



Potentiometric Titrations

* Introduction

The end points of titrations can be determined by various visual methods which depend on the use of indicators. But if the solutions are coloured, very dilute and forming the precipitate, the suitable indicators are not available and end points of such titrations cannot be determined accurately.

In above case end points of titrations are determined by measuring the potential of certain electrodes because the potential of such electrodes depend on the activity or concentration of ions present in the solution. These titrations are called potentiometric titrations.

For any metal-metal ion electrode, the half cell reaction can be written as,



Potential of metal electrode is expressed according to Nernst equation as;

$$E_M = E_M^0 - \frac{2.303RT}{nF} \log \phi_a$$

$$E_M = E_M^0 - \frac{2.303RT}{nF} \log \frac{1}{a_{M^{n+}}}$$

$$E_M = E_M^{\circ} + \frac{0.0591}{n} \log a_{M^{n+}}$$

E_M° = Standard reduction potential of the electrode

n = Number of electrons involved in the electrode reaction.

$a_{M^{n+}}$ = Activity of Metal ions.

* Determination of pH

pH is negative logarithm of H^+ ion concentration of solution.
i.e. $pH = -\log [H^+]$

The concentration of H^+ ions can be determined using electrode reversible to H^+ ion, where such a electrode is set up for half cell with test solution as electrolyte.

The emf of the half cell is determined by coupling it with another standard electrode and the emf of complete cell is measured.

The emf of the cell depends on concentration of H^+ ions.

For standard hydrogen electrode in contact with solution of H^+ ions involving reaction,



Nernst equation can be given as,

R = Ideal gas constant

$$E_{H_2} = E_{H_2}^{\circ} + \frac{2.303RT}{nF} \log C_{H^+}$$

n = No. of electrons involved in Reaction

Where, $E_{H_2}^{\circ} = 0$, $T = 298K$, $R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$ and $F = 96500 \text{ C mol}^{-1}$

$$E_{H_2} = -0.0591 pH$$



Now, standard hydrogen electrode is coupled with a reference electrode like saturated calomel electrode (SCE). The complete cell can be represented as,

$$\text{Pt, H}_2 (\text{g, 1 atm}) | \text{H}^+ (\text{c} = \text{unknown}) || \text{SCE}$$

The emf of cell is determined potentiometrically and is given by,

$$E = E_R - E_L$$

$$= E_{\text{SCE}} - E_{\text{H}_2}$$

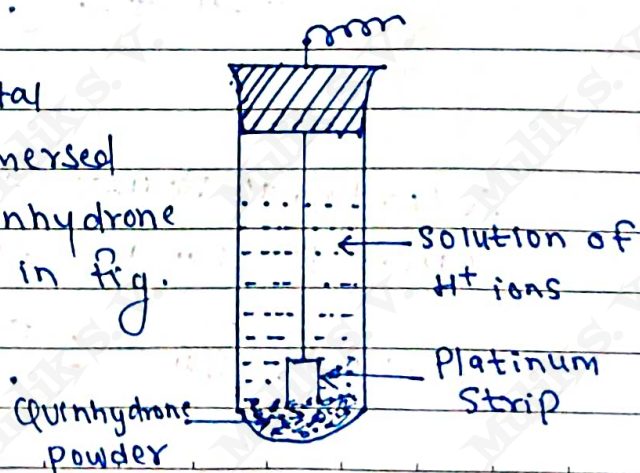
$$= 0.2422 - (-0.0591 \text{ pH})$$

$$\therefore \text{pH} = \frac{E - 0.2422}{0.0591}$$

* Detail study of Quinhydrone and Glass electrodes and their use in determination of pH.

