CONDUCTANCE MEASUREMENTS

11.1 To determine the cell constent of the given conductance cell.

Theory:

The resistance of any conductor varies directly as its length (l cm.) and inversely as its area (a sq. cm.); that is,

$$R = \rho . \frac{l}{a} \qquad \ldots (1)$$

where ρ is a constant, called the specific resistance of the conducting material. It is the resistance in ohms of a specimen 1 cm. in length and 1 sq. cm. in cross section.

The conductance (C) of a solution is the reciprocal of the resistance (R); and its specific conductance (k) is the reciprocal of the specific resistance (ρ). From (1)—

$$\frac{1}{\rho} = \frac{1}{R} \cdot \frac{l}{a}$$

or,

$$k = \mathrm{C} \times \frac{l}{a}$$

$$= \mathrm{C} \times K \text{ or } (1/R) \times K \qquad \ldots (2)$$

where l may be taken as the distance between the two electrodes in the conductance cell and a is the area of each. For a given cell l and a are constants and the quantity l/a is called the cell constant (K)

The cell constant may be obtained by direct measurement, but this is rarely done. (K) is generally obtained by using a solution of known specific conductance. Potassium chloride solutions of known strength are used for this purpose, for they have been measured with great accuracy in cells of known dimensions. A given solution of potassium chloride of known specific conductance (k) is taken in the experimental cell and its resistance or conductance (C) is measured. The cell constant, K is equal to $k \times R$ [from equation (2)].

Once the cell constant of a cell is known, it can be used to measure the specific conductanc (k) of any other solution, because k is equal to $K.(1/R)$ (where R is the observed resistance of the solution in the cell).

Material:

(1) Exactly 1N KCl solution (100 ml.)

Procedure:

The resistance (and hence conductance) can be measured with the aid of a conductivity bridge, using Wheatstone bridge method. The principle of the method is illustrated in fig. 24. The conductivity cell forms one arm *ab* of a Wheatstone bridge, a standard variable resistance box R forms another arm, and a calibrated slide-wire resistance *cb* constitutes the third and fourth arms, *cd* and *db*.

The passage of a current through an electrolytic solution may result in the change of composition of the solution at the electrodes; potentials may thus arise at the electrodes. This is called polarization. There may be serious errors in the conductivity measurements, unless

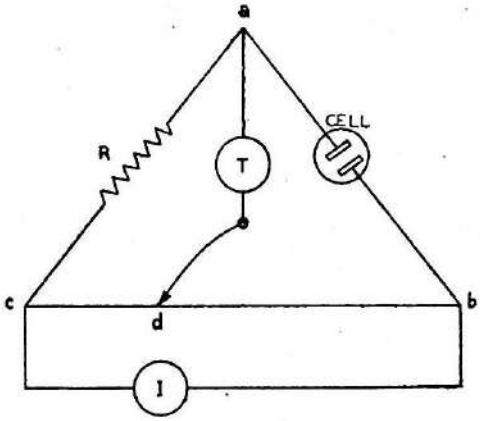


Fig. 24 Wheatstone's Meter Bridge

such polarisation effect is reduced considerably. These difficulties are overcome (*i*) by the use of alternating currents for the measurements so that the polarisation is constantly reversed; (*ii*) by using platinum electrodes covered electrolytically with a light coating of finely divided platinum, known as 'platinum black'; this increases the surface considerably and reduces the polarisation.

Now, in the Wheatstone bridge (fig. 24), the alternating current is provided by an induction coil or a valve oscillator (I) across *cb*. A telephone T (or similar device) connected across *ad* is used to detect the point of balance. With a given resistance at *R*, when the position of the slide contact is adjusted for minimum sound in the telephone, the following relationship holds good—

$$\frac{R_{cell}}{R} = \frac{bd}{cd}$$

where R is the known resistance, and R_{cell} the resistance of the given cell. From this relationship the resistance of the cell can be calculated, since R, bd and cd are known.

A disadvantage of this method is that one must work in a quiet room undisturbed by noise. However, for accurate work it is better to replace the telephone detector by a visual device, *i.e.* a magic-eye electronic detector.

A common type laboratory conductivity bridge is shown in Fig. 25.

Connect the units of the conductivity bridge according to the directions supplied by the manufacturer of the instrument (study the circuit until it is clearly understood that the different parts of the inastrument correspond to those of Fig. 24)

Conductivity cell:

The conductivity cell should be constructed of Pyrex or other resistance glass. The electrodes should be at least 1 sq. cm. in area and welded to thick platinum wires that are fused in glass tubes in which they make contact with mercury (not shown in Fig. 26).

Typical conductivity cells are shown in figure 26. I is "bottle type", suitable for titrations. II is the "immersion type" of cell for dipping into the test sloution (note that it is open at the bottom).

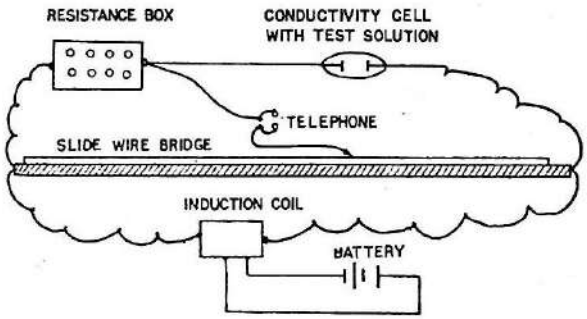


Fig. 25—Schematic Representation of the Set-up of a Conductivity Bridge

Platinising the electrodes:

Clean the conductivity vessel and the electrodes with a warm solution of dichromate and concentrated sulphuric acid. Wash with distilled water until free from acid. Place some quantity of the platinizing solution (prepared from 3 gm. of chloroplatinic acid and 0.025 gm. of lead acetate per 100 ml. water). Connect the electrodes to a current source (battery, 4 volts). The current is so adjusted (use rheostat) that there is only a moderately rapid evolution of hydrogen. Each electrode should be used alternately as anode and cathode (i.e., the current should be reversed every half-minute). The time of electrolysis is 2 to 5 minutes. The platinum coating should be black and shining. After platinising, the electrodes must be freed from traces of occluded chlorine by the following method: Place the electrodes in a solution of dilute sulfuric acid and pass current for about 15 minutes with the reversal of the current every minute (alternatively, using the two platinised electrodes, *connected together*, as cathode and another platinum electrode as anode—in this case current need not be reversed). Wash the electrodes repeatedly with distilled water and keep immersed in distilled water, until required for use.

Prepare carefully exactly 0.1, 0.02, 0.01 and 0.001 *N* KCl solution by quantitative dilution of 1*N* stock solution.

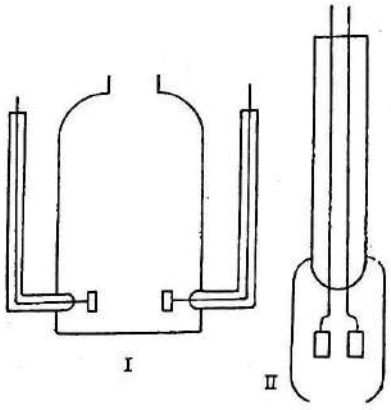


Fig. 26—Conductivity Cells

Set up and connect the apparatus. Fix the cell in a thermostat at 25°C. Fill the cell with conductance water*, and measure its resistance. Rinse and refill the cell and measure the resistance again. Repeat this process until the resistance has become essentially constant, showing that contaminating electrolytes in the cell have been rinsed out.

Next rinse the cell two or three times with the most dilute KCl solution (0.001*N*) and measure the resistance with this solution filling the cell. Make additional mesurements on fresh samples of the same solution until successive determinations agree closely.

Repeat the procedure with the other KCl solutions.

Results and Calculations:

Temperature=...

Concn. (N)	Resistance (R) (ohm)	Conductance (C) $=1/R$ (mho)	Sp. conductance (κ) ($ohm^{-1}cm^{-1}$)	Cell const. (K) $=\kappa \times R$ (cm^{-1})	Mean (K) (cm^{-1})

**Conductance water.*—This is obtained by redistilling distilled water with addition of a little potassium permanganate and traces of caustic soda in an all-glass apparatus. The specific conductivity of water should be less than 5×10^{-6} mhos $cm.^{-1}$

11.2 Studies on the conductance behaviour of weak and strong electrolytes.

(a) Determination of equivalent conductivity of some strong electrolytes at different concentrations.

(b) Determination of equivalent conductivity of a weak electrolyte at different concentrations.

(c) Determination of the ionisation constant of the weak electrolyte.

Theory:

(*a*) Strong electrolytes are those like sodium chloride which are practically completely ionised at all dilutions; and weak electrolytes are those which are dissociated only slightly even in very dilute solutions.

Changes in the conductance of an electrolytic solution with concentration may be due to changes both in the number and in the mobility of the ions present.

The increase of the equivalent conductance of solutions of strong electrolytes with dilution is mainly due to increased mobility of the ions. The conductance behaviour of the strong electrolytes has been successfully treated by Debye, Hückel and Onsager. The Debye-Hückel-Onsagar equation may be written as:

$$\Lambda = \Lambda_0 - [A + B\Lambda_0]\sqrt{C} \qquad \ldots (1)$$

where A and B are constants, characteristic of the solvent and dependent on temperature; C is the concentration of the electrolyte. At 25°C, values of A and B for water are 60.2 and 0.229 respectively. Λ represents the equivalent conductance at concentration C, and Λ_0 is the equivalent conductance at infinite dilution.

According to equation (1), a plot of Λ versus $\sqrt{C}$ should yield a straight line with intercept equal to Λ_0.

(*b*) In the case of weak electrolytes, the increase in equivalent conductivity on dilution is not primarily due to an increase of the mobility of the ions, but is largely due to an increase in the number of ions with diluton. Debye-Hückel-Onsager treatment cannot be applied to weak electrolytes.

According to the Arrhenius theory, the dissociation of weak electrolytes is not complete even in dilute solution and the degree of dissociation (α) at any concentration is given by the relation,

$$\alpha = \frac{\Lambda}{\Lambda_0} \qquad \ldots (2)$$

In the case of weak electrolytes, the value of Λ_0 cannot be obtained by extrapolation to infinite dilution of results obtained at finite concentrations. However, it can be calculated from results obtained with strong electrolytes by means of the Law of Kohlrausch concerning the additivity of ionic conductances at infinite dilution. Thus for a weak acid, CH_3COOH, the value of Λ_0 may readily be determined from a knowledge of the Λ_0 values of HCl, NaCl and CH_3COONa:

$$\Lambda_0(CH_3COOH) = \Lambda_0(HCl) + \Lambda_0(CH_3COONa) - \Lambda_0(NaCl) \quad \ldots \quad (3)$$

The Λ_0 values of strong electrolytes are obtained by applying equation (1).

(*c*) The dissociation constant K_a of a weak electrolyte (say, acetic acid) may also be calculated from Ostwald dilution law—

$$K_a = \frac{\alpha^2 C}{1-\alpha} \quad \ldots \quad \ldots \quad (4)$$

Where α = degree of dissociation

C = concentration in moles/lit.

Materials:

(1) Standard KCl solution (for determination of cell constant; (2) 1*N* acetic acid solution; (3) 1*N* HCl solution; (4) 1*N* NaCl solution (5) 1*N* CH_3COONa solution.

Procedure:

For all conductance measurements, the cell is kept immeresed in a thermostat (say, at 25°C).

First the cell constant is determined as described under experiment No. 11.1.

100 ml. of 0.05 *N* acetic acid is prepared by quantitative dilution of 1*N* stock solution with conductance water. Determine the conductance of this solution. Next a 0.025*N* solution is prepared by quantitative dilution of the 0.05*N* solution and its conductance is measured. In this manner, conductance measurements are made on 0.05, 0.025, 0.0125, 0.00625, 0.00312 and 0.00156*N* acetic acid solutions.

