of the alkali from the burette and measure the voltage. Squeeze the bulb 3 or 4 times in order to make the solution homogeneous (inside and outside). Add another portion of the alkali and measure the e.m.f. Repeat the process until a sharp change is observed after certain point—which is the equilvalence point. Add in steps of 1 drop (0.05 ml.) when approaching the equivalence point. Take at least 4 readings after equivalence point. (For this experiment, a direct-reading milli-voltmeter of very high resistance can be conveninently used in place of the potentiometer).

The process is the same for all acids and the acid-mixture.

Results and Calculations:

Expt. (*a*)		Expt. (*b*)		Expt. (*c*)	
Results and Calculations: Expt. (*a*)		Expt. (*b*)		Expt. (*c*)	
Vol. of strong acid = 50 ml.		Vol. of weak acid = 50 ml.		Vol. of strong acid = ...ml Vol. of weak acid = ...ml.	
Vol. of alkali added, (ml.)	$\Delta E/\Delta V$	Vol. of alkali added, (ml.)	$\Delta E/\Delta V$	Vol of alkali added, (ml.)	$\Delta E/\Delta V$

Plot $\Delta E/\Delta V$ vs. vol. of alkali in each case. The nature of the plot in expt. (*a*) and (*b*) is shown in Fig. 39 (*a*) while that in expt. (*c*) is shown in Fig. 39 (*b*).

From expt. (*a*)

From expt. (*a*)—

50 ml. of strong acid = ...ml. alkali

From expt. (*b*)—

50 ml. weak acid = ...ml. alkali

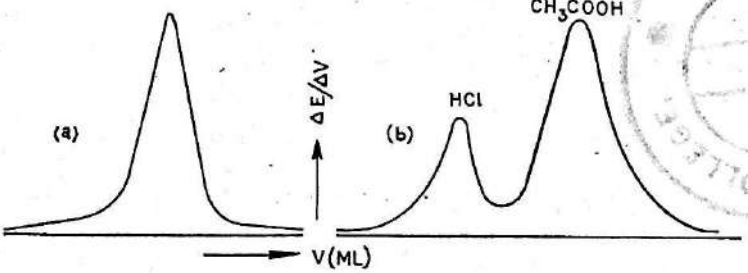

Fig. 39. Plot of $\frac{\Delta E}{\Delta V}$ vs. V

If the strength of alkali is known, calculate the strength of the acid solutions. Check your results from observations in expt. (*c*).

12.13. Determination of the standard oxidation potential of $Fe(CN)_6^{-4}$ — $Fe(CN_6^{-3}$ system.

Theory:

The oxidation potential of the redox system—

$$Fe(CN)_6^{-3} + e \rightleftharpoons Fe(CN)_6^{-4}$$

is given by

$$E = E^\circ + \frac{RT}{F} \ln \frac{a Fe(CN)_6^{-3}}{a Fe(CN)_6^{-4}} \quad (a = \text{activity})$$

$$= E^\circ + \frac{2.303RT}{F} \log \frac{[Fe(CN)_6^{-3}]}{[Fe(CN)_6^{-4}]} + \frac{2.303RT}{F} \log \frac{f Fe(CN)_6^{-3}}{f Fe(CN)_6^{-4}} \quad \ldots (1)$$

From Debye-Hückel limiting law (f = activity coefficient)—

$$\log f = - AZ_i^2 \sqrt{\mu} \quad \ldots (2)$$

where μ is the ionic strength of the medium and is defined by

$$\mu = \tfrac{1}{2} \Sigma C_i Z_i^2 \quad \ldots (3)$$

where C_i is the concentration (or molality) of each ion and Z_i is its valence.

$$\therefore \log \frac{f Fe(CN)_6^{-3}}{f Fe(CN)_6^{-4}} = A(Z^2 Fe(CN)_6^{-4} - Z^2 Fe(CN)_6^{-3}) \sqrt{\mu} \quad \ldots (4)$$

If an equimolar mixure of ferrocyanide and ferricyanide (*i.e.* $\frac{[Fe(CN)_6^{-3}]}{[Fe(CN)_6^{-4}]} = 1$) be used, then from equations (1) and (4)—

$$E = E^\circ + K\sqrt{\mu} \quad \ldots (5)$$

where $K = \frac{2.303RT}{F} A \, (Z^2 Fe(CN)_6^{-4} - Z^2 Fe(CN)_6^{-3})$

The aim of the present experiment is to find out E°.

The cell used for the experiment is—

$$\text{Satd. calomel} \parallel Fe(CN)_6^{-3} - Fe(CN)_6^{-4} \mid Pt$$

The observed e.m.f. of such a cell is given by—

$$E_{obs.} = E - E_{SC}$$

$$= E^\circ - E_{SC} + K\sqrt{\mu} \quad \ldots (6)$$

The plot of $E_{obs.}$ *vs.* $\sqrt{\mu}$ for different solutions will yield a straight line with interecept as $(E^\circ - E_{SC})$. Thus, knowing E_{SC} at the laboratory temperature, the E° can be found out at that temperature.

Materials:

(*a*) ~0.1M $K_3Fe(CN)_6$; (*b*) ~0.1M $K_4Fe(CN)_6$; (*c*) Standard

oxalic acid (N/10) solution; (*d*) ~0.1(N) $KMnO_4$; (*e*) Standard Potassium dichromate (N/10) solution; (*f*) 0.1 (N) Sodium thiosulfate.

Procedure:

Titrate ferrocyanide by standard $KMnO_4$ and ferricyanide by standard $Na_2S_2O_3$. Find out the exact strength of both ferrocyanide and ferricyanide. Dilute each with calculated amount of water to prepare exactly 125 ml. 0.02 *M* solution of each.

In a 500 ml. dry conical flask mix the two 0.02 *M* solutions to prepare 0.01 (*M*) ferroycanide—ferricyanide. Take aliquots of the 0.01*M* solution and dilute properly so as to prepare solutions (ferrocyanide-ferricyanide) of 0.008, 0.005, 0.004, 0.002, 0.001 and 0.0008 (*M*).

Take about 30 ml. of a solution (start from lowest concentration) in a beaker and dip freshly sterilised platinum electrode. Connect this to saturated calomel electrode through KCl-agar salt bridge. Connect the platinum electrode to the positive terminal of the potentiometer and the calomel electrode to the negative electrode (Fig. 30).

Set the rheostats against the standard cadmium cell (1.0182 volts) and then measure the e.m.f. of the experimental cell.

Measure the e.m.f. of the next solution (next higher concentration). In this way note down the *Eobs* of all solutions (the platinum wire is to be sterilised and the standardisation of potentiometer is to be checked each time).

Results and Calculations:

Laboratory temperature=...

Flask No.	Concn. of soln. (*M*)	$\mu=\frac{1}{2}\Sigma C_i Z_i^2$	$\sqrt{\mu}$	Eobs.

Plot Eobs. vs. $\sqrt{\mu}$

From graph—

Intercept = $E^\circ - E_{sc}$

$\therefore$ E° = E_{sc} + Intercept

= ... Volt

[Values of E_{sc} at different temperature are given at the end of expt. No. 12.1, P. 127]

12.14. Determination of the transport numbers of the silver ion and the nitrate ion in a solution of silver nitrate.

Theory:

When an electric current is passed through an electrolyte solution, it is found that the change of concentration at the two electrodes, is, in general, not the same. Since equivalent amounts of positive and negative ions are discharged at the two electrodes, this fact indicates that the cations and the anions move with unequal speeds and do not take equal share in carrying the electric current. The fraction of the total quantity of current carried across by a particular type of ion is called the transport number of that ion. Evidently, the transport number is proportional to the speed of the ion. If the transport number for the cation and the anions is t_c and t_a respectively and their speed is u and v respectively, then

$$t_c = \frac{u}{u+v} \qquad t_a = \frac{v}{u+v}$$

$$\text{and } t_c + t_a = 1$$

In the present experiment the transport number of the silver ion in a silver nitrate solution has been calculated from the change in concentration in the *anode* chamber. If x faradays of current are passed between the electrodes, then x equivalents of silver ion are formed by the electrode reaction in the anode comparatment. However, the actual increase in the number of equivalents of silver ion in this compartment is not equal to x because of the migration of silver ions away from the positive electrode *i.e.* anode. If the actual increase is z, the number of equivalents of silver ion which have migrated out of the anode chamber is $x-z$; so that fraction of the current carried by the silver ions is.

$$t_c = \frac{x-z}{x}$$

Since the sum of the transport numbers of the anion and the cation must be unity, the transport number of the nitrate ion can be calculated.

$$t_a = 1 - t_c$$

Materials:

(1) 0.05*M* silver nitrate solution; (2) standard 0.05*N* potassium thiocyanate solution; (3) saturated ferric ammonium sulfate solution containing sufficient HNO_3 to suppress hydrolysis.

Procedure:

The apparatus is illustrated in figure 40. Into the tubes *A* and *B* there are fixed, by means of corks, two silver electrodes made by fixing

pieces of thick silver rod to copper wires and cementing the latter into glass tubes so that only the silver is exposed; use epoxy adhesive.

Fill the tubes *A*, *B* and *C* (U-Shaped) with the solution of silver nitrate, the composition of which by weight is determined by titration.

