Electrolyte Concentration Cell

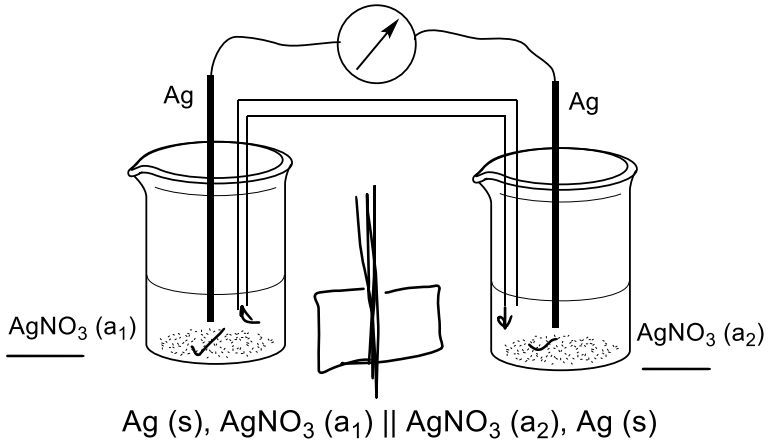
In these kind of concentration cells, the same electrode is dipped to solutions of the same ions but with different activities.

These are of two types: (i) Electrolyte concentration cell with transference

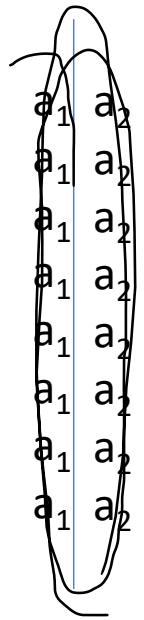
(ii) Electrolyte concentration cell without transference

Concentration Cell without transference

The activities of the electrolytes in which the electrodes are dipped are different. However the electrolytes are separated *via* a salt bridge. The electrolytes with different activities as such do not mix. The liquid-liquid junction potential does not exist.

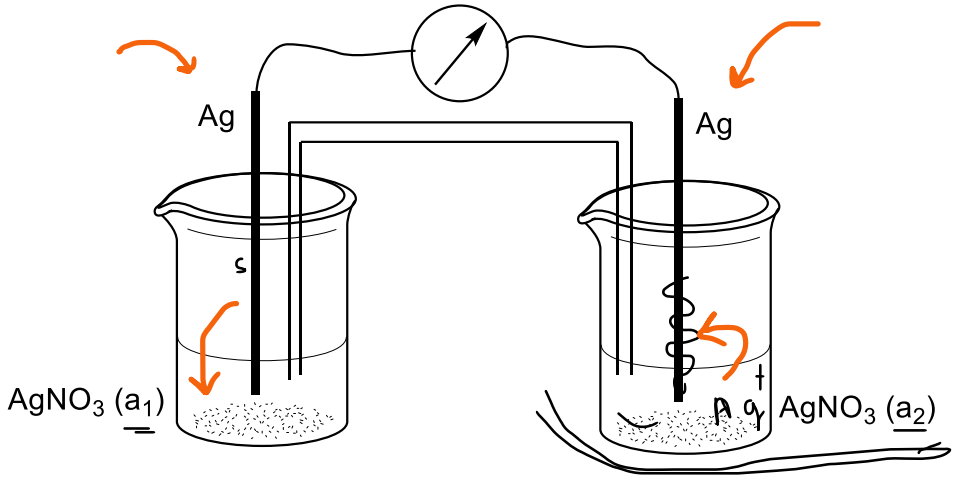


Ag (s), $AgNO_3$ (a_1) || $AgNO_3$ (a_2), Ag (s)



$H_2(P_1) \rightarrow H_2(P_2)$

Let two similar silver electrodes be dipped into two solutions of silver nitrate with different activities a_1 and a_2 respectively. The two solutions being connected to each other *via* a salt bridge. In such a case an emf is shown by the potentiometer.
Let in the left electrode , oxidation takes place (anode) and in the right electrode reduction takes place (cathode)



Ag (s), $AgNO_3$ (a_1) || $AgNO_3$ (a_2), Ag (s)