(A) The Quinhydrone electrode

A bright platinum an inert metal (for electrical contact), is immersed in a solution containing quinhydrone (about 0.15g/100ml): as show in fig.





$$E_{QH} = E_{QH}^{\circ} - \frac{2.303 RT}{2F} \cdot \log \frac{1}{a_{H^+}}$$

$$E_{QH} = E_{QH}^{\circ} + \frac{2.303 RT}{2F} \cdot \log a_{H^+} \quad \therefore \log a_{H^+} = 2 \log [H^+]$$

$$E_{QH} = E_{QH}^{\circ} + \frac{2.303 RT}{F} \log a_{H^+}$$

Since, $E_{QH}^{\circ} = 0.6998V$ and $pH = -\log a_{H^+}$,

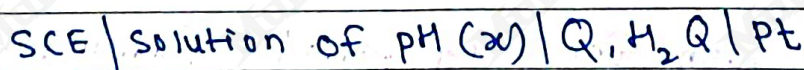
$$E_{QH} = 0.6998 - \frac{2.303 RT}{F} \cdot pH$$

and at 298K $E_{QH} = 0.6998 - 0.0591 pH$

So, potential of quinhydrone depends upon H^+ ions and can be used for determining the pH of solution.

Determination of pH:

Quinhydrone electrode is dipped in the solution of unknown pH, is coupled with saturated calomel electrode (SCE) as reference electrode. The cell formed is as follows.



Emf of the cell (E_c) can be given as.

$$E_c = E_R - E_L$$

$$E_c = E_{QH} - E_{SCE}$$

R = Right (Cathode)

L = Left (Anode)

From equation

$$E_{\text{SCE}} = E_{\text{QH}} = 0.6998 - 0.0591 \text{pH}$$

and

$$E_{\text{SCE}} = 0.2458 \text{ V at } 298 \text{ K,}$$

$$E_c = 0.6998 - 0.0591 \text{pH} - 0.2458$$

$$E_c = 0.4540 - 0.0591 \text{pH}$$

$$\therefore \text{pH} = \frac{0.4540 - E_c}{0.0591}$$

* Advantages:-

1. It is easy to construct.
2. It attains equilibrium rapidly.
3. It can be used in many solutions in which hydrogen electrode is not applicable.
4. It is not easily poisoned as that of the hydrogen electrode.

* Disadvantages

1. It cannot be used in solutions of pH greater than 8. As equilibrium between quinone and hydroquinone which is the basis of potential equation.
2. Potential of the electrode may be slightly affected by high concentrations of salts.
3. It is not stable for long periods; particularly above 303 K.

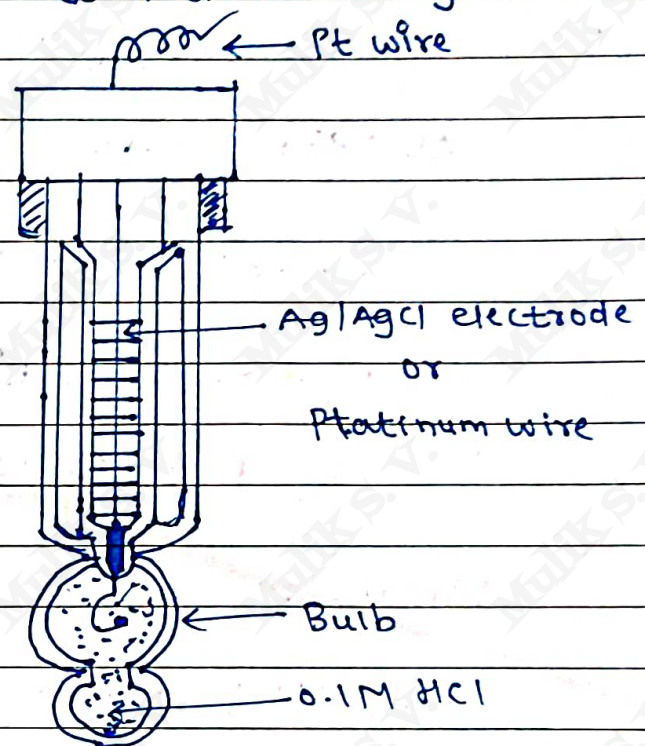


* Glass electrode

The glass electrode consists of a special glass (pH responsive glass) of relatively low melting point and high electrical conductivity. It is blown in the form of a bulb which is then sealed to the bottom of a hard glass tube.

