Experiment No. 1:

Equivalent conductance of strong electrolytes

Aim of experiment:

Estimate the equivalent conductance of strong electrolyte and determinate it's equivalent conductance at infinite dilution from extrapolation to zero concentration.

Theory:

Equivalent conductance is given by the equation :

$\mathbf{\Lambda = 1000\ L / C}$

Where C : is equivalent concentration in unit (gram equivalent / lit)
L : is the specific conductance (S / cm or ohm^{-1} cm^{-1})
S : unit of conductance (Siemens)

The equivalent conductance has the meaning of the conductance of the electrolyte between two electrodes, 1 cm a part, and of such an area that the volume between these electrodes contains one gram equivalent of electrolyte.

For further theoretical treatment as well as for many practical purposes we need to know equivalent conductance obtained under the conditions where the dissociation would be complete and interioinc forces negligible. The conditions are fulfilled at infinite dilution denoted by ($\Lambda_\circ$ in some text book). Where $\Lambda_\circ$ = equivalent concentration at infinite dilution.

It's obvious that this value ($\Lambda_\circ$) can not be reached experimentally therefore, convenient methods of extrapolation must be used.

For strong electrolytes an empirical formula, first introduced by kohlrausch, can be used.

$$\mathbf{\Lambda = \Lambda_\circ - aC^b}$$

Where : (a) and (b) are constants, values of (b) being between 1/2 and 1/3. Later on a formula of nearly the same shape was derived by Debye and Onsager. The extrapolation using the plot of Λ against C^b with b put equal to 1/2 gives usually a straight line which can be extrapolated to C = 0 with sufficient precision.

Procedure:

1. Checking cell constant (k):

For determination of cell constant prepare (25 ml), (0.1N) KCl and measure its conductance, using the following equation of calculating the cell constant

$$\mathbf{K = L_{KCl} \times R_{KCl}}$$

L_{KCl} at 25 °C is 0.01288 $S.cm^{-1}$

R is Resistance = 1/C'   C'= concentration (ohm^{-1} or S)

2. Measurements of conductivity:

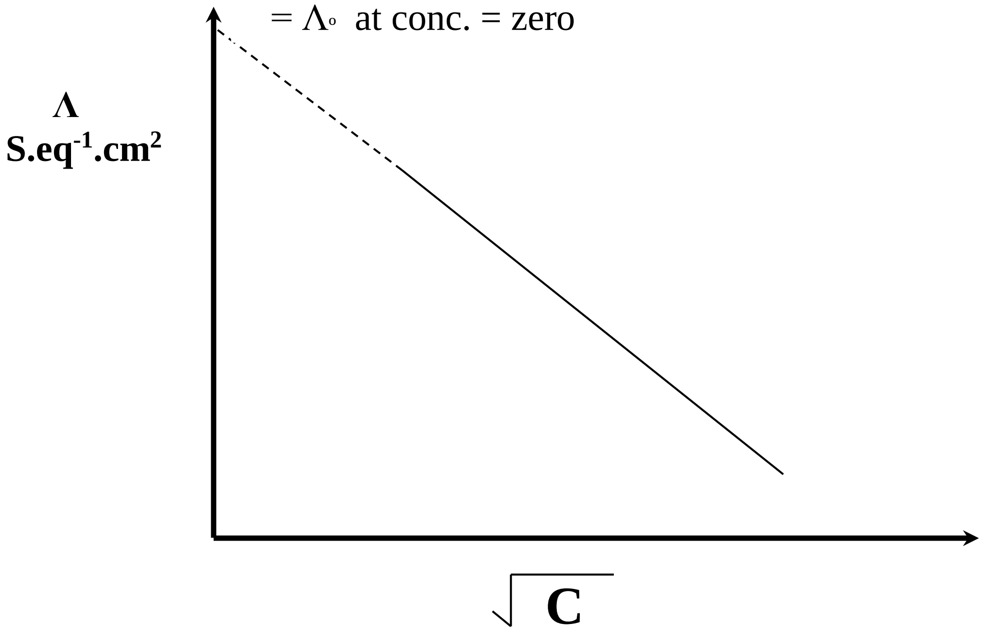
- **a)** Bring (100 ml) from (0.1N) of strong electrolyte (HCl) .
- **b)** Prepare by dilution 8 solutions from the above electrolyte in the range (0.09, 0.08, 0.07, 0.06, 0.05, 0.03, 0.02, 0.01 N), (25ml) for each one.
- **c)** Measure the conductance by conductometer.

Result and calculation:

Arrange your results in table below:

Conc. gm eq. / lit.	C' S	L = C' × K $S.cm^{-1}$	Λ $S.eq^{-1}.cm^2$	$\sqrt{Conc.}$

Plotting Λ (y axis) against $\sqrt{Conc}$ (x axis) then calculate $\Lambda_\circ$ from extrapolation to zero concentration



Experiment No. 2:

Dissociation constant of weak electrolytes from conductivity measurements

Aim of experiment:

To estimate the dissociation constant of weak electrolyte from measurements of its conductance at different dilutions.