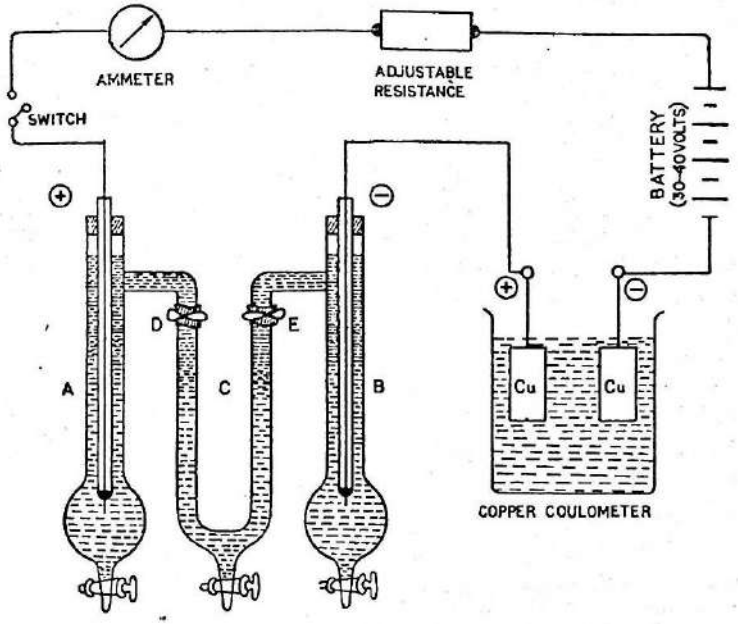

Fig. 40. Determination of transport number

Connect the apparatus with a battery. A current of about 0.02 amp. is sent through the solution. A milliammeter, a copper coulometer and a sliding resistance should also be inserted in the circuit, all in series. The ammeter is to be used for the approximate regulation of current, and the coulometer for the determination of the total amount of electricity passed through the solution. A potential of 30-40 volts will be necessary.

As copper coulometer one may employ a beaker containing a copper solution of the composition given below:

Copper sulfate	: 150 g.
Sulfuric acid	: 50 g.
Alcohol	: 50 g.
Water	: 1000 g

Two electrodes about 1.5 to 2 sq.cm., cut from a copper sheet is dipped in the copper sulfate solution. The copper plate to be used as cathode must be cleaned and weighed. Check the connections. The rubber tubes with *D* and *E* should be kept open. Pass current for about two hours and note down the exact time period.

After the conclusion of the experiment, the rubber tubes are closed by means of the clips D and E, and the anode liquid is run off through the tap at the bottom of the tube A, into a weighed flask. Wash this tube and electrode with a little of original silver nitrate solution and allow this portion also to run into the weighed flask. Weigh the solution and determine its composition by titration with thiocyanate solution using ferric alum as indicator as follows: Pipette out 25 ml. of the solution in a weighed conical flask containing 50 ml. of distilled water and 1 ml. of ferric ammonium sulfate solution. Weigh the whole and then titrate with standard KCNS until a permanent red tint is obtained.

Open the clip D and run the intermediate solution contained in C into a separate flask (do not rinse this comparatment) and analyse similarly. The composition of the solution should remain unchanged.

Remove the cathode from the coulometer, wash with distilled water and then with alcohol, heat in an oven at 110°C, cool in a desiccator and weigh.

Results and calculations:

Duration of the experiment = ... mins.
Current strength used = ... amp.

(A) Original $AgNO_3$ solution

Weight of flask = W_1 gm.
Weight of flask + 20 ml of solution = W_2 gm.
$\therefore$ weight of solution = $(W_2 - W_1)$ gm. = W gm

20 ml. of $AgNO_3$ solution required...ml. $N/20$ KCNS
$\therefore$ Concentration of $AgNO_3$ = X (N)
$\therefore$ Amount of $AgNO_3$ = m gm
$\therefore$ Amount of water = $(W-m)$ gm.

Hence, initially $(W-m)$ gm. of water contained $\frac{m \times 107.88}{169.89}$ gm. of Ag.

$$= \frac{m}{169.89} \text{ equiv. of Ag.}$$

(B) After electrolysis

(*a*) Middle comparatment (C):
20 ml of solution required ... ml. $N/20$ KCNS .

(*b*) Anode compartment (A):
Weight of flask = W_3 gm.
weight of flask + anode solution = W_4 gm.
$\therefore$ Weight of solution = $(W_4 - W_3)$ gm. = W_5 gm
Anode solution required.....ml. $N/20$ KCNS solution.
$\therefore$ Amount of $AgNO_3 = m_1$ gm.
$\therefore$ Amount of water = $(W_5 - m_1)$ gm.

Hence, after electrolysis $(W_5 - m_1)$ gm. of water contained $\frac{m_1}{169.89}$ equivalents of Ag.

If there had been no change in concentration, this quantity of water would have contained

$$\frac{m \times (W_5 - m_1)}{169.89 \times (W-m)} \text{ equivalents of Ag.}$$

Therefore the increase in the number of equivalents of silver ion in the anode chamber is—

$$\frac{m_1}{169.89} - \frac{m(W-m_1)}{169.89\,(W-m)} = z$$

(C) Initial weight of cathode in coulometer $= W_6$ gm. and final weight of cathode after electrolysis $= W_7$ gm.

$\therefore$ Increase of Weight of cathode $= (W_7 - W_6)$ gm.

$$= \frac{(W_7-W_6)}{31.77} \text{ equivalent of Cu or Ag.}$$

$$= x$$

Therefore, the migrated amount is $(x-z)$ equivalents of Ag; and this number is proportional to the velocity of silver ion. Hence the fraction of the total current carried by the cation is $\frac{x-z}{x}$. This value is t_c. $\therefore\ t_c = \frac{x-z}{x}$

The fraction of current carried by the anion $= t_a = 1 - t_c$.

12.15. Determination of the transport number of hydrogen ion by E.M.F. measurements.

A concentration cell with transport of the following type may be made up from two silver/silver chloride electrodes and two solutions of HCl:

$$\underset{}{\text{Ag, AgCl}} \mid \underset{(C_1)}{\text{HCl}} \,\vdots\, \underset{(C_2)}{\text{HCl}} \mid \text{AgCl, Ag}$$

The E.M.F. arises partly at the two electrodes and partly at the liquid junction; the sum of these contributions is

$$E = -2t_+ \frac{RT}{F} \ln\ (f''_+ C_2 / f'_+ C_1) \qquad \ldots\ (1)$$

where f''_+ and f'_+ are the mean activity coefficients of H^+ and Cl^- at concentrations C_2 and C_1 respectively, and t_+ is the transport number of the hydrogen ion. With the aid of equation (1), the transport number can be obtained from measurements of E, provided the activity coefficients are known.

Set up a cell with 0.05 *N* HCl in one beaker (I), 0.5*N* HCl in another beaker (II) and a mixture of roughly equal volumes of 0.05 and 0.5*N* HCl in a separate beaker (III) is placed between them. Add one drop of approximately *N*/100 $AgNO_3$ to I and to II. Immerse two silver wires as electrodes in I and II; they will function as Ag/AgCl electrodes owing to the AgCl present in the solution and the formation of a small amount of AgCl on the surface by reaction of surface oxides with HCl. Connect both I and II with III by two strips of filter paper soaked in ammonium nitrate solution.

Measure the E.M.F. and calculate t_+ using eqn. (1)

The activity coefficients are as follows:

When $C_1 = 0.05\ N$, $f'_+ = 0.830$ and

when $C_2 = 0.50\ N$, $f''_+ = 0.757$.

EXPERIMENT NO. 13: POLAROGRAPHY

13. Studies on the use of dropping mercury electrode (or Polarography) in the qualitative and quantitative determination of electroreducible substances.

Theory:

Qualitative as well as quantitative determination of many electroreducible substances in dilute solution may be made by means of a suitably conducted electrolysis of the solution in a cell in which the cathode is mercury-falling dropwise from a glass capillary tube and the anode is a pool of mercury. At the initial stages of the electrolysis, as the applied voltage is gradually increased no appreciable current will pass through the electrolytic cell until the decomposition potential of the electrolyte is reached. When the applied voltage goes beyond the decomposition potential, ions get deposited on the electrodes and exchange of electrons occurs between the electrodes and electrolytes resulting in a sudden increase in current (*vide* Fig. 41). [The small gradual rise in current at the initial stages (i.e. before decomposition potential is reached) as shown in the figure is attributed to the continous formation of an electrical double layer of positively and negatively charged ions at the interface between the continuously increasing surface of the mercury and the solution. This current is called the 'residual current'. The reduction of traces of impurities in the solution may also add to the residual current].

When the decomposition potential of the electroreducible substance is reached, ions of the substance are discharged at the surface of the mercury drop. As the applied voltage is increased further,

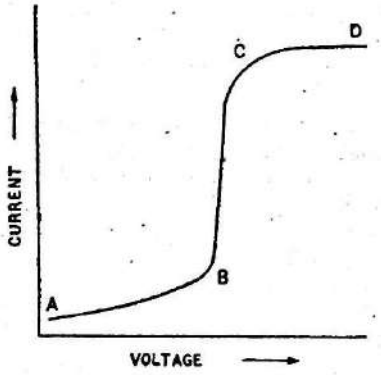

Fig. 41—Current—Voltage curve.

the discharge rate of the ions increases, thereby resulting in a decrease

in the concentration of the ions at the drop surface. However, the ions discharged are replaced by fresh ions coming from the bulk of the solution by diffusion. The rate of diffusion is proportional to the difference in concentration of the ions existing between the drop surface and the bulk of the solution. With gradual increase in the applied e.m.f., the concentration at the drop surface decreases and the rate of diffusion proportionately increases. When the potential reaches a value such that the reducible ions are effectively being reduced as fast as they reach the surface of the drop, both the concentration gradient and the rate of diffusion reach maximum values. At this stage, the part of the current depending on the rate of diffusion of ions reaches a limit, independent of the e.m.f. and proportional to the concentration of the reducible substance. The current at this stage is called the 'limiting current'. In Figure 41, *A*—*B* corresponds to residual current; decomposition potential is reached at *B*; *B*—*C* represents the sudden increase in the current; at *C* the rate of diffusion of ions reaches the maximum and *C*—*D* corresponds to limiting current. The limiting current minus the residual current is called 'diffusion current' (i_d).