The oxidation half reaction can be written as : $Ag(s) \rightarrow Ag^+(a_1) + e^-$
The reduction half reaction can be written as: $Ag^+(a_2) + e^- \rightarrow Ag(s)$
The overall reaction can be given as: $Ag^+(a_2) \rightarrow Ag^+(a_1)$
The Nernst equation can be written as:

$$E_{cell} = E^o_{cell} - \frac{RT}{nF} \ln \frac{a_1}{a_2}$$

$$E_{cell} = 0 - \frac{RT}{nF} \ln \frac{a_1}{a_2}$$

At 25 ^oC,

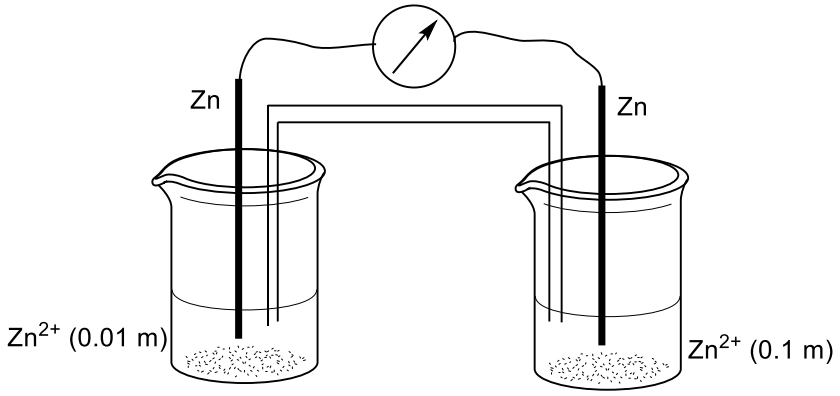
$$E_{cell} = -\frac{0.0591}{n} \log \frac{a_1}{a_2} = \frac{0.0591}{n} \log \frac{a_2}{a_1} = \frac{0.0591}{n} \log \frac{a_{cathode}}{a_{anode}}$$

$E_{cell} > 0$ if, $a_2 > a_1$

The electrolyte with higher activity will act as the cathode

Q1. Calculate the emf of a cell obtained by dipping two similar zinc electrodes into two different Zn^{2+} solutions of molality 0.01 m and 0.1 m respectively. The mean ionic activity coefficients of the electrolytic solutions is 1.

Answer:



The electrolytic compartment with higher activity will act as cathode.

$$Zn^{2+}\ (0.1\ m) + 2e^- \rightarrow Zn\ (s)$$

The electrolytic compartment with lower activity will act as anode.

$$Zn\ (s) \rightarrow Zn^{2+}\ (0.01\ m) + 2e^-$$

Overall reaction, $Zn^{2+}\ (0.1\ m) \rightarrow Zn^{2+}\ (0.01\ m)$; $\quad E_{cell} = +\frac{\mathbf{0.0591}}{\mathbf{n}}\mathbf{log}\frac{\mathbf{a_{0.1}}}{\mathbf{a_{0.01}}} = \frac{\mathbf{0.0591}}{\mathbf{2}}\mathbf{log}\frac{\mathbf{0.1}}{\mathbf{0.01}} = \mathbf{(0.0591/2)\ log\ 10}$

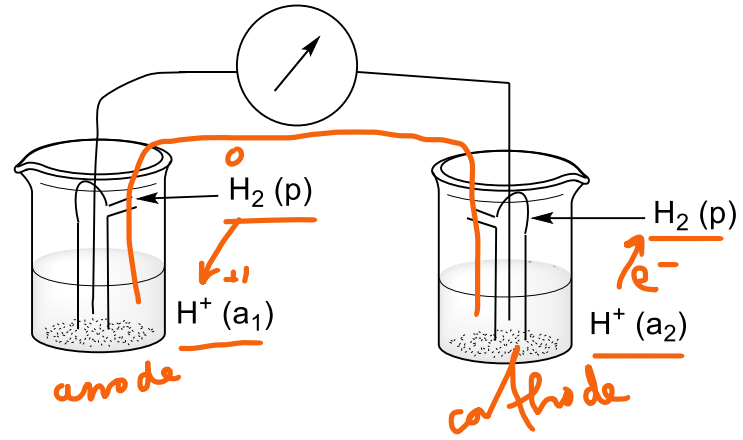
The activity of an electrolyte is directly proportional to the concentration: $\mathbf{a} \propto \mathbf{c} \Rightarrow \mathbf{a} = \gamma\,\mathbf{c}$

