at least five minutes before mixing the two solutions. During this period stir the solutions. Then, at a particular moment (note the time) pour the acid as rapidly as possible into the alkali. Mix the two solutions and note the temperature every half-minute for about 10 minutes after mixing, until it is found that the fall of temperature after the initial rise becomes uniform. At first the temperature rises rapidly, then more slowly, and then begins to fall. Since, as the temperature rises above that of the room, radiation from the calorimeter takes place and thus the highest temperature registered by the thermometer will be lower than if no loss of heat by the calorimeter occurred. In order to obtain the true rise of temperature produced by the heat of neutralisation, plot the thermometer readings (before and after mixing) against the time (Fig. 17).

In Fig. 16 the mean of the temperatures of acid and alkali solutions is represented as rising slowly previous to mixing; but other possibilities

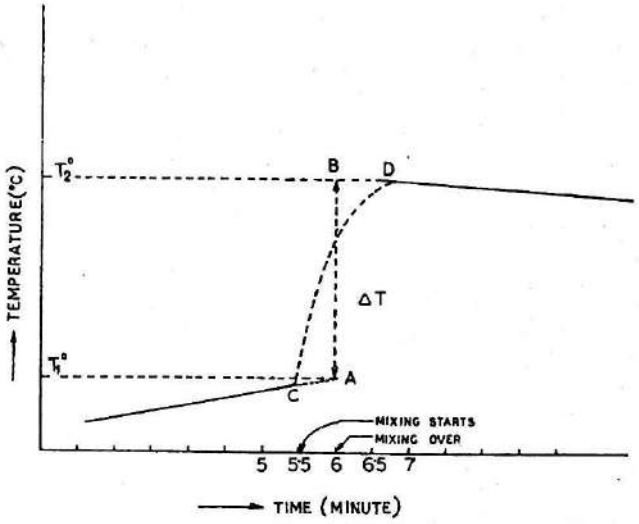


Fig. 16 Temperature-Time Plot

also exist, that is, the temperature may remain constant with time or there may be gradual fall in temperature. If the time of mixing was, say, at the sixth minute, the mean temperature (T_1° C) at that instant is determined from the graph by extrapolation. This corresponds to the point *A*. The highest temperature (T_2°C) which would have been reached in the absence of radiation is obtained by drawing a straight line through the last set of readings (which the fall of temperature has become uniform), and extrapolating this line so as to cut the perpendicular at the sixth minute. This gives the point *B*. The distance *AB* then gives the true rise of temperature (T_2°C—T_1°C). The dashed line *CD* shows the temperature rise after mixing. At the end of the experiment, add a drop of phenolphthalein and be sure that all hydrochloric acid has been neutralised.

Results and Calculations:

Record the temperature and time in the following way:

Time (min.)														
Temperature (°C)														

Plot a graph of temperature against time, and obtain the temperature rise from extrapolation of the readings to the time of mixing. Let the temperature rise be T_2°C—T_1°C = ΔT°C.

$\therefore$ Heat evolved $= (m_1S_1+m_2S_2+m_3S_3+m_4S_4)\Delta T$

where m_1, m_2, m_3 and m_4 are the masses of the solution, calorimeter, thermometer and stirrer respectively, and S_1, S_2, S_3, and S_4 their specific heats. As regards the specific heat of the solution, this will vary more or less from that of pure water according to the concentration of the dissolved salt. With the solutions of the concentrations used above, it will be sufficiently accurate for the present purpose to take the water equivalent of the solution (i.e. its mass $\times$ sp. heat) as being equal to that of the water contained in it. (In the present case, m_1S_1=500 cal *per degree.*)

In the case of the thermometer, which consists of glass and mercury, the weight of which can not be determined separately, the water equivalent is obtained by making use of the fact that the specific heat on volume basis (i.e. per ml.) of glass and mercury is practically the same and equal to 0.47 per millilitre. (1 cc of glass has the water equivalent, $2.5\times0.19=0.47$, as 1 cc. of mercury, $13.6\times0.034=0.46$). To obtain the volume of the immersed portion of the thermometer, a beaker of water is counterpoised on the balance, and then the thermometer is supported on a stand so that the bulb is immersed in the water. The weight which has now to be added in order to obtain equipoise gives the volume of the portion of the thermometer under water. Multiply the weight of displaced water by 0.47 to obtain the water equivalent of the bulb (immersed portion of the thermometer).

Now, number of gram molecules of HCl=.....

Heat of neutralisation per mole of HCl=.....Cal.

[The following are the specific heats of the usual metals employed for calorimeter and stirrer:—Platinum—0.032; Silver—0.046; Copper—0.092; Nickel—0.109]

8.2 DETERMINATION OF HEAT OF IONIZATION OF PHENOL

Theory:

The heat of neutralisation of a strong acid with a strong base is 13.7 kcal/mole. Since some energy is required to ionize a weak acid, the heat of neutralisation of a weak acid with a strong base is generally less than 13.7 kcal/mole. According to Hess's law, the resultant heat change in a chemical reaction is the same whether the reaction takes place in one stage or by several intermediate stages. The neutralisation of phenol by a strong base can be represented in the following manner:

$$C_6H_5OH + Na^+ + OH^- \xrightarrow{\Delta H\text{neutralisation}} Na^+ + C_6H_5O^- + H_2O$$

$$\downarrow \Delta H \text{ ionization} \qquad \uparrow -13.7\text{kcal.}$$

$$C_6H_5O^- + H^+ + Na^+ + OH^-$$

Following Hess's law, $\Delta H\text{neutralisation} = \Delta H\text{ionization} - 13.7$ kcal ... (1)

Materials:

Simple calorimeter, 0.5N sodium hydroxide and 0.5 N phenol solutions.

Procedure:

Follow the same procedure as given in Experiment No. 8.1

Results and calculations:

Calculate the heat of ionization with the help of equation (1).

Suggestions for further work:

Heat of ionization of acetic acid can be determined in the same manner.

Heats of Neutralisations of Weak acids with strong bases :—

(*a*) $CH_3COOH + NaOH$ aq. $\Delta H = -13.3$ Kcal

(*b*) $C_6H_5OH + NaOH$ aq. $\Delta H = -6.5$ kcal

8.3 Determination of heat of solution of potassium chloride

Theory:

The integral heat of solution is defined as the heat absorbed or liberated when one gram mole of a substance is dissolved in a given quantity of a solvent. When the resultant solution is very dilute the integral heat of solution is almost constant and is sometimes called the total heat of solution.

The heat change involved in dissolution of a salt in water occurs by two stages.

(*a*) heat required to separate the anions and cations from their positions in the crystal lattice (*i. e.* lattice energy). (This is endothermic).

(*b*) heat evolved when the ions become hydrated. (This is exothermic)

In most cases, however, the lattice energy is greater than the sum of the heats of hydration. The total heat change is, therefore, endothermic.

Materials:

Potassium chloride (powdered).

Procedure:

Weigh about 20 gm of potassium chloride on a watch glass. Take 200 ml. of distilled water in a calorimeter. Allow the apparatus to stand for 15 minutes. Then stir the water and read the temperature

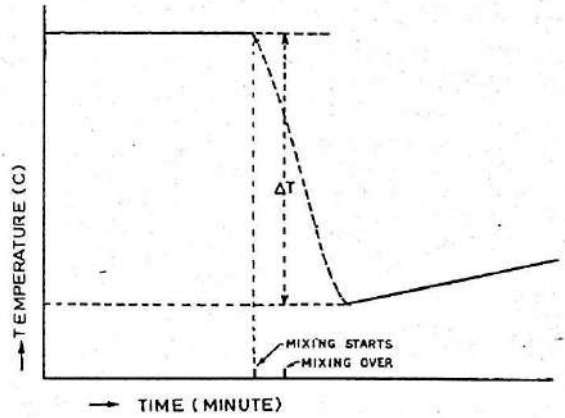


Fig. 17. Temperature-Time Plot (calorimetry).

every minute for 5 minutes. Next add the salt into the water, stir and read the temperature every half minute until the rate of change becomes steady for 5 minutes. Find out the fall in temperature corrected to the time of mixing as discussed in expt. No. 8.1 (see Fig. 16).

Results and calculations:

Heat absorbed (x) $= \Delta T$ [mass of water + (mass of calorimeter $\times$ sp. heat. of calorimeter) + mass of potassium chloride $\times$ sp. heat of potassium chloride.

$\therefore$ Heat absorbed when 1 mole of potassium chloride is dissolved

$$= \frac{\text{Molecular weight of KCl} \times x}{\text{Weight of KCl}}$$

Suggestions for further work:

Heats of solutions of other salts can be determined.

Salt	sp. heat. (cal/gm.)	Heat of solution (Kcal/mole)
Ammonium chloride ...	0.36	—3.90
Ammonium nitrate ...	0.40	—6.33
Copper sulfate, pentahydrate ...	0.25	—2.80
Potassium chloride ...	0.16	—4'44
Potassium nitrate ...	0.21	—8.46
Sodium chloride ...	0.20	—1.28
Sodium thiosulfate, pentahydrate ...	0.35	—11.37

EXPERIMENT NO. 9

OPTICO-CHEMICAL METHODS

9.1 TO VERIFY WHETHER BEER'S LAW IS OBEYED BY THE GIVEN COLOURED SOLUTION.

Theory:

When a beam of monochromatic light of intensity I_o passes through a medium of thickness d which absorbs at the particular wavelength, the intensity of the emergent beam, I, is less than I_o , According to Lambert's law the following relationship is obeyed—

$$\log_{10}\left[\frac{I_o}{I}\right] \propto d \qquad \ldots \quad (9.1)$$

The quantity $\log_{10}\left[\frac{I_o}{I}\right]$ is termed the optical density O.D. Lambert's law may be tested by using different lengths of the absorbing medium (usually with different cell thickness) and measuring the optical density (at each thickness).