In addition to the diffusive force, an electrical force also tends to supply ions to the drop surface. The part of the limiting current

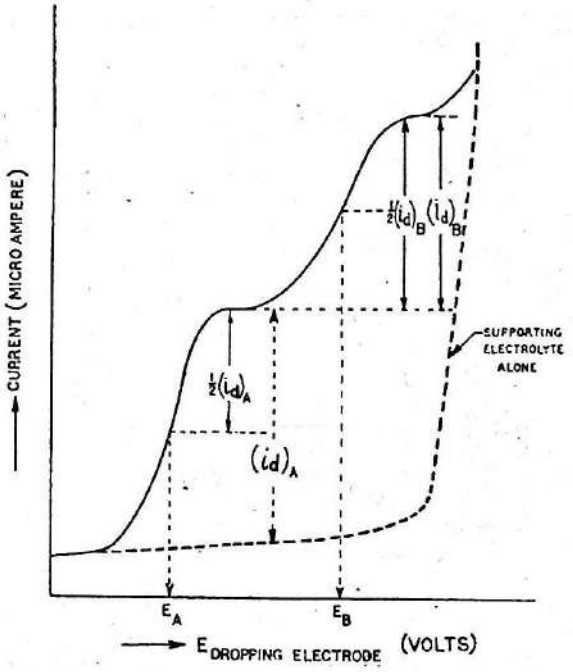

Fig. 42—Diffusion currents and half-wave Potentials

due to such electrical migration of ions may be eliminated by the

addition of a large excess of an 'indifferent' (also called 'supporting') electrolyte. The supporting electrolyte is such that it is not reduced at the potential at which the test salt undergoes reduction. Under the circumstances the current through the solution will be effectively caried by the ions of the supporting electrolyte. Potassium chloride is commonly used as a supporting electrolyte. In the presence of an excess of such an electrolyte, the limiting current (corrected for residual current) is directly proportional to the concentration of the test salt. Thus a quantitative estimation of the test salt is made possible. Qualitatively, the reducible ions are characterised by 'half-wave' potential, the potential at which the diffusion current reaches half its maximum value. When several reducible substances are present, each will make its own contribution to the total limiting current when the applied voltage reaches its own decomposition potential and exceeds it. The concentration of each ion will then be proportional to the height of the corresponding current wave (i.e. diffusion currents (i_d) Fig. 42)

The usefulness of the dropping mercury electrode was first demonstrated by Prof. J. Heyrovsky. Since the method involves the polarisation of the dropping mercury electrode, the apparatus

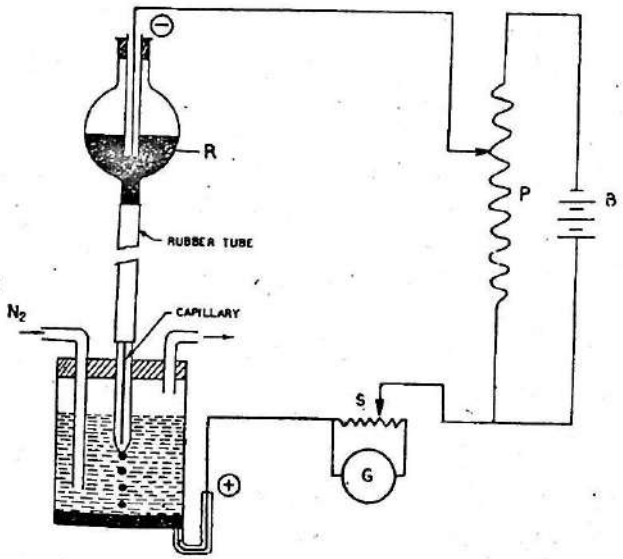

Fig. 43—Dropping Mercury Electrode

is called a *polarograph* and the current-voltage record, a *polarogram*. The method is also known as *polarography*. It is applicable to solutions of small concentrations (10^{-2} to $10^{-5}M$). An added advantage of the method is that the sample is not destroyed by the analysis.

Principle of the method:

The experimental arrangement is shown in Figure 43. The mercury reservoir (*R*) is a 100 ml. levelling bulb, connected with the capillary tube by a sulfur-free, heavy-walled rubber tubing (80-100 cm. long). Neoprene tubing is generally employed. The capillary tube has a length of 5 to 10 cm. and a bore diameter of 0.05 mm. The outside diameter of the capillary tube is about 6 mm. and the delivery tip is cut perfectly horizontal. If a 0.05 mm. bore is not available, a broken thermometer tube can be drawn out and cut off.

A galvanometer (*G*) with a variable shunt (*S*) for regulating the sensitivity is connected in series for the measurement of the current through the cell circuit. The current source is a battery (*B*). The current through the cell circuit is of the order of 10^{-5} ampere.

As the mercury drops form and fall, the current oscillates at each value of the applied e.m.f. Therefore, some means of measuring the average current is required. For this reason, a galvanometer of long period (about 15 seconds) is used and the mercury drops from the capillary should fall at such a rate that one drop takes 3 to 6 seconds to form and fall. The desired drop time is obtained by choice of capillary size and pressure from the reservoir of mercury. This pressure can be varied by adjusting the distance between the capillary tip and the mercury reservoir.

Since the anode is made very large in area (compared to the cathode area) and the current flowing through the cell is very small, polarisation at this electrode (anode) will be negligible. The anode can be used as a reference electrode. Since the cathode is made very small compared to the anode, polarisation of the cathode will be very high and variation in the e.m.f. of the cell would be effectively due to the changes in potential of the cathode. Consequently, this electrode functions as an indicator electrode to measure the changes in potential when current is flowing.

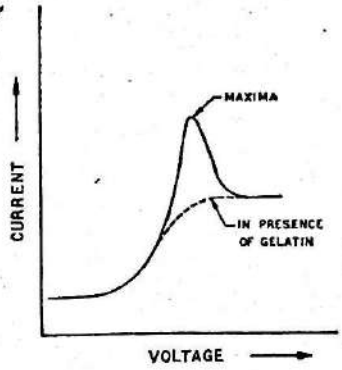

Fig. 44—Suppression of maxima in current-voltage curve,

Since oxygen is readily reduced at the dropping electrode and usually interferes with current-voltage curves of other substances, it is necessary to remove the dissolved air from the test solution by bubbling an inert gas through the cell before (and not during) the electrolysis.

The adsorption of reducible substances in the surface of the mercury may cause a current to flow which is greater than the limiting current due to diffusion. Undesirable maxima may then occur in the current-voltage curve (Fig. 44). In order to measure the true diffusion current, this maxima must be eliminated or suppressed. This

can be easily done by the addition of a surface-active agent (such as, sodium methyl red, gelatin, methyl cellulose) which is strongly adsorbed but is not reduced at the given potential.

Procedure:

Take 50 ml. of the solution ($\sim 10^{-3}M$) of the reducible substance (say, $CdCl_2$) in the electrolytic cell. Add calculated amount of $1N$ KCl so as to make the solution $0.1N$ in KCl. Next add sufficient gelatin so as to make a 0.01 per cent solution in gelatin. Pass purified H_2 (or N_2) through the solution for about 30 minutes in order to remove the dissolved air.

Standardise the potentiometer against the standard cadmium cell (not shown in the figure) and check all electrical connections. Apply about 0.1 Volt and measure the current as shown by the galvanometer deflection. Increase the applied voltage by increments of about 0.1 volt and note down the galvanometer deflection in each case. Take readings until the applied e.m.f. reaches 2 volts.

Convert the galvanometer deflections to microamperes by means of the calibration curve provided. (If the calibration curve is not provided, it can be constructed by performing a separate experiment, that is, by measuring galvanometer deflections at different current strengths in a circuit consisting of the galvanometer with shunt, battery, 10,000 ohm resistor and a potentiomter).

Results and Calculations:

Applied e.m.f. (volt)								
Galvanometer deflection (cm.)								
Current (micro-amp.)								

Plot current *vs* applied e.m.f.; find out half-wave potential and diffusion current from the graph.

Suggestions for further work:

1. The procedure can be repeated at other concentrations of $CdCl_2$ (i.e., 5×10^{-4}, 5×10^{-5}, 10^{-5} M) under identical experimental conditions and a calibration curve (diffusion current vs. concentrations) can be constructed. Concentration of the 'unknown' $CdCl_2$ solution can be then read directly from the calibration curve provided the diffusion current of the unknown solution has been found out at the same experimental conditions as in the calibrating ('known') solutions.

2. Half-wave potentials of other reducible substances ($CuCl_2$, $ZnCl_2$, $MnCl_2$) can be determined.

3. Half-wave potentials of two reducible ions (*say*, Cd^{++} and Zn^{++}) in a mixture can also be determined.

EXPERIMENT NO. 14 : Differential Thermal Analysis

14. To analyse the given sample by Differential Thermal Analysis (D. T. A.) and to construct and interpret the thermogram obtained.

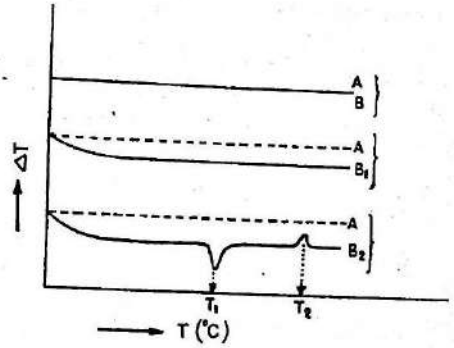

Fig. 45—ΔT *vs.* T plot

Theory:

The principle of D.T.A. is based on the measurement of the difference in temperature between the sample and a reference material (inert) by means of a differential thermocouple, when heat is supplied to the two samples at the same rate.

When two similar inert materials (A, B) are placed in a furnace and the temperature raised slowly, it will be found that the temperature of the two materials rises uniformly and no difference of temperature develops between them (i.e., $\Delta T=0$; Fig. 45). When B is replaced by another material B_1 which has different thermal characteristics but is otherwise similar to A, a difference in temperature arises between the two as the furnace temperature is raised slowly. This difference becomes more of less constant after some time. Let us suppose that B_1 is replaced by another material B_2 which undergoes some chemical or physico-chemical changes on being heated. If heat is absorbed at any particular temperature during this change, then at that temperature there will be a sudden retardation in the rate at which the temperature of B_2 increases. This will make a large difference of temperature between the sample (B_2) and the reference material (A) at that temperature (Fig. 45). Similarly, if there is evolution of heat during any chemical or physico-chemical change, there will be a difference in temperature between the sample and the inert material. But this time the difference in temperature will be in the opposite direction. Figure 45 shows the plot of ΔT (difference in temperature) vs. T (temperature of the furnace); the resulting curves constitute what are known as *thermograms*. Generally the thermograms are so plotted that the endothermal peaks are shown downwards and exothermal peaks upwards with respect to the base line $\Delta T=0$.