Similarly, conductance measurements are made on solutions of HCl, NaCl and CH_3COONa at various concentrations of, say, 0.04, 0.02, 0.01, 0.0025 and 0.00125(*N*). The solutions are prepared as in the case of acetic acid by quantitative dilution of a stock solution with conductance water.

Results and Calculations:

Cell constant (K) =

Table I

Temperature = ...

Electrolyte	Concentration (C) equivalent /lit.	Observed Resistance (R) ohm	Conductance ($1/R$) mhos	$k = K \times 1/R$ mhos cm^{-1}	$\Lambda = 1000k/C$ mho cm^2 equivalent^{-1}	Λ_0 (from graph)
HCl	... ...					
NaCl	... ...					...
CH_3COONa	... ...					...

Table II

Results of Acetic acid

$$\Lambda_0(CH_3COOH) = \Lambda_0(HCl) + \Lambda_0(CH_3COONa) - \Lambda_0(NaCl)$$

C equivalent per litre	R ohm	$1/R$ mhos	$k = K \times 1/R$ mhos cm^{-1}	$\Lambda = 1000k/C$ mhos cm^2 equivalent^{-1}	$\alpha = \frac{\Lambda}{\Lambda_0}$	$K_a = \frac{a^2C}{1-a}$
... ...						

Mean K_a = ...(at 25°C)

Suggestions for further work:

The influence of structure on the dissociation constants of organic acids may be studied. For example, the dissociation consta nts of monochloroacetic acid ($ClCH_2COOH$) and propionic acid (CH_3CH_2COOH) may be determined and compared with the dissociation constant of acetic acid.

11.3. Studies on some conductometric titrations.

Theory:

Since the specific conductance of a solution is proportional to the concentration of the ions in it, conductometric method can be used to determine the end points of ionic titrations. This method can be applied (*i*) to acidimetric titrations, (*ii*) to some precipitation titrations, and (*iii*) to titrations involving the formation of complex ions.

For example, when hydrochloric acid is titrated with sodium hydroxide the highly mobile hydrogen ions ($\lambda_0(H^+) \simeq 350$ ohm^{-1}cm^{-1}) are progressively replaced by the slower moving sodium ions ($\lambda_0(Na^+) \simeq 50$ ohm^{-1}cm^{-1}) and the conductance of the solution decreases. After the end point has been reached., the conductance rises sharply as there is now an excess of hydroxide ions, which are also highly mobile ($\lambda_0 \simeq 198$ ohm^{-1}cm^{-1}).

Similarly, the neutralisation of a strong base by addition of a strong

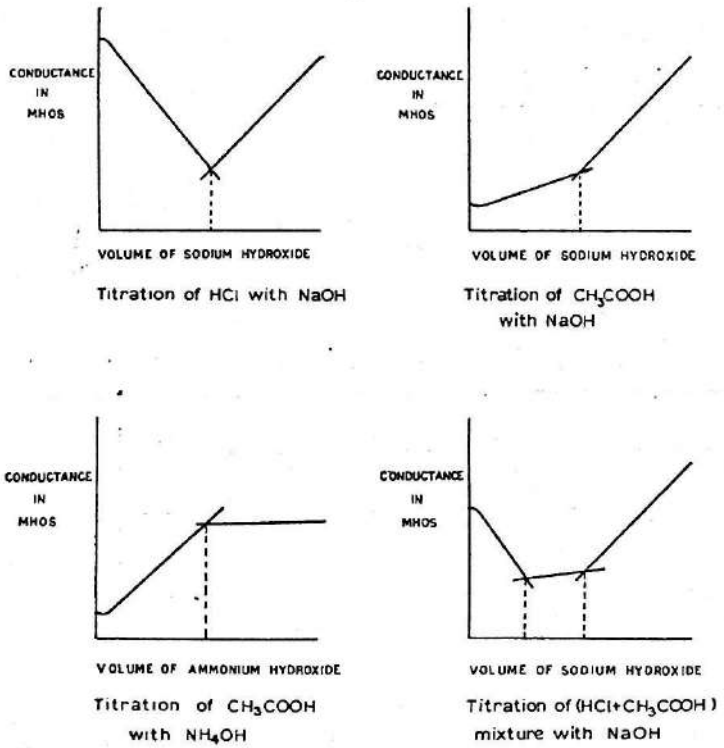


Fig. 27—Conductometric Titrations

acid leads to a minimum conductance at the end point. This is due to the disappearance of the OH^- ions and their replacement by the less

mobile anions (Cl^-) of the acid, followed by addition of highly mobile free H^+ ions after the end point. When, therefore, the conductance of the solution is plotted against the volume of titrant, a curve of the form shown in figure 27 is obtained.

The present experiment consists of two titrations, the first of a strong acid and the second of a weak acid, both with standard NaOH.

The same experimental methods can be used in conductometric titrations as are used in any other type of conductance measurements. Any cell may be used which permits of stirring by shaking or otherwise and to which the reagent can be added from a burette. It is usually convenient to avoid a large increase in volume during the titration. This is done by titrating with a reagent which is 10 or 20 times as concentrated as the solution to be titrated; use of a low-speed magnetic stirrer is most convenient for stirring.

Materials:

(1) 0.01 *N* HCl (100 ml.); (2) 0.01 *N* CH_3COOH(100 ml.); (3) 0.20 *N* NaOH (50 ml.)

Procedure:

Rinse the cell a number of times with conductance water.

Pipette 25 ml. of HCl into the cell. Set up the conductivity apparatus. Note the temperature of the cell (or, keep the cell in a thermostat at 25°C or so). Add small portions of alkali from the microburette, stir the solution and measure the resistance of the cell after each addition. Take at least five readings beyond the end point.

Repeat the procedure with acetic acid.

Results and Calculations:

HCl			CH_3COOH		
Vol. of NaOH added (ml.)	Observed resistance (R) ohm	Conductance $1/R$ ohm^{-1}	Vol. of NaOH added (ml.)	Observed resistance (R) ohm	Conductance $(1/R)$ ohm^{-1}

Plot conductance against volume of titrant. Two intersecting straight lines

would be obtained, the point of intersection being the equivalence point. Check the correctness of the equivalence point thus obtained.

Note that the conductometric titration curve for CH_3COOH is quite different from that of HCl. The latter is a V-shaped one while the former is not (Fig. 27).

Suggestions for further work:

1. Titrations of weak acid with a weak base and of a mixture of acids ($HCl+CH_3COOH$) with NaOH can be done. The nature of conductance titration graphs are shown in Fig. 27.

2. The conductometric method has been applied successfully to determine the end point of various electrolytic reactions. Thus, in the case of the reaction,

$$KCl+AgNO_3 = AgCl+KNO_3$$

the conductance of the solution remains almost unchanged on addition of silver nitrate to potassium chloride, bacause the conductance of potassium nitrate is similar to that of potassium chloride, When however, an excess of silver nitrate is added, the conductance shows a sudden increase.

3. The conductometric method may be applied to the determination of analytical precipitations. In the case of the reaction.

$$MgSO_4+Ba(OH)_2 = Mg(OH)_2+BaSO_4$$

the products are both sparingly soluble and separate out from the solution. Thus the conductance decreases initially and after the end point has been reached, on adding excess of barium hydroxide, the conductance rapidly increases.

4. Conductometric titration has been applied to study the formation of compounds between the alkali fluoride and aluminium fluoride similar to $3NaF, AlF_3$. The formation of complexes such as K_2HgI_4 has also been studied by this method.

11.4. To determine the hydrolysis constant of aniline hydrochloride in aqueous solution at 25°C by conductance measurements.

Theory:

When a salt of a weak acid or base is dissolved in water, hydrolysis occurs, so that the conductance of the solution is now due partly to the ions of the salt and partly to the ions (H^+ or OH^-) or the acid or base formed by hydrolysis. An excess of the weak acid or base in the presence of its salt can be regarded as completely unionised. Therefore, addition of weak acid or base to the salt solution supresses the hydrolysis, but the ionisation will be unaffected.

Aniline hydrochloride ($C_6H_5NH_3^+Cl^-$), the salt of a weak base and a strong acid is hydrolysed in water giving $(1-\alpha)$ equivalents of un-

hydrolysed salt and α equivalents of free acid and free base, where α is the degree of hydrolysis—

$$\underset{(1-\alpha)}{C_6H_5NH_3^+} \rightleftharpoons \underset{\alpha}{C_6H_5NH_2} + \underset{\alpha}{H^+}$$

The weak undissociated base aniline does not contribute to the total equivalent conductance (Λ) of the solution, which may therefore be written as follows.

$$\Lambda = (1-\alpha)\Lambda_c + \alpha\Lambda_{HCl}$$

$$\text{or,} \quad \alpha = \frac{\Lambda - \Lambda_c}{\Lambda_{HCl} - \Lambda_c} \qquad \ldots (1)$$

where Λ_c and Λ_{HCl} are the equivalent conductances of the unhydrolysed salt and the free acid at the same concentration. Λ_c, as has been pointed out, can be determined by measuring the equivalent conductivity in the presence of excess aniline. The values of Λ_{HCl} at concentrations of $\frac{M}{32}$, $\frac{M}{64}$, and $\frac{M}{128}$ are known to be respectively 393, 399 and 401. Thus α being determined from equation (1) the hydrolysis constant K_h is easily obtained [$K_h = \alpha^2[C/(1-\alpha)]$].

Materials:

(1) Aniline hydrochloride: (2) Freshly distilled aniline; (3) Bottle type conductance cell; (4) Standard KCl solution (for measuring cell constant).

Procedure:

Determine the cell constant of the conductance cell, Expt No. 11.1.

Prepare $\left(\frac{M}{32}\right)$ solution of aniline hydrochloride in pure water. From this stock solution, make $\frac{M}{64}$ and $\frac{M}{128}$ solutions. Determine the conductivity of each solution at 25°C, the cell being placed in a thermostat.

Now make a stock $\frac{M}{32}$ solution of aniline hydrochloride, not in pure water, but in an $\frac{N}{32}$ solution of aniline in water. Dilute this solution with $\frac{N}{32}$ aniline to make $\frac{M}{64}$ and $\frac{M}{128}$ solutions of aniline hydrochloride in the aniline solution. Determine the conductivity of each solution at 25°C, the conductance cell being placed in a thermostat.

Results and calculations:

Cell constant = ...

Table I

Temperature = 25°C

Solution of aniline hydrochloride	Observed Resistance (R) (ohm)	Conductance $\frac{1}{R}$ (mho)	Sp. conductance $k = \frac{1}{R} \times$ cell const.	k^*	Equiv. Cond. $= \Lambda = \frac{1000k^*}{C}$	$\alpha = \frac{\Lambda - \Lambda_c}{\Lambda_{HCl} - \Lambda_c}$	$K_h = \frac{\alpha^2 C}{1-\alpha}$
$\frac{M}{32}$ in water					$= \Lambda$		
$\frac{M}{32}$ in aniline soln.					$= \Lambda_c$		
$\frac{M}{64}$ in water					$= \Lambda$		
$\frac{M}{64}$ in aniline soln.					$= \Lambda_c$		
$\frac{M}{128}$ in water					$= \Lambda$		
$\frac{M}{128}$ in aniline soln.					$= \Lambda_c$		

*k represents corrected values (that is, specific conductance of aniline hydrochloride in solution – specific conductance of water)

11.5. To determine the solubility of the given sparingly soluble salt by conductance measurements.

(Lead sulfate, silver iodate, silver chromate, strontium sulfate, etc. may be used).

Theory:

In a saturated solution of a difficultly soluble salt, the solution is so dilute that the effects of interionic attraction are negligible. The equivalent conductance of such a solution may be assumed to be practically equal to the limiting value obtained by extrapolation to infinite dilution (Λ_0).