According to Beer's law, in a medium with a single absorbing substance, the optical density (O.D.) is proportional to the concentration, C of that substance:—

$$\text{O.D.} = \log_{10}\left[\frac{I_o}{I}\right] \propto C \qquad \ldots \quad (9.2)$$

Combination of the two laws gives

$$\text{O.D.} = \log_{10}\left[\frac{I_o}{I}\right] = \epsilon Cd \qquad \ldots \quad (9\ 3)$$

It is usual to measure the concentration C in moles/litre and the thickness in cms. In this case, ϵ is the molar extinction coefficient with the unit litre mole^{-1} cm^{-1}.

For any solute the validity of Beer's law may be tested by measuring the optical density at several concentrations in a cell of fixed length. In a graph paper optical density is plotted against concentration and a straight line passing through the origin should be obtained.

In practice the above linear relationship is subject to the following limitations:—(*a*) the light is nearly monochromatic; (*b*) the coloured material absorbs only this light; (*c*) the nature of the absorbing material remains unchanged on dilution, *i.e.* it does not ionise, dissociate, or combine with the solvent in such a way as to change colour.

Apparatus:

There are various types of colorimeter (the directions supplied by the manufacturer should be followed). A schematic description of a common type (Fig. 18) is given below:—

Filters are used for obtaining monochromatic light (light source is generally the tungsten filament operated at low voltage and high

current and constancy of light is obtained by a special transformer, and a stablized voltage supply). A set of six or more filters is necessary so that a suitable one may be selected for a particular solute. After passing through the absorption cell containing the sample, the

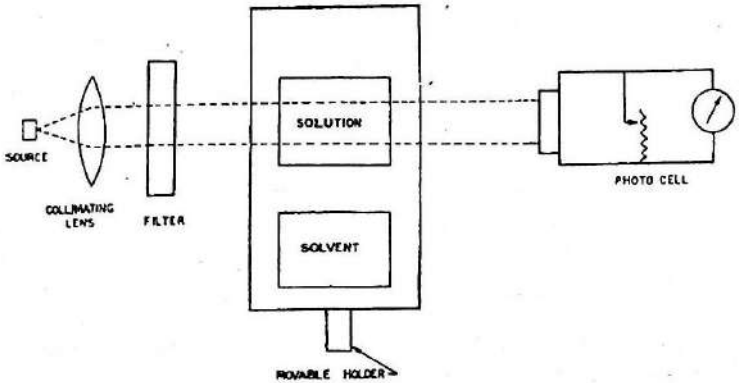


Fig. 18—Colorimeter [schematic]

intensity of the transmitted light is measured. The photoelectric cell with suitable amplifiers is the most sensitive measuring apparatus.

(Modern instruments usually read directly the percentage transmission and/or optical density).

With relatively simple equipments of this type it is better not to take optical density measurements at values higher than unity (that is, with samples of less than 10% transmission). As the light transmitted is further reduced, any errors in its measurement become increasingly serious in terms of optical density. The concentration of solute should be so adjusted that the optical density is less than one.

Materials:

Experimental solution.

Procedure:

Clean and wash the cells. Take the given solution in one cell and solvent in another cell. Take one filter and measure the optical density (following the direction supplied by the manufacturer). Remove this filter and use successively all the filters and note down the optical density (O.D.) in all cases. Select the filter for which O.D. is maximum and use this filter for further work (Table II).

Let the strength of the given solution be X(N). From this solution prepare by exact dilution solutions of different strengths say, X/2(N), X/4(N), X/8(N), X/16(N). Using that particular filter (preceding paragraph) measure the optical density of each of the above solutions.

TABLE I

Filter No.	Optical density

TABLE II

Filter No. (corresponding to maximum O.D.) =.....

Concentration (moles/lit)	Optical density

Plot O.D. *vs.* *C* and verify whether Beer's law is obeyed or not.

Suggestions for further work:

1. The following coloured solutions may be used for this experiment:

(*a*) Copper sulfate solution to which has been added an excess of ammonium hydroxide.

(*b*) Potassium permanganate solution.

(*c*) Iodine solution in acetone.

(*d*) Solutions of various dyes viz., methylene blue, crystal violet in water/alcohol.

2. From the calibration curve (O.D. vs *C*) obtained by this experiment, the unknown concentration of a solute can be found out just by measuring the O.D. of the "unknown" solution with the proper filter.

9.2 To study the ferric-salicylic acid complex absorptiometrically by Job's method of continued variation.

Theory:

A number of phenolic compounds (for example, salicylic acid) form coloured complexes with Fe^{+++} salts—

$$Fe^{+++} + \text{Salicylic acid} \rightleftharpoons \text{Complex (coloured)}$$

The stoichiometry of the complex can be determined by the method due to Job. When equimolar solutions of the two reactants are mixed in varying porportions, the maximum amount of the complex at equilibrium is formed when the proportion of the reactants employed corresponds to the empirical formula of the complex. That is, in $aA+bB \rightleftharpoons A_aB_b$, the maximum amount of A_aB_b is present if a parts of x molar solution of A be mixed with b parts of x molar solution of B. If $a/b=1$, the composition of the complex is AB.

Reagents:

1. $N/500$ HCl; 2. $10^{-3}M$ salicylic acid in $N/500$ HCl;
3. $10^{-3}M$ ferric ammonium alum in $N/500$ HCl.

Procedure:

The optimum pH for the stability of the complex is about 2.6-2.8. This is obtained by using solutions of the reactants in $N/500$ HCl.

Mix the Fe^{+++} and salicyclic acid solutions in different proportions (see Table below) in properly labelled stoppered glass tube (test tube size).

Measure the transmission (or optical density, if possible) for a particular solution (say, solution No. 4), using different filters (i.e., at different wave lengths); and thus choose the filter corresponding to the $\lambda max.$ (*vide* expt. No. 9.1). Using that filter, measure the transmission (or optical density) of each solution.

Results and Calculations:

Filter (corresponding to $\lambda max.$) = ...

Solution No.	Vol. of Fe^{+++} (ml.)	Vol. of Salicylic acid (ml.)	Transmission (or Optical density)
1	9	1	
2	8	2	
3	7	3	
4	6	4	
5	5	5	
6	4	6	
7	3	7	
8	2	8	
9	1	9	

Plot transmission vs. vol. of salicylic acid (Fig. No. 19). Verify whether solution No. 5 shows minimum transmission (i.e. maximum absorption of light). If it does so, the composition of the complex can be suggested as [Fe (salicylic acid)]$^{++}$.

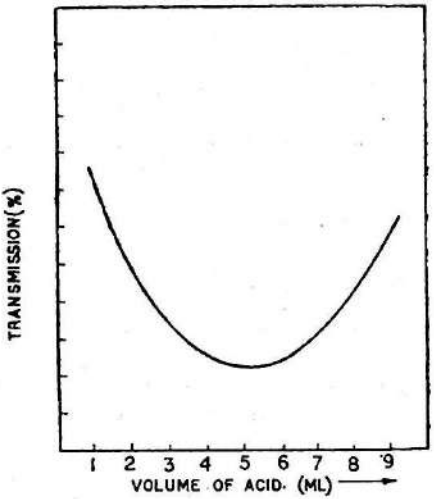


Fig. 19—Job's Method

In case you choose to plot optical density (instead of transmission) *vs.* volume of salicylic acid, solution No. 5 should show *maximum* optical density (i.e., maximum absorption).

9.3 To determine the dissociation constant of phenolphthalein (indicator) absorptiometrically.

Theory:

Weak acids and bases which exhibit one colour when dissociated and another when undissociated are called indicators. Phenolphthalein is an example of an acid indicator.

If we represent an acid indicator by the general formula HIn, it may ionise in solution as follows:

$$HIn \rightleftharpoons H^+ + In^-$$

In an alkaline medium, phenolphthalein gives In^- (red coloured) because of the shift of the equilibrium point to the right due to the concentration of H^+ being reduced. In acid solutions, however, the point of equilibrium is shifted to the left and phenolphthalein exists as HIn (colourless). According to the law of mass action—

$$K_{in} = \frac{[H^+]\,[In^-]}{[HIn]} \quad \ldots (1)$$

$$= \frac{[H^+].\ \alpha.C}{(1-\alpha).C} = \frac{[H^+]\alpha}{(1-\alpha)} \quad \ldots (1a)$$

where $[H^+]$, $[In^-]$ and [HIn] are the respective concentrations; K_{in} is the dissociation constant of the indicator, also called indicator constant; α is the degree of dissociation of the indicator *i.e.*, the fraction present in the alkaline from (i.e. as In^-); C is the total concentration of the indicator. From equation (1a) it follows that—

$$pK_{in} = pH - \log\left(\frac{\alpha}{1-\alpha}\right) \quad \ldots (2)$$

where $pK_{in} = -\log [K_{in}]$ and $pH = -\log [H^+]$.

It is evident from equation (2) that as the pH of the solution increases, $\log\left(\frac{\alpha}{1-\alpha}\right)$ increases ($\because$ pK_{in} = constant). That is, there will be greater dissociation (larger α). At pH $\approx$ 10, phenolphthalein is practically completely dissociated (i.e. $\alpha \approx 1$). On the other hand, at pH = 7 and below, it is assumed to exist practically completely in the undissociated form.

Now, αC = Concentration of the dissociated form;

and $(1-\alpha)C$ = Concentration of the undissociated form.

According to Beer—Lambert law,

$$\text{Optical density} = \log\left(\frac{I_o}{I_t}\right) = \epsilon ct, \quad \ldots (3)$$

Where I_o = Intensity of incident light.

I_t = Intensity of transmitted light,

ϵ = Extinction coefficient of the solute.

c = Concentration of the coloured solute in moles/lit $= \alpha C$.

and t = Thickness of the solution tube in cm.