In curve 3, there are two inflexions due to absorption and evolution of heat at $T°_1$ and $T_2°C$ respectively. Explanation of these inflexions in the thermograms provides useful information as regards the chemical or physico-chemical changes occurring in B_2. *These changes may be due to dehydration, transition from amorphous to crystalline form, transition from one crystalline form to another, oxidation, decomposition, etc.*

In practice, the sample to be studied and the inert material are placed in two holes (H_1 and H_2) of a specimen holder (Fig. 46). The inert material generally used is calcined aluminium oxide (since it

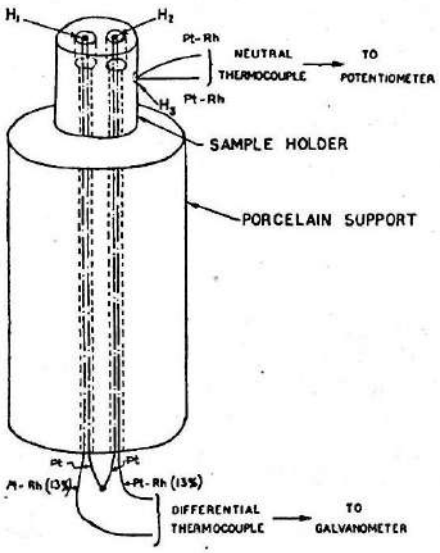

Fig. 46—Specimen holder and porcelain support.

does not undergo any thermal changes over a wide temperature range). One junction of a differential thermocouple is placed in the center of the inert material and the other in the sample. Another thermocouple junction is placed in the third hole (H_3) of the specimen holder and records the temperature of the holder. After being packed with the sample and the inert material, the specimen holder mounted on a porcelain support is placed in the furnace along with the thermocouples. If the temperature of the furnace is raised at a uniform rate, the temperature of the sample and that of the inert material rise at equal rates and there will be no difference of temperature. However, when there is any chemical or physico-chemical change at any instant, the temperature of the sample will be greater or less than that of the inert material (depending on exothermic or endothermic nature of the change) at the instant. When the change is over, the temperature of the sample again becomes the same as that of the inert material.

Thus, for an interval of time, an e.m.f. is set up in the differential thermocouple circuit. In the actual experimental procedure, this e.m.f. is recorded in terms of deflections in a galvanometer included in the circuit. A graphical plot of galvanometer deflection against the furnace temperature during a course of experiment constitutes a thermogram.

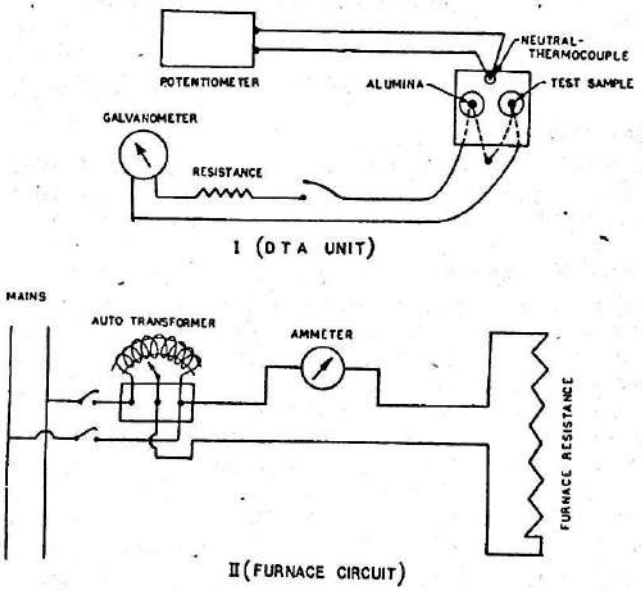

Fig. 47.—Experimental Set-up for D.T.A.

Apparatus:

Fig. 47 represents the experimental set-up used for D.T.A. The experimental unit essentially consists of a furnace, a metallic specimen holder, a porcelain suport for the specimen holder, a potentiometer, a reflecting type galvanometer, an ammeter, a variac transformer and thermocouples.

Furnace:

A vertical type furnace is generally used. It is constructed by winding two lengths of kanthal wire in parallel on an alundum tube of 10″ long and 2.2″ inside diameter. The tube consists of external grooves for winding the wire. (While kanthal wire is suitable upto 1350°C, platinum-rhodium wire is used for temperatures upto 1500°C and nichrome wire is suitable at lower temperatures upto 1000°C). The temperature of the furnace (hence, that of the specimen holder) can be varied using a variac transformer. The electrical connections of the furnace are shown in Fig. 47.

Specimen holder:

The metallic specimen holder is generally of cylindrical shape made of pure nickel, 1.5″ long and 1.0″ in diameter, with two holes 0.7″ apart. The holes are of diameter 0.35″ each.

The holes are 0.5″ deep on the top, narrowing down at the opposite end. The holes of the specimen holder at this end have diameter equal to that of the porcelain supporter (*vide* below) on which the holder rests. The third hole of diameter 0.1″ is made at one of the side arms of the holder. The third hole should be of sufficient depth for the fused end of the neutral thermocuple to pass through.

Porcelain supporter:

The porcelain support should stand a temperature of about 1300°C without deformation. It is about 7″ long and 2″ diameter with two holes through which the thermocouple wires can pass.

Differential thermocouple:

Pt-Pt.Rh (13%) thermocouples are generally used for measuring the specimen holder themperature and the differential temperature. Two ends of the platinum wires of the differential thermocouple (T_D) are connected together and the other two ends constituting the differential leads are connected to the galvanometer. The neutral thermocouple, T_N (embedded in the third hole) is connected to a sensitive potentiometer (run by a 3 volt battery).

Galvanometer:

The galvanometer is usually of the Tynsley type. The deflections due to the potential difference in the differential thermocouple are recorded.

A resistance in series with the differential circuit is generally included, since the thermal changes are sometimes so large that the pointer goes off the scale.

Potentiometer:

Temperature of the holder (or furnace temperature) is measured by a sensitive potentiometer having a sensitivity of at least 10 mV. Two leads of the neutral thermocouple are connected to the potentiometer and readings in mV are noted.

Procedure:

Part I: Calibration of the neutral thermocouple (T_N):

The thermocouple, Pt—Pt.Rh(13%) is calibrated using high-boiling liquid (glycerol, silicone liquid, conc. H_2SO_4, etc.). Heat the liquid and at different temperatures note down the corresponding mV readings. Plot temperature vs. mV; the resulting straight line constitutes the calibration curve for the thermocouple.

Part II: Calibration of the D.T.A. unit:

In order to check the experimental set-up, D.T.A. of "known" substances should be carried out. Melting point and inversion point of some calibrating ("known") substances are given in the following table.

Table I

Calibrating substance	Melting (*M*)/Inversion (*I*) point (°C)		
NH_4NO_3	I I M	85 125 170	
AgI	I M	147 552	
$NaNO_3$	M	314	
$NaMo_2O_4$	I M	642 687	

Clean the two holes of the specimen holder and dry them. Fill up one hole with the inert material (calcined alumina) and the other hole with the calibrating substance. Packing of the inert substance and the calibrating sample should be done at moderate pressure. Place the specimen holder mounted on the procelain support inside the furnace. Check the electrical connections in the neutral thermocouple and differential thermocouple circuits, and also in the furnace circuit.

Raise the temperature of the furnace slowly (using the variac transformer) at the rate of $10° \pm 1°C$/min. Note down the galvanometer readings at 1 minute intervals. Initially the galvanometer reading will remain constant, but as the temperature of melting or inversion is reached it will move to the right or left of the scale, depending on the absorption or evolution of heat. [Note the direction of the galvanometer pointer when the melting point is reached (i.e. absorption of heat). If the pointer moves in the opposite direction at any other temperature, it can be predicted that at that temperature a chemical/physico-chemical change with evolution of heat occurs. The nature of thermal changes in the given sample ("unknown") can thus be identified]. When the thermal change is over, the pointer will come back to the original position. A typical thermogram for a 'known' substance is shown in figure 48. Note the galvanometer readings against mV (in the potentiometer). mV readings will correspond to the temperature of the furnace (strictly speaking, temperature of the specimen holder).

Part III: D. T. A. of the given sample:

Clean and dry the holes. Instead of the calibrating substance, now pack the given sample. Repeat the procedure as outlined in

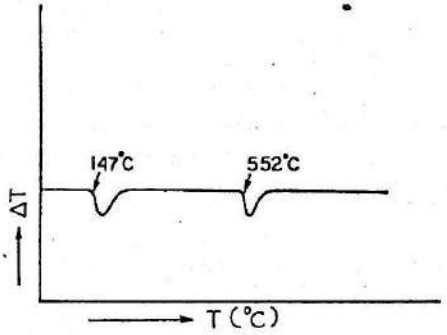

Fig. 48.—D.T.A. of AgI.

Part II. Note the galvanometer readings corresponding to the mV reading (potentiometer). Continue the process until the upper limit of temperature (as given in the instructions) is reached.

Results and calculations:

Part I: Calibration of the neutral thermocouple (T_N):

Table II

Temperature (°C)									
mV									

Part II: Calibration of the D.T.A. unit:

Table III

mV									
Temperature, °C (corresponding to mV—from Part I)									
Galvanometer deflection (cm.)									

Plot galvanometer deflections against temperature and compare the 'inflections' in your thermogram with the values given in Table I.

Part III: **D. T. A. of the given sample:**

Table IV

mV									
Temperature, °C (corresponding to mV—from Part I)									
Galvanometer deflection (cm.)									

Plot galvanometer readings against temperature and discuss the possible chemical or physicochemical changes.