If the specific conductance (κ) of the saturated solution and that of the water used as solvent are determined, the specific conductance of the ions of the salt may be calculated by simple subtraction.

$$\kappa_{solution} - \kappa_{water} = \kappa_{ions} \quad \ldots (1)$$

By definition the equivalent conductance Λ is given by

$$\Lambda = \kappa_{ions} \times V \times 1000 = \kappa_{ions} \frac{1000}{C} \quad \ldots (2)$$

where V=volume containing 1 g-equiv. of solute in ml. and C=concentration in gm equiv./liter.

Since Λ is assumed to be equal to equivalent conductivity at infinite dilution, Λ_0 we get.

$$C = \frac{1000\ \kappa_{ions}}{\Lambda_0} \quad \ldots (3)$$

The value of Λ_0 can be obtained from the sum of the ionic conductivities. From equation (3), we can determine the number of gram equivalents of salt in 1 litre of solution. *To obtain the number of gram-molecules per liter, the solublity in gram-equivalents per liter must be divided by the valency of the cation or the anion* (higher value).

Materials:

(1) Standard KCl solution (for determining cell constant); (2) given sparingly soluble salt.

Procedure:

The cell constant for the conductance cell employed is determined as described under experiment No. 11.1.

For all conductance measurements the cell is kept immersed in a thermostat, preferably at 25°C. The cell is filled with conductance water, and its resistance is measured; it is then rinsed, refilled, and the resistance measured again. This process is repeated until the resistance has become essentially constant.

The salt whose solubility is to be determined is shaken repeatedly with conductance water to remove any soluble impurities. The well-washed salt is suspended in conductance water in a conical flask which has been thoroughly cleaned and rinsed with conductance water. The suspension is warmed moderately, then placed in the thermostat at constant temperature, say 25°C, and stirred vigorously until it has come to equilibrium at the temperature of the thermostat. The specific conductance of this solution is determined by repeated measurements on fresh samples of the solution until a constant value is obtained.

Results and calculations:

Table I

$\Lambda_0 = \lambda_{0\,(Cation)} + \lambda_{0\,(Anion)} = \ldots\ldots$

Cell constant= .....

	No. of observations	Resistance (R), ohm	Conductance, $\left(\frac{1}{R}\right)$ mhos	k = Cell Const. $\times \frac{1}{R}$ mho cm^{-1}
Water			= ..... (Mean Value)	... = k_{water}
Solution			= ..... (Mean Value)	... = $k_{solution}$

$\therefore \quad k_{ion} = k_{solution} - k_{water}$

Thus, Solubility in gm-equiv./lit. $= \dfrac{1000\, k_{ions}}{\Lambda_0}$

Note that the solubility product of a sparingly soluble binary salt of the type AB is simply the square of the solubility determined as above, *provided the solubility is expressed in gm-mols per liter.*

11.6: Studies on the kinetics of saponification of ethyl acetate by sodium hydroxide by conductance measurements. Determination of (*a*) the rate constant at different temperatures and hence (*b*) activation energy of the reaction.

Theory:

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

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

is given by the second order rate expression (expt. No. 10.6):

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

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

provided both the reactants are at the same intial concentration (a); the rate constant k can be determined from the slope of the plot of $1/(a-x)$ *vs.* t.

In this system, since the fast moving OH^- ions are being replaced by slower CH_3COO^-, the conductance will decrease with time. If R_0, R_t and R_∞ be the resistance of the reaction mixture at time zero, t and infinity respectively, then—

$$x \text{ is proportional to } \left(\frac{1}{R_0} - \frac{1}{R_t}\right) \text{ i.e. } (C_0 - C_t)$$

$$(a-x) \text{ is proportional to } \left(\frac{1}{R_t} - \frac{1}{R\infty}\right) \text{ i.e. } (C_t - C\infty)$$

$$\text{and } a \text{ is proportional to } \left(\frac{1}{R_0} - \frac{1}{R\infty}\right) \text{ i.e. } (C_0 - C\infty)$$

This is because the total change of conductivity (*i.e.* $C_0 - C\infty$) is evidently proportional to the total amount of ethyl acetate, a; conductivity change at any time t is $C_0 - C_t$ which is evidently proportional to the extent of reaction during this period (i.e. x).

Therefore k can be determined from the slope of the plot of

$$\left\{\frac{1}{\frac{1}{R_t} - \frac{1}{R\infty}}\right\} \text{ vs. } t. \text{ i.e. } \left(\frac{1}{C_t - C\infty}\right) \text{vs. } t.$$

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

$$k = A \exp. [-E/RT]$$

$$\text{or, } \log k = A' - \frac{E}{2.303\ RT}$$

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}) and T is the absolute temperature.

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

Materials:

(1) 0.02M NaOH; (2) 0.02M ethyl acetate; (3) Bottle-type conductance cell.

Procedure:

The conductance cell, one dry stoppered 500 ml. conical flask and two conical flasks containing NaOH and ester respectively are placed in the thermostat maintained at a definite temperature (say, 25°C).

25 ml. of NaOH is pipetted into the dry conical flask. Next 25 m. ethyl acetate solution is pipetted into the same flask. Start the stol watch at half-discharge of the pipette. The reaction mixture in the the flask is well shaken and transferred as quickly as possible to the conductance cell, after rinsing the cell with the reaction mixture. The resistance of the solution is noted at intervals of one minute or so.

After about ten minutes the solution is poured back into the flask and kept overnight for noting $R\infty$.

The procedure is repeated at least at two other temperatures.

Results and Calculations:

Table I

Temp °C T	Time t	R ohm	$\frac{1}{R}$ mho	$\frac{1}{R_t} - \frac{1}{R_\infty}$ (mho)	$\frac{1}{a-x} = \frac{R_\infty . R_t}{R_\infty - R_t}$ (ohms)	k ($M^{-1}t^{-1}$)
	∞	...	...	—	—	
	∞	...	...	...	—	
	∞	...	...	...	—	

Plot $1/(a-x)$ (last column) against t (time) at each temperature. Three straight lines intersecting at one point (intercept, $1/a$) would be obtained the slope of each line giving the k at the corresponding temperature.

Now plot log k against 1/T. From graph (log k *vs* $1/T$)—

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

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

11.7: Conductometric determination of the kinetic order of saponification of Ethyl acetate by Sodium hydroxide.

Theory:

For a reaction of the n-th order, the time τ taken to complete a definite fraction (say, one half) of the reaction is given as—

$$\tau \propto \frac{1}{a^{n-1}}$$

provided the reactants are all at the same initial concentration, a. If in two different experiments the concentrations are a_1 and a_2 and the corresponding, *say*, half-life periods are τ_1 and τ_2 then

$$\frac{\tau_1}{\tau_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

$$\text{or, } n = 1 + \frac{\log (\tau_1/\tau_2)}{\log (a_2/a_1)}$$

τ_1 and τ_2 can be obtained by plotting x, the extent of the reaction, against the corresponding time t.

For the saponification of ethyl acetate,

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

the OH^- is replaced by slower CH_3COO^-, as a result of which the conductance decreases with time (*vide*—Expt. No. 11.6). If R_0, R_t and $R\infty$ be the resistances of the reaction mixtures at times zero, t and infinity respectively, then—

$$a \propto \left(\frac{1}{R_0} - \frac{1}{R\infty}\right)$$

$$(a-x) \propto \left(\frac{1}{R_t} - \frac{1}{R\infty}\right)$$

$$\text{and } x \propto \left(\frac{1}{R_0} - \frac{1}{R_t}\right)$$

Materials:

(1) 0.02*M* ethyl acetate; (2) 0.02*M* NaOH; (3) Bottle-type conductance cell.

Procedure:

The conductance cell and stoppered conical flasks containing ethyl acetate and NaOH are kept in a thermostat maintained at say, 25°C.

25 ml. alkali solution is pipetted into 2 dry 500 ml. conical flasks (I, II) fitted with stopper; they are also placed in the same thermostat.

25 ml. ester is pipetted into flask I and stop-watch started at the time of half-discharge of pipette. The mixture is well shaken and is poured inside the conductance cell as quickly as possible after rinsing the cell. The resistance of the reaction mixture is noted from time to time. After about ½ hour the contents of the cell is poured back into flask I and kept overnight for noting R_∞ reading.

50ml. water is poured into flask II containing 25 ml. NaOH solution, and 25 ml. of ester is pipetted into it. The stopwatch is started at the half-discharge of the ester. The reaction mixture is transferred quickly into the conductance cell, previously rinsed with the same solution. The resistance is noted as before.

Results and Calculations:

Reaction mixture I				Reaction mixture II			
Time	R ohm	$\frac{1}{R_t}$ mho	$\frac{1}{R_0}-\frac{1}{R_t}$ mho	Time	R ohm	$\frac{1}{R_t}$ mho	$\frac{1}{R_t}-\frac{1}{R_\infty}$ mho
0	...	...		0	...	...	
∞				∞			

Plot $(1/R_t - 1/R_\infty)$ *vs* time and from each graph find out the time in which this quantity falls to half. This time is the time of half reaction.

From graph,

T_1, time for half reaction (mixture I) = ...

T_2, time for half reaction (mixture II) = ...

$$\therefore \text{ Order} = 1 + \frac{\log \frac{T_1}{T_2}}{\log \frac{a_2}{a_1}}$$

POTENTIOMETRIC EXPERIMENTS

12.1: Determination of Standard Electrode Potential

Theory:

In E.M.F. studies different authors unfortunately follow different conventions. The student should try to master one convention and then it would be easy to follow different authors. The convention we shall follow in this book is as follows:

(*i*) All cells are constituted of two half cells. If it is known which one of the two half-cells is positive, we shall strictly follow the convention of writing it on the right-hand side and the other half-cell on the left-hand side. So a complete cell would be represented as follows (the separating double line indicates a salt-bridge to eliminate junction potential).

(−) Left-Hand Half-Cell || Right-Hand Half-Cell (+)

Where the polarity is unknown, for theoretical treatment we shall still consider the right-hand cell positive. Therefore if the potential of the right-hand cell is E_{Right} and that of the left-hand cell is E_{Left}, we have for the observed E.M.F. of the cell, E_{Cell} as follows:

$$E_{Cell} = E_{Right} - E_{Left} \qquad \ldots \quad (12.1)$$

It may be noted that E_{Right} or E_{Left} can be the potential of the corresponding electrode above any arbitrary half-cell, but conventionally this arbitrary half-cell is the normal hydrogen electrode. This is a universally followed convention.

(*ii*) The conventional value of the potential of any electrode (E_{el}) therefore is its potential measured against the normal hydrogen electrode. So, the electrode reaction is the reduction reaction: $M^{n+} + n\epsilon = M$ and the electrode potential ($E_{el.}$) of any electrode reversible to metal ions M^{n+} is given by the famous Nernst equation as given below.

$$E_{el.} = E^{\circ}_{el.} + \frac{RT}{nF} \ln a \qquad \ldots \quad (12.2)$$

$$\text{or } E_{el.} = E^{\circ}_{el.} + \frac{0.0591}{n} \log a \text{ (at 25°C)} \qquad \ldots \quad (12.3)$$

where $E_{el.}$ = The conventional potential of any electrode i.e. the potential against the normal hydrogen electrode. To avoid any ambiguity we shall call this value the Reduction Potential of an electrode (*i.e.* a half-cell).

$E°_{el.}$ = Standard electrode potential (reduction) of the electrode; also called standard reduction potential. Tables of $E°$-values for all electrodes or half-cells are available in standard text books. Note that $E°=E$ when $a=1$, i.e. the standard electrode potential of any given electrode is the potential against the normal hydrogen electrode when the reversible ion is of unit activity.

n = valency of the cation.

a = activity (effective concentration) of the cation, M^{+n}.

F = one Faraday of electricity.

The student should do well to memorise equation 12.2 and its corollary, equation 12.3. (Also, *vide* eqn 12.4, & discussion (p. 140) under 12.7).

Note (1) — If the electrode is reversible to anion (for example, if the cell reaction is $(F_2+2\epsilon=2F^-$ the plus sign in eqn. 12.2 has to be changed to minus sign.