Theory:

Equivalent conductance (Λ) of an electrolyte is related to its specific conductance by the equation:

$\Lambda = 1000\ L / C$

And the degree of dissociation is given by : $\alpha = \Lambda / \Lambda_\circ$ (where $\Lambda_\circ$ equivalent conductance at infant dilution for the dissociation of weak acid as :

$$\underset{C(1-\alpha)}{CH_3COOH} \rightleftharpoons \underset{C\alpha}{CH_3COO^-} + \underset{C\alpha}{H} \quad , Ka = \frac{C\alpha \ . \ C\alpha}{C(1-\alpha)} = \frac{\alpha \ C}{(1-\alpha)}$$

$K_C = (1-\alpha)$

Therefore we can write Ostwald's dilution law in the form:

$K_C = [(\alpha^2 C) / (1-\alpha)] = (\Lambda^2 C) / (\Lambda_\circ - \Lambda_\circ \Lambda)$

Knowing Λ at a concentration C and $\Lambda_\circ$ from the tables we can calculate the dissociation constant, K_C.

Ostwald's law can also be given in the form:

$1 / K_C = (\Lambda_\circ^{\ 2} / \Lambda^2 C) - (\Lambda_\circ / \Lambda_\circ^{\ 2} C)$

And multiplying last equation by the factor $C\Lambda / \Lambda_\circ^2$ we get the final form.

$$\frac{1}{\Lambda} = \frac{1}{\Lambda_\circ} + \frac{C\Lambda}{K_C \Lambda_\circ^2}$$

Procedure:

1. Checking cell constant (k):

For determination of cell constant, prepare (25 ml) of (0.1N) KCl and measure its conductance, using the following equation to calculating the cell constant

$$K = \frac{L_{KCl}}{C'_{KCl}}$$

L_{KCl} at 25 °C is 0.01288 $S.cm^{-1}$

C' : is the conductance of 0.1 N KCl (ohm^{-1} or S).

2. Measurements of conductivity:

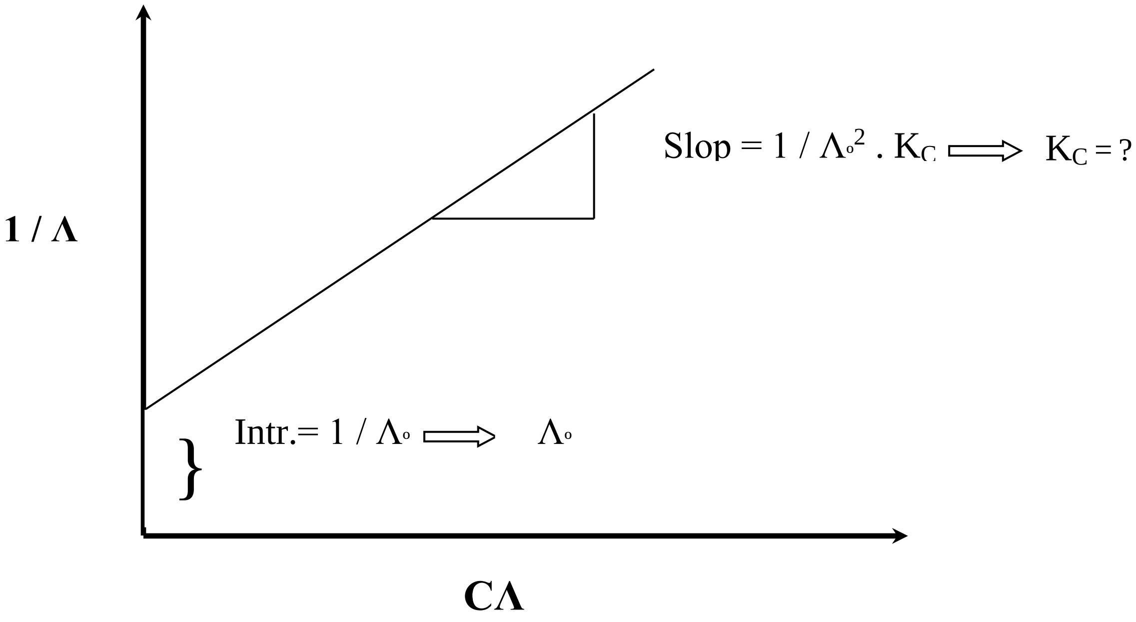
- **a)** Bring (25 ml) from (0.1N) of weak electrolyte (CH_3COOH) .
- **b)** Prepare by dilution 8 solutions from the above electrolyte in the range (0.08, 0.06, 0.05, 0.04, 0.03, 0.02, 0.01, 0.08 N), in volume (25 ml) for each one.
- **c)** Measure the conductance by conductometer.