EXPERIMENT NO 15 : GAS ADSORPTION

15. Determination of the surface area of the given powdered catalyst sample by the B.E.T. method.

Theory:

The determination of surface area is of paramount importance particularly in the field of industrial catalysis. The preparation of the specific catalysts and a comparison of their relative activities largely depend on the surface areas of the respective catalysts. Of the various methods used for determing surface area, gas adsorption method of Brunauer, Emmett and Teller (or briefly B.E.T. method) is rather simple and widely used.

The B.E.T. multilayer adsorption isotherm is given by—

$$\frac{P}{V(P_0-P)} = \frac{1}{V_mC} + \frac{C-1}{V_mC} \cdot \frac{P}{P_0} \quad \ldots (1)$$

where P_0 is the saturation pressure of the gas; V is the volume at N.T.P. of the gas adsorbed at a pressure P of the system; V_m is the volume at N.T.P. of the gas adsorbed when the surface of the adsorbent is completely covered with a monolayer of the adsorbate; C is constant for a given system. It follows from equation (1) that the plot of L.H.S. of the equation vs. P/P_0 should yield a straight line, from the slope and intercept of which V_m can be calculated, that is—

$$V_m = \frac{1}{(\text{intercept} + \text{slope})} \quad \ldots (2)$$

If the cross-section of the gas molecule (i.e. the area of the surface

covered by each adsorbed molecule) is known, then the surface area of the adsorbent can be calculated as follows:—

22414 ml. of the gas at N.T.P. contains 6.023×10^{23} molecules.

$\therefore$ V_m ml. at N.T.P. contains $\frac{6.023 \times 10^{23} \times V_m}{22414}$ molecules

If x=Wt. of the solid adsorbent

and A=Cross-section of each adsorbed molecule (M.^{2}), then

$$\text{Surface area per gm} = \frac{6.023 \times 10^{23} \times V_m \times A}{22414 \times x} \text{ (meter)}^2 \quad \ldots \quad (3)$$

The gas commonly used in the B.E.T. method is nitrogen. At liquid nitrogen temperatures, value of A for nitrogen is 16.2 A^2 or

$\frac{16.2}{10^{20}}$ (meter)^2

Adsorption Apparatus

A conventional B.E.T. unit is shown in Fig. 49. B is a calibrated burette (50 c.c. capacity) connected to a mercury reservoir R_1. A manometer M is connected to the burette through a three-way stop-

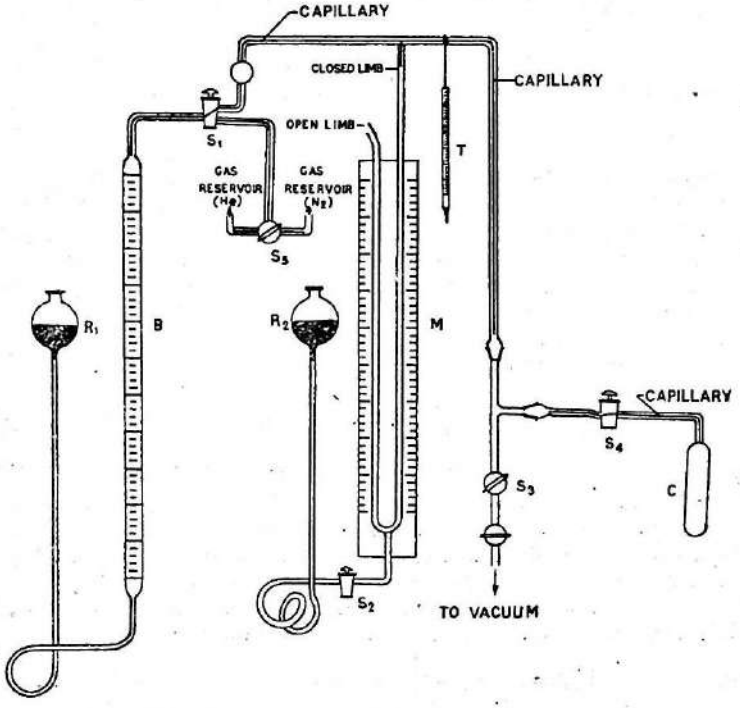

Fig. 49.—B.E.T. unit for surface area measurement.

cock S_1. The third line of the stopcok is connected to the gas reservoir. The manometer is joined to a mercury reservoir R_2 through a stopcock S_2. Both R_1 and R_2 are fixed to adjustable stands and can be moved upwards or downwards. The levels of the mercury in the manometers and burette can be adjusted by adjusting the positions of these reservoirs. The manometer is connected to the vacuum line through the stop cock S_3. The closed limb of the manometer is connected to a B_{10}-socket which can be fitted to the catalyst tube C through the stopocks S_3. The three-way stopcock S connects the apparatus with the two gas reservoirs. Thermometer T reads room temperature.

The stopcocks and ground glass joints in the adsorption unit are specially processed for operation under high vacuum. All the gas joints and stopocks are lubricated with high vacuum grease.

Principle of the method

Any adsorption measurement involves the addition of a known quantity of the gas to the previously evacuated apparatus containing the sample and determination of the volume of the gas adsorbed in the system after attainment of adsorption equilibrium. This can be done as follows:—

Close S_2 and S_5. Open S_4 and connect B with M through S_1. Through S_3 evacuate the apparatus for 2 hours. Now close S_3. Make the mercury levels in R_1 and B same. Open the three-way stop cock S_1 so as to connect the burette B with the gas reservoirs. Connect the apparatus with the helium gas reservoir through the three-way stop cock S_5. Collect some amount of He gas (say, 25 c.c.) in B. Now close S_5. Through S_1 (slowly and carefully move it) introduce about 4 ml. of He into the other parts of the apparatus. Make mercury levels in R_1 and B same and note the exact volume of the gas transferred. Wait for 15 minutes for equilibrium to reach. Corresponding to this volume, note down the readings of both limbs of the manometer, i.e., closed-scale reading (C.S.R.) and open scale reading (O.S.R.). The pressure of the gas is then: Atmospheric pressure—(C.S.R.—O.S.R.).

Introduce another increment (*say*, 3ml) of the He gas through S_1 (Be careful while moving S_1). Note down the corresponding pressure as before. Repeat this procedure until six readings have been taken.

Helium is inert and does not get adsorbed on the sample. Therefore measurement of the volumes of the gas at different pressures produces a calibration curve (Volume vs. pressure). Repeat this procedure with another gas (instead of helium) which gets absorbed on the given sample. Suppose that at a particular pressure P_1 cm., the adsorbable gas has a volume V_1 c.c. From the calibration curve, read the volume (*say* V_2 c.c.) corresponding to the same pressure P_1 cm. Since some amount of gas has been adsorbed, $V_1 > V_2$. The difference $V_1 - V_2$ is equal to the volume of the gas adsorbed at P_1. Similarly,

calcuate the volume of the gas adsorbed at other pressures. Convert these volumes to N.T.P. values. This will give V (*vide* eqn. 1).

Procedure:

Part I:

Construct the calibration curve with helium as outlined above.

Part II:

The adsorbable gas commonly used for surface area measurements is nitrogen. The adsorption experiment is done at liquid air temperature (i.e. the catalyst tube C is placed in a thermoflask containing liquid air). At this temperature, value of P_0 (*vide* eqn. 1) for N_2 is 80 cm.

Before starting the adsorption experiment, the helium gas is to be removed by evacuation. Through S_3 evacuate the apparatus for about 3 hours. Close S_3. Connect B to the gas reservoirs through S_1. Through S_5 introduce (*say* about 25 ml.) N_2 gas to B. Now close S_5. Immerse C in a thermoflask containing liquid air. Through S_1 (slowly and carefully move it) introduce about 3ml. of the gas into other parts of the apparatus. Note down the volume of the gas transferred (adjust the mercury levels in B and R_1) and the corresponding pressure (*i.e.*, note the C.S.R. and O.S.R. readings in the manometer). Repeat this procedure until at lest five readings have been taken.

Read the atmospheric pressure from the barometer. Note down the room temperature.

Results and calculations:

Room Temperature = ...°C
Atomospheric pressure = ...cm
= P' cm
Wt. of sample taken = ...gm
= ...x gm.

Part I:

Table I

Volume of He (c.c)	C.S.R. (cm.)	O.S.R. (cm.)	$P=P'-$(C.S.R.$-$O.S.R.) cm.

Plot volume against P and construct the calibration curve.

Part II :

Table II

Volume of N_2 V_1,(c.c)	C.S.R. cm.	O.S.R. cm.	$P=P'-$ (C.S.R $-$O.S.R) cm.	V_2 (from calibration curve) c.c.	$V_3 = V_1 - V_2$ (c.c.)	V_3 converted to N.T.P$=V$ (c.c.)

N.B. Values of V_2 at different pressures P in part II are obtained from the calibration curve obtained in Part I of the experiment.

Table III

P (from Table II) cm.	P_0-P	$\frac{P}{V(P_0-P)}$	$\frac{P}{P_0}$

Plot $\frac{P}{V(P_0-P)}$ vs $\frac{P}{P_0}$. From the slope and the intrecept of the straight line, find out V_n (*vide* equation 2).

Using equation (3), calculate the surface area of the given adsorbent.

EXPERIMENT NO. 16 (THERMOSTAT)

16 To set up a thermostat.

Theory:

A thermostat is an essential apparatus in any physico-chemical laboratory. Basically, it is a vessel in which a fluid is maintained at a constant temperature automatically. The fluid may be air, water or oil, and the corresponding thermostat is respectively called an air thermostat, a water thermostat or an oil thermostat. The principle of operation is the same for all these thermostats and the most common type, viz. a water thermostat, is described below.