Note (2) — Note that some authors use an opposite convention and use oxidation potential which is the negative of the value of reduction potential

Note (3) — Note that according to our convention, one can find the electrode potential of *any* electrode by writing the electrochemical reaction as a reduction process. If the activity quotient which is similar in form to equilibrium constant, of this reaction is K', the electrode potential is given by—

$$E = E° - RT/nF \ln K' \qquad \ldots \quad (12.4)$$

We shall use this equation extensively later and so the student should master it carefully. Eqn. 12.2 is a special case of eqn. 12.4.

In the present experiment, the metal-metal ion electrode will be combined with a calomel electrode to form a cell. The E.M.F. of the cell is measured by a potentiometer. If the calmel electrode is the negative electrode, equation (12.1) for the given cell at 25°C becomes—

$$E_{Cell} = \left[E°_{el.} + \frac{0.0591}{n} \log a \right] - \text{Ecalomel} \qquad (12.5)$$

If the potassium chloride concentration in the calomel electrode is 1N, the cell is written as—

$$Hg \mid Hg_2Cl_2;\ KCl(1N) \parallel M^{n+}(a) \mid M,$$

the two vertical lines indicating that junction potential effects have been eliminated by the use of a salt bridge.

However, if the calomel electrode is the positive electrode, the cell is represented as—

$$M \mid M^{n+}(a) \parallel KCl(1N);\ Hg_2Cl_2 \mid Hg.$$

the cell potential is given by the expression

$$E_{Cell} = Ecalomel - \left[E^{\circ}el + \frac{0.0591}{n} \log a \right] \quad \ldots \quad (12.6)$$

If the measured cell potential (E_{Cell}), the valence of the metal ion (n), and the ionic activity (a) are known, it is possible to calculate the standard electrode potential (E°_{el}) of the particular metal-metal ion couple by using either equation (5) or (6). The ionic activities (a) can be obtained by multiplying the molarities of the ions by the proper activity coefficients (vide Table at the end of this experiment).

Materials:

Cadmium electrode in the form of wire and 0.1M and 0.01M solutions of cadmium chloride; Potentiometer with necessary accessories (Standard cell, galvanometer, resistances, etc.); Calomel electrode.

Procedure:

Preparation of Calomel Electrode

Various forms of the calomel electrode are illustrated in Fig. 29; 0.1N, N, or saturated potassium chloride may be used, but the last-

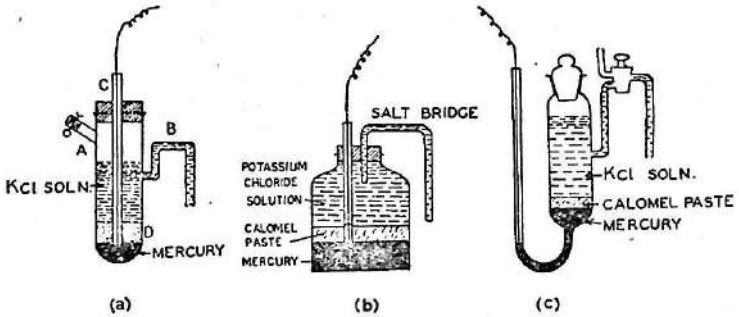


Fig. 29. Calomel Electrodes

named is generally used for class work. One of these, *viz.* type (*a*) will be described here in detail; the others will then be self-explanatory. Cell of type (*a*) consists of a glass vessel provided with a bent side tube B and another side tube A, over the end of which a piece of rubber tubing is placed which can be closed by a screw clip. Electrical connection with the electrode is made by means of a platinum wire, sealed through a glass tube C; the latter contains a little pure mercury into which an amalgamated copper wire dips. To set up the electrode, a saturated solution of analytically pure potassium chloride containing some of the solid salt is first prepared. Pure mercury to a depth of 0.5—1 cm is placed in the bottom of the dry electrode vessel; the mercury is then covered with a layer of calomel paste D. The latter is prepared by rubbing pure calomel, mercury, and saturated potassium chloride

solution together in a glass mortar; the supernatant liquid is poured off and the rubbing process repeated twice with fresh quantities of saturated potassium chloride solution. The rubber bung carrying the glass tube and platinum wire is then inserted, care being taken that the platinum wire dips into the mercury. The vessel is then filled with a saturated solution of potassium chloride (previously saturated with calomel by shaking with the solid salt) by drawing in the solution through the bent tube B, and then closing the rubber tube A with a clip. The electrode is then ready for use. In electrode (*b*), salt bridge may be filled with a jelly of 3 per cent agar in saturated potassium chloide solution. The electrode (*c*) is suitable for precison work; it has a three-way stop-cock for flushing away the contaminated potassium chloride after it has been employed in a titration.

Use of the potentiometer ;

The electromotive force of the experimental cell is determined by means of the potentiometer, using Poggendorff's compensation method. The principle of the method is to balance the unknown e.m.f. against a known e.m.f. which can be easily varied. When the two e.m.f.'s are made exactly equal, no current will flow through a galvanometer placed in the circuit. The principle of the method is shown in Fig. 30. The current is supplied from a steady source, *B*, which is either a storage battery or a few dry cells in series. This is connected in series with a rheostat *R* and with the terminals of a slide wire *AC* (also called "potentiometer wire"). *AC* is a thin wire of uniform cross-section. The cell, the emf. of which is to be determined, is connected to one end *A* of the potentiometer wire and to a siliding contact *D* through a galvanometer *G* and a key, K_1. The sliding contact *D* can be moved along *AC*. A special double-throw switch K_2 is placed in

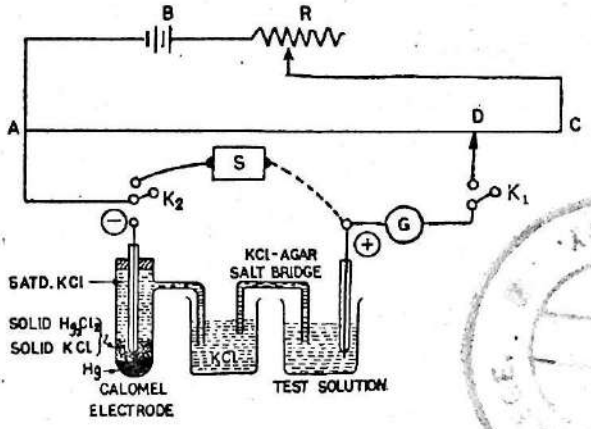


Fig. 30. E.M.F. Measurement

order to permit the standard cell *S* to be placed in the circuit. While

connecting the battery and the experimental cell to the bridge, note that the positive poles should be connected to the same end of the bridge; under these conditions, the experimental cell will then send a current through the circuit in a direction opposite to that supplied by the battery.

Since the sliding wire is of uniform resistance and the same current passes through each section of it, there will be a uniform fall of potential per unit length in the direction A to C. The difference of potential between A and any point, say D, will be proportional to the length AD, and will be equal to the fraction, AD/AC of the total fall of potential along the wire. Now, say, the experimental cell is placed in the circuit and the switch k_1 is pressed; the galvanometer will usually show a deflection. By moving the sliding contact, a point, say D_1, is reached when no current passes through the galvanometer. The e.m.f. the experimental cell is then given by—

$$\frac{\text{E.M.F. of exptl. cell}}{\text{E.M.F. of } B} = \frac{\text{Length } AD_1}{\text{Length } AC}$$

That is, the e.m.f. of the experimental cell is equal to that of the battery multiplied by AD_1/AC.

The potentiometers manufactured for laboratory use are so designed that the fall of potential per unit length of wire can be adjusted to some decimal fraction of a volt; and then the unknown voltage can be read directly from the scale. This can be done by means of the rheostat R and a standard cell (Weston cell). The Weston cell S has a voltage of 1.0183 volts at 25°C or, 1.0183—0.000046 (t - 20) at any other temperature t°C. The standard cell is put in the circuit with the help of the swith K_2. If the bridge is divided into 2000 equal parts, then the point D is so adjusted (using rheostat in order to get no deflection in the galvanometer) that AD corresponds to 1018.3 divisions. This means that the fall of potential along AD is 1.0183 volts and the fall of potential per unit length is 1 milli-volt. Having once adjusted the potentiometer with the rheostat against the standard cell, the readings thereafter are obtained directly in volts.

Connect the units of the potentiometer system according to the directions supplied by the instrument makers (study the circuit until you clearly understand the different parts of the instrument in terms of Fig. No. 30).

Measurement of e.m.f. of the cell:

The cell consists of a calomel electrode in combination with cadmium-cadmium ion electrode. The cell assembly is shown in Figure 30. The negative electrode is connected to the negative binding post of the potentiometer. If the electrodes are not properly connected to the potentiometer, it will be impossible to obtain a reading, since the galvanometer will always deflect in the same direction.

Make 0.1M and 0.01M solutions of cadmium chloride gravimetrically and then check the concentrations by proper analytical procedures. Measure the e.m.f. of the cell using both 0.1M and 0.01M solutions.

Results and Calculations:

Calculate the standard reduction potential of Cd-Cd^{++} system by using either equation (5) or equation (6), as the case may be.

Suggestions for further work:

Standard reduction potentials of other electrodes can be determined by a similar procedure. $E°_{el.}$ values of some common electrodes and other parameters are given in the following table.

In case of silver electrode, ammonium nitrate instead of potassium chloride should be used in the salt bridge. A silver wire cleaned with nitric acid (1:1) can be used as a silver electrode. Alternatively, the electrode can be made by electrolytic precipitation of silver on platinum foil.

Standard Electrode Potential (Reduction; 25°C)

Electrode	Electrode Reaction	$E°_{el.}$ (Volts)
Ag; Ag^{++}	$Ag^{+} + e = Ag$	+ 0.799
Cu; Cu^{++}	$Cu^{++} + 2e = Cu$	+ 0.345
Pb; Pb^{++}	$Pb^{++} + 2e = Pb$	− 0.126
Cd; Cd^{++}	$Cd^{++} + 2e = Cd$	− 0.402
Zn; zn^{++}	$Zn^{++} + 2e = Zn$	− 0.762

Potentials of the Calomel electrodes at t°C

$$E_t = E_{25} - a\,(t-25)$$

(KCl Concn.)	E_{25}, Volt	a
0.1N	0.3338	0.00007
1N	0.2800	0.00024
Staturated	0.2415	0.00076

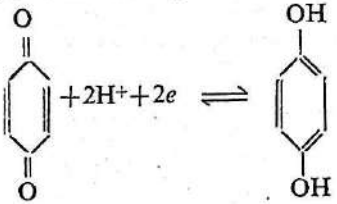
Mean Activity Coefficients (γ) of some Electrolytes at 25°C ($a = \gamma C$)

Electrolyte	0.01M	0.1M
$CdCl_2$	0.524	0.228
$CuSO_4$	0.404	0.158
$Pb(NO_3)_2$	0.692	0.367
$AgNO_3$	0.902	0.723
$ZnSO_4$	0.400	0.161

12.2: Potentiometric titration of acetic acid with NaOH and determination of the dissociation constant of acetic acid using quinhydrone electrode.

Theory:

Quinhydrone is a compound which in solution dissociates, giving equal concentrations of quinone (Q) and hydroquinone (H_2Q) according to the following electrochemical equation (reduction):



$$\therefore K' = \frac{(QH_2)}{(Q)\,(H^+)^2} = \frac{1}{(H^+)^2}$$

$$\therefore E = E^\circ - \frac{RT}{nF} \ln K'$$

The reduction potential of the system is therefore given by the Nernst equation, which in its most general form in given by (eqn. 12.4)—

$$E = E^\circ - \frac{RT}{nF} \ln K' \quad \ldots \quad \ldots \quad \ldots \quad (12.4)$$

where K′ is the activity quotient in the reduction equation.

$$\therefore \quad E = E^\circ - \frac{RT}{2F} \ln \frac{[H_2Q]}{[Q]\,[H^+]^2} \text{ (\textit{vide} eqn. 12.4)}$$

$$= E^\circ + \frac{RT}{F} \ln [H^+] \left(\because \frac{[Q]}{[H_2Q]} = 1\right) \quad \ldots \quad \ldots \quad (12.7)$$

$$= E^\circ + 0.0591 \log [H^+] \left(\because \frac{RT}{F} \times 2.303 = 0.0591 \text{ at } 25^\circ C\right) (12.7)$$

The value of E° at 25°C is 0.6990 volts, measured against a standard hydrogen electrode.

