Antimony Electrode (Sb/Sb_2O_3 electrode)

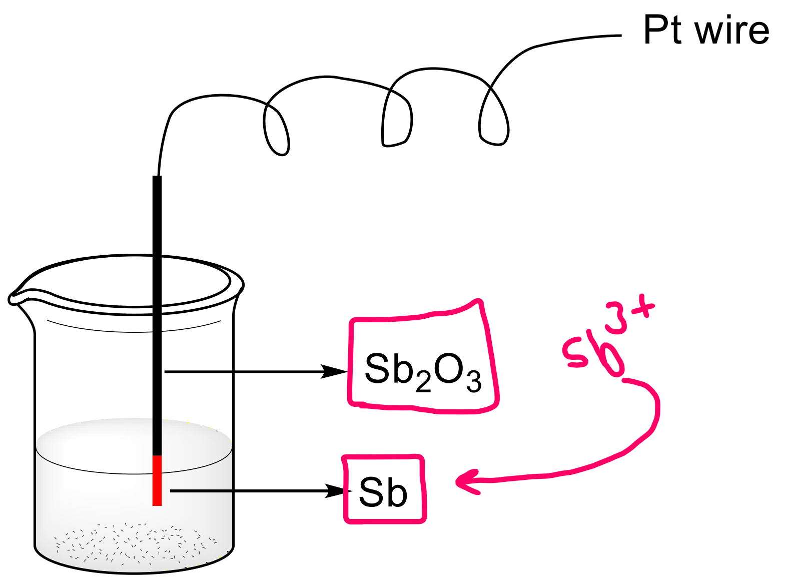
It consists of an antimony rod dipped into a solution whose pH is to be determined. Upon exposure to air the antimony partially gets oxidized to antimony oxide (Sb_2O_3). It is linked to the circuit via a platinum wire.

The oxidation state of Sb in Sb_2O_3 is +3.

The electrode reaction can be given as (reduction)

+3 0

$$Sb_2O_3 + 6H^+ + 6e^- \rightarrow 2Sb + 3H_2O$$



The Nernst equation for the electrode can be given by:

$$E_{Sb2O3/Sb} = E^o_{Sb2O3/Sb} - \{RT/nF\} \times \ln \{1/[H^+]^6\}$$

$$E_{Sb2O3/Sb} = E^o_{Sb2O3/Sb} - \{2.303RT/nF\} \times \log \{1/[H^+]^6\}$$

$$E_{Sb2O3/Sb} = E^o_{Sb2O3/Sb} + \{2.303RT \times 6/nF\} \log [H^+]$$

$$E_{Sb2O3/Sb} = E^o_{Sb2O3/Sb} + \{2.303RT \times 6/6F\} \log [H^+] \quad \{\text{since } n = 6\}$$

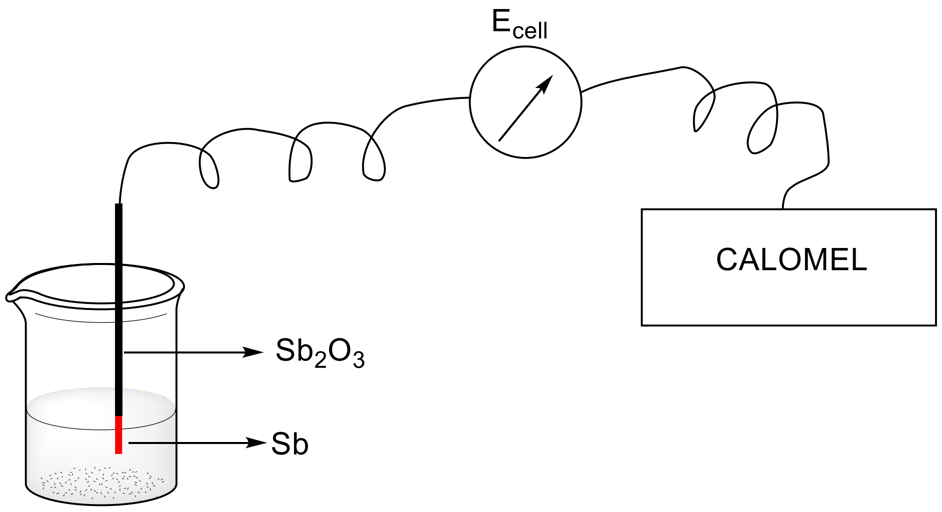
$$E_{Sb2O3/Sb} = E^o_{Sb2O3/Sb} - \{2.303RT /F\}\, pH \quad \{\text{since } n = 6\}$$