A water thermostat consists of a vessel made of glass or metal containing water. It is provided with a stirrer run by an electric motor. Into the bath is dipped an electric heater (an electric bulb may also serve as a heater) which is controlled by a thermoregulator through a relay. The thermoregulator is the *crucial component* of this

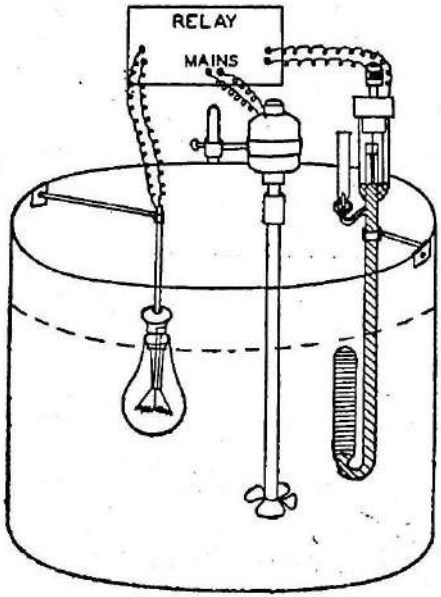

Fig. 50.—Thermostat.

set-up. It is generally of the liquid expansion type, for example, toluene thermoregulator or mercuty thermoregulator. The mechanism of working is simple to understand. Suppose the thermoregulator is set at 35°C. This means that the liquid will expand with rise of temperature such that an electrical contact is established when the temperature attains 35°C. This will energise the relay which would cut off the heating circuit. So the temperature cannot go above 35°C. As soon as the heater is cut off, the thermostat would start cooling

off and as soon as the temperature falls below 35°C, the electrical contact within the thermoregulator will be broken. This would de-energise the relay and so the heater will be again switched on. Thus the heater will be automatically switched 'off-and-on' so that the temperature will remain close to a predetermined point (here 35°C)

The essential *elements* of a thermostat are the following:

(*i*) A bath
(*ii*) A stirrer
(*iii*) A heater
(*iv*) A thermoregulator
and (*v*) A relay.

The set-up is shown schematically in Fig. 50 where the relay is shown to coordinate the operation of the heater and the thermoregulator. (*Vide* also Fig. 53).

Materials:

(*i*) **Thermostat Vessel:** This may be an ordinary glass jar or a large beaker or a metal vessel of a few litres capacity with a glass window if necessary. This should be properly insulated by felt or glass wool or plastic magnesia or asbestos fibre. Sometimes, insulation is done by cork slab or polystyrene foam.

(*ii*) **Stirrer:** A glass or metal stirrer of any suitable shape : A fan-type or screw-type or centrifugal type strirrer may be used with a fractional horse-power motor (1/8 H.P. or less) fixed on a heavy stand or on wall.

(*iii*) **Heater:** An electrical heater of a suitable wattage may be used. For not too high temperature *say* between room temperature and 50°C, only one 75 to 100 watt electric bulb is found very convenient. For higher precision particularly at a higher temperature, it is better to have an auxiliary heater of wattage just sufficient to keep the temperature slightly below the desired point. This one is kept constantly switched 'on'. The other heater may be a bulb of low wattage and it should be connected through the relay.

(*iv*) **Thermoregulator:** Thermoregulators may be of various types of which the following are common: (*a*) Toluene thermoregulator; (*b*) Mercury-in-glass thermoregulator; (*c*) Vapour-liquid type (also called J-type) thermoregulator; (*d*) Bimetallic type. The bimetallic type has not sufficient sensitivity so as to be used in precision thermostats as required in a physico-chemical laboratory and hence will not be further discussed.

(*a*) A toluene thermoregulator is easily assembled in the laboratory. It is an almost U-shaped bulb (see Fig. 51). The filling up of the bulb with toluene and mercury requires some ingenuity. The thermoregulator is closed with a rubber stopper through which passes a glass T-tube provided with two stopcocks. Suction with the help

of a pump (or water-pump) is applied through the side tube through the corresponding stop-cock. This stop-cock is now closed and the apparatus is inverted. The mouth of the other stop-cock is now kept under toluene taken in a beaker, and the latter stop-cock is now opened. Toluene now rushes up and almost fills the bulb. By repeating the process and by careful manipulation, the thermoregulator is completely filled with toluene and a moderate amount of mercury as shown in Fig. 51. Electrical contacts are now made by two nickel-chromium wires (the central one being of adjustable height) dipped into mercury in the capillary and in the annualar space (or side tube) respectively. By adjusting the amount of mercury and by lowering or raising the central wire in the capillary the thermoregulator is set for any desired temperature. In some types the elongated bulb is replaced by a coil to obtain higher surface to volume ratio for better thermal sensitivity.

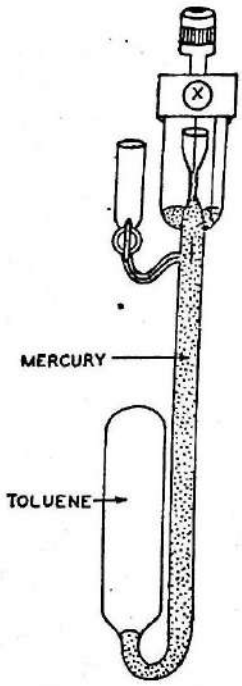

Fig. 51.—Toluene Thermoregulator.

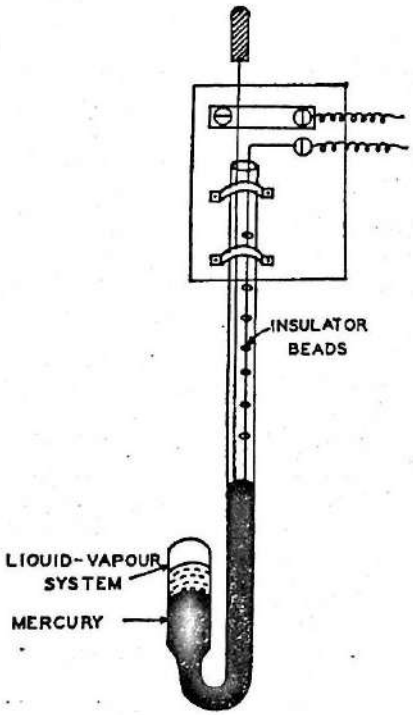

Fig. 52.—J-type Thermoregulator.

(*b*) **Mercury-in-glass thermoregulator:** This is also a liquid expansion type thermoregulator; here mercury is the only fluid used and this expands and makes the electrical contact. In this type the knob is rotated to lower or to raise the naked wire to fix up the

temperature of the bath at any desired point. The fabrication of this type is difficult in the laboratory and so is usually purchased.

(*c*) **Gas-liquid type thermoregulator:** In this handy type, commonly called J-type thermoregulator, the expanding fluid is a

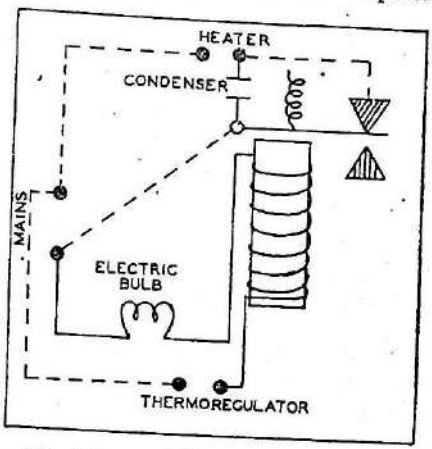

Fig. 53.—Set-up of Relay in a thermostat.

two-phase system, *viz.* a liquid in contact with its saturated vapour near its boiling point, enclosed in a small bulb over mercury. This

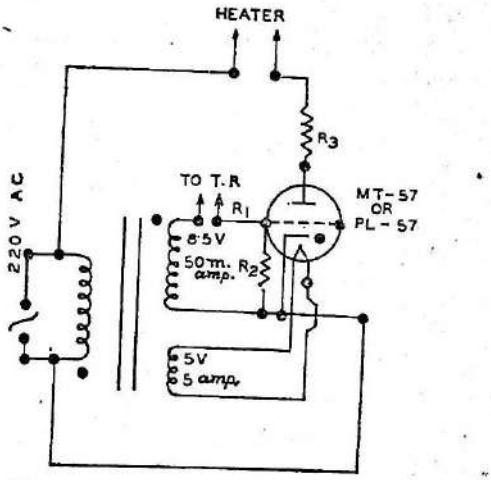

Fig. 54.—Thyratron Electronic relay.

is shown in Fig. 52. The liquid (a pure compound or a mixture) is chosen to have a boiling point close to *say* within 4°C of the desired temperature. This is a neat simple device which under proper condition is capable of regulating to ± 0.01°C or somewhat better.

(v) **Relay:** Relays are mere electromagnetic devices such that when the circuit is closed through the thermoregulator it energises the electromagnet which attracts a piece of iron as a result of which the circuit is broken. Such "Normally on" relays can be made in a laboratory or easily purchased. They are sometimes called "Telegraph relays". The relay lay-out is shown in Fig. 53.

Electronic relays have become very common nowadays. They are readily purchased. One simple but highly efficient type using a thyratron valve is shown in Fig. 54. This is easily assembled with a thyratron valve, a suitable transformer and a couple of resistances purchased from a supplier of radio components. The authors can unreservedly recommend the same.

Procedure:

The set-up is shown in Fig. 50. Fill up the thermostat to the necessary level with water (preferably distilled water). Add an anti-fungal agent (dilute solution of copper sulphate or mercuric chloride). Fit up the strirrer and regulate the speed of the stirrer so that there is brisk circulation throughout the available space. Put the thermoregulator inside the thermostat so that the whole bulb is immersed. The heater bulb is also kept immersed under water upto its metal neck (i.e. the glass portions only). The heater or the auxiliary heater is allowed to heat the water up to the desired point. As soon as this is achieved, the thermoregulator is now adjusted so that it starts doing 'make and break'. The final adjustment is done by rotating the knob at the top of the thermoregulator so that the thermometer reads the exact temperature. The thermostat is now ready for use. The thermostat is to be fitted with a sensitive thermometer (not shown in Fig.) which is graduated to at least one-tenth of a degree (°C).

For use at a temperature higher than say, 60°C it is advisable to put a little transformer oil over the water in the thermostat. This effectively prevents evaporation of water from the open surface so that the need for periodic replenishment of water in the thermostat becomes minimal. However for all temperature higher than 50°C or so it is best to use cheap lub oil (obtainable from motor oil dealers) or silicone oil (not easily available in India).