The cell used for the experiment is—

$Hg|Hg_2Cl_2$, KCl(satd.) ‖ solution, quinhydrone, $H^+|Pt$

In this cell calomel undergoes oxidation while the quinhydrone reduction. Hence the observed e.m.f. of the cell is (*vide* eqn. 12.1)

$$E_{obs} = E_R - E_L$$
$$= E - E_{calomel}$$

where E = Potential of the Quinhydrone electrode as given by eqn. 12.7.

and $E_{calomel}$ = Electrode potential of the saturated calomel electrode = 0.2415 volts.

$$\text{or, } E_{obs} = E^\circ - E_{calomel} + 0.0591 \log (H^+) \quad \ldots \quad 12.8$$
$$= (0.6990 - 0.2415) - 0.0591\ pH.$$

$$\text{or, } pH = \frac{0.4575 - E_{obs}}{0.0591} \text{ at } 25^\circ C \quad \ldots \quad 12.8(a)$$

One serious objection to the application of the quinhydrone electrode is that it cannot be used in solution more basic than about pH 9, because hydroquinone, a weak acid, is neutralised by base, giving incorrent values of pH.

The observed e.m.f. thus varies linearly with *p*H or with the logarithm of hydrogen ion concentration. In practice, the potential is measured after successive additions of small volumes of titrating solution (NaOH). E_{obs}. (*or* pH) is then plotted against the added volume of reagent; the neutratisation point is indicated by a sudden change (an inflection) in E (*or* pH) versus volume of titrant curve (Fig. 31 (*a*)).

The precision of the experiment depends upon the steepness of the slope of the inflection in the curve. The curve will be less steep if the sample is more dilute, or if either the acid or the base is weakly ionised. In case both the acid and the base are weak, the titration curve is far from steep and it is very difficult to obtain useful results. If the slope is not very sharp, better results are obtained by constructing a plot of $\triangle pH/\triangle V$ against V, where $\triangle(pH)/$ is the change in *p*H due to the volume change ($\triangle V$) of the reagent. Such plot is known as differential curve. The equivalence point is apparent as a maximum in the differential plot (Fig. 31*b*). Sometimes the "analytical" method is used to locate the end point. The method depends on the fact that the second derivative, $\triangle^2(pH)/\triangle V^2$ of the curve is zero at the point where the slope of the curve, $\triangle(pH)/\triangle V$ is a maximum (Fig. 31*c*).

According to Henderson's equation,

$$pH = pK_a + \log \frac{[Salt]}{[Acid]} \quad \ldots \quad (12.9)$$

where $pK_a = -\log K_a$ (K_a = dissociation constant of the acid). When the acid is half neutralised (i.e., [Salt]=[Acid]), $pH = pK_a$. Therefore the dissociation constant of an acid can be easily found out from the *p*H at the half-neutralisation point.

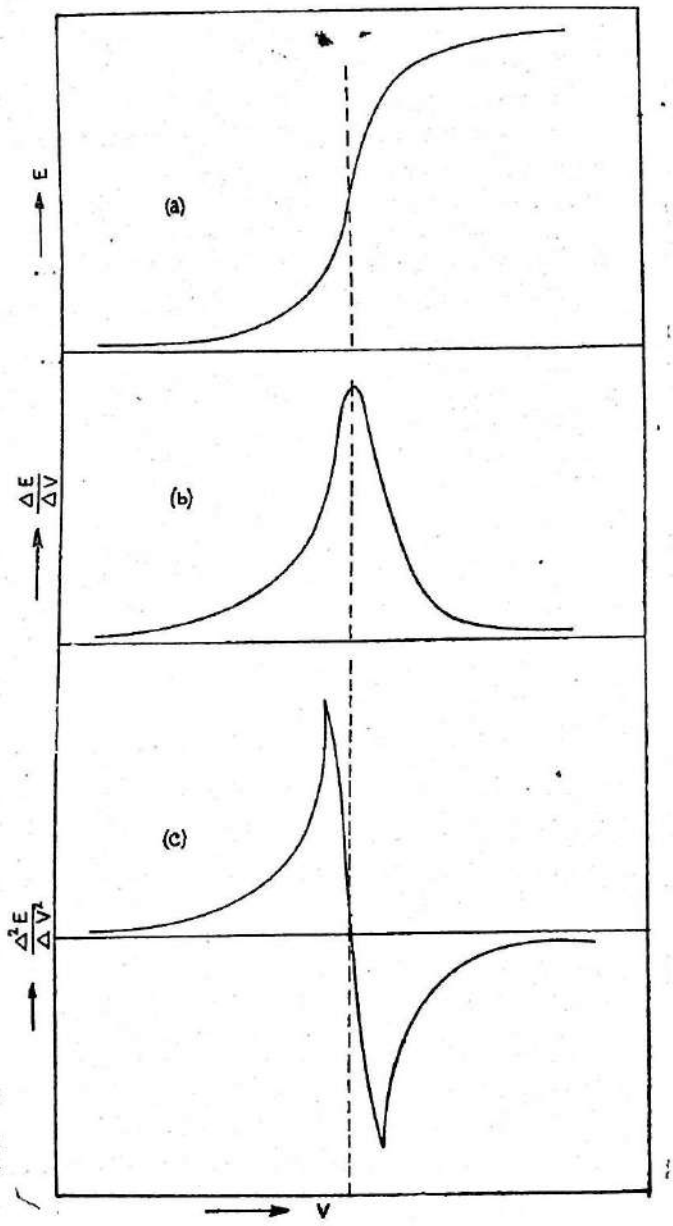


Fig. 31. (*a*) E vs. V, (*b*) $\triangle E/\triangle V$ vs. V and (*c*) $\triangle^2 E/\triangle V^2$ vs. V plots
Here E stands for e.m.f. and V for volume of titrant

Materials:

(1) Acid; (2) Alkali; (3) Quinhydrone.

If quinhydrone is not available, it may be prepared as follows; 30 gms. of ferric ammonium sulfate is dissolved in 300 ml. water at 65°C. This solution is poured into a warm solution of 25 gm. of hydroquinone in 300 ml. water. Quinhydrone precipitates in fine dark needles. The mixture is cooled in ice water, filtered by suction, washed with cold water. The product is recrystallised from water and dried.

Measurement of e.m.f. of the cell

Take 25 ml. of the acid in a 100 ml. beaker and add about 0.1 gm. of quinhydrone and stir the solution vigorously to prepare a saturated solution. Immerse the bright platinum electrode and lower the end of the salt bridge arm in the solution. The arrangement of apparatus, is shown in Fig. 30. Connect the calomel electrode to the negative terminal of the potentiometer and the quinhydrone electrode to the positive terminal. Set the rheostats against the E.M.F. of the standard cadmium cell (Expt. 12.1) and then meausure the E.M.F. of the experimental cell.

Add NaOH from burette and note down the voltage after each addition. (5 ml. portions may be added initially, followed by drop-by-drop additions near the end point). Take at least 5 readings after the equivalence point. (From time to time it is necessary to clean the bright wire electrode. This is most readily done by heating the wire in an alcohol flame).

Results and Calculations:

Volume of CH_3COOH = ...ml.

Vol. of NaOH (ml.)	E*obs.*	*p*H Calculated by equation 12.8	$\frac{\Delta pH}{\Delta V}$	$\frac{\Delta^2 pH}{\Delta V^2}$

Plot *p*H obs. *vs* vol. of NaOH. Also plot $\frac{\Delta pH}{\Delta V}$ vs. vol of NaOH, and $\frac{\Delta^2 pH}{\Delta V^2}$ *vs.* vol. of NaOH on the same graph paper. The nature of the plots is shown in fig. 31

pH at the neutralisation point = ... (from graph).

∴ pH at half neutralisation point = ...

= pK_a

Suggestions for further work:

1. Oxalic acid may be taken instead of acetic acid. In the titration curve, two inflexions will be observed. Applying Henderson's equation, the two dissociation constants of oxalic acid can be found out.

12.3: Potentiometric titration of phosphoric acid with sodium hydroxide using hydrogen electrode.

Theory:

When placed in a solution in which a reaction involving the transfer of an electron may take place, an inert electrode, such as a platinum electrode, assumes an electric charge. Thus when hydrogen gas is passed on an electrode of platinum foil, covered with platinum black and immersed in a solution containing hydrogen ions, an electrical potential is developed between the electrode and the solution. The reduction potential is then given by (*vide* eqn. 12.4)—

$$H^+ + e \rightleftharpoons \tfrac{1}{2} H_2$$

$$E = E^\circ + \frac{RT}{F} \ln \frac{[H^+]}{[H_2]^{\frac{1}{2}}} \quad \ldots (12.10)$$

where $[H_2]$ and $[H^+]$ are the activities (or effective concentrations) of hydrogen gas and hydrogen ions respectively. The value of E° for this reaction is zero, by convention. Assuming the activity of the hydrogen gas to be equal to the pressure expressed in atmspheres and letting $pH = -\log [H^+]$, the equation (12.10) at 25°C and 1 atm. pressure becomes.

$$E_{obs} = 0.0591 \log [H^+]$$
$$= -0.0591\ pH \quad \ldots (12.11)$$

The complete cell used for the experiment is

Pt, H_2 (1 atm.); $H^+ \parallel$ KCl (sat.); Hg_2Cl_2,Hg.

The observed e.m.f. of such a cell is

$$E_{obs.} = E_R - E_L$$
$$= E_{calomel} - E_L$$
$$= 0.0591\ pH + E_{calomel}$$

$$\text{or, } pH = \frac{E_{obs.} - E_{calomel}}{0.0591} \quad (\text{at } 25°C,\ E_{calomel} = 0.2415 \text{ volts})$$

$$= \frac{E_{obs} - 0.2415}{0.0591} \quad \ldots \quad \ldots (12.12)$$

Materials:

(1) Phosphoric acid; (2) NaOH

Procedure:

A diagram of the apparatus is shown in the figure 32. The hydrogen electrode is connected to the negative terminal of the potentiometer and the saturated calomel electrode is connected to the positive terminal. Close the switch in the battery circuit and tap the key of the potentiometer. If a deflection of the galvanometer is noted, change the setting of the resistor slide until no deflection

occurs when the key is lightly tapped. Only slight currents should be allowed to pass as otherwise the hydrogen electrode will become polarised. The H_2-electrode shown in Fig. 32 (*left*) is more convenient.