$\log \frac{1}{a^x} = -x \log a$

At 25 °C,

$+\log H^+ = -pH$

$$E_{Sb2O3/Sb} = E^o_{Sb2O3/Sb} - 0.0591pH \quad \{\text{since } n = 6\}$$



$$E_{cell} = E_{ant} - E_{cal}$$

- Advantages

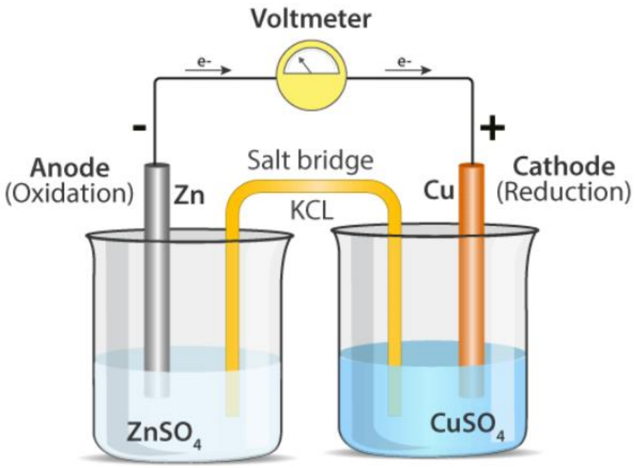
- It can be used in the pH range 3 to 8
- It is not easily poisoned or damaged
- It can be used with viscous fluids

- Disadvantages
- The electrode can not be used in the presence of strong oxidizing and reducing agents

Concentration Cells

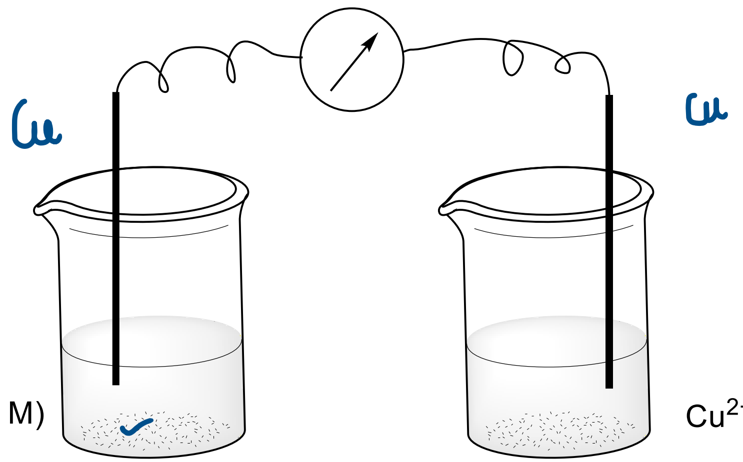
Concentration cells are a type of electrochemical cells in which emf (E_{cell}) is seen not due to some chemical reaction occurring within the cell but due to the transfer of matter from one half cell to the other due to some concentration difference.

The transfer of matter will take place only in that direction in which Gibbs free energy decreases ($\Delta G < 0$). The transfer of matter can be from the electrode or the electrolyte



$Zn(s)\,|\,ZnSO_4(aq)\,||\,CuSO_4(aq)\,|\,Cu(S)$

Case 1



Cu^{2+} (1 M)

Cu^{2+} (1 M)