Result and calculation:

Arrange your results in table like below:

Conc. gm eq. / lit.	C' S	$L = C' \times K$ $S.cm^{-1}$	Λ $S.eq^{-1}.cm^2$	$\frac{1}{\Lambda}$	$C\Lambda$

Plotting $1/\Lambda$ (y axis) against $C\Lambda$ (x axis) then calculate K_C from results


Slop = 1 / Λ∘² . K_C ⟹ K_C = ?
1 / Λ
Intr.= 1 / Λ∘ ⟹ Λ∘
CΛ

Experiment No. 3:

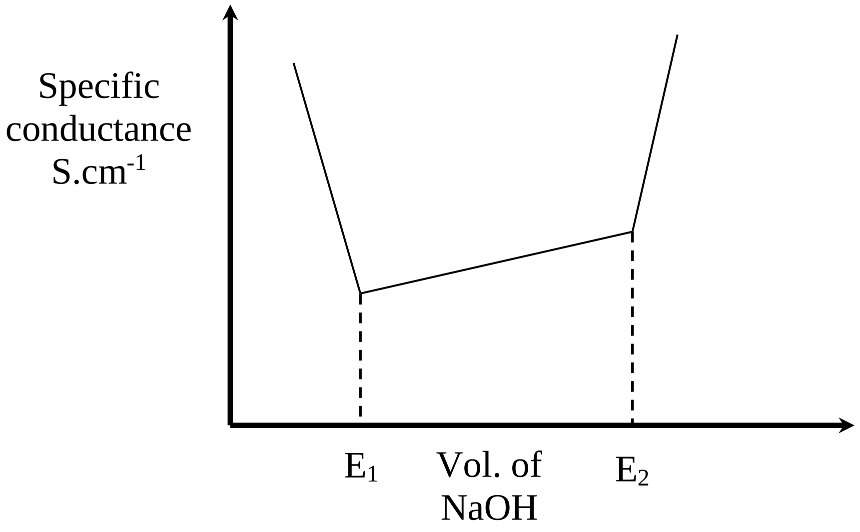
Conductometric titration

Aim of experiment:

Determine the concentration of HCl and CH_3COOH in a given sample.

Theory:

When a mixture of strong acid (e.g. HCl) and weak acid (e.g. CH_3COOH)titrated with strong base (e.g. NaOH) the conductance of solution is decreased steadily due to replacement of H^+ ion by metal ion Na^+ which have lower conductance, then after an equivalent amount of the base added the conductance of the solution increase steadily due to formation of the salt, e.g CH_3COONa which is strong electrolyte and hence is more highly ionized than the weak acid CH_3COOH, after an equivalent amount of the strong base added the conductance increase again because OH^- ion have higher conductance and still increase as OH^- ion added to the solution, the two breaks in the curve (No.1) correspond to equivalent points of HCl and CH_3COOH respectively.



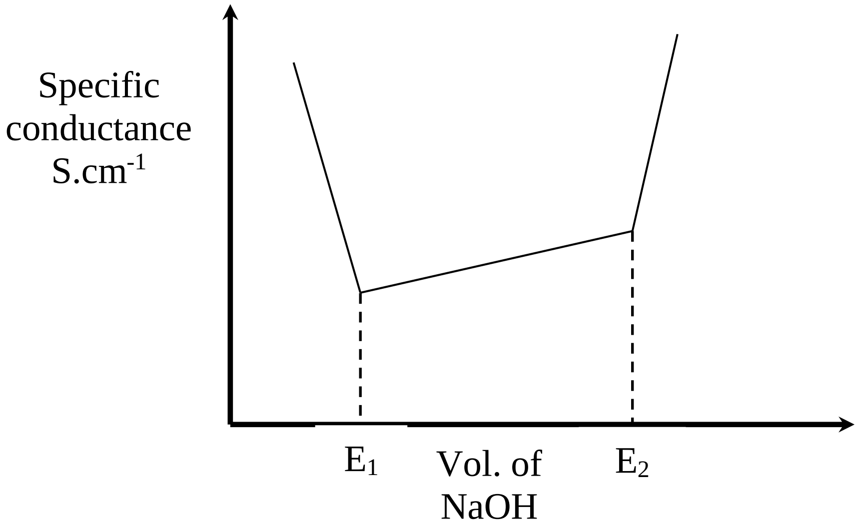
Procedure:

1. Bring (50 ml) of (0.1N) NaOH .
2. Bring (20 ml) of the unknown sample (the mixture of HCl and CH_3COOH) titrate with NaOH (add 0.5 ml each time) and measure the conductance (C').

Specific conductance (L) = conductance (C') × cell constant (K).

Result and calculation:

Plot specific conductance (L) (y axis) against volume of NaOH (x axis). Then find intersection corresponding to both equivalent point of HCl and CH_3COOH, if there are not enough points at any of branches for linear relation, continue the titration and then calculate the original concentration of HCl and CH_3COOH.



[HCl] $N_1V_1 = N_2V_2$

$0.1 \times E_1 = N_2 \times 20$

[CH_3COOH] $N_1V_1 = N_2V_2$

$0.1 \times (E_2 - E_1) = N_2 \times 20$

Experiment No. 4:

The quinhydrone electrode

Aim of experiment:

1. Estimate the standard electrode potential (E°Q) value of quinhydrone electrode by extrapolating its E values to pH = zero.
2. Find the range over which quinhydrone electrode can be used for pH measurements .