A solution of 0.1 M HCl which provides a constant H^+ ion concentration (constant pH) is placed inside the bulb and Ag/AgCl electrode or a platinum wire is inserted to make the electrical contact.

The electrode can be represented as follows:



Glass electrode...

Experimental soln. (pH = x) | glass | 0.1 M HCl | AgCl | Ag.

At 298 K the potential of glass electrode is given by,

$$E_G = E_G^\circ - 0.0591 \times \text{pH}$$

E_G° = constant for the given glass electrode.

* Determination of pH.

For determining pH of solution, glass electrode is dipped into it and is coupled with saturated calomel electrode (reference electrode) through a salt bridge to form a cell as follows:



Emf of the cell (E_c) is measured potentiometrically

$$E_c = E_{\text{SCE}} - E_g$$

$$\text{At } 298 \text{ K, } E_{\text{SCE}} = 0.2458 \text{ V}$$

$$\therefore E_c = 0.2458 - (E_g^\circ - 0.0591 \text{ pH})$$

$$E_c = 0.2458 - E_g^\circ + 0.0591 \text{ pH}$$

$$E_c = k + 0.0591 \text{ pH}$$

Where, $k = (0.2458 - E_g^\circ) = \text{constant}$ dependent upon the composition of glass.

* Advantages

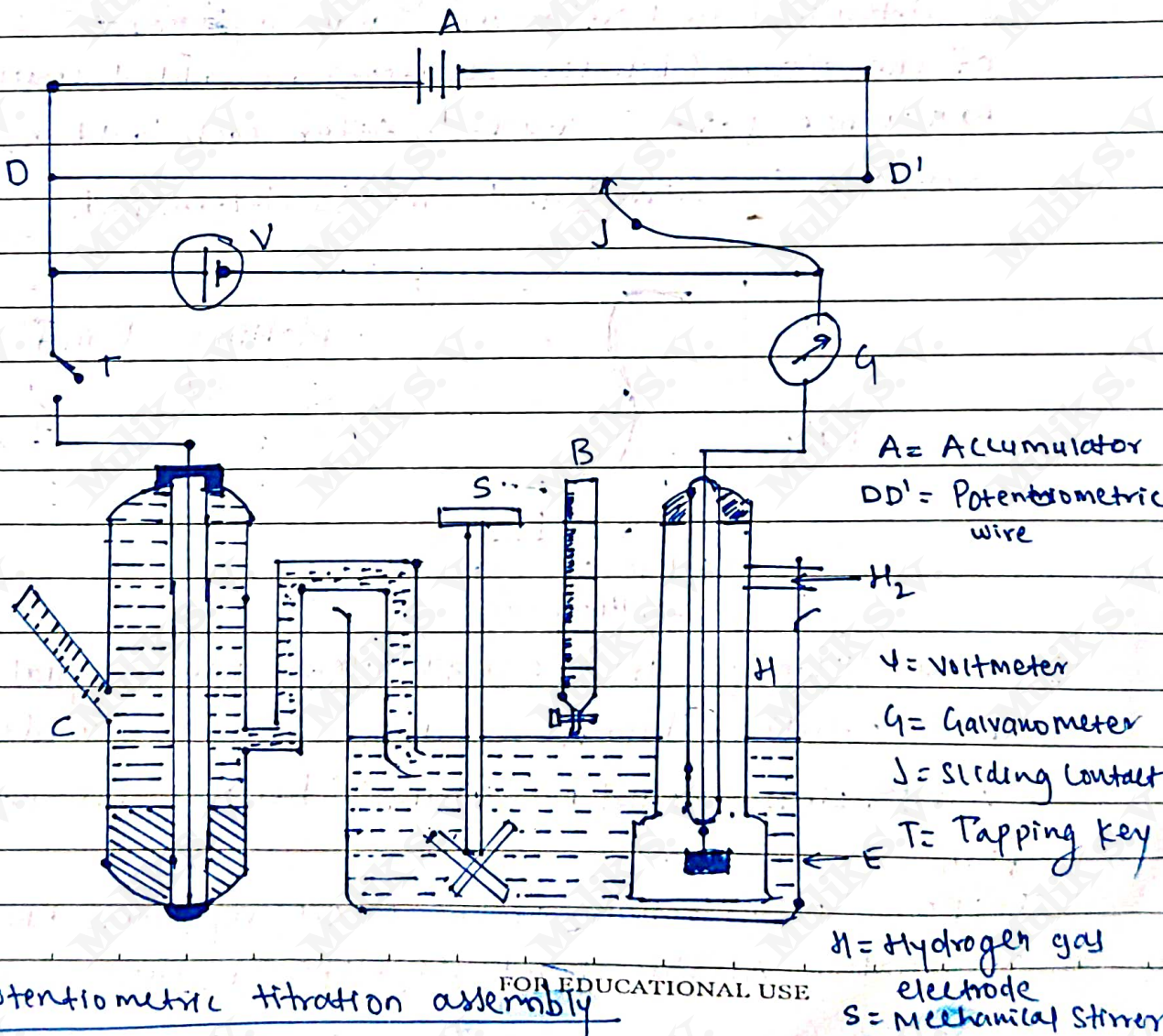
1. It is not affected by strong oxidising or reducing agents (solutions).
2. It can also be used in the presence of metallic ions, poisons, etc.
3. It can be used in solutions of pH values even upto 12 with special glass.
4. It is simple to operate.