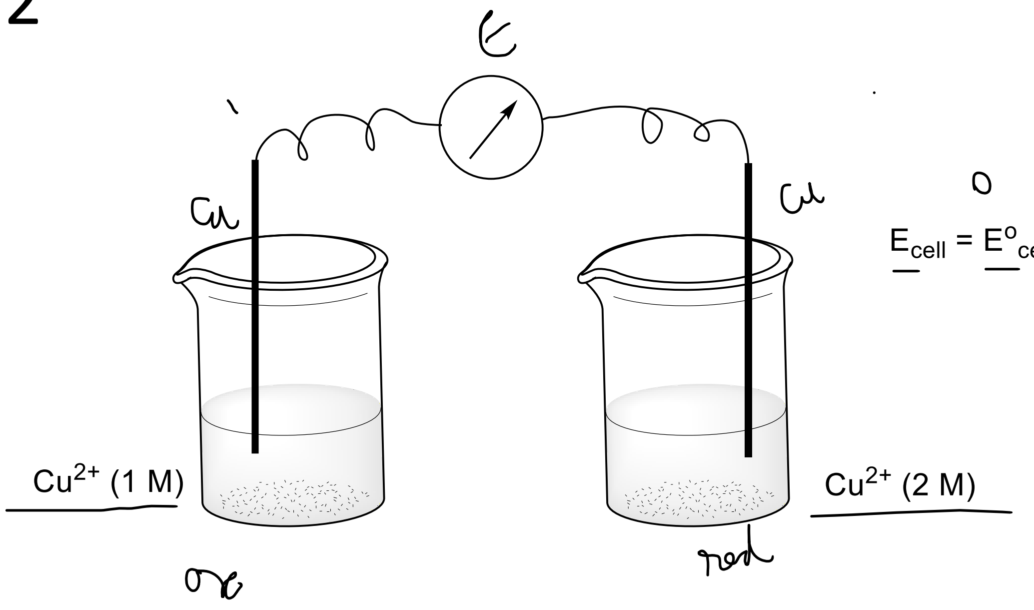
$E_{cell} = E^o_{cell} - (0.0591/n) \log \{[Cu^{2+}]/[Cu^{2+}]\}$

$E_{cell} = E^o_{Cu2+/Cu} - E^o_{Cu2+/Cu}$

$E_{cell} = 0$

$$E^o_{cell} = E^o_{red} - E^o_{oxid} = E^o_{Cu^{2+}/Cu} - E^o_{Cu^{2+}/Cu} = 0$$

Case 2



$$\underline{E_{cell}} = \underline{\overset{o}{E^{o}_{cell}}} - (0.0591/n)\{\underset{1}{\overset{a}{[Cu^{2+}]}}/\underset{2}{\overset{c}{[Cu^{2+}]}}\}$$

Concentration cell

- Electrode concentration cell ✓
- Electrolyte concentration cell
  - with transference
  - without transference

- **Electrode Concentration cell.**

The concentration cells in which electrodes of the same material, having different concentrations/pressures are dipped into, same electrolytes with same concentrations.

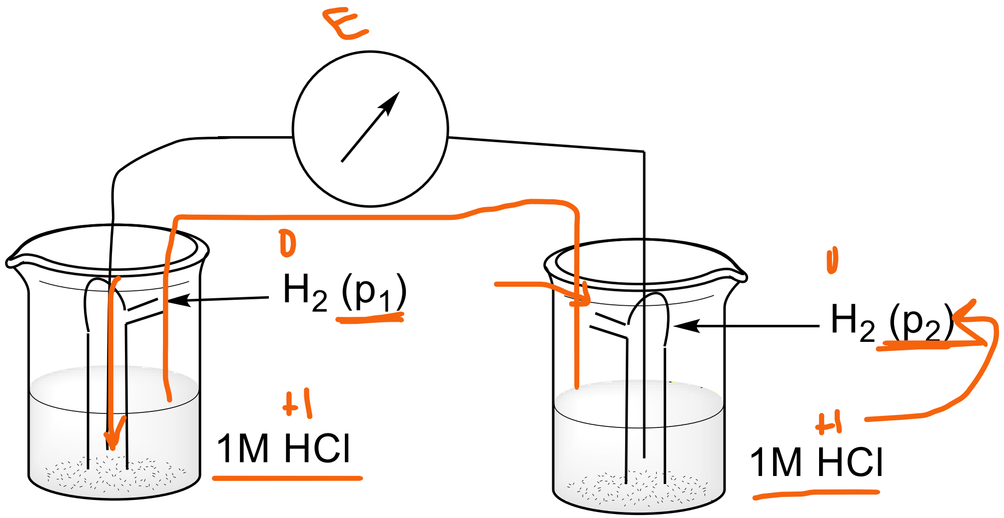
It can be of two types:

1. Cells with gaseous electrodes

In these cells, the electrodes are gaseous and have different pressures which are being dipped into the same solution (of that of the gas) with the same concentration

Let two hydrogen electrodes with hydrogen
gas at different pressures be connected to each other as shown in the figure .
The concentration of the acid used in both the electrodes being same in both the cases.