In the present case, equation (3) can therefore be written as—

$$\text{O. D.} = \log\left(\frac{I_o}{I_t}\right) = \epsilon(\alpha C)t \quad \ldots (4)$$

If, instead of measuring optical density, the instrument reads transmittance, T where $T = \left(\frac{I_t}{I_o}\right)$, it follows—

$$-\log T = \epsilon.\ (\alpha Ct.) \quad \ldots (5)$$

Equation (5) shows that with increase in α, the degree of dissociation, the solution absorbs more light and transmittance decreases. When $\alpha = 1$ (i.e., at pH 10), we get from eqn. (5)—

$$-\log T_{min.} = \epsilon\ Ct \quad \ldots (6)$$

where $T_{min.}$ corresponds to the light transmitted at complete dissociation (i.e., minimum transmittance), Dividing equation (5) by equation (6), one gets—

$$\frac{\log T}{\log T_{min.}} = \alpha \quad \ldots (7)$$

If α be known the pK_{in} can be calculated using equation (2).

Materials:

(1) Exactly 0.2 *M* NaOH; (2) Exactly 0.2*M* Boric acid (1.2368 gm. per 100 ml.); (3) Freshly prepared phenolphthalein indicator solution (dissove 0.1 gm. of indicator in 50 ml. of 95 per cent alcohol and then take 5 ml. of this solution and mix with 45 ml. of water); (4) saturated solution of sodium carbonate.

Procedure:

Prepare the buffer solutions of different pH in properly labelled dry concial flasks by mixing proper amounts of 0.2 *M* NaOH and 0.2 *M* boric acid as shown in table I.

To each solution (from No. 1 to No. 10) add three drops of the indicator. Take solution No. 10 and then measure the λ_{max}.

At λ_{max} (use proper filter) measure the transmittance of each solution. Transmittance of solution No. 10 corresponds to T_{min}.

Results and Calculation:

Filter No. (corresponding to λ_{max}) = ...

Table I

Solution No.	Volume of 0.2*M* NaOH ml.	Volume of 0.2*M* boric acid ml.	pH of the buffer solution	Transmission % (T)	$\alpha = \log T / \log T_{min}$	pK_{in}	Mean pK_{in}
1	0	10.0	6.90				
2	0.5	9.5	7.49				
3	1.0	9.0	7.94				
4	1.5	8.5	8.30				
5	2.0	8.0	8.66				
6	2.5	7.5	8.78				
7	3.0	7.0	8.99				
8	3.5	6.5	9.12				
9	4.0	6.0	9.46				
10	Saturated Na_2CO_3 solution (10 ml).			...T_{min}			

If the instrument gives values of optical density instead of transmittance, equations (5) to (7) should be changed accordingly.

9.4 To determine the pH of the given solution colorimetrically.

Theory:

(Consult experiment No. 9.1).

Equation (2) of experiment No. 9.3 can be written as—

$$pH = pK_{in} + \log \frac{[\text{Basic form}]}{[\text{Acid form}]} \quad \ldots \quad \ldots \quad (1)$$

Both forms of the indicator are present at any hydrogen-ion concentration. It must be realised that the human eye has a limited ability to detect either of the two colours when one of them predominates. Experience shows that the solution will appear to have the "acid" colour when [Acid from]/[Basic form] is above approximately 10, and the "alkaline" colour when [Basic form] / [Acid from] exceeds approximately 10.

Thus, for "acid" colour, equation (1) reduces to

$$pH = pK_{in} - 1$$

whereas for "alkaline' colour.

$$pH = pK_{in} + 1$$

Therefore, the colour-change interval is—

$pH = pK_{in} \pm 1$ (i.e. approximately ovei two pH units).

Within this range the indicator will appear to change from one colour to the other. Moreover, the colour change will be gradual, since it depends on the ratio of the concentrations of "acid" and "basic" forms. Thus, phenolphthalein is said to have pH range of 8.3—10.0. Now, if the given solution has a pH within this range (i.e., 8.3—10.0), then phenolphthalein can be used to determine its pH. The method consists of:—(*i*) to prepare a number of buffer solutions in the range of the indicator, (*ii*) then to add the same quantity (2 or 3 drops) of indicator to equal volumes of all buffer solutions as well as of the unknown solution, and (*iii*) to match the colour of the unknown solution against the colour of the buffer solutions. The one which gives the same tone and intensity of colour as the unknown solution correspnds to the desired pH.

Meterials:

1. Buffer solutions; 2. Indicators (or indicator solutions) (*See* Table-1)

Procedure:

Colorimetric determination of pH consists of two steps—(*i*) Choice of the correct indicator; (*ii*) Matching of colour.

Choice of correct indicator:

Take 5 ml. of the given solution in a test tube; add three drops of an indicator (Start from indicator No. 1 in the following table). If

the buffer shows strongly alkaline colour, evidently this indicator is unsuitable. Repeat the experiment with indicator No. 2 and successively with other indicators in the series until an indicator showing mixed colour is found. This is the "correct" indicator.

Once the "correct" indicator is chosen, the next step is to prepare buffer solutions of graded pH (in steps of, *say*, 0.1 pH) covering its entire pH range.

Take equal volumes (say, 10 ml.) of buffer solutions as well as the same volume of the given solution in properly labelled stoppered glass tubes of identical dimensions (small test tube size). Add equal volumes (2 or 3 drops) of the indicator solution to each solution and shake carefully.

Matching of Colour:

Match the colour of the given solution of unknown pH against the colour of the buffer solutions and find out the particular buffer solution which has the same colour intensity as that of the given solution. pH of that buffer corresponds to the unknown pH.

Matching of the colours by visual means has many limitations and for more accurate work, a colorimeter should be used (See expt. No. 9.1).

Table I

Serial No.	Indicator	Composition* of solution, per cent.	pH range	Colour	
				alkaline	acid
1.	Thymol blue	0.04	1.2-2.8	yellow	red
2.	Bromo phenol blue	0.04	4.0-4.6	blue	yellow
3.	Chloro phenol red	0.04	4.8-6.4	red	yellow
4.	Bromo thymol blue	0.04	6.0-7.6	blue	yellow
5.	Phenol red	0.02	6.8-8.4	red	yellow
6.	Phenolphthalein	0.02	8.3-10.0	red	colourless
7.	Alizarin yellow R	0.01	10.1-12.0	orange red	yellow

*Stock solutions of indicators are usually made by dissolving 0.1 gm. of the indicator in 50 ml. of 95 per cent alcohol. Mix 10 ml. of the stock solution with 40 ml. of water in order to make 0.04 per cent. Similarly, for 0.02 per cent, mix 5 ml. of the stock solution with 45 ml. of water; for 0.01 per cent, mix 2.5 ml. of the stock solution with 47.5 ml. of water.

Suggestions for further work:

Instead of using such laborious colorimetric procedure, universal indicators covering a wide pH range may be used. pH papers sensitive over definite pH ranges are also in extensive use nowadays. pH meters with glass electrode are very convenient for measuring pH of a variety of substances in the laboratory and in industries.

9.5 To determine the index of refraction of a given liquid and to find its specific and molecular refractivity.

Theory:

When a monochromatic ray of light passes from one transparent isotropic medium into another, it is refracted. According to Snell's law, the degree of refraction is such that the ratio (n) of the sine of the angle of incidence to the sine of the angle of refraction is constant. This ratio is equal to the ratio of the velocities of the light in the two media. Hence,

$$n = \frac{\text{Sin } i}{\text{Sin } r} = \frac{V_1}{V_2}$$

where V_1 is the velocity of light in vacuum and V_2 is that in the other medium; this makes the ratio, n a characteristic constant which is always greater than unity and is called refractive index.

In practice, the reference medium is air instead of vacuo. Therefore, the refractive index with respect to air should be multiplied by the ratio $V_{vacuum}/V_{air}=1.00029$ in order to get the true refractive index. This correction is unnecessary except for work of very high accuracy.

The refractive index of a liquid varies with temperature and pressure, but the specific refraction (r) defined by Lorenz and Lorentz is independent of these variables. According to Lorenz and Lorentz,

$$r = \frac{n^2-1.}{n^2+2} \cdot \frac{1}{d}\ ;\ R = \frac{n^2-1}{n^2+2} \cdot \frac{M}{d}$$

where d is the density of the liquid. When specific refraction is multiplied by the molecular weight, M one obtains the molecular (or molar) refraction, R.

Principle of the method:

Abbe refractometer is widely used for general laboratory practice, because it is easy to handle and so constructed that it can be worked with ordinary daylight and manipulated to give refraction values corresponding to the sodium D lines.

The apparatus (Fig. 20) consists of two prisms; the lower prism (P_1) has a ground glass diagonal face and is used to confine and illuminate the test sample; the upper prism (P_2) is the refracting prism. While light is reflected into P_1, where it is scattered at different angles at the ground-glass surface, some of the scattered light passes into the liquid (held between the two prism) at nearly grazing incidence (i.e., i=90°, *critical ray*) and produces a sharp boundary (position N) in the telescope. The position of this boundary is calibrated in terms of refractive index on a scale. Since white light is used, critical rays

having different wave lengths are produced. Therefore, the critical boundary is diffuse and coloured because of the dispersion of these rays by the sample and the prism. The colour of the critical boundary is removed by two identical Amici prisms A_1 and A_2 which can be

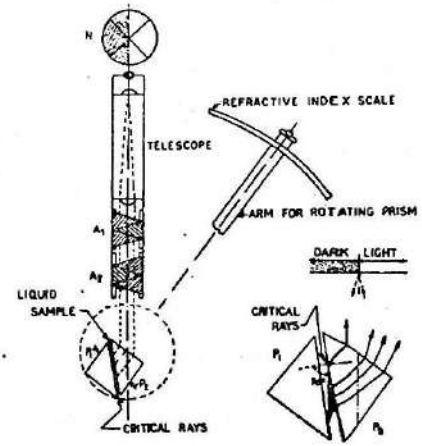


Fig. 20—Principle of Abbe Refractometer.

so adjusted as to produce a dispersion which is equal and opposite to that caused by the sample and the prism. When this adjustment has been done, the critical boundary is sharp and colourless. The Amici prisms are so constructed that the rays for the sodium D line are not deviated while rays of all other wave lengths are deviated. Thus, the refractive index is obtained for the sodium D line.