Theory:

Quinhydrone is an equimolecular mixture compounds of quinons (Q) and quinhydrone (QH_2). Quinhydrone is a redox system, the potential of which depends upon pH. The reversible equilibrium existing between quinon and hydroquinone is given by the equation:

$$Q + 2H^+ + 2e^- \rightleftharpoons QH_2$$

And on applying the general equation to such an equilibrium we obtain

$$\mathbf{EQ = E^oQ + (RT/nF)\ ln\ (a_Q\ .\ a^2_{H+}) / a_{QH2}}$$

In solution, equimolecular compound is dissociated into equal concentrations of quinone and hydroquinone, therefore the ratio a_Q / a_{QH2} is stay constant, and the equation reduces to

$$\mathbf{E_Q = E^o_Q + (2.303RT)/F\ log\ a_{H+}}$$
$$\mathbf{E_Q = E^o_Q + 0.0591\ log\ a_{H+}} \qquad \textbf{At 25 °C}$$
$$\mathbf{E_Q = E^o_Q - 0.0591\ pH}$$

E^o_Q, the standard electrode potential for quinhydrone, is calculated as (0.6994 volt) at 25 °C.

Procedure:

1. Prepare exactly standard series of buffer mixtures covering the pH from (1-10), example the Britton-Robinson buffer mixtures as follows:

Mixture of phosphoric acid, boric acid and acetic acid that its concentration is 0.04 M , its prepare from :

20 ml (0.12 M) phosphoric acid
20 ml (0.12 M) boric acid
20 ml (0.12 M) acetic acid

2. Bring 50 ml from (0.2M) NaOH (in burrate).
3. To 50 ml buffer solution soluble an equal amount from quinine and hydroquinone, then add (a mls) of NaOH as in the table:

" a " ml	pH	" a " ml	pH	" a " ml	pH
1.2	1.89	13.8	4.35	28	7.54
5.0	2.21	17.5	5.02	31.2	8.36
8.8	2.87	20.0	5.72	35.0	9.15
11.2	3.78	25.0	6.80	37.5	9.62

The pH of the prepared buffer solutions should be checked with glass electrode (pH meter).

4. The quinhydrone electrode (half cell) consiste of a platinium electrode (dipping) into the buffer solutions (solution must be slightly yellow, saturated with quinhydrone).
5. Combine this electrode with a saturated Calomel electrode and measure the E.M.F for each addition of NaOH to buffer by the potentiometer, and calculate the potential of the quinhydrone electrode, by using this equation :

$$\mathbf{E_{cell} = E_Q - E_{Calomel}}$$

$$\mathbf{E_{Calomel} = 0.246\ volt\ at\ 25\ ^\circ C}$$

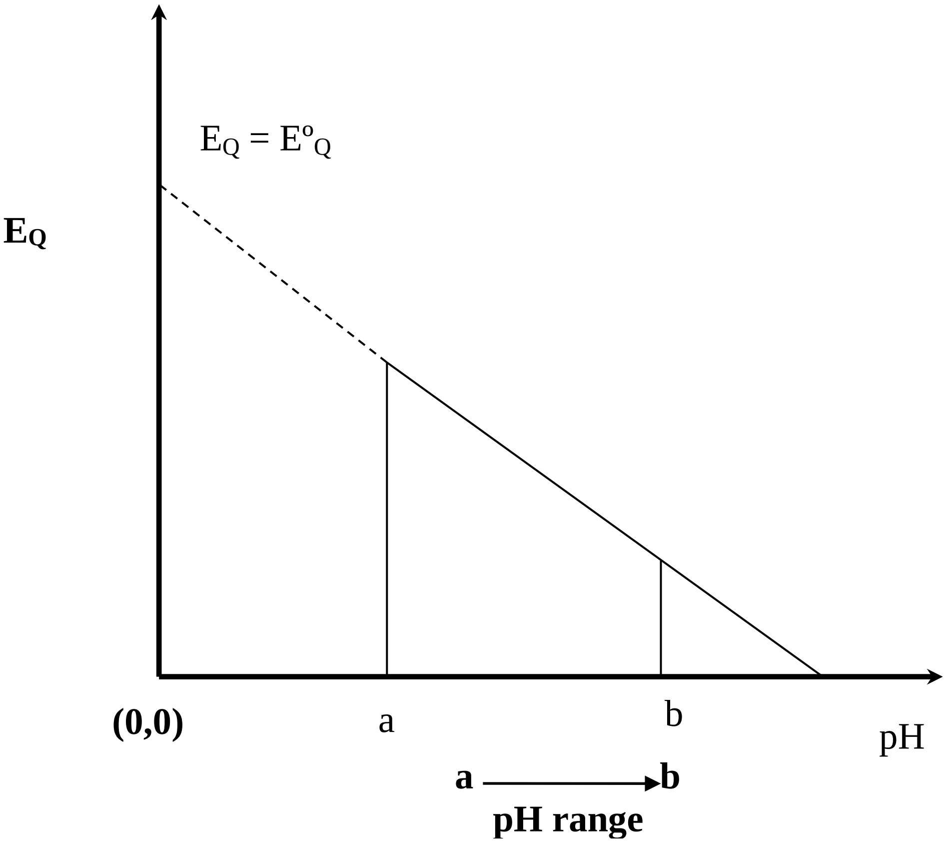
Result and calculation:

1. Arrange your results in table below:

" a " ml of NaOH	pH	E_{cell} volt	E_Q volt

Plot the values of the potential of quinhydron electrode (E_Q) (y axis) against pH (x axis) .

2. By extrapolating the curve to pH = zero, estimate E^o_Q.
3. To find the pH range over which quinhydrone electrode can be used for pH-measurements determined the first point on curve and the last point on it, it will be the pH range of quinhydrone electrode.