Disadvantages:-

1. As glass membrane has extremely high resistance, the ordinary potentiometer cannot be used to measure the potential of electrode but we can use special electronic potentiometers.
2. Electrodes are costly and fragile.

* Potentiometric Titrations

(A) classical methods for locating end points:



Potentiometric titration assembly

S = Mechanical stirrer

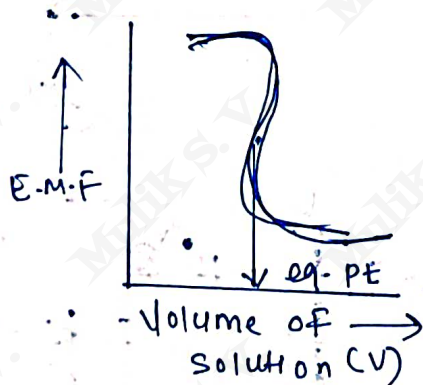
B = Burette with solution

E = Experimental solution (ion^n to be titrated)

In this method equivalence point (end point) of the reaction is obtained from sudden change in potential in the plot of emf vs Volume of titrating solution (burette solution).

In this method a cell is constructed by using two electrodes out of which one electrode used is of known potential i.e. reference electrode like calomel electrode. The other electrode is an indicator electrode, the potential of which depends on the concentration of particular ions present in the solution in which it is dipped.

The emf of the cell containing the initial (original) solution is determined and relatively large increments (1 to 5 ml) of the titrant (burette solution) are added until the equivalence point is reached. After each addition, the solution is stirred and emf is determined.



Plotting E.m.f vs Volume of solⁿ (V)

In the vicinity of the equivalence point, equal increments (about 0.1 ml) of burette solution should be added.

Several points should be obtained beyond the equivalence point.

The point of inflection of the curve represents the end point of titration. At this point the slope of curve is maximum.