Where γ is a constant called the mean ionic activity coefficient. In the given question $\gamma = 1$.

$$E_{cell} = -\frac{\mathbf{0.0591}}{\mathbf{2}}\log\frac{\gamma \text{ X } 0.01}{\gamma \text{ X } 0.1} = -\frac{0.0591}{2}\log\frac{1}{10} = (0.0591/2) \text{ x } \log 10 = 0.0295 \text{ V}$$

Electrolyte concentration cells without transference may also involve gaseous electrodes. Same gaseous electrodes with the same pressure of the gas dipped into acidic solutions of different activities may result in the generation of emf.

The figure on the right shows two hydrogen electrodes dipped into acidic solutions of activities a_1 and a_2 respectively. The two compartments formed as such are connected through platinum wires and *via* a salt bridge.



Let oxidation takes place at the left electrodic compartment (anode) while reduction takes place at the right electrodic compartment (cathode)
The oxidation half reaction can be given by

$$H_2\ (p) \rightarrow 2H^+\ (a_1) + 2e^-$$

The reduction half reaction can be given by

$$2H^+\ (a_2) + 2e^- \rightarrow H_2\ (p)$$

The overall reaction can be given by: $2H^+\ (a_2) \rightarrow 2H^+\ (a_1)$

The Nernst equation can be given as: $E_{cell} = E^o_{cell} - \frac{0.0591}{n} \log \frac{(a_1)^2}{(a_2)^2}$

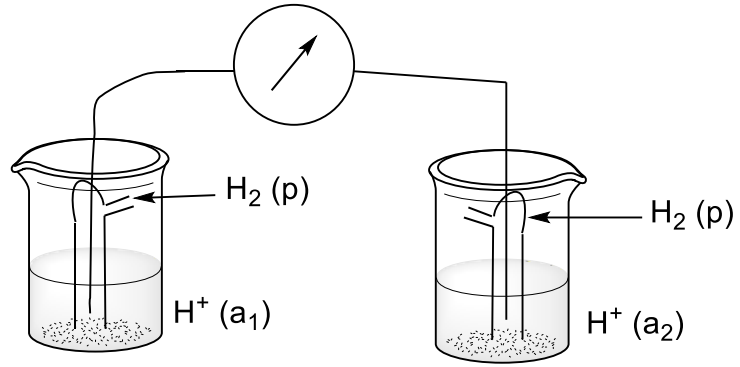
$$E_{cell} = E^o_{cell} - \frac{0.0591}{2} \times 2 \log \frac{a_1}{a_2}$$

$E_{cell} = -0.0591 \log \frac{a_1}{a_2} = +0.0591 \log \frac{a_2}{a_1}$; $a_2 > a_1$ (the electrolytic compartment with electrolyte with more activity will act as the cathode)

$$\log \frac{a^x}{b^x} = \log \left(\frac{a}{b}\right)^x = x \log \frac{a}{b}$$

$E_{cell} = 0.0591 \log (a_{cathode}/a_{anode})$

Q. In the figure on the right, the concentrations of the solutions on the left and the right compartments respectively are 0.01 m and 0.1 m respectively. If the mean ionic activity coefficients at 25 ^{o}C are 0.95 and 0.85 respectively, find the emf of the cell produced.