Experiment No. 5:

The glass electrode

Aim of experiment:

1. Estimate the standard electrode potential (E^o_G) for the glass electrode by extrapolating its E_G to pH = zero.
2. Find the range over which glass electrode can be used for pH-measurements.

Theory:

The glass electrode consist of the following combineation:

Reference electrode (1) In solution of known pH	Glass membrane	Solution (2) of unknown pH

$$\mathbf{E_G = E^o_G + 0.0591 \log a_{H^+}}$$
$$\mathbf{E_G = E^o_G - 0.0591\ pH}$$

At 25 ºC

When E_G is the potential of the glass electrode at any pH and E^o_G is the standard glass electrode potential at pH = zero or $a_{H^+} = 1.0$

Procedure:

1. Standardized the glass electrode against a buffer solution known pH.
2. Prepare exactly a standard series of buffer mixture covering the pH-range from 1-10 for example the Britton-Robinson buffer mixtures as follows:
   Mixture of phosphoric acid, boric acid and acetic acid that its concentration is 0.04 M , its prepare from :
   20 ml (0.12M) phosphoric acid
   20 ml (0.12M) boric acid
   20 ml (0.12M) acetic acid
3. Bring 50 ml from (0.2M) NaOH (in burrite).
4. To 50 ml buffer solution add (a mls) of NaOH as in the table:

" a " ml	pH	" a " ml	pH	" a " ml	pH
1.2	1.89	13.8	4.35	28	7.54
5.0	2.21	17.5	5.02	31.2	8.36
8.8	2.87	20.0	5.72	35.0	9.15
11.2	3.78	25.0	6.80	37.5	9.62

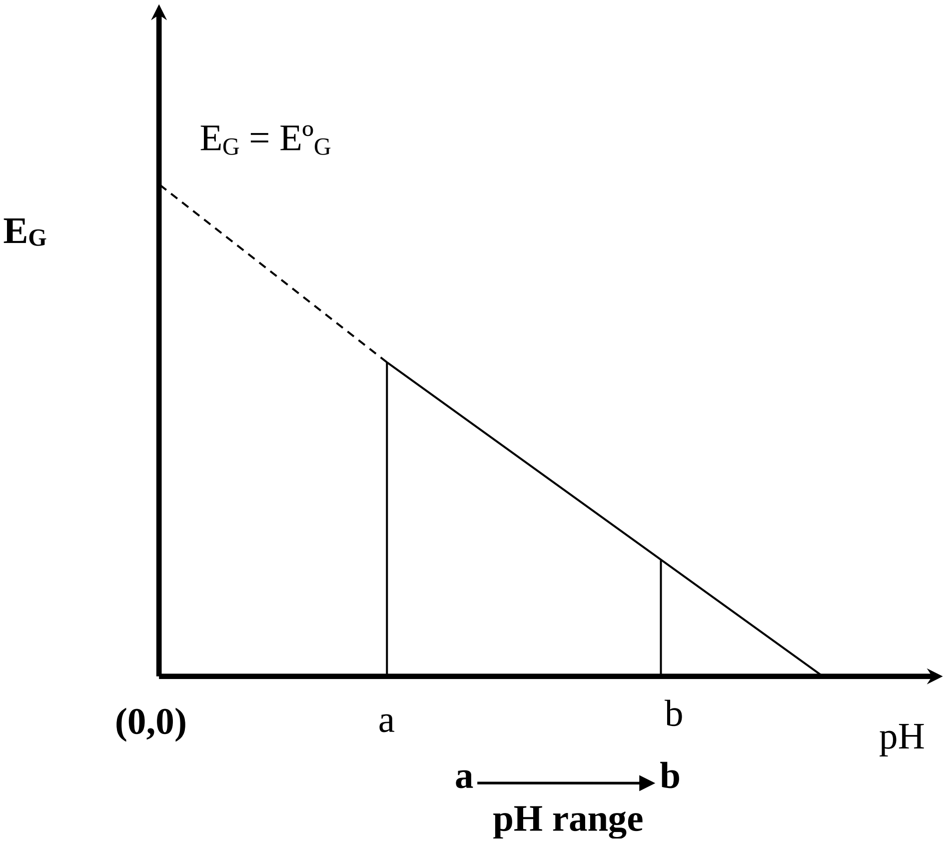
5. Measure the e.m.f and the pH for each addition of NaOH to buffer by using glass electrode in combination with pH-meter

Result and calculation:

1. Arrange your results as this table :

" a " ml of NaOH	pH	E_G (mv.)

2. Plot the values of the potential of glass electrode (E_G) (y axis) against pH (x axis) .
3. By extrapolating the curve to pH = zero, estimate E^o_G.
4. To find the pH range over which glass electrode can be used for pH-measurements , by determined the first point on curve and the last point on it, it will be the pH range of glass electrode.



Experiment No. 6:

Disociation constant (Ka) of a weak acid from its neutralization curve

Aim of experiment:

Estimate the dissociation constant of given weak acid from titration curve. Measure pH by means of the glass electrode.