APPENDIX

Atomic Weights of Some Common Elements

Element	Symbol	Atomic number	Atomic weight
Aluminium	Al	13	26.9815
Argon	Ar	18	39.948
Arsenic	As	33	74.9216
Barium	Ba	56	137.34
Beryllium	Be	4	9.0122
Bismuth	Bi	83	208.980
Boron	B	5	10.811
Bromine	Br	35	79.909
Cadmium	Cd	48	112.40
Calcium	Ca	20	40.08
Carbon	C	6	12.0111
Cerium	Ce	58	140.12
Chromium	Cr	24	51.996
Cobalt	Co	27	58.9332
Copper	Cu	29	63.54
Fluorine	F	9	18.9984
Gold	Au	79	196.967
Helium	He	2	4.0026
Hydrogen	H	1	1.00797
Iodine	I	53	126.9044
Iron	Fe	26	55.847
Krypton	Kr	36	83.80
Lead	Pb	82	207.19
Lithium	Li	3	6.939
Magnesium	Mg	12	24.312
Manganese	Mn	25	54.9380

Element	Symbol	Atomic number	Atomic weight
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.94
Neon	Ne	10	20.183
Nickel	Ni	28	58.71
Nitrogen	N	7	14.0067
Oxygen	O	8	15.9994
Palladium	Pd	46	106.4
Phosphorus	P	15	30.9738
Platinum	Pt	78	195.09
Potassium	K	19	39.12
Silicon	Si	14	28.086
Silver	Ag	47	107.87
Sodium	Na	11	22.9898
Strontium	Sr	38	87.62
Sulfur	S	16	32.064
Tin	Sn	50	118.69
Titanium	Ti	22	47.90
Uranium	U	92	238.03
Vanadium	V	23	50.942
Xenon	Xe	54	131.30
Zinc	Zn	30	65.37

Concentration Units for Solutions

Name	Symbol	Definition
Weight per cent	%	(grams of solute/grams of solution) × 100.
Mole fraction	X_A	Moles of *A*/total number of moles.
Molarity	M	Moles of solute per liter of solution.
Normality	*N*	Equivalents of solute per liter of solution.
Formality	F	Formula weights of solute per liter of solution.
Molality	M	Moles of solute per 1000 gm. of solvent.
Weight formality	f	Formula weights of solute per 1000 gm. of solvent.

Table I

Solubility (gms./100 gms. of water)

Substance	20°C	30°C	40°C	50°C	60°C
BaC_2	35.7	38.2	40.7	43.6	46.4
KBr	65.2	70.6	75.5	80.2	85.5
NaCl	36.0	36.3	36.6	37.0	37.3
$NaNO_3$	88.0	96.0	104.0	114.0	124.0
$SrCl_2,6H_2O$	52.9	58.7	65.3	72.4	81.8
KCl	34.0	37.0	40.0	42.6	45.5
K_2SO_4	11.11	12.97	14.76	16.50	18.17
$FeSO_4,7H_2O$	26.5	32.9	40.2	48.6	—

Table II

Transition points of salt hydrates

Substance	Temperature (°C)
$Na_2CrO_4,10H_2O \rightleftharpoons Na_2CrO_4,6H_2O$	19.71
$Na_2SO_4,10H_2O \rightleftharpoons Na_2SO_4$	32.48
$NaBr,2H_2O \rightleftharpoons NaBr$	50.78
$MnCl_2,4H_2O \rightleftharpoons MnCl_2,2H_2O$	58.33
$Na_2CO_3,10H_2O \rightleftharpoons Na_2CO_3,7H_2O$	32.12

Table III

Surface Tension (dynes/cm.)

Substance	20°C	25°C	30°C	40°C	50°C
Water	72.75	71.97	71.18	69.56	67.91
Benzene	28.88	—	27.56	26.26	25.00
Toluene	28.43	—	27.32	26.13	25.00
Chlorobenzene	33.20	—	—	—	29.60
Chloroform	27.10	—	—	—	—
Cyclohexane	25.30	—	—	—	—
Ethyl acetate	23.90	—	—	—	20.20
Ethyl alcohol	22.30	—	21.43	20.60	19.80
n-Hexane	18.40	—	—	—	16.30
Carbon tetrachloride	26.77	—	25.53	—	23.10
Glycol	47.70	—	—	—	—
Methyl alcohol	22.61	—	—	—	—
Methyl acetate	24.60	—	—	—	—
Acetone	23.70	—	—	21.16	—

Table IV

Viscosity (Centipoises)

Substance	20°C	25°C	30°C	40°C	50°C
Water	1.005	0.8937	0.8007	0.6560	0.5494
Acetone	—	0.316	0.295	—	—
Aniline	4.40	3.71	3.16	2.37	1.85
Benzene	0.652	—	0.564	0.503	0.442
Toluene	0.590	—	0.526	0.471	0.426
Chloroform	0.480	0.542	0.514	0.464	0.424
Ethyl alcohol	1.20	—	1.003	0.834	0.702
Ethyl acetate	0.455	0.441	0.400	—	0.345
n-Hexane	0.326	0.294	—	0.271	0.248
n-Heptane	0.409	0.386	—	0.341	—
Carbon tetrachloride	0.969	—	0.843	0.739	0.651
Methyl alcohol	0.597	0.547	0.510	0.456	0.403
Methyl acetate	0.381	—	—	0.230	—

Table V

Physical constants of some common liquids

Substance	Mol. wt.	Index of refraction*	Density (gm./ml.)
Acetic acid	60.05	1.3721 (20°C)	1.049 (20°C)
Acetone	58.08	1.35886(19.4°C)	0.792 (20°C)
Pyridine	79.10	1.50919(21°C)	0.982 (20°C)
Aniline	93.12	1.5863 (20°C)	1.622 (20°C)
Benzene	78.11	1.50112(20°C)	0.879 (20°C)
Carbon disulfide	76.13	1.6255 (20°C)	1.2628(20°C)
Carbon tetrachloride	153.84	1.46305(15°C)	1.595 (20°C)
Chloroform	119.39	1.44643(18°C)	1.4984(15°C)
Ethyl alcohol	46.07	1.3611 (20°C)	0.785 (25°C)
n-Heptane	100.20	1.38764(20°C)	0.6837(20°C)
n-Hexane	86.17	1.37490(20°C)	0.6603(20°C)
Methyl alcohol	32.04	1.3288 (20°C)	0.7917(20.C)
Phenol	94.11	1.54247(40.6°C)	1.0722(20°C)
Toluene	92.13	1.49693(20°C)	0.8669(20°C)

*for the D-line of Sodium.

Table VI

Dissociation constants (K_a) in aqueous solutions at 25°C.

Acid	$pK = -\log_{10}K_a$	Acid	$pK = -\log K_a$
Acetic	4.75	Succinic	4.21 (Step 1) 5.64 (Step 2)
Benzoic	4.21	Oxalic	1.27 (Step 1) 4.27 (Step 2)
Monochloracetic	2.86	Phosphoric	2.12 (Step 1)
Dichloracetic	1.48		7.21 (Step 2)
Trichloracetic	0.70		12.30 (Step 3)

Table VII

Specific conductivity of aqueous KCl solutions

Temperature °C	Sp. cond. (mhos cm^{-1}) for 1*N* Soln.	Sp. cond. (mhos cm^{-1}) for 0.1*N* Soln.	Sp. cond. (mhos cm^{-1}) for 0·01*N* Soln.
20	0.10207	0.01167	0.001278
22	0.10594	0.01215	0.001332
25	0.11180	0.01288	0.001413
27	0.11574	0.01337	...
30	...	0.01412	...
32	...	0.01462	...
35	...	0.01539	...

Table VIII

Ionic conductivities at infinite dilution

Ion	18°C	25°C	50°C
H^+	314	350	465
K^+	64.6	74.5	115
Na^+	43.5	50.9	82
NH_4^+	64.5	74.5	115
Ag^+	54.3	63.5	101
$\frac{1}{2}Ba^{++}$	55	65	104
$\frac{1}{2}Ca^{++}$	51	60	98
$\frac{1}{2}Pb^{++}$	61.5	72	—
$\frac{1}{2}Mg^{++}$	45	53.1	—
Cl^-	65.5	75.5	116
Br^-	67.2	77.4	—
I^-	66.4	76.2	—
NO_3^-	61.7	70.6	104
CH_3COO^-	34.6	40.8	67
OH^-	172	192	284
$\frac{1}{2}SO_4^{2-}$	68	79	125
$\frac{1}{2}C_2O_4^{2-}$	63	73	115

Table X.