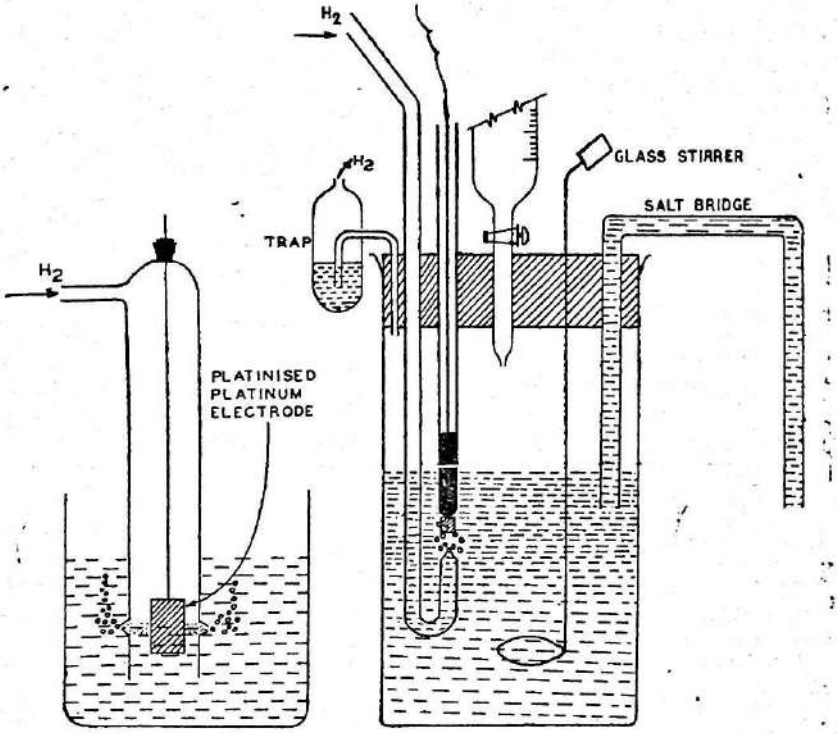


Fig. 32 Hydrogen Electrode (Two types shown)

The hydrogen electrode consists of a piece of platinum foil (or wire), the surface of which is coated with finely divided platinum (platinum black) and is saturated with hydrogen gas. The wire carrying the platinum foil is fused through a glass tube. This tube is put in a jacket with an inlet for hydrogen gas. Before use the electrode is cleaned with chromic acid cleaning solution and washed repeatedly in distilled water. It is then immersed in a 2 to 3 per cent solution of platinic chloride containing a trace of Pb-acetate and then made the cathode in an electrolysis cell in which the anode is another platinum wire or foil. The current may be supplied from two $1\frac{1}{2}$ volt dry cells in series. After a thin black film is deposited on the cathode, electrolysis is stopped. The electrodes are then placed in a small beaker of distilled water to which a drop of conc. H_2SO_4 has been added and the electrolysis is allowed to proceed as before. This treatment produces hydrogen and removes any impurities. The electrode should be washed and stored in distilled water. It must be replatinsed from

time to time, as the coating of platinum black becomes "poisoned" with use.

Hydrogen from a tank is purified by passing through wash bottles containing solutions of alkaline pyrogallol, potassium permanganate and distilled water. Hydrogen can also be generated in a Kipp's apparatus.

Take 25 ml. of the 0.5 N H_3PO_4 in a 250 ml. beaker and add enough water such that the electrode is at such a level as to prevent air diffusing back into the region of the electrode. Pass hydrogen at a steady rate. Add NaOH solution slowly from a burette. Stir the solution after each addition and measure the voltage. At intial stages 2 ml. portions of NaOH is added, but as the neutral point is approached, readings are taken more frequently (in stepts of 0.1 ml.), and after passing the end point larger amounts can again be added. (In case of phosphoric acid two sharp changes in E_{obs} should occur).

Results and Calculations:

Vol. of H_3PO_4 taken = ...

Vol. of NaOH (*ml.*)	Eobs. (volts)	$\Delta E/\Delta V$	$\Delta^2E/\Delta V^2$	*p*H(eqn. 12.12)

The nature of one of the plots (*p*H vs. vol. of NaOH) is shown in fig. 33. From graph,

*p*H at 1st ½-neutralisation

= .....

$\therefore$ pK_1 = ...

*p*H at 2nd ½-neutralisation

= ...

$\therefore$ pK_2 = ...

Suggestions for further work:

The following acid-base titrations can also be performed with hydrogen electrode. (1) HCl—NaOH; (2) HCl —Na_2CO_3 ; (3) CH_3CO OH—NaOH; etc.

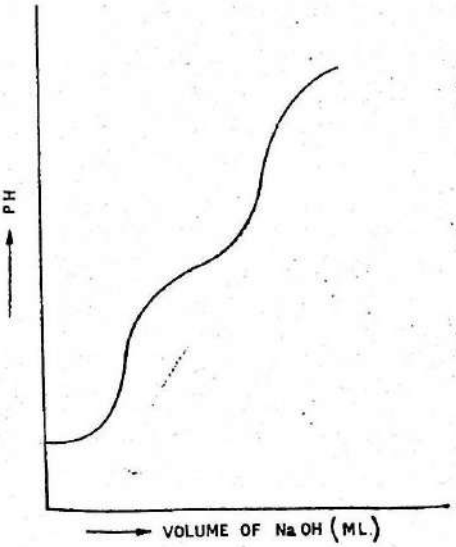


Fig. 33. Plot of *p*H *vs* Volume of NaOH

12.4: Determination of the hydrolysis constant of aniline hydrochloride using the hydrogen electrode.

Theory:

Aniline hydrochloride, the salt of a weak base and a strong acid, hydrolyses according to the following equation—

$$C_6H_5NH_2.HCl \rightleftharpoons C_6H_5NH_2 + HCl$$

The hydrolysis constant is given by, $K_k = \frac{\alpha^2 C^2}{(1-\alpha)C}$ ... (12.13)

where α is the degree of hydrolysis and C is the total concentration of salt in moles the per liter. $C\alpha$ (the concn. of free acid), may be taken as equal to C_{H^+}(as HCl is completely ionised) where C_{H^+} is the concentration of hydrogen ions in solution. The hydrolysis constant can be written as—

$$K_h = \frac{C_{H^+}C_{H^+}}{C - C_{H^+}} = \frac{C_{H^+}^2}{C} \quad \ldots (12.14)$$

as C_{H^+} can be neglected in comparison to C. From equation (14), it follows that by measuring the concentration of hydrogen ions in a salt solution of known concentration, the hydrolysis constant can be found out.

The cell employed is

Pt, H_2 (1 atm.); H^+ ‖ KCl (Satd.); Hg_2Cl_2, Hg

The observed e.m.f. is given by (*vide* expt. No. 12.3)—

$$E_{obs} = 0.0591\ pH + E_{calomel} \text{ (at } 25°C)$$

$$\therefore pH = \frac{E_{obs} - 0.2415}{0.0591} \quad \ldots (12.15)$$

The pH (i.e.—log C_{H^+}) of the solution may be calculated by means of Eqn, (15); The value of C_{H^+} thus obtained when substituted in eqn. (14) gives K_h.

Materials:

Aniline hydrochloride crystals.

Procedure:

Prepare solutions of aniline hydrochloride of different strengths $\left(\frac{M}{10} \text{ to } \frac{M}{500}\right)$.

Measure pH of each of the solutions by hydrogen electrode (*see* expt. No. 12.3 for detailed procedure).

Solution No.	C (moles/lit.)	$E_{obs.}$ (volts)	pH	C_{H^+} (gm. ion/lit.)	K_h (moles/lit.)	Mean K_h (moles/lit.)
	...					

The calculation of K_h can be done either with the approximate version or without the approximation with the help of eqn. (13). Note that the approximate form used is accurate enough for our purpose.

Suggestions for further work:

A glass electrode (*vide* expt. No. 12.8) may be used instead of hydrogen electrode.

12.5: Determination of the standard electrode potential of the quinhydrone electrode.

Theory:

For theory of the quinhydrone electrode *vide* Expt. 12.2

The electrode pontential of this sytem is given by eqn. 12.7,

$$E = E^\circ + 0.059 \ pH \qquad \ldots (12.7)$$

The aim of the present experiment is to determine E°.

The cell used for the experiment is the same as in Expt. 12.2 :—

Hg | Hg_2Cl_2,KCl (satd.) || solution, quinhydrone H^+ | Pt

The observed e.m.f. of the cell is given by (*vide* Expt. 12.2)—

$E_{obs} = E - E_{calomal}$ where $E_{calomel}$=Reduction potential of the saturated calomel electrode)

$$= E^\circ + 0.0591 \ pH - E_{calomel}$$

$$= (E^\circ - E_{calomel}) + 0.0591 pH \qquad \ldots (12.16)$$

The e.m.f.'s of solutions with different pH values are measured. The plot of E vs. pH will yield a straight line with intercept $(E^\circ - E_{calomel})$. Thus by knowing $E_{calomel}$ at the laboratory temperature, the E° can be found out at that temperature.

Materials:

(1) 0.4(N) NaOH; (2) 0.4(N) CH_3COOH; (3) Quinhydrone.

Procedure:

Prepare exactly 0.2 (N) CH_3COONa from the NaOH and CH_3COOH solutions. This can also be done by direct weighing and dissolving analytically pure *dry* anhydrous sodium acetate. Also the 0.4 (N) CH_3COOH is diluted properly so as to produce exactly 0.2(N) CH_3COOH.

Take six dry 250 ml. conical flasks. The following buffer solutions are to be prepared:

Flask No.	Vol of 0.2N CH_3COOH	Vol of 0.2N CH_3COONa	pH of the buffer solution
I	45	5	3.72
II	40	10	4.05
III	35	15	4.27
IV	30	20	4.45
V	25	25	4.63
VI	15	35	4.99

Take a 100 ml. clean beaker and wash it with the buffer solution (say, of flask No. 1). Put about 30 ml. of this buffer, saturated with quinhydrone and connect to saturated calomel electrode through KCl-agar salt bridge. Connect the platinum—quinhydrone electrode to the positive terminal of the potentiometer and the calomel electrode to the negative terminal (*vide* Fig. 30)

Set the rheostats against the e.m.f. of the standard cadmium cell (1.0183 volts) and then measure the e.m.f. of the experimental cell.

Measure the e.m.f. of the other buffer solutions in a similar manner (the platinum wire is to be sterilised each time, and also the standardisation of the potentiometer is to be checked before each reading).

Results and Calculations:

Laboratory temperature = ...

Flask No.	pH	E*obs.*

Plot E*obs.* vs. pH.

From graph, find the intercept.

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

$\therefore$ $E^\circ = E_{calomel} + \text{Intercept}$

= .....Volt.

12.6: Potentiometric redox titration of $K_3Fe(CN)_6$ with Co(II) and hence to find out the concentration of the latter in the given solution.

Theory:

Cobalt (II) can be estimated by $K_3Fe(CN)_6$ in strongly alkaline medium in presence of ammonium citrate. $Co^{II}(NH_3)_6$ formed in alkaline medium is oxidised to $Co^{III}(NH_3)_6$ by ferricyanide.

The oxidation potential of any redox system is given by—

$$E = E^\circ + \frac{RT}{nF} \ln \frac{[\text{Oxidised Form}]}{[\text{Reduced Form}]} \quad \ldots \quad \ldots \quad (12.17)$$

Therefore, for $Fe(CN)_6^{-3} + \epsilon \rightleftharpoons Fe(CN)_6^{-4}$

$$E = E^\circ + \frac{RT}{F} \ln \frac{[Fe(CN)_6^{-3}]}{[Fe(CN_6^-)^4]} \quad \ldots \quad (12.18)$$

Note that equation 12.17 is none other but eqns. 12.4 expressed in a simpler form.

The cell used for the experiment is—

Satd. calomel $\|$ $Fe(CN)_6^{-3}$—$Fe(CN)_6^{-4}$ | Pt.

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

$$E_{obs} = E - E_{calomel}$$

$$= (E^\circ - E_{calomel}) + \frac{RT}{F} \ln \frac{[Fe(CN)_6^{-3}]}{[Fe(CN)_6^{-4}]} \quad \ldots \quad (12.19)$$

When Cobalt (II) is added to the system, $Fe(CN)_6^{-3}$ is removed and the concentration $Fe(CN)_6^{-4}$ increases. From eqn. (12.19) it is evident that with the progressive addition of Cobalt (II), the observed e.m.f. will gradually diminish (*vide* P. 142). At the end point there will be a sharp decrease due to the sudden removal of all ferricyanide ions.

Materials:

(1) $K_3Fe(CN)_6$ (2) $Na_2S_2O_3$; (3) $K_2Cr_2O_7$; (4) Liquor. ammonia; (5) Cobaltous nitrate solution; (6) Petroleum ether; (7) Ammonium citrate (It can be prepared from the following: 50 gm. citric acid + 100 ml. water + 67.5 ml. liq. NH_3).

Procedure:

Titrate $K_3Fe(CN)_6$ with standard $Na_2S_2O_3$ and find out the strength of ferricyanide.