Theory:

For partially neutralized acid we can write Henderson-Hesselbach's equation.

$$\mathbf{pH = pK_a + \log C_s/C_A}$$

Where C_s is molar concentration of the salt either added directly or formed by the addition of alkali, and C_A is molar concentration of the free acid, from the above equation we can see that $C_s = C_A$, then $pH = pK_a$
Therefore pH of half neutralized acid is thus equal to its pK_a.

Procedure:

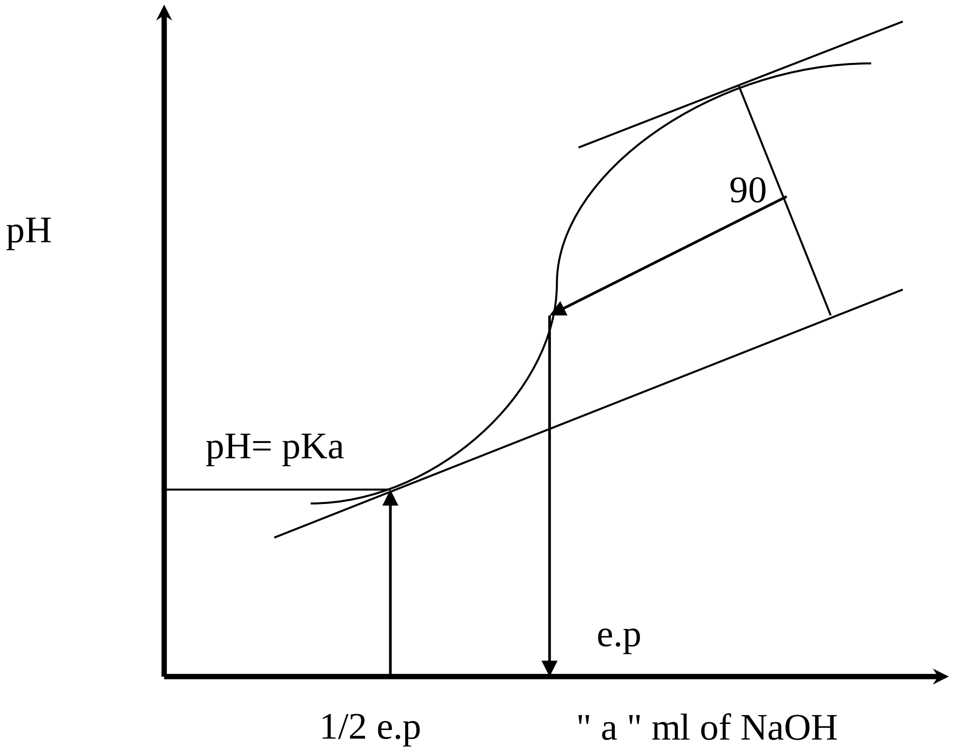
1. Prepare (50ml) 0f (0.02M) from weak acid (CH_3COOH) by dilution.
2. Titrate the solution above with (0.2M) from NaOH using glass electrode in combination with pH meter.
3. Measure the pH after the addition of every (0.5ml) of (0.2M) NaOH (until the pH will be partially constant by the addition of excess alkali).

Result and calculation:

1. Arrange your results as this table :

" a " ml of NaOH	pH

2. Plot the values of pH(as coordinate) (y axis) against " a " ml of NaOH (x axis) , from the curve estimate pKa.



pKa = -log Ka
Ka = 10^{-pKa}

Experiment No. 7:

A. Measurement of the E.M.F of a concentration cell

Aim of experiment .A.:

To measure the E.M.F of the glavanic element

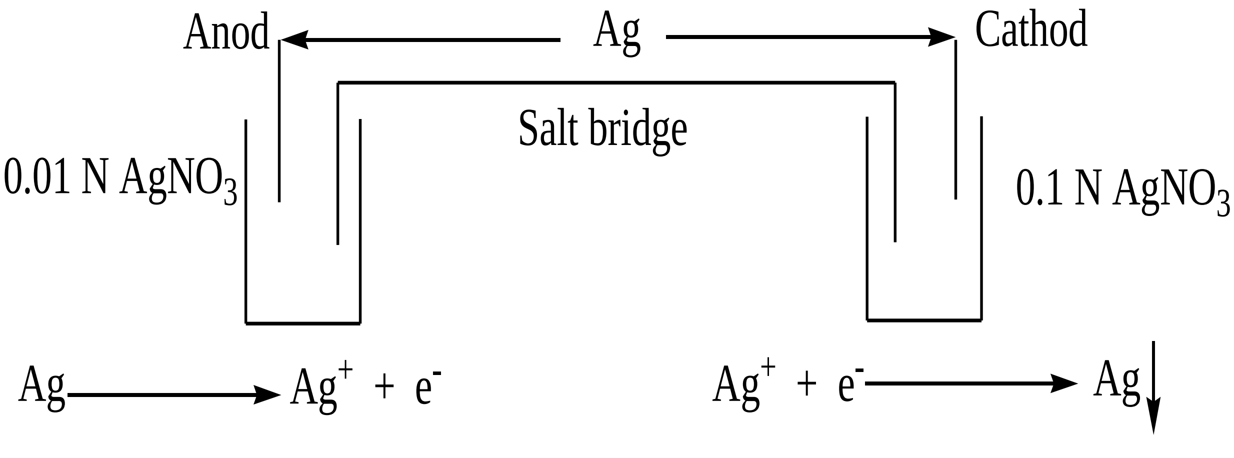
$\mathbf{Ag / AgNO_3, C_1 // AgNO_3, C_2 / Ag}$