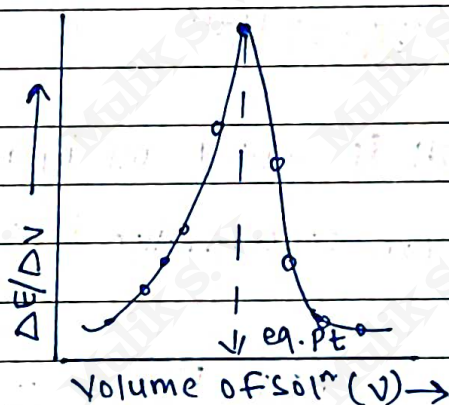


(B) Analytical (or derivative) methods for locating end points:

In classical method, the accuracy of the results obtained will depend on the skill with which the titration curve has been drawn. Thus, there may be personal errors in locating the end points. Therefore, it is preferable to employ analytical or derivative methods.

(a) First derivative method:

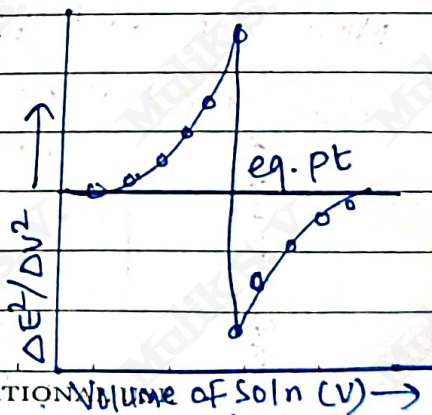
Here, a curve is obtained by plotting the graph of $\Delta E/\Delta V$ vs. Volume of titrant V , where ΔE = change of electrode potential for the maximum addition of ΔV volume of the burette solution.



(b) Second derivative method

Here, $\Delta E^2/\Delta V^2$ is plotted against Volume of Solution V , added from the burette.

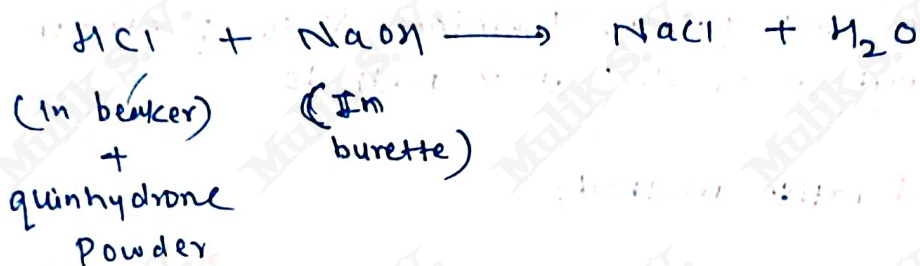
The second derivative ($\Delta E^2/\Delta V^2$) is zero at the point of inflection i.e. at the end point.



* Acid-Base Titrations (Neutralisation Reactions)

In neutralisation reaction of acid by base, the concentration of H^+ ions is changed with addition of base.

Hence Any electrode whose potential depends upon H^+ ion concentration can be used as an indicator electrode.
e.g. Hydrogen, quinhydrone or glass electrode.



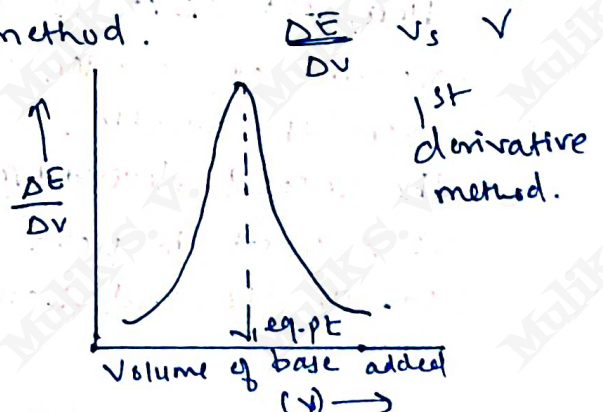
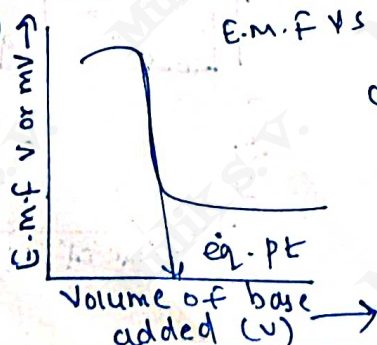
Platinum wire is dipped in beaker and is coupled with saturated Calomel electrode. The cell constructed can be represented as follows.