Buffer Solutions

I		II		III		IV		V		VI		VII		VIII		IX	
pH	X	pH	X	pH	X	pH	X	pH	X	pH	X	pH	X	pH	X	pH	X
1.0	67.0	2.2	49.5	4.1	1.3	6.0	5.6	8.0	20.5	9.2	0.9	10.0	10.7	11.0	4.1	12.1	8.0
1.1	52.8	2.3	45.8	4.2	3.0	6.1	6.8	8.1	19.7	9.3	3.6	10.1	12.2	11.1	5.1	12.2	10.2
1.2	42.5	2.4	42.2	4.3	4.7	6.2	8.1	8.2	18.8	9.4	6.2	10.2	13.8	11.2	6.3	12.3	12.8
1.3	33.6	2.5	38.8	4.4	6.6	6.3	9.7	8.3	17.7	9.5	8.8	10.3	15.2	11.3	7.6	12.4	16.2
1.4	26.6	2.6	35.4	4.5	8.7	6.4	11.6	8.4	16.6	9.6	11.1	10.4	16.5	11.4	9.1	12.5	20.4
1.5	20.7	2.7	32.1	4.6	11.1	6.5	13.9	8.5	15.2	9.7	13.1	10.5	17.8	11.5	11.1	12.6	25.6
1.6	16.2	2.8	28.9	4.7	13.6	6.6	16.4	8.6	13.5	9.8	15.0	10.6	19.1	11.6	13.5	12.7	32.2
1.7	13.0	2.9	25.7	4.8	16.5	6.7	19.3	8.7	11.6	9.9	15.7	10.7	20.2	11.7	16.2	12.8	41.2
1.8	10.2	3.0	22.3	4.9	19.4	6.8	22.4	8.8	9.6	10.0	18.3	10.8	21.2	11.8	19.4	12.9	53.0
1.9	8.1	3.1	18.8	5.0	22.6	6.9	25.9	8.9	7.1	10.1	19.5	10.9	22.0	11.9	23.0	13.0	66.0
2.0	6.5	3.2	15.7	5.1	25.5	7.0	29.1	9.0	4.6	10.2	20.5	11.0	22.7	12.0	26.9		
2.1	5.1	3.3	12.9	5.2	28.8	7.1	32.1	9.1	2.0	10.3	21.3						
2.2	3.9	3.4	10.4	5.3	31.6	7.2	34.7			10.4	22.1						
		3.5	8.2	5.4	34.1	7.3	37.0			10.5	22.7						
		3.6	6.3	5.5	36.6	7.4	39.1			10.6	23.3						
		3.7	4.5	5.6	38.8	7.5	40.9			10.7	23.8						
		3.8	2.9	5.7	40.6	7.6	42.2			10.8	24.25						
		3.9	1.4	5.8	42.3	7.7	43.5										
		4.0	0.1	5.9	43.7	7.8	44.5										
						7.9	45.3										
						8.0	46.1										

I : 25 ml. of 0.2 M KCl + X ml. of 0.2 M HCl
II : 50 ml. of 0.1 Potassium hydrogen phthalate + X ml. of 0.1M HCl.
III : 50 ml. of 0.1M Potassium hydrogen phthalate + X ml of 0.1 NaOH
IV : 50 ml. of 0.1M Potassium dihydrogen phosph ate + X ml. of 0.1M NaOH
V : 50 ml. of 0.025M borax + X ml. of 0.1M HCl.
VI : 50 ml. of 0.025M borax + X ml. of 0.1MNaOH
VII : 50 ml. of 0.05 M Sodium bicarbonate + X ml. of 0.1M NaOH
VIII : 50 ml. of 0.05M disodium hydrogen phosphate + X ml. of 0.1M NaOH.
IX : 25 ml. of 0.2M KCl + X ml. of 0.2M NaOH.

Table IX

Solubility product of difficultly soluble salts

Substance	Solubility product (at temperature noted)
$BaSO_4$	1.08×10^{-10}(25°C)
CaC_2O_4, H_2O	2.57×10^{-9} (25°C) 1.78×10^{-9} (18°C)
$PbCrO_4$	1.77×10^{-14}(18°C)
AgBr	7.7×10^{-13} (25°C)
AgCl	1.56×10^{-10}(25°C)
AgI	1.5×10^{-16} (25°C)
SrC_2O_4	5.61×10^{-8} (18°C)
ZnC_2O_4, $2H_2O$	1.35×10^{-9} (18°C)

Table XI

Colour changes and pH range of Indicators (Also See Expt. No. 9.3; P. 73)

Indicator	pH range	Colour in		pK_{in}
		acid medium	alkaline medium	
Methyl orange	3.1— 4.4	Red	Orange	3.7
Bromophenol blue	3.0— 4.6	Yellow	Blue	4.1
Methyl red	4.2— 6.3	Red	Yellow	5.0
Bromothymol blue	6.0— 7.6	Yellow	Blue	7.1
Phenolphthalein	8.3—10.0	Colourless	Red	9.6

Table XII

Standard electrode potentials (Reduction) at 25°C

Electrode	Electrode reaction	E°(volts)
Pt, MnO_4^-, Mn^{++}, H^+	$MnO_4^- + 8H^+ + 5e = Mn^{++} + 4H_2O$	1.52
Pt, Cl_2(g); Cl^-	$\frac{1}{2}Cl_2 + e = Cl^-$	1.36
Hg, Hg_2^{++}	$Hg_2^{++} + 2e = 2Hg$	0.799
Ag, Ag^+	$Ag^+ + e = Ag$	0.798
Pt; Fe^{+++}, Fe^{++}	$Fe^{+++} + e = Fe^{++}$	0.771
Calomel electrode	$\frac{1}{2}Hg_2Cl_2 + e = Hg + Cl^-$	0.280
Pt; H_2,H^+	$H^+ + e = \frac{1}{2} H_2$	0.000
Pb, Pb^{++}	$Pb^{++} + 2e = Pb$	—0.122
Sn, Sn^{++}	$Sn^{++} + 2e = Sn$	—0.136
Zn, Zn^{++}	$Zn^{++} + 2e = Zn$	—.672

Table XIII

Volumetric standards

Standards	Formula	Mol. wt.	Equivalent weight
Sodium carbonate	Na_2CO_3	106.00	53.00
Sodium Oxalate	$Na_2C_2O_4$	134.00	67.00
Oxalic acid (crystal)	$H_2C_2O_4,2H_2O$	126.06	63.04
Benzoic acid	C_6H_5COOH	122.13	122.13
*Ferrous sulfate	$FeSO_4,7H_2O$	278.03	278.03
*Ferrous ammonium sulfate	$FeSO_4.(NH_4)_2SO_4,6H_2O$	392.16	392.16
*Potassium Ferrocyanide	$K_4Fe(CN)_6,3H_2O$	422.41	422.41
*Potassium bromate	$KBrO_3$	167.016	27.836
*Potassium dichromate	$K_2Cr_2O_7$	294.222	49.037
*Potassium ferricyanide	$K_3Fe(CN)_6$	329.26	329.26
*Potassium Permanganate	$KMnO_4$	158.03	31.606
*Sodium thiosulfate	$Na_2S_2O_3,5H_2O$	248.21	248.21
*Iodine (resublimed)	I	126.91	126.91
Potassium chloride	KCl	74.56	74.56
Silver nitrate	$AgNO_3$	169.89	169.89

*In redox reaction.

Table XIV

Molal Boiling-point Constants of some common Solvents

Solvent	Boiling point at 760 mm (°C)	Molal Boiling point constant (K_b) °C.
Acetone	56.0	1.71
Benzene	80.2	2.53
Chloroform	60.2	3.63
Ethanol	78.3	1.22
Water	100.0	0.51
Carbon tetrachloride	76.5	5.05

Table XV

Molal freezing point constants of some common solvents

Solvent	Freezing point (°C)	Molal depression(K_f)
Acetic acid	16.7	3.9
Benzene	5.5	5.12
tert-Butanol	25.1	8.37
cyclohexane	6.5	20.0
Camphor	178.4	37.7
Cyclohexanol	25.1	37.7
Naphthalene	80.2	6.9
Heptachloropropane	29.5	12.0
Nitrobenzene	5.7	8.1
Phenol	42.0	7.27
Water	0.0	1.855

Table XVI

Index of Refraction (for sodium D-line)

Temp. °C.	Water, relative to air	Ethyl alcohol (99.89%) relative to air	Carbon disulfide, relative to air
20	1.33299	1.36048	1.62546
22	1.33281	1.35967	1.62387
24	1.33262	1.35885	1.62226
26	1.33241	1.35803	1.62064
28	1.33219	1.35721	1.61902
30	1.33192	1.35639	1.61740
32	1.33164	1.35557	1.61577
34	1.33136	1.35474	1.61413
36	1.33107	1.35390	1.61247
38	1.33079	1.35306	1.61080
40	1.33051	1.35222	1.60914

Table XVII

Refraction equivalents (for Sodium D line)

Carbon	2.418	Chlorine	5.967
Hydrogen	1.100	Bromine	8.865
Oxygen (In CO gr.)	2.211	Iodine	13.900
Oxygen (in ethers)	1.643	Double bond	1.733
Oxygen (in OH gr.)	1.525	Triple bond	2.398

Table XVIII

(I) *Critical Solution Temperature (C.S.T) and Composition*

System	Temperature	Composition
Water—Phenol	65.9°C	66%
Methanol-cyclohexane	49.1°C	29%
Isopentane-Phenol	63.5°C	51%

(II) *Systems with lower and upper C.S.T.*

System	Lower Temperature	Upper Temperature
Methyl ethyl ketone-water	−6°C	133°C
Glycerol-m-toluidine	6.7°C	120°C
Nicotine-water	60.8°C	208°C

Table XIX

Parachor Equivalents

Carbon	4.8	Sulfur	48.5	Nitrogen	12.5
Hydrogen	17.1	Chlorine	53.8	Double bond	23.2
Oxygen	20.0	Bromine	68.0	Triple bond	46.6
O in esters	60.0	Iodine	90.0	6-membered ring	6.1

Table XX

Respresentative Flocculation values (C) for As_2S_3 (Negative) Sol.

Electrolyte	Cation valence	*C (m, equiv./liter)*
NaCl	1	51
KNO_3	1	50
$\frac{1}{2}$ K_2SO_4	1	63
HCl	1	31
$MgSO_4$	2	0.81
$BaCl_2$	2	0.69
$ZnCl_2$	2	0.68
$AlCl_3$	3	0.093

Table XXI

Vapour pressure (P) and density (d) of water at different temperature

t (°C)	*P* (mm.Hg)	*d* (gm./ml.)	*t* (°C)	P (mm. Hg)	*d* (gm/ml.)
20	17.54	0.9982	28	28.35	0.9962
21	18.65	0.9980	29	30.04	0.9959
22	19.83	0.9978	30	31.82	0.9956
23	21.07	0.9975	31	33.69	0.9953
24	22.38	0.9973	32	35.66	0.9950
25	23.76	0.9970	33	37.63	0.9947
26	25.21	0.9968	34	39.90	0.9944
27	26.74	0.9965	35	42.18	0.9940

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LOGARITHMS OF NUMBERS

	0	1	2	3	4	5	6	7	8	9	Differences								
											1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9

	0	1	2	3	4	5	6	7	8	9	Differences								
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55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9

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