Theory:

Cells with this kind of connections are called without transport and transfer don't appear in the expression for this E.M.F. . In our experiment we shall eliminate the liquid junction potential by using a salt bridge with saturated KNO_3 in which the tips of electrod vessels of both half cells with be dipping or as shown in the fig. The E.M.F of the concentration cell thus formed is given by the equation :

E.M.F. = E = RT / F ln C_1 / C_2

Where C_1 & C_2 are the concentrations precisely activities of silver ion in the two half cells C_1 & C_2. Using this equation the first element can be directly calculated and compared with E.M.F found.



Procedure:

1. For construction of the cell use two silver electrods washed with ammonia and with redistilled water dipped in the solution of (0.1N) $AgNO_3$ and (0.01N) $AgNO_3$.
2. After filling the each two beaker the solution mentions above (0.1 & 0.01N) $AgNO_3$), dip both tips of the half cells with salt bridge, as in the fig. this concentration
3. Measure the E.M.F of cell by potentiometer.
4. Compare the E.M.F obtained with the theoretical value calculated from "Nernst equation" and comment on the results.

B . Liquid junction potential

Aim of experiment .B.:

Determination of liquid junction potential of a concentration cell.

Theory:

The E.M.F of a concentration cell is given by the equation :

$$E = (2t^- - RT) / F \ln C_1 / C_2 \text{ ---------- } (1)$$

t^- : transference number of the anion, the transference number can be defined as :

The fraction of the total current carried by each ionic species. C_1 & C_2 are the concentration of the first and second solution which is experimentally replacing the activities by diluted solution. In this equation is included the liquid junction potential which is formed at the junction between the two solution. If this potential could be eliminated, for example by using salt bridge the E.M.F of the concentration cell would be given by :

$$E = RT / F \ln C_1 / C_2 \text{ ---------- } (2)$$

The difference between equation 1 and 2 thus given the values of the liquid junction potential E_L:

$$E = (2t^- - 1) RT/ F \ln C_1 / C_2 \text{ ---------- } (3)$$

Procedure and calculation:

1. Construct a cell consisting of two silver electrodes immersed in solution of $AgNO_3$ (0.1N) and (0.01 N) $AgNO_3$ (25 ml of each one) .
2. Measure the E.M.F of this cell with and without salt bridge (using daniell cell).
3. Subtract the E.M.F in both cases in order to get the liquid junction potential.
4. Calculate the transference number of the anion using equation (3).

C . Determination of the solubility product of silver chloride

Aim of experiment .C.:

Determination the solubility of AgCl.

Procedure:

1. Bring (25 ml) of (0.1N) of each of $AgNO_3$ and KCl.
2. Construct the cell described above using two silver wires as electrode, silver chloride is produced by two drops of silver nitrate solution to the potassium chloride environment.
3. Measure the E.M.F of the cell as described before.

Calculation:

1. Knowing that the activity of (0.1N) $AgNO_3$ is (0.075), calculate the activity of Ag in KCl using the relation.

   $$\mathbf{E = 0.0591 \log a_{Ag^+} (AgNO_3) / a_{Ag^+} (KC1)}$$

2. Assuming that KCl is completely dissociated, calculate Ksp as:

   $$\mathbf{Ksp = a_{Ag^+} (KC1) \times 0.1}$$

   Compare the value obtained with the theoretical one calculated above.

D. Determination of the stability constant of complex $[Ag(NH_3)_2]^+$

Aim of experiment .D.:

Determination of the stability constant of complex $[Ag(NH_3)_3]^+$.

Theory:

The formation of complex ions its usually a reversible reaction where the complex ion dissociates to the original ions.

$$Ag^+ + 2(NH_3) \rightleftharpoons [Ag(NH_3)_2]^+$$

The equilibrium constant of the reaction mentioned above give us an idea about the stability of the complex ion and therefore it is called its stability constant.

Procedure:

1. Prepare (25ml) (0.01N) $AgNO_3$ solutions by dilution from (0. 1N) $AgNO_3$.
2. Prepare (25ml) (1N) NH_4OH, then prepare (0.025N) of $AgNO_3$ in NH_4OH (ammonia solutions).
3. Construct the following concentration cell.

Ag / 0.025 N $AgNO_3$ in IN NH_3 solution // sat. solu. of KNO_3 / 0.01 N $AgNO_3$ / Ag

4. Measure the E.M.F of cell.

Calculation:

1. The stability constant for complex $[Ag(NH_3)_2]^+$ can be estimate from the reaction mentioned above.

$$K = \frac{[Ag(NH_3)_2]^+}{[Ag]^+_{free} \quad [NH_3]^2}$$

2. From equation :

$$E = \frac{RT}{nF} \ln \frac{C_{Ag+} ①}{C_{Ag+} ②}$$

We can calculate the concentration of the $[Ag^+]_{free}$ in the formula C_{Ag+} (2) in the half cell containing ammonia, C_{Ag+}(1) is the concentration of Ag^+ in the half cell containing no NH_3 (0.01N).