Meterials:

(1) Unknown liquid; (2) Distilled water; (3) Lens paper (or cotton moistened with alcohol) to clean the prisms of the refractometer.

Apparatus:

A schematic representation of the apparatus is shown in Fig. 21. The prisms can be rotated by means of a movable arm A, so as to set the critical boundary of the cross hairs in the eyepiece. The position of the critical border line is observed through the fixed telescope T and by turning A it is made to coincide with the intersection of the cross-hairs in the telescope (Position N, Fig. 20. The position of the arm is read on a curved scale (S) which is graduated directly into refractive indices (between 1.3 and 1.7) so as to read the values to the third decimal place directly. The fourth decimal is estimated with an accuracy of 2 units by means of the lens L. The compensator C, composed of two similar Amici prisms, rotated simultaneously in opposite directions by the milled head G, is used to produce a dis-

persion equal but opposite to that of the liquid and allows the border line to be changed from a coloured band to a sharp, colourless line.

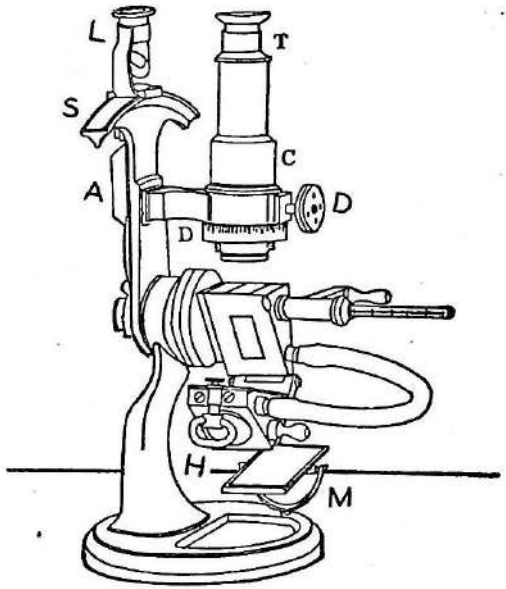


Fig. 21—Abbe Refractometer.

Procedure:

Place the instrument on a table near the window (but not in direct sunlight), and make connections for the circulation of water through the casings in a slow but steady stream, the water being supplied from a constant temperature bath.

Turn the latch *H*, and release the lower prism. Clean the prisms by swabbing them gently with cotton moistened with alcohol. Be careful not to scratch the soft glass of the prisms.

In order to test the correctness of the adjustment of the instrument, place a drop of distilled water on the glass surface and close the prisms with the help of the latch. Next rotate the prisms with the movable arm until the border line appears in the field. It may be necessary to rotate the mirror (*M*) so that light enters the window prism.

Turn the screw head *D* and thus adjust the compensator so that the colour band due to dispersion disappears and a sharp boundary line is obtained. Next rotate the arm *A* until this line coincides with the intersection of the cross hairs and read the refractive index reading to the fourth decimal place.

Note down the temperature. Repeat the readings at least three times and take the mean. Compare the result with the data given in the Appendix.

Open the latch, release the lower prism, clean the polished glass surfaces with a little alcohol and cotton (or lens paper). Measure the refractive index of the liquid assigned for investigation in exactly the same manner as outlined above. Repeat three times and take the mean value.

Determine the density of the liquid at the temperature at which refractive index measurements were made. Use pyknometer for this purpose (*vide*, Expt. No. 1.).

Results and Calculation :

Temperature = ...
n for water = ...
(Literature value)

Water		Liquid				
n	mean n	n	Mean n	density d gm/ml.	$r=\frac{n^2-1}{n^2+2}\cdot\frac{1}{d}$	Molar refraction $=M\times r$
	...		...	...		

Compare your value with that calculated from refraction equivalents of atoms and structural units—(*Appendix*, Table XVII)

Suggestions of further work:

1. Determine the molar refraction of the following pairs of liquids: (*i*) Methyl acetate and ethyl acetate; (*ii*) Acetic acid and propionic acid; (*ii*) Benzene and toleuene. Find out the contribution of $>CH_2$ group to the molar refraction.

2. Concentration of a solute in a solution (*say*, of KCl in aqueous solution) can be determined by refractivity measurements.

Prepare solutions of known concentration and measure refractive index (n) of each. Plot n vs c, the concentration; this gives the calibration curve. Measure n of the "unknown" solution and read the concentration of the solute from the calibration curve.

9.6 To determine the specific rotation of cane sugar.

Theory:

It is well known that when ordinary light is passed through a Nicol prism, the emergent light has the vibrations in ether in one plane, and the light is said to be plane-polarised. When a second Nicol prism is placed at right angles to the first (*crossed Nicols*), no light can pass through and the field of view appears dark. However, on rotating

the second prism, the field of view appears alternatively light and dark, the maximum of darkness following the minimum as the prism is rotated through an angle of 90°. The first prism, by which the light is polarized is called the polarizer; and the second prism by which the light is analysed is called the analyzer.

Let us suppose that the axes of the two prisms are at right angles to each other (i.e. crossed position) so that the field of view appears dark. At this set-up, if a tube containing a solution of cane sugar is placed between the two prisms, light can be seen through the analyzer; and the analyzer must be turned through a certain angle, α, in order to make the field of view dark again. The solution of cane sugar has therefore the power of rotating the plane of polarised light through a certain angle. Besides cane sugar, solutions of camphor, tartaric acid and many other substances behave similarly. All these substances are said to be *optically active*. The angle through which the analyzer must be rotated to darken the field again is the measure of the optical rotation. If the analyzer is turned clockwise (i.e. to the right), the optically active substance is said to be dextro-rotatory; and if the analyzer has to be turned anticlockwise (i.e., to the left), the substance is said to be laevo-rotatory.

The extent of rotation depends on the following:—(1) the nature of the substance; (2) the length of the tube containing the solution through which the light passes; (3) the temperature; (4) the nature of the solvent; and (5) the wave length of the light used (the shorter the wave length, the greater the angle of rotation). In order to take these factors into account, one defines a quantity, *the specific rotation*, by the following relation:

$$[\alpha]_{\lambda}^{t} = \frac{100\alpha}{lC} \qquad \ldots (1)$$

where $[\alpha]^t\lambda$ is the specific rotation of the substance at t°C and the wave length of light is λ; l is the length of the light path in *decimeters*. C is the concentration of the solute in gms per 100 ml. solution. Thus, $[\alpha]_D^{25°}$ means the specific rotation for the D line (sodium light) at the temperature 25°C.

Materials:

Sugar.

Procedure:

The arrangement of the optical parts of a polarimeter is shown schematically in Fig. 20.

S is the light source for monochromatic light and
L is the lens which makes the rays of light parallel.
P is the polarizing prism and
T is the observation tube;
A is the analyzing prism and *EF* is the telescope.

G is a graduated disc provided with verniers which can be caused to rotate along with the analyzer and the telescope.

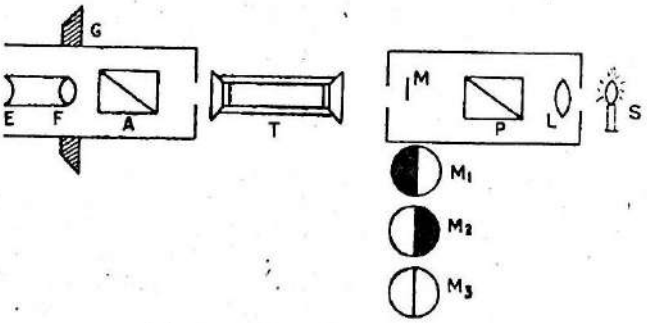


Fig. 22—Polarimeter (*Schematic*).

M is a small Nicol prism which covers half of the opening at the end of the polarizer tube; on passage through M, the light is altered in phase by half a wave length, but still remains plane-polarised. In this way, two beams of polarised light are produced. If the polarizer is rotated so that the plane of polarization forms an angle θ with the optical axis of the Nicol prism, the two planes of polarization will also be inclined at an angle equal to 2θ. This is called the half-shadow angle. Now, on rotating the analyzer, a position will be obtained when only one half of the field of view will appear dark while the other half will remain bright (in Fig. 22 position M_1). On rotating the analyzer further through an angle of 2θ, another position will be obtained when that half of the field which was previously bright will now appear dark and that formerly dark will appear bright (Position M_2). However, an intermediate position of the analyzer can be obtained when the field of view will appear of uniform brightness (position M_3); this is the position where the analyzer is to be set and the corresponding reading of the scale is to be recorded. The scale is usually graduated directly into quarters of degrees and with the aid of verniers and a magnifying glass, the angles may be read to 0.01°. It is be noted that by diminishing the angle, θ, the sensitiveness of the instrument can be increased (because, now the angle 2θ through which the analyzer must be rotated in order to get the field of uniform illumination, is diminished); but with decrease in the half-shadow angle, difficulty (i.e. straining of the eyesight) may arise in determining the field of uniform illumination. The angle of the half-shadow is to be so adjusted (by rotating the polarizer) that there is least difficulty (i.e. without unduly straining the eyesight) in determining the field of uniform illumination.

For ordinary laboratory work, monochromatic yellow light of incandescent sodium vapour is used as the light source. The light source should be placed at the focal distance from the end of the polarimeter (about 20 cm.) and should not be too close to heat the instrument.

The observation tubes are generally 1 dcm.(10 cm.) long. In many cases these tubes are made equal to some multiple of 1 dcm., e.g., 2 or 4 dcm., or even a fraction, e.g., 0.5 dcm. The observation tube is surrounded by metal jackets through which water at constant temperature (i.e., from a thermostatic bath) can be circulated by means of a pump.