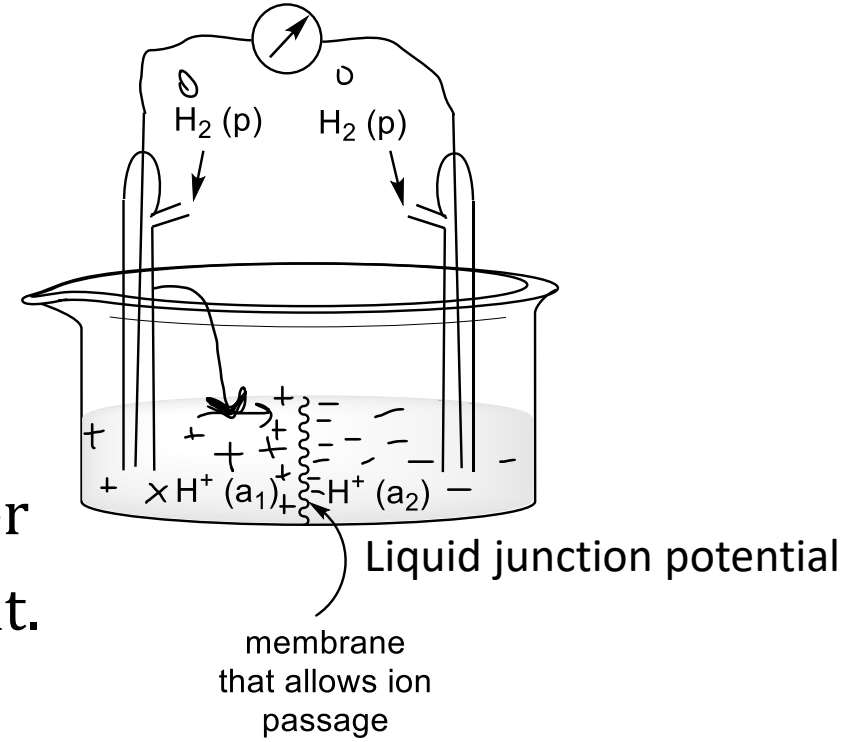
Ans : $E_{cell} = 0.0591 \log\{ a_{cathode}/a_{anode} \} = 0.0591 \log \{(\gamma_{cathode} \times c_{cathode})/ (\gamma_{anode} \times c_{anode})\}$

$= 0.0591 \log \{(0.85 \times 0.1)/(0.95 \times 0.01)\} = +0.056$ V

$a = \gamma \times c$

Electrolyte Concentration Cell with transference

As shown in the figure, a cell is constructed by dipping two hydrogen electrodes with hydrogen at a pressure **p** immersed into two acidic solutions with activities $\mathbf{a_1}$ and $\mathbf{a_2}$ respectively. The solutions are separated from each other by a membrane that allows the movement of ions through it.



The oxidation half reaction can be written as $H_2\ (p) \rightarrow 2H^+\ (a_1) + 2e^-$ (anode)

The reduction half reaction can be written as $2H^+\ (a_2) + 2e^- \rightarrow H_2\ (p)$ (cathode)

$$\mathbf{E_{cell} = E_{cathode} - E_{anode} + E_{LJP}}$$

Ionic Mobility (u_+/u_-)

It is the terminal/drift speed acquired by an ion per unit potential difference.

Transport Number (t_+/t_-)

The transport number of a ion in a electrolyte is the fraction of the total current carried by the ion.

t_+ = (current carried by the cation)/(total current) = $(u_+)/(u_+ + u_-) = (\lambda_+/\Lambda^o_m)$

t_- = (current carried by the anion)/(total current) = $(u_-)/(u_+ + u_-) = (\lambda_-/\Lambda^o_m)$

$t_+ + t_- = 1$

Let at the left compartment, oxidation takes place while at the right compartment, reduction takes place.

The emf of the cell with transference is obtained as: $E_{w.t} = 2t_- \, X \, \frac{0.0591}{n} \log \frac{a_2}{a_1}$

The electrolyte with higher activity acts as the cathodic half cell

The emf of the cell without transference is: $E_{w.o.t} = \frac{0.0591}{n} \log \frac{a_2}{a_1}$