Now, when NaOH is added ml by ml from the burette decrease in H^+ ion concentration is observed with increase in pH

$$\text{As } pH = \frac{0.454 - E_{\text{cell}}}{0.0591} \text{ for quinhydrone electrode}$$

Now, the end point or equivalence point can be analysed using classical or 1st derivative method.

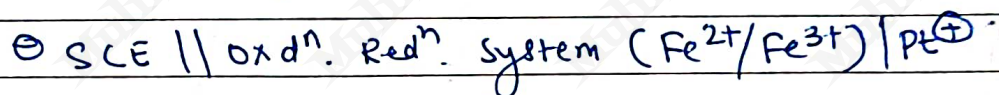




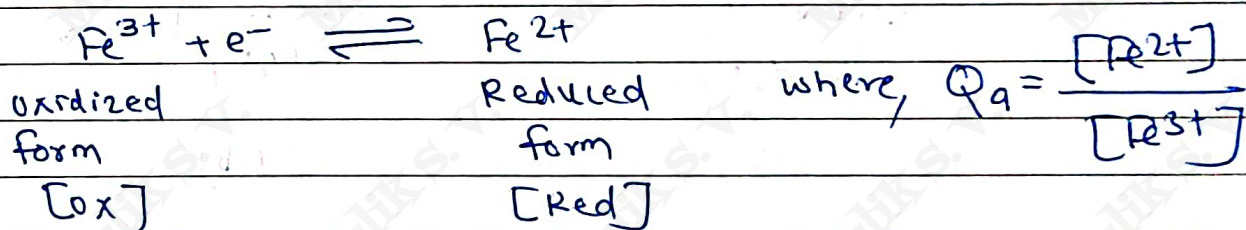
* Redox - Titrations (Oxidation-Reduction Reactions):-

To determine the end point of titration between ferrous sulphate, FeSO_4 (reducing agent) and potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$ (oxidising agent).

In the experimental procedure, a definite quantity of FeSO_4 is taken in a beaker with some quantity of H_2SO_4 . which is stirred well and platinum wire is dipped into it and is further coupled with saturated calomel electrode through salt bridge as follows,



Now with respect to SCE, Pt is +ve electrode where 'redⁿ' will take place as follows.



Now by applying Nernst equⁿ we have

$$E = E^{\circ} - 0.0591 \cdot \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$

$$T = 298 \text{ K}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

Above equⁿ can also written as

$$n = 1$$

$$F = 96500 \text{ C mol}^{-1}$$

$$E = E^{\circ} - \frac{0.0591 \cdot \log \frac{[\text{Red}]}{[\text{Ox}]}}{n}$$

for general redox reaction

or

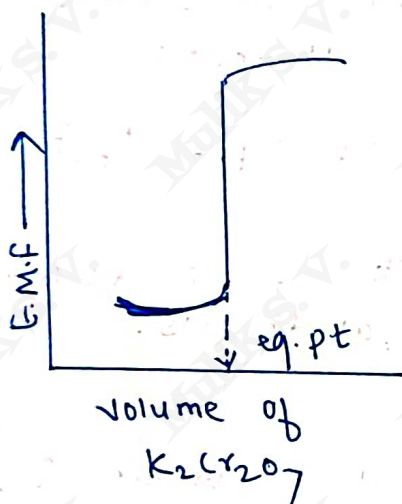
$$\therefore E = E^{\circ} + \frac{0.0591}{n} \log \frac{[\text{Oxd}]}{[\text{Red}]}$$