Determination of zero points: Set up the polarimeter as described above. Wash the observation tube (previously cleaned with chromic acid) several times with distilled water and fill up the tube with distilled water (take care that no air bubbles remain inside). The glass plates at the two ends of the tube must be clean and the outer surfaces of the plates must be dry. Focus the telescope eyepiece on the line bisecting the field of view. Rotate the analyzer so as to get unequal illumination of the two halves of the field of view. Rotate the analyzer further in suitable directions until equal illumination of both halves of the field of view (position M_3) is obtained. Note down the readings on each side of the scale. This gives the right and left zero points. These zero readings when subtracted from the corresponding readings on solutions of the optically active substance give the angles of rotation. The zero readings should be taken at the beginning and at the end of each set of determinations.

Determination of the angle of rotation: Prepare a 10% solution of cane sugar (the crystallized sugar should be previously heated to about 105°C, cooled in a desiccator and weighed out accurately). Rinse the observation tube with the sugar solution and fill up the tube with the solution as before. Determine the position of the analyzer at equal illumination of the two halves, as described in the preceding paragraph. The difference between the reading on the right and the zero on the right gives the angle of rotation. Since, however, the circular scale may not be exactly centred, one should take the *average* of the readings on the right and the readings on the left side as the angle of rotation (α).

Find out the specific rotation of cane sugar at the experimental temperature, using equation (1).

[The value of $[\alpha]_D^{28°}$ for cane sugar varies slightly with concentration and is $+66.67°-0.0095C$, where C is the weight of the sugar in grams per 100 ml. of solution. The following relation holds good over the temperature range 14° and 30°C.

$$[\alpha]_D^t = +66.67-0.0247\ (t-20)]$$

Suggestions for further work

(1) Concentration of sugar in an unknown solution can be determined polarimetrically as follows:

Prepare 10%, 7.5%, 5%, 2.5% and 1.25% sugar solutions by weight. Measure the angle of rotation (α) in each case. Plot α against C, the concentration; this gives the calibration curve. Measure the

angle of rotation of the unknown solution; from the calibration curve, find out the concentration of the unknown solution. [Note that the slope of the calibration curve multiplied by 100 (with a decimeter long observation tube) gives the specific rotation].

2. Other optically active substances, such as tartaric acid or camphor may be studied in the same manner as sugar. Nonaqueous solution may also be used (for example, camphor in benzene or carbon tetrachloride).

3. The effect of wave length of the light on the rotation can be studied, provided there is arrangement for obtaining lights of different wave lengths.

4. Kinetics of some reactions (for example, inversion of sucrose) can be studied by polarimetric means (see expt. No. 10.3).

EXPERIMENT NO. 10

REACTION KINETICS

10.1 To determine the rate constant of the hydrolysis of methyl acetate catalysed by an acid.

Theory:

When methyl acetate reacts with water it is hydrolysed, the reaction being catalysed by acid (e.g. HCl)—

$$CH_3COOCH_3 + H_2O \rightleftharpoons CH_3COOH + CH_3OH$$

In the presence of a large amount of water the reaction is a pseudo-unimolecular reaction for which the following rate equation applies—

$$-\frac{dC}{dt} = kC \qquad \ldots (1)$$

where C represents the concentration of methyl acetate at time t and k is the rate constant or velocity constant. The hydrochloric acid is not consumed during the reaction and the reaction produces acetic acid. Consequently the progress of the reaction can be followed by withdrawing measured samples and titrating with alkali at timed intervals and at the end of the reaction.

Let the titre at infinite time be T_∞, the titre at time zero be T_0 and the titre at time t be T_t. Thus the initial concentration of ester C is proportional to the total change in titre, $(T_\infty - T_0)$ and the concentration, C at any time t is proportional to the titre value yet to change, *i.e.*, $(T_\infty - T_t)$. Equation (1) can be integrated as follows,

$$-\int \frac{dC}{C} = k \int dt$$

$$\text{or } -ln\ C = kt + \text{Const.}$$

$$\text{at } t = 0,\ C = C_0 \qquad \therefore\ -ln\ C_0 = \text{Const.}$$

$$\text{Thus, } ln\ \frac{C_0}{C} = kt$$

$$\text{or} \qquad k = \frac{2.303}{t} \log \frac{C_0}{C} \qquad \ldots (2)$$

where C_0 is the initial concentration of the ester. Eqn. (2) can also be written in the form

$$k = \frac{2.303}{t} \log_{10} \frac{T_\infty - T}{T_\infty - T_0}$$

$$\text{or } \frac{kt}{2.303} = \log (T_\infty - T_0) - \log (T_\infty - T_t)$$

$$\text{or } \log (T_\infty - T_t) = \log (T_\infty - T_0) - \left(\frac{kt}{2.303}\right) \qquad \ldots (3)$$

Hence a graph of $\log (T_\infty - T_t)$ against t should give a straight line with slope equal to $-\frac{k}{2.303}$, from which the rate constant (k) can be calculated.

Reagents:

(1) Methyl acetate; (2) 150 ml. HCl $\left(\frac{N}{2}\right)$; (3) 500 ml. NaOH (0.1N); (4) phenolphthalein indicator.

Procedure:

Take 100 ml. of HCl solution in a clean, dry conical flask and place in a thermostat maintained at close to room temperature (25° to 40°C). Also take about 20 ml. of ester in a dry, clean test tube; cork it and place it in the same thermostat. Allow to stand for 30 minutes to attain the temperature of the thermostat.

Take six 250 ml. conical flasks, each containing 25 ml. of water and some pieces of ice.

Now pipette 5 ml. of the ester into the HCl solution, shake well and record the time at which the pipette is half-emptied. After 5 minutes 5 ml. of the reaction mixtures is withdrawn and delivered into a conical flask containing ice-cold water and titrated immediately with sodium hydroxide solution, using phenolphthalein as indicator. Similar titrations are made at 10,20,30,40,50 and 60 minute intervals after mixing.

In addition to the above, titrate 5 ml. of HCl solution (that is, 5ml. HCl+100 ml. water) directly with the alkali. This is for determining T_o.

The remaining reaction mixture is allowed to stand for 48 hours Take 5 ml. *sample* and titrate with alkali as before. This gives T_∞.

If such a long time is not available, heat the *samples* not too tightly corked, over a water-bath at about 80°C for a couple of hours under refluxing conditions, cool and titrate. This titres is T_∞.

Results and Calculations :

Temperature of the thermostat =...
Volume of NaOH required to neutralise 5 ml. of reaction mixture after 48 hours delay=T_∞ =.....ml.

Time in mins. (t)	Titre (T_t) (ml.)	$T_\infty - T_t$(ml.)	log ($T_\infty - T_t$)
0	... = T_o		
...			
...			
...			
...			
...			
...			
...			
...			
∞	... = T_∞	—	

Plot log ($T_\infty - T_t$) against t.

Slope (from graph) $= -\frac{k}{2.303}$ $\therefore$ k = ... (min.$^{-1}$).

10.2 Studies on the kinetics of iodination of acetone.

Theory:

Iodine reacts with acetone to form acetonyl iodide—

$$CH_3COCH_3 + I_2 = CH_3COCH_2I + HI.$$

This reaction is catalysed by hydrogen ions. If acetone is in large excess, its concentration may be regarded as constant. It is an interesting fact of reaction kinetics that the observed rate $\left(-\frac{d[I_2]}{dt}\right)$ is independent of iodine concentration *i.e.* the rate is of zero order with respect to iodine. That is,

$$-\frac{d[I_2]}{dt} = k\, C_{I_2}{}^0 = k \text{ (here } C_{I_2} = \text{Concentration of iodine)}$$

or, $\quad -d[I_2] = kdt$

or, $\quad [I_2] = -kt + \text{Constant} \qquad \ldots\ (1)$

The rate of the reaction is determined by withdrawing samples from the reaction mixture at known times and measuring the iodine concentration in these samples.

Since the reaction is zero order with respect to iodine, the rate-determining step does not involve the interaction between the ketone and the iodine molecule. The usually accepted mechanism is as follows—

$$HA + CH_3COH_3C \underset{\text{(slow)}}{\rightleftharpoons} H_3C-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}=OH^+ + A^-$$

$$HI + CH_2ICOCH_3 \xleftarrow[\text{(rapid)}]{+I_2} CH_2=\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}-OH + H^+ \quad \text{(rapid)}$$

(enol form)

So in reality what is being measured is the rate of enolisation of acetone.

Materials:

(1) Acetone; (2) 100 ml. $N/2$ H_2SO_4; (3) 60 ml. $N/10$ I_2; (3) 300 ml. N CH_3COONa; (5) 250 ml. $N/100$ $Na_2S_2O_3$.

Note: Iodine Solution is prepared by dissolving 12.692 gms. of resublimed iodine in a saturated solution of 16 gm. KI and diluting to a litre; use proportionately less amount of I_2 and KI to prepare less volume at a time.

Procedure:

Acetone, iodine solution and acid are kept in the thermostat for ½ hr. to attain the constant temperature of the thermostat. The following reaction mixture is prepared in a dry clean stoppered bottle:

Bottle No. I.

Acetone...	10 ml.
Water...	60 ml.
$N/2$ H_2SO_4...	20 ml.

Then run in 10 ml. iodine solution (with a pipette) and start the stopwatch immediately. After suitable interval (*say*, 2 minutes), withdraw 10 ml. sample and run this into 10 ml. *N* sodium acetate in a conical flask, thereby checking the reaction. Immediately titrate the sample with *N*/100 sodium thiosulfate, using starch as an indicator. At least five readings with progress of reaction should be taken. The titre values may be taken as proportional to the iodine concentration, $[I_2]$.

The procedure is to be repeated while varying the acetone concentration, iodine concentration and acid concentration. For this the following mixtures are to be prepared (the total volume remaining constant, 100 ml.):

	Bottle No. II (Iodine conc. halved)	Bottle No. III (Acetone conc. halved)	Bottle No. IV (Acid conc. halved)
Acetone ...	10 ml.	5 ml	10 ml
Water ...	65 ml	65 ml	70 ml
N/2 H_2SO_4 ...	20 ml	20 ml	10 ml
N/10 I_2 ...	5 ml	10	10 ml

Results and Calculations:

Table I

Bottle I		Bottle II		Bottle III		Bottle IV	
Time	Titre value (ml.)	Time	Titre value (ml.	Time	Titre value (ml.)	Time	Titre value (ml.)