The liquid junction potential is therefore:

$$E_J = E_{w.t} - E_{w.o.t}$$

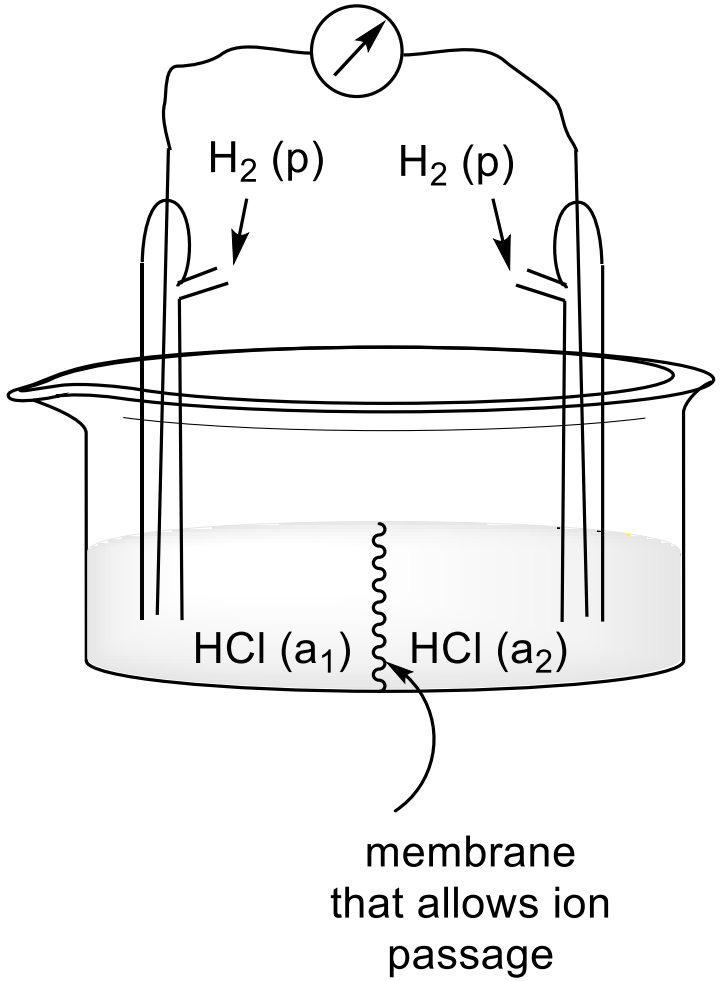
$$E_J = [\, 2t_- \, X \, \frac{0.0591}{n} \log \frac{a_2}{a_1} \,] - [\frac{0.0591}{n} \log \frac{a_2}{a_1} \,]$$

$$E_J = \{2t_- - 1\} \, [\frac{0.0591}{n} \log \frac{a_2}{a_1} \,]$$

$$E_J = \{2t_- - (t_+ + t_-)\} \, [\frac{0.0591}{n} \log \frac{a_2}{a_1} \,]$$

$$E_J = \{t_- - t_+\} \, [\frac{0.0591}{n} \log \frac{a_2}{a_1} \,]$$

(for concentration cell without transference, however $a_2 < a_1$)



Potentiometric Titrations

These are the titrations which involve the measurement of electrode potentials with the addition of a titrant.

It is used in the determination of the concentration of an unknown solution.

Two kinds of electrodes are used in potentiometric titrations:

A cell is first formed by combining the two electrodes

(i) Indicator electrode

To the compartment containing the indicator electrode, the titrant is added slowly. The electrode is dipped in such an electrolytic solution which is reversible with respect to the electrode. For example, the Hydrogen electrode is reversible to the H^+ ions, Zn electrode is reversible to the Zn^{2+} ions. Upon the slow addition of the titrant, the electrode potential of the indicator electrode changes which results in the change in the cell potential. This change is measured after each addition.

(ii) Reference electrode

It is an electrode whose potential remains constant throughout the titration. The potential is normally known such as the standard calomel electrode.

In addition, a salt bridge is also present in the setup.

It is of three types:

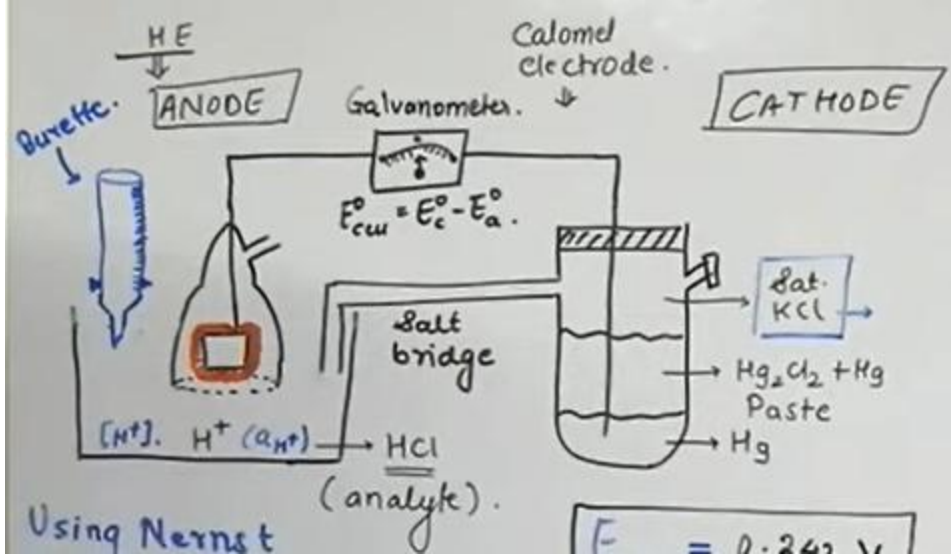
(I) Acid-Base titration

(II) Oxidation-Reduction titration

(III) Precipitation titration

- Acid – Base Titration

In such a titration, an acid is titrated with a base. The potential of the indicator electrode is measured after each addition of the titrant.



Let us consider a solution of HCl is to be titrated against a solution of NaOH. Any electrode whose concentration depends on the concentra-tion of H^+ ions is placed in the HCl solution and is taken as the indic-ator electrode (such as hydrogen electrode, glass electrode etc.). It is connected to a reference electrode such as the calomel electrode to form a galvanic cell as shown in the figure.

If a saturated calomel electrode is used as the reference electrode (E^o_{cal} = +0.2422 V), and a hydrogen electrode is used as the indicator electrode (E^o_{SHE} = 0 V), then the hydroden electrode behaves as the anode and the calomel electrode behaves as the cathode. Now, if a solution of NaOH of known concentration/activity is slowly added to the HCl solution the electrode potential of the hydrogen electrode will continuously change due to the change in the pH of the HCl solution (pH will increase).

The oxidation reaction in the Hydrogen electrode is given by: H_2 (g) → $2H^+$ (aq) + $2e^-$

Therefore the Nernst equation for the electrode can be written as:

$$E_{H2/H+} = E^o_{H2/H+} - \frac{0.0591}{2} \times \log[H^+]^2 = 0 - \frac{0.0591}{2} \times 2 \log[H^+] = 0.0591 \times (-\log[H^+]) = 0.0591\ pH$$

- The equation $E_{H2/H+} = 0.0591\ pH$ represents the oxidation potential of the hydrogen electrode. The reduction potential of the electrode will therefore be $E_{H+/H2} = -0.0591\ pH$.

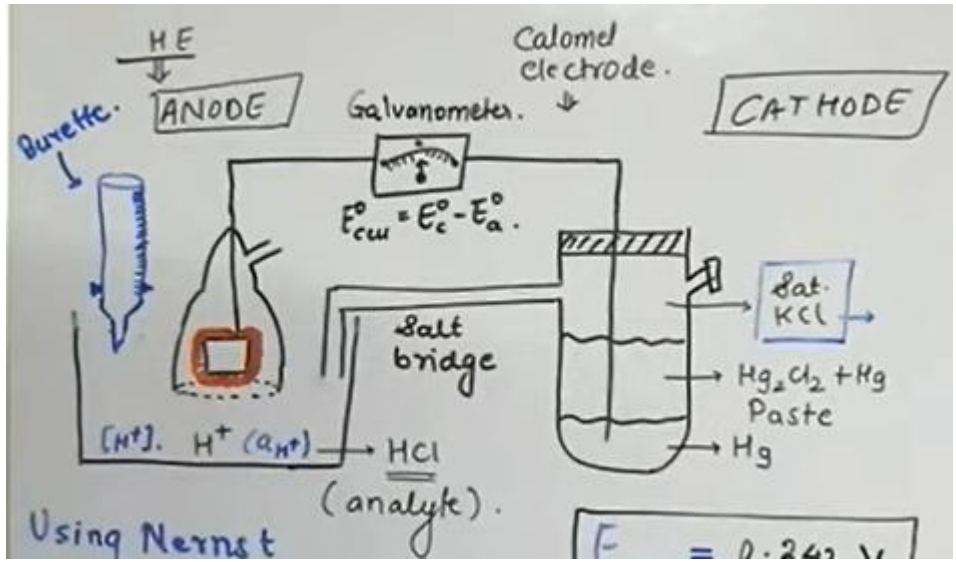
- The cell potential for the cell is given by: $E_{cell} = E_{cathode} - E_{anode} = +0.2422 - (-0.0591pH$
- $E_{cell} = 0.2422 + 0.0591\ pH$