3. The difference between the original concentration of Ag^+ in the cell containing NH_4OH (0.025N) and the $[Ag^+]_{free}$ calculated from E.M.F is the concentration of Ag^+ in the complex $[Ag(NH_3)_2]^+$ and thus is the concentration of the complex ion.
   i.e. $[Ag(NH_3)_2]^+ = 0.025 - [Ag^+]_{free}$
4. The difference between original concentration of NH_4OH (1N) and concentration of the complex ion multiplied by two is the concentration of NH3 at equilibrium .
   i.e. $[(NH_3)] = 1 - [Ag(NH_3)_2]^+ \times 2.$
5. The stability constant is obtained from the relationship

$$K = \frac{[Ag(NH_3)_2]^+}{[Ag]^+_{free} \quad [NH_3]^2}$$

Experiment No. 8:

Thermodynamics of cells

Aim of experiment:

Calculate the three thermodynamic parameters

1. The free energy change (ΔG).
2. The entropy change (ΔS).
3. The change in enthalpy (ΔH).

Theory:

A famous example of reversible cell is the Daniell cell consisting of zinc electrode immersed in an aqueous solution of zinc sulphate, and a cupper electrode in cupper sulphate solution.

$$Zn \,/\, \underset{\substack{\text{solu.}\\ 0.1\ N}}{ZnSO_4} \;\vdots\; \underset{\substack{\text{solu.}\\ 0.1\ N}}{CuSO_4} \,/\, Cu$$

The two solution being usually separated by porous partition if the external circuit is closed by an E.M.F just less than that of the Daniell cells the chemical reaction taking place in the cell is:

$$Zn + Cu^{+2} \rightleftharpoons Zn^{+2} + Cu$$

i.e. zinc dissolve from zinc electrode to form zinc ions, in solution while cupper ions are discharged and deposit cupper on the other electrode. On the other hand, if the external E.M.F is slightly greater than that of the cell the reverse process is takes place.

The E.M.F of Daniell cell depends upon temperature. From temp. coefficient of E.M.F and aknowlegle of E.M.F at a particular temp. three thermodynamic quantities associated with the reversible reaction occurring in the cell can be evaluated. These thermodynamic quantities are the free energy increase (ΔG), the entropy increase (ΔS) and the enthalpy (ΔH) given by equation 1, 2, 3 severally.

$\Delta G = -nFE$ -------------(1)

$\Delta S = nF\,(\Delta E/\Delta T)_P$-------------(2)

$\Delta G = nF\,[T(\Delta E/\Delta T)_p - E]$-------------(3)

Where E is the E.M.F of the cell.

F is the Faraday number and equal 96500 coloumb

n is the number of electrons involved in the reaction.

T is the absolute temp.in Kelvin.

$(\Delta E/\Delta T)_P$ is the temp. coefficient in volt per degree.

Procedure:

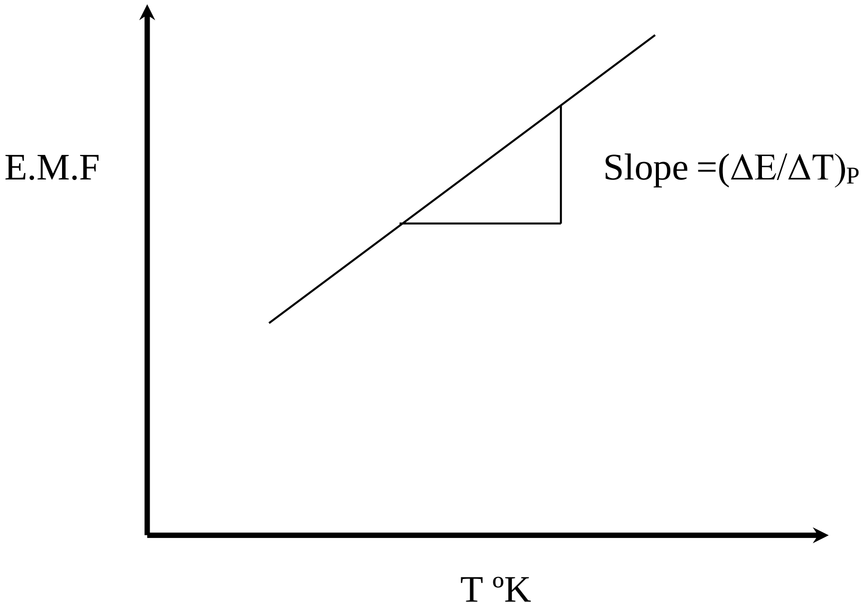
1. Bring (50ml) of (0.1N) from $ZnSO_4$ & $CuSO_4$ every one on beaker.
2. Prepare Daniell cell as outlined before, measure its E.M.F at room temperature.
3. Place the cell in thermostat and continue for measuring its E.M.F at a temp. ranging from 15-40 ºC.

Result and calculation:

1. Arrange your results as this table:

Temp. ºC	E.M.F	T ºK

2. Plot a curve between E.M.F (y axis) and temp. In (x axis) and calculate the temp. coefficient of the cell and temp. in Cx.



Calculate ΔG, ΔS & ΔH by using equation above.