Plot directly the titre values (representing I_2 concn. in terms of thiosulfate) *vs.*, time for each bottle and find out rate constant (k) from the slope.

Compare the k's for bottle (I) and (II), (I) and (III), and (I) and (IV)

Table II

Bottle No.	Rate constant, (M. time^{-1})
I	
II	
III	
IV	

Suggestions for further work:

Try if the kinetics of bromination of acetone (acid catalysed) can be studied by similar methods. The Br_2 concentration can be determined by adding fixed amounts of KI in each aliquot and titrating the liberated I_2 with $Na_2S_2O_3$ solution.

10.3 To determine the rate constant of inversion of cane sugar in the presence of an acid.

Theory:

The reaction for the inversion of sucrose (cane sugar) catalysed by an acid is as follows:

$$\underset{\text{(Sucrose)}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{(Glucose)}}{C_6H_{12}O_6} + \underset{\text{(Fructose)}}{C_6H_{12}O_6}$$

The rate of the reaction depends upon the concentrations of sucrose and water and also upon the concentration of hydrogen ion, which acts as catalyst. The concentration of water may be regarded as constant since a large excess is normally present. Under a fixed hydrogen ion concentration the reaction is thus first order with respect to sucrose.

In order to follow the rate of the reaction, use is made of the property of the solution of rotating the plane of polarized light. Whereas cane sugar is dextro-rotatory, invert sugar (mixture of glucose and fructose) is laevo-rotatory, so that, after the reaction, the sign of rotation changes from right to left.

Let A_o represent the initial angle of rotation, A_t the angle at any time t and A_∞ the angle after complete inverstion has occurred. Thus the initial concentration of cane sugar (C_o) is proportional to the total range of change, i.e. $(A_o - A_\infty)$ and the concentration (C) at time t is proportional to the range of angle yet to change, i.e., $(A_t - A_\infty)$.

In accordance with the following expression for a first order reaction (*vide* expt. No. 10.1)—

$$k = \frac{2.303}{t} \log \frac{C_o}{C} \quad \ldots (1)$$

where C_o is the intial concentration, C is the concentration at time t and k is the velocity constant, we can write,

$$k = \frac{2.303}{t} \log_{10} \frac{A_o - A_\infty}{A_t - A_\infty}$$

or, $$\frac{kt}{2.303} = \log_{10} (A_o - A_\infty) - \log_{10} (A_t - A_\infty)$$

or, $$\log_{10} (A_t - A_\infty) = \log_{10} (A_o - A_\infty) - \frac{kt}{2.303} \quad \ldots (2)$$

Hence a graph of log $(A_t - A_\infty)$ against t should give a straight line with a slope equal to $-\frac{k}{2.303}$, from which the rate constant can be calculated.

Materials:

(1) 4*N* HCl (100 ml.); (2) suga.r

Procedure:

Prepare a 20% solution of cane sugar by dissolving 20 gm. of pure cane sugar in water and making the volume upto 100 ml. (if the solution is hazy, filter). Place the sugar solution and HCl solution in separate flasks in the thermostat maintained at room temperature.

Set up the polarimeter and determine the zero (read procedure in expt. No. 9.6). Place a jacketed observation tube in the polarimeter and circulate water through the mantle of the observation tube. The circulation of water through the mantle be so regulated and checked from time to time that the temperature remains constant to $\pm 0.5°C$ throughout the experiment.

The observation tube is dried and replaced in the polarimeter. When the temperature has become constant, pipette out 25 ml. of HCl solution and deliver it into the sugar solution, and, as soon as possible pour the mixture into the observation tube (take care that no air bubble remains). Preserve the remaining mixture for the final reading. Determine quickly the angle of rotation and note the time at which the reading is made. Take subsequent readings after 3,6,10, 15, 20, 30, 40, 60 minutes.

The final reading (A_∞) is taken after 48 hours delay. Alternatively, the temperature of the circulating water is raised to about 70°C and take readings every minute until five successive constant values have been obtained. Then bring back the temperature to room temperature and again take readings every minute until five consecutive constant values have been obtained. At higher temperature the reaction runs to completion quite rapidly and the value at room temperature after complete conversion represents the value of A_∞.

Results and calculation:

Temperature = ...

Time in minutes	Scale reading in degrees	Rotation in degrees (A)	$(A_t - A_\infty)$	log $(A_t - A_\infty)$
0		A_0 = ...	$(A_0 - A_\infty)$ = ...	
.				
.				
.				
.				
.				
.				
.		A_∞ = ...	———	

$$\text{slope} = -\frac{k}{2.303} \text{ (from graph).}$$

$$\text{or, } k = \text{.....(min.}^{-1}\text{).}$$

Suggestions for further work:

1. Different concentrations of the same acid may be used. Thus for two sets of experiments, if k_1 is the rate for acid concentration C_1 and k_2 is the rate for acid concentration C_2, then it will be found that

$$\frac{k_1}{k_2} \approx \frac{C_1}{C_2}$$

2. At a fixed acid concentration, the reaction may be studied at different temperature and the activation energy (E) is calculated from the slope of the plot of $\log k$ against $\frac{1}{T}$ (*vide* Expt. No. 10.5).

3. Instead of hydrochloric acid, trichloroacetic acid, sulfuric acid and monochloroacetic acid (each $4N$) may be used as catalysts. The relative strength of trichloroacetic acid and monochloroacetic acid can be determined from the relative order of rate constants and should be explained on the basis of molecular structure.

10.4 Studies on the kinetics of reaction between hydrogen peroxide and hydriodic acid. (*i*) Determination of the rate constant (*ii*) Determination of activation energy.

Theory:

The reaction

$$2HI + H_2O_2 \longrightarrow I_2 + 2H_2O$$

is believed to proceed in two stages

$$(a)\ HI + H_2O_2 \xrightarrow{\text{slow}} HIO + H_2O$$

$$(b)\ HI + HIO \xrightarrow{\text{rapid}} I_2 + H_2O$$

The rate of the first stage is slow, while the second reaction is almost instantaneous. The order is obviously that of the slower stage (*i.e.* second order).

If the condition of the experiment be so adjusted that there is a constant excess of HI in the reaction mixture, the kinetic order of the reaction with respect to H_2O_2 will be one.

The course of the reaction is followed by allowing the reaction to proceed in the presence of a known (small) amount of sodium thiosulfate and timing the interval which elapses before this is used up, i.e., before iodine appears. Sodium thiosulfate regenerates I^- while removing I_2. The constant excess of HI is thus obtained expermentally by using a large volume of the reaction mixture and continually adding small amounts of thiosulphate solution. The small increase in volume due to addition of thiosulfate is negligible. Thus the concentration of iodide ion is made constant.

The following first order rate equation is thus applicable:

$$k = \frac{2.303}{t}\log\frac{C_o}{C}$$

$$\text{or, } kt/2.303 = \log C_o - \log C \quad \ldots (1)$$

$$\text{or, } \log C = \log C_o - \frac{kt}{2.303}$$

where C_o is the initial concentration of H_2O_2. Therefore, from the plot of log C vs. t, we can get k at any temperature.

From the values of k at different temperatures, the activation energy can be determined by applying Arrhenius equation—

$$k = A.\ \exp.\ [-E/RT] \quad \ldots (2)$$

$$\text{or } \log k = \log \text{A (constant)} - \frac{E}{2.303RT} \quad \ldots (3)$$

where E (the activation energy) and A (the temperature-independent factor) are constants characteristic of the reaction, R is the gas constant (1.987 calories mole^{-1} degree^{-1}) and T is the absolute temperature.

A plot of log k against $1/T$ will have a slope of $-\frac{E}{2.303\ R.}$

Materials:

(1) A 2 vol. solution of H_2O_2 (by necessary dilution of commercial H_2O_2); (2) Dilute H_2SO_4 (1 vol. conc. acid with 2 vol. water, (*Caution!*); (3) A standard solution of sodium thiosulfate (about *N*/5); (4) Freshly prepared starch solution.

Procedure:

Dissolve 2g. of KI in 500 ml. water in a litre flask. Add by means of a graduated cylinder 30 ml. dil H_2SO_4 and well mix with the iodide solution. Place the flask in a thermostat and keep it upright with a retort stand and a ring in such way as to allow sufficient freedom for the flask to be shaken without removal from the bath. Pour into two separate large test tubes 20 ml. H_2O_2 solution and 10 ml. starch solution (with the aid of pipettes). Keep all the solutions in the thermostat for 1/2 hr. During this period titrate the H_2O_2 solution in the following way.

Place 20 ml. of dil. H_2SO_4, 80 ml. water and 2' gm. of KI in a stoppered conical flask. Add 20 ml. of H_2O_2 solution. Mix by shaking and allow to stand for 20 min. Finally titrate the I_2 liberated with the standard thiosulfate. Let this titre value be x.

Note the temperature of the thermostat. Arrange a burette (containing $Na_2S_2O_3$) so that it will deliver into the large flask.

Pour into the flask first the starch solution and the 20 ml. of H_2O_2 from the test tubes. Start the stop watch as the latter is added. Run

from the burette (directly into the solution) about 1 ml. $Na_2S_2O_3$ solution. Note the volume of thiosulfate added and shake the reaction mixture immediately. The blue colour of starch-iodine which developed on the addition of H_2O_2 will be discharged after addition of sodium thiosulfate. After about 3 min. this colour will suddenly reappear and note the time at which this happens. (Do not stop the watch). The colour is again discharged by the addition of another 1 ml. of thiosulfate, which is immediately well mixed by shaking and the time of reappearance of blue colour again noted. Proceed in this way with addition of 1 ml. portions of thiosulfate and timing the reappearance of the blue colour, until 10 ml. in all have been added.