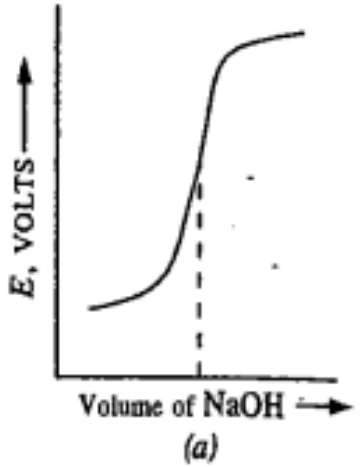
The cell potential will therefore increase with the increase in the pH of the solution.

The overall cell can be shown as

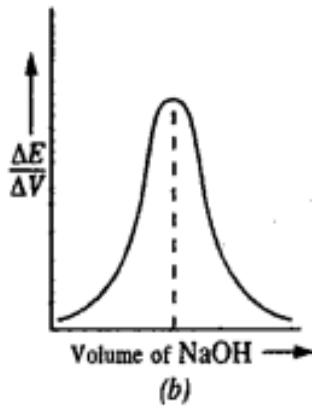
Pt, H_2(g, 1 atm), HCl (a_1) || Hg (s), Hg_2Cl_2 (s), KCl

The plot of E_{cell} vs volume of base (NaOH) appears to be a sigmoid curve as shown in the figure on the right. The point at which the all H^+ ions are exactly neutralised by the base is called the equivalence point. Th emf initially rises gradually and thereafter more rapidly near the equivalence point.





- At the equivalence point where almost all of the H^+ ions are neutralized, further addition of NaOH does not change the pH and the emf of the cell.
- In the same way, a DE/DV vs volume of NaOH is shown in the figure below. The highest point in the curve represents the equivalence point and the volume of NaOH at that point represents the volume of NaOH required for the titration i.e., the volume of NaOH that exactly neutralises the HCl solution.



Example 31. 25 ml of a solution of HCl (0·1 M) is being titrated potentiometrically against a standard (0·1 M) solution of NaOH using a hydrogen electrode as the indicator electrode and saturated calomel electrode (SCE) as the reference electrode. What would be the EMF of the cell initially and after the addition of 20, 24·9, 24·95, 25·00 25·05, 25·10 and 30·00 ml of NaOH solution ? Comment on the data obtained.

Answer: $E_{cell} = 0.2422 + 0.0591\ pH$

Molarity of HCl = 0.1 M = 0.1 mol L^{-1} => 0.1 mol HCl in 1000 mL
$\Rightarrow$ no of moles of HCl in 25 mL of 0.1 M solution = (25 x 0.1)/1000 = 2.5 x 10^{-3} mol

Molarity of NaOH = 0.1 M = 0.1 mol in 1000 mL

(i) Addition of 20 mL NaOH :
No of Moles of NaOH in 20 mL of 0.1 M NaOH = 2 x 10^{-3} mol

The addition of 20 mL of 0.1 M NaOH to HCl solution means 2 x 10^{-3} moles of NaOH have been added and 1 mol NaOH neutralises 1 mol HCl. therefore 2 x 10^{-3} mol NaOH will neutralise 2 x 10^{-3} mol HCl

Remaining HCl after neutralisation = 2.5 x 10^{-3} – 2 x 10^{-3} = 5 x 10^{-4} mol
New volume = 25 mL + 20 mL = 45 mL => New molarity = (5 x 10^{-4} mol/45 x 10^{-3} L) = 0.011 M