Now when $\text{K}_2\text{Cr}_2\text{O}_7$ is added ml by ml it converts Fe^{2+} ions to Fe^{3+} ions. Increasing E of the system as it is directly proportional to Oxidation (Fe^{2+} ions)

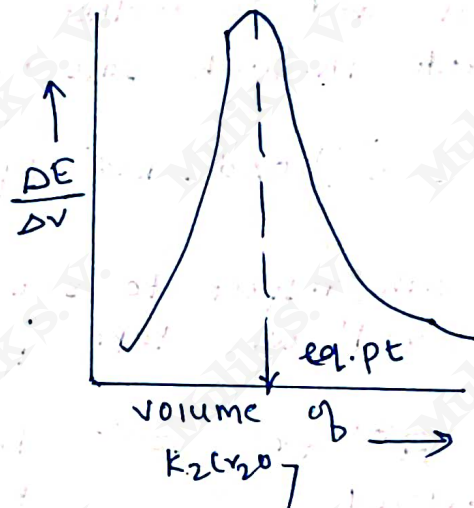
Now equivalence point can be determined by two ways

(a) Classical method] $E.M.F$ Vs volume of $\text{K}_2\text{Cr}_2\text{O}_7$

(b) 1st Derivative method $\frac{\Delta E}{\Delta V}$ Vs volume of $\text{K}_2\text{Cr}_2\text{O}_7$



(a)



(b)

* Precipitation Titrations

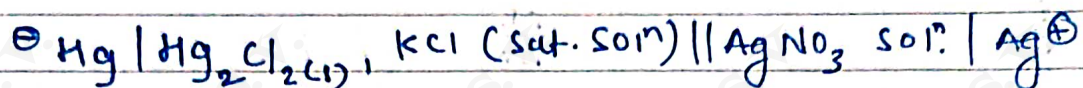
In titrations where precipitation takes place, the ordinary indicator method is not useful.

In this method, indicator electrode which is reversible to one of the ions of precipitate is used

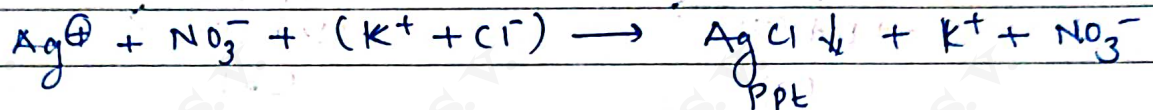
e.g. AgNO_3 Vs KCl soln
(Pipetted out) (In burette)



Electrodes used :- Silver electrode - Indicator electrode
 SCE - Reference electrode
 KNO₃ - Salt bridge



Reaction :-



So, at Ag electrode reduction take place as,



$$\therefore E_{\text{Ag}} = E_{\text{Ag}}^\ominus - \frac{0.0591}{n} \log \frac{a_{\text{Ag(s)}}}{a_{\text{Ag}^\oplus}}$$

$$\therefore = E_{\text{Ag}}^\ominus - 0.0591 \log \frac{1}{a_{\text{Ag}^\oplus}} \quad (\because n=1 \text{ and } a_{\text{Ag(s)}}=1)$$

$$= E_{\text{Ag}}^\ominus + 0.0591 \log a_{\text{Ag}^\oplus}$$

Total cell potential

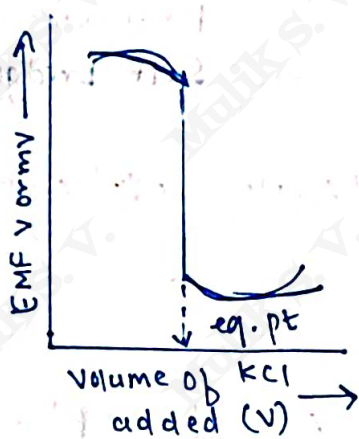
$$E_c = E_{\text{Ag}} - E_{\text{SCE}}$$

Now, we know that during titration, concentration of Ag⁺ ions decreases and accordingly decreasing E_{Ag} and E_c.