In a 250 ml. beaker take 20 ml. of ferricyanide, 20 ml. of ammonium citrate and 100 ml. of 5(*N*) ammonia. The mixture is covered with sufficient petroleum ether whose function is to prevent aerial oxidation of $Co(NH_3)_6^{+2}$ and to prevent evaporation of NH_3. Dip the freshly sterilised platinum electrode and connect to saturated calomel electrode through KCl-agar salt bridge. Connect the platinum electrode and the calomel electrode to the terminals of the potentiometer. The arrangement of the apparatus is shown in Fig. 34

Set the rheostats against the standard cadmium cell (1.0183 volts).

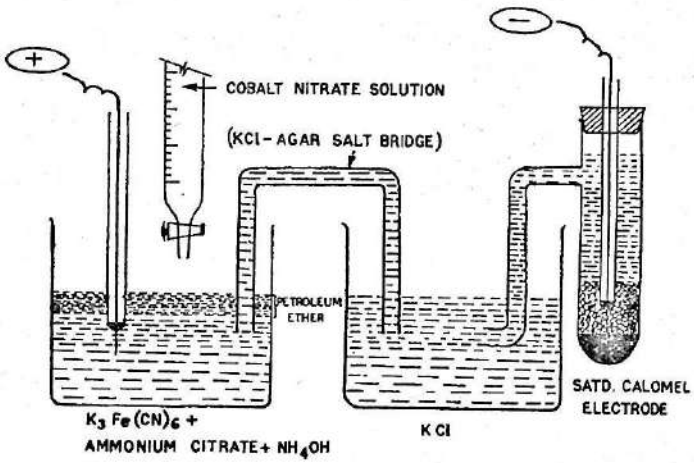


Fig. 34.—Potentiometric titration of Co (II)

and then measure the e.m.f. of the experimental cell. Add cobaltous nitrate solution from a burette; stir the solution and note down the observed e.m.f. Initially larger amounts (say, 1 ml. each time) may be added, but as the end-point is approached, readings are taken more frequently (0.1 or 0.05 ml.) and after the end point amounts in larger steps can again be added.

Dilute the original cobaltous nitrate solution so that its concentration is exactly half of that of the original one. Repeat the above procedure with this dilute solution.

Results and Calculations:

Strength of $K^3Fe(CN)$ =.....

Expt. (1)		Expt. (2)	
Vol. of $K_3Fe(CN)_6$=20ml.		Vol. of $K_3Fe(CN)_6$=20 ml.	
Vol. of Co (II) (ml.)	E (volt)	Vol. of Co (II) Diluted Solution (ml.)	E (volt)

Plot E_{obs} *vs* vol. of Co (II) solution. The nature of the plots is shown in Fig. 35.

From expt. (I)—

Vol. of Co (II) for 20ml. $K_3Fe(CN)$ = ...

∴ Strength of Co (II) = ...

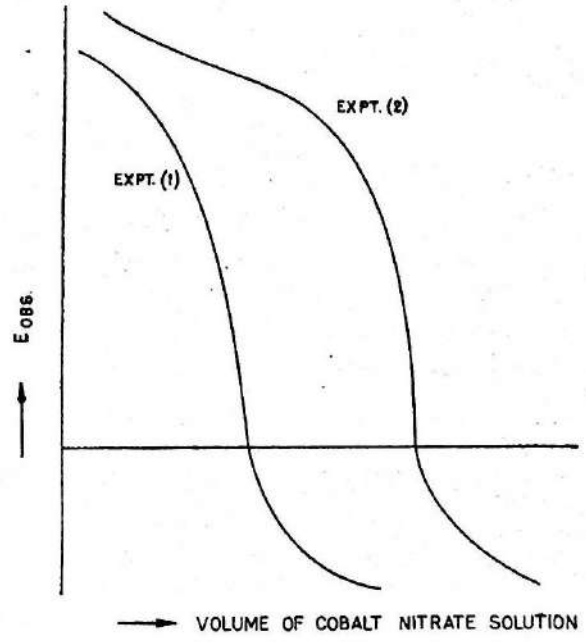


Fig. 35—E_{obs} *vs.* vol. of Co (II).

From expt. (2)—

Vol of Co (II) for 20 ml. $K_3Fe(CN)_6$ = ...

∴ Strength of Co)II) = ...

12.7: A Note on E.M.F. (Sign before Ion-Terms).

Students often find difficulty in writing down the equation for $E_{el.}$ (electrode potential) and E.M.F. They will find no difficulty if they follow the following rules based on reduction potential convention.

Half-Cells.—Write down all cell reactions irrespective of whether it is the positive or the negative electrode as reduction equations (i.e. electrons on left). Then write down the equation for activity quotient K′ (which is similar to equilibrium constant K in form) assuming by convention unit activity for solids and electrons. Some typical examples are shown below.

Electrode	Reduction Equation	Activity Quotient, K′
(1) Cu | Cu^{++}	$Cu^{++}+2e=Cu$	$K'=1/(Cu^{++})$
(2) Ag | AgCl, Cl^-	$AgCl+e=Ag+Cl^-$	$K'=(Cl^-)$
(3) Calomel electrode	$Hg_2Cl_2+2e=2Hg+2Cl^-$	$K'=(Cl^-)^2$

The electrode potential is then given by eqn. 12.4 (P. 124)

$$E_{el.} = E^\circ_{el.} - \frac{RT}{nF} \ln K' \qquad \ldots (12.4)$$

For Cell No. 1: $E_{el.} = E^\circ[Cu^{++} \rightarrow Cu] + \frac{RT}{2F} \ln (Cu^{++})$

For Cell No. 2: $E_{el.} = E^\circ[AgCl \rightarrow Cl^-] - \frac{RT}{F} \ln (Cl^-)$

For Cell No. 3: $E_{el.} = E^\circ\text{Calomel} - \frac{RT}{F} \ln (Cl^-)$

where E°'s are the standard electrode potential (reduction) of the corresponding half-cells, and first bracket indicates activity (effective concentration).

Complete Cells.—Always write the positive electrode (where known) on the right-hand (R) side and the negative electrode on the left-hand (L) side. The E.M.F. (E) is then given by eqn. 12.1 (P. 123)

$$E = E_R - R_L \qquad \ldots (12.1)$$

where E_R and E_L are given by eqn. 12.4. So with the help of eqn. 12.1 and eqn 12.4 one can easily write the E.M.F. of *any* cell.

Sign Rule.—In the final equation for E.M.F. check the correctness of the sign before each ion-term with the help of the following rule first given by the senior author:

Multiply the electrode polarity sign with the sign of the oxidation rank of the reversible ion; the product gives the sign of the ion term. The sign of oxidation rank is (+) for simple positive ions, and (—) for simple negativeions; (+) for oxidants, and (—) for reductants of a redox pair.

Thus, H^+ at positive (+) electrode must be preceded by (+) sign (eqn. 12.8); H^+ at negative (−) electrode by a(−) sign (eqn. 12.12); Ferricyanide (oxidant; ∴ rank symbol +) at positive electrode by (+) sign and ferrocyanide (reductant; rank symbol−) by (−) sign (eqn. 12.19). *The student should do well to memorise eqn.* 12.1, *eqn.* 12.4 *and the sign rule*, and then he will be able to write down correctly the $E_{el.}$ for all half-cells and E for all complete cells with perfect ease.

E.M.F. Change during Titration.—The above rule can also predict how E.M.F. changes during potentiometric titration. The rule is: Multiply the electrode polarity sign of the tiration cell by the rank symbol of the titrant. If the product is (+), the E.M.F. increases during titration; if negative, the E.M.F. decreases.

Thus, in Expt. 12.2 we are adding alkali i.e. a negative (−) OH^- ion to the positive (+) electrode; so since (−) × (+) = (−), we predict that Eobs. will decrease with progress of titration.

Similarly, in Expt. 12.3 we are adding the negative (−) OH^- ions to the negative (−) electrode; since (−) × (−) = (+) we predict that the Eobs. will increase with progress of titration.

In Expt. 12.6, we add Co(II) [Cobatous, a reductant, so rank symbol (−)] to the positive (+) electrode. So we predict that the Eobs. will decrease with titration (Fig. 35).

All these predictions are borne out by experiment.

E.M.F. SIGN RULE (TABULAR SUMMARY)

	Sign before Ion-term in EMF eqn,		EMF change during titration with titrant shown in column 1	
	In Positive Half-Cell (+)	In Negative Half-Cell (−)	Titrant added to Positive Half-Cell (+)	Titrant added to Negative Half-Cell (−)
Positive Ion or Oxidant Ion in redox pair (+)	+	−	+ (Increase)	− (Decrease)
Negtive Ion or Reductant Ion in redox pair (−)	−	+	− (Decrease)	+ (Increase)

12.8. Potentiometric estimation of Fe(II) with $K_2Cr_2O_7$ and determination of the formal redox potential of the ferrous-ferric system.

Theory:

The oxidation potential of any redox system is given by the equation

$$E = E^\circ + \frac{RT}{nF} \ln \frac{[\text{Oxidised form}]}{[\text{Reduced form}]}$$

Hence for ferrous-ferric system ($Fe^{+3} + e \rightleftharpoons Fe^{+2}$) we have

$$E = E^\circ + \frac{RT}{F} \ln \frac{[Fe^{+3}]}{[Fe^{+2}]} \quad \ldots (1)$$

The experimental cell is:

Saturated calomel $\|$ Fe^{+3}—Fe^{+2} | Pt

The observed e.m.f. of such a cell $E_{obs.}$ is given by—

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

$$= E^\circ - E_{SC} + \frac{RT}{F} \ln \frac{[Fe^{+3}]}{[Fe^{+2}]} \quad \ldots (2)$$

When $K_2Cr_2O_7$ is added to the system, Fe^{+2} is removed and the concentration of Fe^{+3} increases. From equation (2) it is evident that with the progressive addition of $K_2Cr_2O_7$, the observed e.m.f. will gradually increase (also *vide* Rule in Section 12.7). At the end point there will be sharp change due to sudden removal of all Fe^{+2} ions.

At half-equivalence point (e.g. $[Fe^{+2}] = [Fe^{+3}]$)—

$$\therefore \quad (E_{obs.})_{\frac{1}{2}} = E^\circ - E_{SC}$$

$$\text{or,} \quad E^\circ = E_{SC} + (E_{obs})_{\frac{1}{2}} \quad \ldots (3)$$

where E° is the formal redox potential of the Fe^{+2}—Fe^{+3} system.

Materials:

(1) Standard $K_2Cr_2O_7$ solution ($\sim 0.2N$); (2) $FeSO_4$ solution ($\sim 0.1N$); (3) H_2SO_4 ($\sim 2N$).

Procedure:

The arrangement of apparatus is the same as in the other potentiometric titrations (see fig. 34).

Take 25 ml. of Fe(II) solution in a small beaker. Add an equal volume of $2N$ H_2SO_4 to this solution. Place the bright platinum electrode in the solution and connect this with a saturated calomel electrode. Connect the platinum electrode and the calomel electrode to the terminals of the potentiometer.

Standardise the potentiometer against the standarad cadmium cell and then measure the e.m.f. of the experimental cell. Add $K_2Cr_2O_7$ solution from a burette, stir the solution, allow to

stand for 1-2 mins. and then note down the observed e.m.f. (Initially and after the end point larger amounts of $K_2Cr_2O_7$ may be added, but near the end point, readings should be taken more frequently, *say* at intervals of 0.1 ml.).

Results and Calculations:

Room temperature = ...

Volume of Fe(II) solution = 25 ml.

Vol. of $Cr_2O_7^{=}$ V(ml.)	$E_{obs.}$ (Volts)	$\Delta E/\Delta V$

Find out the equivalence point from E *vs* V plot (or from $\Delta E/\Delta V$ *vs* V plot). Determine E°, using equation (3) or from a graphical plot using eqn. (2).