The whole procedure is repeated at different temperatures with the same quantities and concentrations of solutions. Readings for at least 3 different temperatures should be taken. At higher temperature more concentrated $Na_2S_2O_3$ should be used, otherwise the time interval may be too short for accurate observation.

Results and calculations:

20 ml. of $H_2O_2 = x$ ml. of thiosulfate

Table I

Time (min.)	Vol. of thiosulfate (ml.) y	Thiosulfate equivalent of H_2O_2 $C = x-y$	$\log C$

Similar tables will be made for three different temperatures (that is, *Table II*, *Table III* and *Table IV*).

Table V

Temp °K	$1/T$	k (time^{-1})	$\log k$

Slope of the plot of $\log k$ vs. $1/T = -E/2.303$.

$\therefore$ Activation energy (E) = ... K. Cal/mole.

10.5 Studies on the kinetics of the reaction between potassium persulfate and potassium iodide. (*i*) Determination of rate constant; (*ii*) Studies on the influence of ionic strength on the rate constant.

Theory:

The rate of the reaction $S_2O_8^{=}+2I^{-}=2SO_4^{=}+I_2$ probably depends upon the bimolecular slow stage—

$$(I^{-}+S_2O_8^{=}) \rightarrow (S_2O_8I)^{3-}$$

followed by the rapid decomposition of the triply charged anion as $(S_2O_8I)^{3-}+I^{-} \rightarrow I_2+2SO_4^{=}$. The reaction rate can be followed by measurihg the rate of liberation of I_2. The bimolecular velocity coefficient is give by the kinetic expression—

$$\frac{dx}{dt} = k[S_2O_8^{=}]\,[I^{-}]$$

$$= k[a-x]\,[b-2x]$$

which on integration gives

when $b > 2a$, $kt = \frac{2.303}{b-2a} \log \frac{a(b-2x)}{b(a-x)}$ ... (1)

when $b < 2a$, $kt = \frac{2.303}{2a-b} \log \frac{b(a-x)}{a(b-2x)}$ ... (2)

when $b = 2a$ $kt = \frac{1}{2a} \cdot \frac{x}{a-x}$ ... (3)

where a is the initial concentration of $K_2S_2O_8$ in moles/lit. and b that of KI in moles/lit. in the reaction mixture.

For the sake of simplicity of calculation, reaction conditions are to be so chosen that equation (3) is made applicable. This means, KI concentration is to be made double the $K_2S_2O_8$ concentration.

The influence of ionic strength on k:

According to Bronsted-Bjerrum equation, for a dilute solution $\log k = \log k_0 + 1.02\, Z_a Z_b \sqrt{\mu}$, where k is the rate constant at ionic strength μ; k_0 is equal to the rate constant at $\mu=0$; Z_a, Z_b are the charges of the ions in the reaction (here $Z_a Z_b=2$); $\mu=\frac{1}{2}\sum C_i Z_i^2$, C_i is the concentration in gm-ion/lit, and Z_i is the valence of the ion and the sum is over all the different kinds of ions in solution.

Materials:

The following solutions are to be prepared: (1) Standard $N/5$ $K_2Cr_2O_7$ (250 ml.); (2) Standard 0.4 M KI solution (250 ml.); (3) Standard 1M KCl solution (250 ml.); (4) Standard $N/100$ $Na_2S_2O_3$ solution (1 lit); (5) 1% starch starch solution (50 ml.). (6) Standard solution of potassium persulfate. This is prepared as follows:—At first about 100 ml. of saturated solution of $K_2S_2O_8$

is prepared. This is diluted to 500 ml. in a volumetric flask with water. The strength of this solution is determined by pipetting 20 ml. of the solution in a conical flask, followed by addition of 4gm. of solid KI (wait for 15 min.). Add 1—2 ml 6(N) acetic acid and titrate with $N/10$ thiosulfate. The strength of the persulfate solution prepared thus is about 0.07(N) (7). Dilute the 0.4M KI with water so that its strength is exactly four times that of persulfate. (Volume of KI in the reaction mixture will be such that its strength will be twice that of persulfate).

Find out the strength of thiosulfate with standard potassium dichromate solution (consult a book on Quantitative Inorganic Analysis).

Procedure:

The following reaction mixtures are to be prepared in four dry stoppered one liter bottles or conical flasks.

	Bottle I	Bottle II	Bottle III	Bottle IV
Water	250 ml.	225 ml.	200 ml.	175 ml.
$K_2S_2O_8$ soln.	100 ml.	100 ml.	100 ml.	100 ml.
KCl soln	0 ml.	25 ml.	50 ml.	75 ml.
KI soln	50 ml.	50 ml.	50 ml.	50 ml.

The first three components (water, $K_2S_2O_8$ and KCl) are added first and kept in the thermostat for 15 mins. Then from the stock solution of KI (also in thermostat) withdraw 50 ml. of KI (by pipette) and run into bottle I. Start the stopwatch at the time of mixing. At intervals of 5 to 10 mins., withdraw 50 ml. of the reaction mixture and deliver into 100 ml. ice-cold water in a 250 ml. conical flask to freeze the reaction and titrate with $N/100$ sodium thiosulfate. Five such samples are to be so withdrawn and titrated at suitable intervals to determine the progress of the reaction with time.

Similarly, KI is added to other bottles and the procedure repeated as above.

Results and Calculations:

Table I

$b = 2a$ = ... moles/lit

$\therefore\ a$ = ... moles/lit

	Time (min.)	Titre value (ml.)	Titre $\times Ss_2o_3$ / 50 = $2x$ mole/lit.	x moles/lit	$(a-x)$ moles/lit	$x/a-x$
Bottle I						
Bottle II						
Bottle III						
Bottle IV						

Plot $x/(a-x)$ against t and from the slope $(=2ak)$ find k for each set of experiments

Table II

Bottle No.	Slope (from graph)	k lit. mol^{-1} $min.^{-1}$	log k	μ	$\sqrt{\mu}$
I					
II					
III					
IV					

Plot log k against $\sqrt{\mu}$ and find the slope, which should be two in this case.

Discussion:

The Brönsted equation of salt effect follows from the Debye-Hückel equation for activity coefficient. Hence, a verification of the former is in a sense a confirmation of the Debye-Hückel equation.

10.6 Studies on the kinetics of saponification of ethyl acetate by sodium hydroxide (*i*) Determination of rate constant; (*ii*) Studies on the influence of ionic strength on the rate constant.

Theory:

The rate of saponification of ethyl acetate represented by the equation—

$$CH_3COOC_2H_5 + OH^- \rightleftharpoons C_2H_5OH + CH_3COO^-$$

can be followed by measuring the rate of change of the concentration of NaOH with time. The rate equation for a second order reaction is given by—

$$kt = \frac{x}{(a-x)}$$

or
$$kt = \frac{1}{a-x} - \frac{1}{a} \quad \ldots (1)$$

where both the reactants are at the same initial concentration, a and $(a-x)$ is the amount remaining at time t; k is the rate constant, which can be determined from the slope of the plot of $1/(a-x)$ vs. t.

The influence of ionic strength on the rate constant is given by the Brönsted equation (*Vide* expt. No. 10.5)—

$$\log k = \log k_0 + 1.02\, Z_A\, Z_B \sqrt{\mu} \quad \ldots (2)$$

where k is the rate constant at ionic strength μ; k_0 is the ideal value of the rate constant *i.e.* when the reaction occurs at infinite dilution ($\mu=0$); Z_A and Z_B are the charges on the reactants (A,B,). In the present case involving a neutral molecule ($Z_A=0$) and a univalent ion ($Z_B= -1$) the specific rate is expected to be independent of the ionic strength provided the latter is low enough for the Debye-Hückel theory to be applicable.

Materials:

(1) Exactly $N/30$ NaOH solution (from$\approx N/25$ NaOH) (2) Exactly $N/6$ Ethyl acetate solution; (3) $N/30$ HCl; (4) $N/30$ Succinic acid; (5) 1M KCl solution;

Take 25 ml $N/30$ succinic acid and titrate with $N/25$ alkali. Knowing the strength of alkali calculate how much water is to be added to a known volume of $N/25$ NaOH to make it exactly $N/30$ ($=S_{NaOH.}$)

Find out the density of ethyl acetate. Knowing its molecular weight calculate how many ml. of the ester is to be taken to prepare a known volume of exactly $N/6$ ethyl acetate.

Procedure:

The following reaction mixtures are to be prepared in 4 clean, stoppered 500 ml. bottles or conical flasks.

	Bottle No. I	Bottle No. II	Bottle No. III	Bottle No. IV
N/30 NaOH	125 ml.	125 ml.	125 ml.	125 ml.
Water	100 ml.	50 ml.	25 ml.	0 ml.
1*M* KCl	0 ml.	50 ml.	75 ml.	100 ml.
N/6 ethyl acetate	25 ml.	25 ml.	25 ml.	25 ml.

The first 3 components (alkali, water, KCl) are added first and the mixtures are thermostated. The stock ester solution is also kept in the thermostat. After about 10 to 15 mins (for temperature equilibrium), pipette 25 ml. ester and run into bottle No. I; start the stopwatch at the half discharge of the ester. 25 ml. of sample is withdrawn at intervals of 1 minute for the first 5—6 minutes and afterwards at intervals of 4 minutes, then run into 25 ml. N/30 HCl. The excess HCl is titrated back with *N*/30 NaOH using phenolphthalein indicator.

Similarly run 25 ml. of *N*/6 ester into bottle II, bottle III and bottle IV. The procedure is repeated as above.