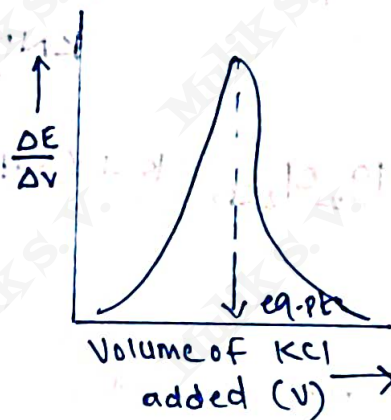
So, equivalence point according to

(a) classical method :- E.M.F ν or mV Vs Volume of KCl

(b) 1st derivative method :- $\frac{\Delta E}{\Delta V}$ Vs Volume of KCl



(a)

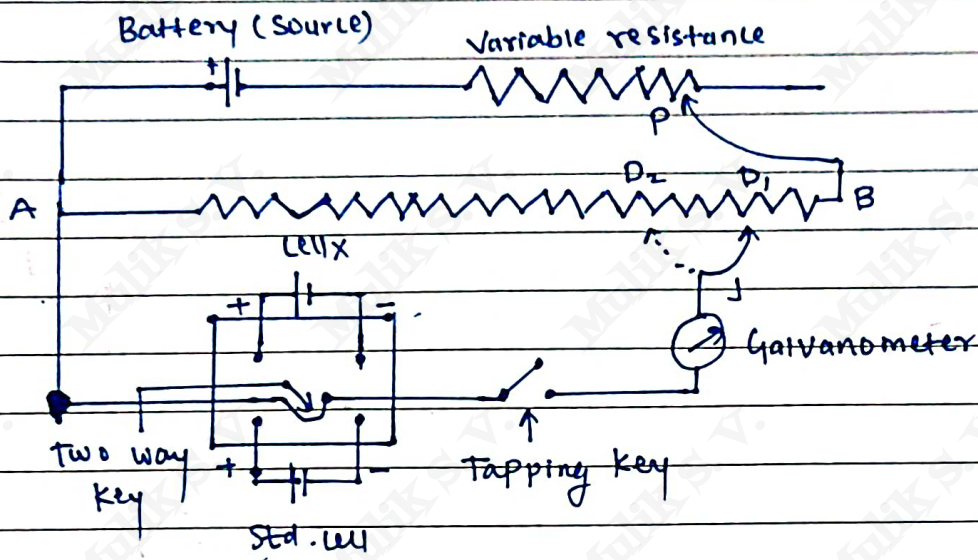


(b)

* Advantages of Potentiometric Titrations :-

1. Potentiometric method can be used in case of dilute and coloured solutions like vinegar or inks.
2. In Potentiometric method we do not require the knowledge of relative strengths of acids and bases used in titrations.
3. This method can be used for the titration of poly basic acids or of mixtures of strong acid and weak acid with a base.
4. Using Potentiometric method it is possible to titrate various oxidising agents against reducing agents and vice-versa.
5. With slight modifications, the apparatus can be automatic.
6. The method can be used for the analysis of chlorides, bromides and iodides.

* Basic Circuit of Direct Reading Potentiometer:-



Standardisation of Potentiometer:

For standardisation, the pointer J is kept at the point D₁ along the wire AB, which corresponds to the emf of standard cell (1.018 volt).

Now, two-way key is shifted towards std. cell, the tapping key is slowly closed and the pointer P is moved along the variable resistance till the galvanometer shows zero deflection. Hence, the potentiometer is standardised.

Once the potentiometer was standardised the variable resistance is kept undisturbed, two way key is shifted towards unknown cell X, the tapping key is closed and pointer J is moved along the wire AB until the Null point D₂ is obtained. The reading of the wire at the point D₂ gives the voltage of the cell X directly.