12.9. Potentiometric estimation of Zn(II) by $K_4Fe(CN)_6$, and to verify the composition of the precipitate, $K_2Zn_3[Fe(CN)_6]_2$, formed during the reaction.

Theory:

The electrode potential for the redox system,

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

is given by (*vide* Expt No. 12·6) $$E = E^\circ + \frac{RT}{F} \ln \frac{[Fe(CN)_6^{-3}]}{[Fe(CN)_6^{-4}]} \quad \ldots (1)$$

The experimental cell is:

Saturated calomel $\| Fe(CN)_6^{-4} - Fe(CN)_6^{-3} \mid Pt$

The observed e.m.f. will be—

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

$$= E^\circ - E_{SC} + \frac{RT}{F} \ln \frac{[Fe(CN)_6^{-3}]}{[Fe(CN)_6^{-4}]} \quad \ldots (2)$$

When Zn(II) is added to the system, $Fe(CN)_6^{-4}$ is removed and the proportion of $Fe(CN)_6^{-3}$ increases. From equation (2) it is evident that with the progressive addition of Zn(II), the observed e.m.f. will gradually increase. At the end point there will be sharp increase due to sudden removal of all $Fe(CN)_6^{-4}$ ions.

Zinc (II) in neutral or acid medium is believed to react with $K_4Fe(CN)_6$ according to the following equation:

$$3Zn^{++}+2K_4Fe(CN)_6=K_2Zn_3[Fe(CN)_6]_2+6K^+$$

The aim of the present experiment is to verify that 3 moles of Zn(II) combine with 2 moles of ferrocyanide in this precipitation reaction.

The strength of $K_4Fe(CN)_6$ can be determined by potentiometric titration against standard $KBrO_3$ in (*N*)HCl medium. Here also there will be a sharp increase in potential of the cell: Satd. calomel $\|$ $Fe(CN)_6^{-3}$—$Fe(CN)_6^{-4}$ | Pt, at the end point during titration.

Meterials:

(1) Standard $KBrO_3$ solution (~0.1*N*); (2) Standard $ZnSO_4$ solution; (3) $K_4Fe(CN)_6$ solution.

Procedure:

Electrical connections are the same as shown in Fig. 34. Take 20 ml. $K_4Fe(CN)_6$ in 1*N* HCl medium, mixed with 2 ml. of a dilute solution of $K_3Fe(CN)_6$. Titrate with $ZnSO_4$ solution and find the end point.

Purify the platinum electrode by burning in an alcohol flame and make the electrical connections as before. Take 20 ml. $K_4Fe(CN)_6$ and 10 ml. 3 *N* HCl. Titrate with standard $KBrO_3$ solution.

Results and Calculations:

Expt. (1) 20 ml. $K_4Fe(CN)_6$+10ml. 2*N*HCl+2ml. dilute $K_3Fe(CN)_6$		Expt. (2) 20 ml. $K_4Fe(CN)_6$+10ml. 3*N* HCl	
Vol. of $K_4Fe(CN)_6$=20 ml.		Vol of $K_4Fe(CN)_6$=20 ml.	
Vol. of Zn (II) (ml.	*Eobs.*	Vol. of $KBrO_3$ (ml.	*Eobs.*

Plot Eobs. *vs.* vol. of titrant in both cases and find out the equivalence point from the inflexion.

Let the no. of moles of $K_4Fe(CN)_6$ present in 20 ml. = x

Say V ml. of Zn (II) combines with 20 ml. $K_4Fe(CN)_6$. Let the no. of moles $ZnSO_4$ in V ml. = y. Check, whether $y/x=3/2$

12.10. Measurement of pH of the given solution using glass electrode.

Theory:

The glass electrode consists of an envelope of soft glass (soda lime glass) containing a dilute solution of hydrochloric acid and the electrode is made of silver covered with a coating of silver chloride. The lowest part of the bulb is very thin (Fig. 36). The potential

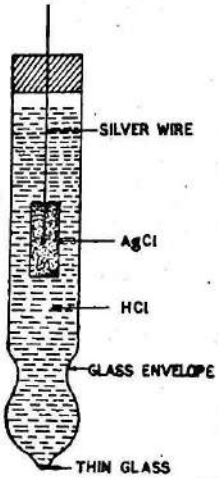


Fig. 36—Glass Electrode

of a cell consisting of this electrode against a reference electrode (commonly, saturated calomel electrode) is a linear function of the pH of the solution in which the glass electrode is kept immersed. In view of the high resistance of the glass membrane (1 to 100 megohms), the e.m.f. of this cell can not be measured with an ordinary potentiometer circuit. This necessitates the use of an electronic voltmeter (as in pH meter).

The exact mechanism of operation of the glass electrode is not clearly understood. It appears to function as a concentration cell. When the H^+ ion concentrations in the two solutions inside and outside the glass membrane are different, a potential difference develops across the membrane. This potential difference is dependent on the pH of the solution outside the glass membrane in the following manner (*vide* expt. No. 12.5)—

$$E = E_0 - \frac{2.303RT}{F} pH$$

where E is the measured e.m.f. of the cell and Eg is a constant for the particular electrode used. The commonly used pH meters directly read pH of the solution.

Two solutions of the same hydrogen-ion activity, with the glass membrane interposed, should show no potential difference. However, glass electrodes usually show a small potential (i.e. asymmetry potential due to the different state of the inside and the outside of the glass electrode bulb) under these conditions. That is why the pH meter is standardised periodically by using a buffer of known pH.

Materials:

(1) Test solution (unknown pH); (2) Buffer of known pH for standardisation.

Procedure:

Standardise the pH meter against the buffer of known pH (for details of operation of the pH meter, consult the bulletin supplied by the manufacturer *or* get advice from the demonstrator).

Put the test solution in a beaker; rinse the electrodes with test solution; dip the electrodes into it. The pH meter will directly read the pH of the solution.

Note that both the glass and the reference electrode should be thoroughly washed with distilled water after each measurement. The glass electrode should not be allowed to become dry; it should be kept immersed in distilled water. The electrodes are fragile and should be handled with great care.

Suggestions for further work:

(1) The glass electrode may be used to measure the pH of a variety of substances (for example, milk, blood, orange juice, tap water, etc.).

(2) Acid-base titrations can be followed using the glass electrode.

12.11. Potentiometric precipitation tiration using silver electrode.

(a) Titration of I^- with $AgNO_3$

(b) Titrations of CNS^- with $AgNO_3$

Theory:

The potential of the electrode system,

$$Ag^+ + e \rightleftharpoons Ag$$

is given by eqn. 12.4 (P. 141)

$$E = E^\circ + \frac{RT}{nF} \ln \frac{[\text{Oxidised Form}]}{[\text{Reduced Form}]} = E^\circ + \frac{RT}{F} \ln [Ag^+] \quad \ldots (1)$$

The experimental cell is:

Saturated calomel $\| Ag^+ | Ag$

The observed e.m.f. is given by

$$\begin{aligned} E_{obs.} &= E - E_{SC} \\ &= E^\circ - E_{SC} + \frac{RT}{F} \ln [Ag^+] \\ &= (0.798 - 0.2415) + 0.0591 \log [Ag^+], \text{ at } 25^\circ C \\ &= 0.5565 + 0.0591 \log [Ag^+] \quad \ldots (2) \end{aligned}$$

When I^- (or CNS^-) is added to the system, Ag^+ is removed as the insoluble Ag-salt. It is evident from equation (2) that at the end point there will be sudden fall in $E_{obs.}$ due to the removl of all Ag^+ ions.

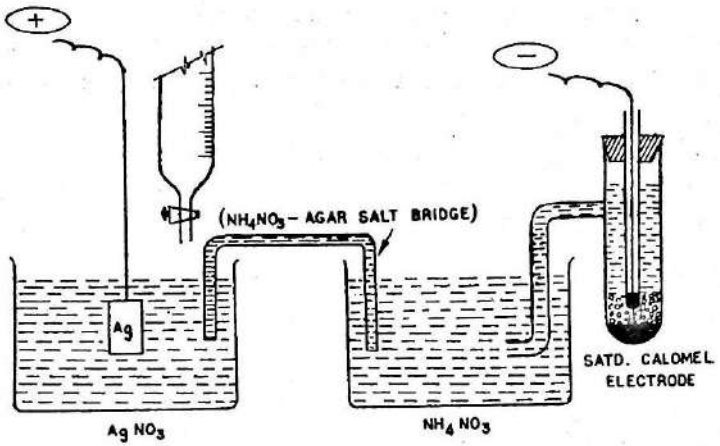


Fig. 37—Potentiometric titration using silver electrode.

Materials:

(1) Standard $AgNO_3$(~0.01*N*); (2) KI(~0.1*N*); (3) NH_4CNS (~0.1*N*).

Procedure:

A silver wire (or foil) is used as the silver electrode. This is cleaned by nitric acid (1:1) and then washed.

The arrangement of the apparatus is shown in Fig. 37. The potentiometric connections and the procedure are similar to other experiments. In the present experiment, the salt bridge from the calomel half-cell must be free from halides, and an ammonium nitrate salt bridge is used.

Results and Calculations:

Expt. (*a*)		Expt. (*b*)	
Titration with KI		Titration with NH_4CNS	
Vol. of $AgNO_3$ taken=25 ml		Vol. of $AgNO_3$ taken=25 ml.	
Vol. of KI added, ml.	*Eobs*, volts	Vol. of NH_4CNS added, ml.	*Eobs*. volts.,

Plot *Eobs*. against vol of titrant in both cases and find out the end points.

From expt. (*a*)

25 ml. of $AgNO_3$=.....ml. KI

∴ strength of KI=.....

From expt. (*b*)—

25 ml. of $AgNO_3$ = ...ml. NH_4CNS

∴ strength of NH_4CNS = ...

12.12. Some differential potentiometric titrations of:

(a) Strong acid—strong base

(b) Weak acid—strong base

(c) Mixture of strong acid and weak acid—strong base

Theory:

This is a method of obtaining a differential curve (Fig. 33*b*) directly. In the adjacent figure (Fig. 38) the electrodes *A* and *B* are platinum wires of identical properties; *A* is sealed into a dropper or syringe of the form shown in the figure. The other electrode *B* is wound around the stem of the dropper. Simply by squeezing the bulb a portion of the liquid is withdrawn and caused to surround the inner electrode, while electrolytic contact is maintained through the capillary tip.

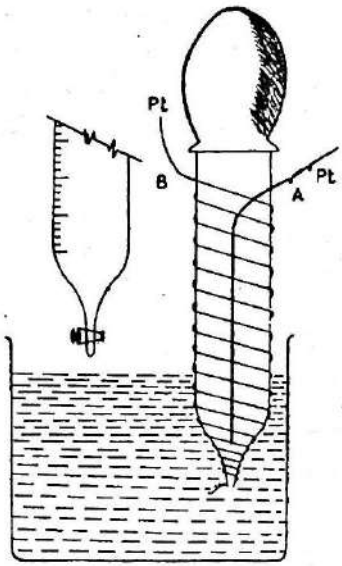


Fig. 38.—Differential potentiometric titration

As long as the solution inside the dropper is the same as that outside, no potential difference will be observed. The addition of a few drops of reagent to the beaker will change the concentration of the outside solution and so a potential difference will be observed. Such potentials are small at points remote from the equivalence point, but much more marked near the end point. In practice, the potential is read after each addition of reagent, the bulb is squeezed several times to mix the whole solution, then another portion of the reagent is added, and the potential difference is again noted. This is continued beyond the equivalence point. The observed potentials plotted against the volume of the reagent will form the differential curve, from which the equivalence point can be read directly. As a matter of fact the drop of reagent which produces the maximum potential corresponds to the equivalence point.

Meterials:

(1) Acid; (2) Base; (3) Quinhydrone.

Procedure:

Take 50ml. of the acid in 100 ml. beaker and saturate with quinhydrone. Fit the apparatus as shown in Fig. 38. Add a portion