Results and Calculations:

Table I

25 ml. *N*/30 HCl = *x* ml. *N*/30 NaOH

	Time	Titre value of *N*/30NaOH, *y*(ml.)	Vol. of *N*/30 unreacted NaOH in the reaction mixture, $(x-y)$ ml.	$\frac{(a-x)=(x-y)}{25} \times S_{NaOH}$ moles/lit.	$\frac{1}{a-x}$	k (from graph) slope of $\frac{1}{(a-x)}$ *vs.t*
Bottle I						
Bottle II						
Bottle III						
Bottle IV						

Table II

Bottle No.	k lit. mole^{-1}sec^{-1}	log k	μ	$\sqrt{\mu}$
I				
II				
III				
IV				

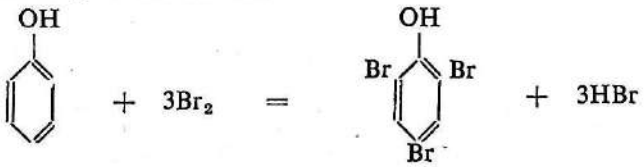
10.7 Studies on a "Clock reaction. Determination of the activation energy of the bromide-bromate reaction.

Theory:

The initial rate of the reaction—

$$KBrO_3 + 5KBr + 3H_2SO_4 = 3K_2SO_4 + 3Br_2 + 3H_2O$$

is measured by the time taken to produce a definite amount of bromine which is consumed by a definite quantity of phenol present in the system according to the reaction—



When the fixed amount of bromine has been used up, the excess bromine liberated is allowed to react with methyl red. The indicator turns colourless. Therefore, in the presence of the indicator (methyl red) the colour change (from red to colourless) corresponds to a definite extent of the reaction. If t is the time taken for this colour change to occur, then

$$k \propto \frac{1}{t} \qquad \ldots (1)$$

where k is the apparent velocity constant of the reaction.

If the same extent of reaction is allowed to occur in identical solutions at different temperature, the activation energy can be estimated following the Arrhenius equation,

$$k = A\, e^{-E/RT} \qquad \ldots (2)$$

where A (temperature-independent factor) and E (the activation energy of the reaction) are both constants, R is the gas constant (1.987 calories mole^{-1} deg^{-1}) and T is the absolute temperature. In the present experiment, equation (2) can be rearranged as:

$$\log_{10}\left(\frac{1}{t}\right) = \text{Constant} - \frac{E}{2.303\ \text{R}} \cdot \frac{1}{\text{T}} \qquad \ldots (3)$$

and consequently a graph of $\log_{10}(1/t)$ against $\left(\frac{1}{\text{T}}\right)$ will have slope of $-(E/2.303\ \text{R})$.

Materials:

(1) 100 ml. bromide-bromate solution (To prepare this mixture mix 50 ml. of M/30 BrO_3^- and 50 ml. of M/6 Br^-); (2) 500 ml. $N/10$ H_2SO_4; (3) 100 ml. 0.01% phenol; (4) Methyl red indicator.

Procedure:

Mix 10 ml. of the bromide-bromate solution with 10 ml. of the phenol solution in a small conical flask and add 3 drops of methyl red. Take 50 ml. of sulfuric acid in another flask. Place the flasks in a thermostat until they attain the thermostat temperature. Add the contents of the first flask into sulfuric acid solution and note the time of mixing (start the stopwatch immediately). Stir the mixture while in the thermostat and note the time when the colour is discharged.

Repeat the experiment under the same conditions at 5 different temperatures.

Results and Calculation:

Temp., °C	Temp. T°K.	$\frac{1}{T}$	Time for a definite fraction of the reaction, t, min.	$\frac{1}{t}$ min^{-1}	$\log\left(\frac{1}{t}\right)$

Plot $\log (1/t)$ vs. $1/T$.

$$\text{Slope} = -\frac{E}{2.303R}$$

$$\therefore \quad E = \ldots \text{ calories per mole.}$$

Suggestions for further work:

1. "*Formaldehyde clock*"—Determination of activation energy of the reaction between formaldehyde and bisulfite.

The initial rate of the reaction—

$$HCHO + Na_2SO_3 + H_2O = Na(O_3SOHCH_2) + NaOH$$

is measured by the time taken to produce a definite amount of NaOH which is consumed by a definite amount of $NaHSO_3$ according to the equation—

$$NaOH + NaHSO_3 = Na_2SO_3 + H_2O$$

When a fixed amount of $NaHSO_3$ has reacted and has been used up, the excess NaOH is allowed to react with phenolphthalein indicator. The indicator turns red. So in the presence of the indicator the colour change from colourless to red corresponds to a definite extent of the reaction. If t is the time taken for this colour change, then

$$k \propto \frac{1}{t}$$

If the same extent of reaction is allowed to occur in identical solutions at different temperatures, the activation energy can be determined using equation (3) as before.

The procedure is as follows:

Prepare the following solutions—

(1) Solution A: Put 24 ml. of aqueous formaldehyde (37-40%) in 1 lit. volumetric flask; add 15 ml. of 1% phenolphthalein solution and make volume up to the mark.

(2) Solution B_1: 0.02M sodium bisulfite (20.8 gm. per liter of solution).

Solution B_2: 0.05M sodium sulfite (6.30 gm. per liter of solution). (If sodium bisulfite is not available, use 38.0 gm. of sodium metabisulfite per liter of solution).

Mix B_1 and B_2 in equal volumes (*i.e.*, 50 ml. B_1+50 ml. B_2) and label it solution B. (These solutions should not be kept over 2 days).

Pipette out 10 ml. of solution A in a conical flask. Pipette out 10 ml. of solution B and pour it into another conical flask. Place the flasks in a thermostat. After say, $\frac{1}{2}$ hour or so, add the contents of the first flask into the second flask (start the stop-watch immediately). Shake the mixture and note the time of appearance of red colour.

Repeat the experiment under similar conditions at different temperatures and treat the data as in the foregoing experiment.

2. These clock reactions (including expt No. 10.4) can be utilised as impressive lecture demonstrations.

10.8. Dilatometric study of the kinetics of hydrolysis of acetal.

Theory:

The rate of the reaction,

$$CH_3CH(OC_2H_5)_2 + H_2O \xrightarrow{(H^+)} CH_3CHO + 2C_2H_5OH$$

is directly proportional to the acetal concentration in the presence of an excess of water and a constant amount of the acid (catalyst). In this reaction the products occupy a larger volume than the reactants. Hence, the change in volume is a measure of the extent of the reaction; this can be studied by means of a suitable dilatometer.

Since the reaction is first order with respect to acetal (vide experiment 10.1),

$$k = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t} \quad \ldots (1)$$

where V_∞, V_0 and V_t refer to the volumes at the end, at the beginning and at time t, trespectively. Here the total change in volume (i.e. $V_\infty - V_0$) is evidently proportional to the initial concentration of the acetal, and the change at any time t (*i.e.* $V_\infty - V_t$) is proportional to the concentration of acetal remaining at time t.

Materials:

(1) 0.4M acetal (freshly distilled) solution; (2) 0.1M HCl solution.

Procedure: The dilatometer is shown in figure 23. A is a 75 m

capacity bulb and *B* is a fine capillary with mm. scale and *C* is a stopcock.

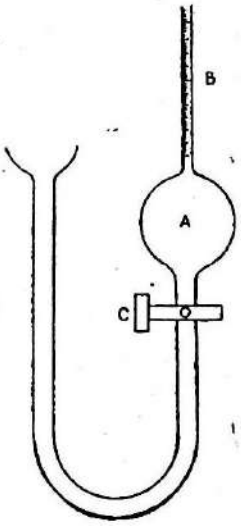


Fig. 23. Dilatometer

Place the solutions in the thermostatic bath. After the solutions have attained the thermostatic temperature, mix 50 ml. of the acetal solution with 50 ml. of acid solution (start the stop watch immediately) and transfer the mixture immediately in the dilatometer (placed in the thermostat). When the level of the reaction mixture reaches the end of the scale, carefully close the stopckock so as to introduce no air bubbles. Record the liquid level in the scale at various intervals of time (i.e. 0, 3, 5, 10, 15, 20, 25, 30, 40, 50, 60, minutes) and call these V_t. When there is no more change in the liquid level (after about 90 minutes), note down the reading, which gives V_∞.

Results and calculations:

Time → (min.)	0	3	5	10	15	20	25	30	40	50	60	∞
V_t → (mm.)	$=V_o$											$=V_\infty$
$(V_\infty - V_t)$ →	$(V_\infty - V_o)$											—
$\log(V_\infty - V_t)$→	$=\log (V_\infty - V_o)$											—

Plot $\log (V_\infty - V_t)$ *vs.* time. From the slope, find out k using equation (1).

Note that V_0 is not directly readable as some time is bound to be lost during filling up and other preliminary manipulations. However V_0 is not at all necessary for calculation of k and if necessary can be obtained by graphical extrapolation.

Suggestions for further work:

The experiment can be repeated at other temperatures and the activation energy can be calculated using Arrhenius equation.

Corrigenda to P. 64

Expt No. 8.1 : Calorimetry

Through oversight the figure of a calorimeter which was to appear on P. 64 as Fig. 16 was omitted. We reproduce below the relevant figure.

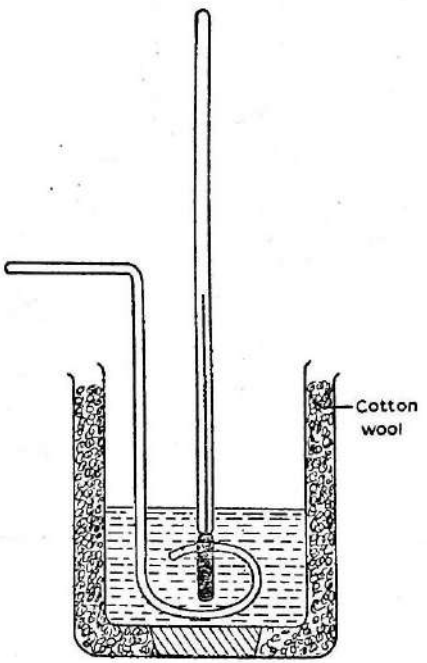


Fig. 16. Calorimeter