In such a case, the potentiometer connected shows a potential difference across the half cells.
Let in the left electrode, oxidation occurs (anode) and in the right electrode reduction occurs (cathode)



$Pt, H_2 (p_1)/HCl (1M) \,||\, HCl (1M), H_2 (p_2), Pt$

• Reduction half reaction (H^+ to H_2), cathode

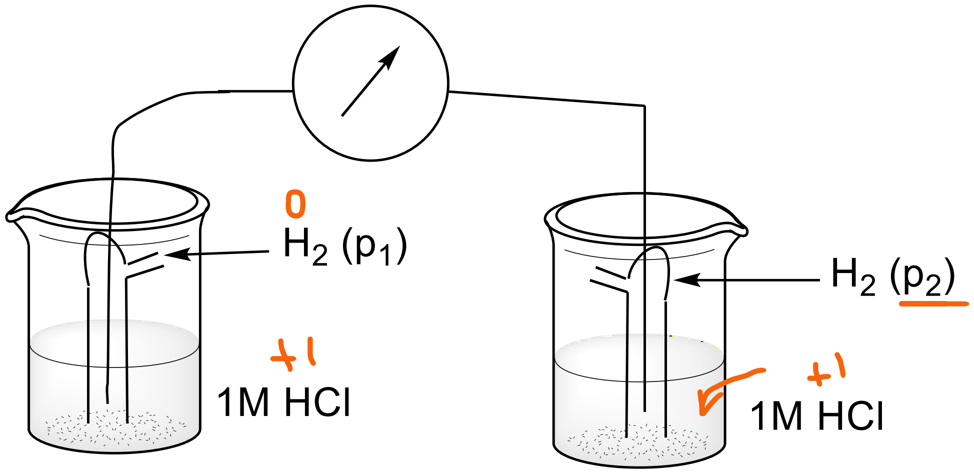
$$2H^+ (1M) + \underline{2e^-} \rightarrow H_2\ (p_2)$$

Oxidation half reaction (H_2 to H^+), anode

$$H_2\ (p_1) \rightarrow 2H^+\ (1M) + \underline{2e^-}$$

Overall reaction,

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



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

The Nernst equation can be written for this cell as:

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n} \log[\frac{P_2}{P_1}]$$

A (g) → B (g); $Q_c = p_B/p_A$

The standard reduction potential for hydrogen electrode is 0

$$E_{cell} = -\frac{0.0591}{n} \log[\frac{P_2}{P_1}]$$

$$E_{cell} = -\frac{0.0591}{n}\log[\frac{P_2}{P_1}] = -\frac{0.0591}{2}\log[\frac{P_2}{P_1}]$$ where, $P_2 < P_1$

If $P_2 > P_1$, then $\log[\frac{P_2}{P_1}] > 0$, then $E_{cell} < 0$, the cell does not produce emf.

If $P_2 < P_1$, then $\log[\frac{P_2}{P_1}] < 0$, then $E_{cell} > 0$, the cell produces emf.

The hydrogen electrode with a higher pressure of H_2 behaves as the anode.

(At moderate pressures , H_2 can be considered as an ideal gas so that ratio of pressure is equal to the ratio of activity.)

$$E_{cell} = -\frac{0.0591}{n}\log[\frac{a_2}{a_1}]$$

2. Cells with amalgam electrodes

Amalgam: Alloy of a metal with mercury.

The concentration/activity of a electrode material can be varied through the formation of its amalgam.

Let two electrodes of Zinc-Amalgam (Zn-Hg) with different activities of Zn be dipped into a solution of $ZnSO_4$ of concentration "***c* M**" as shown in the figure below:

Let oxidation happens in the left electrode (anode)and reduction happens in the right electrode (cathode).

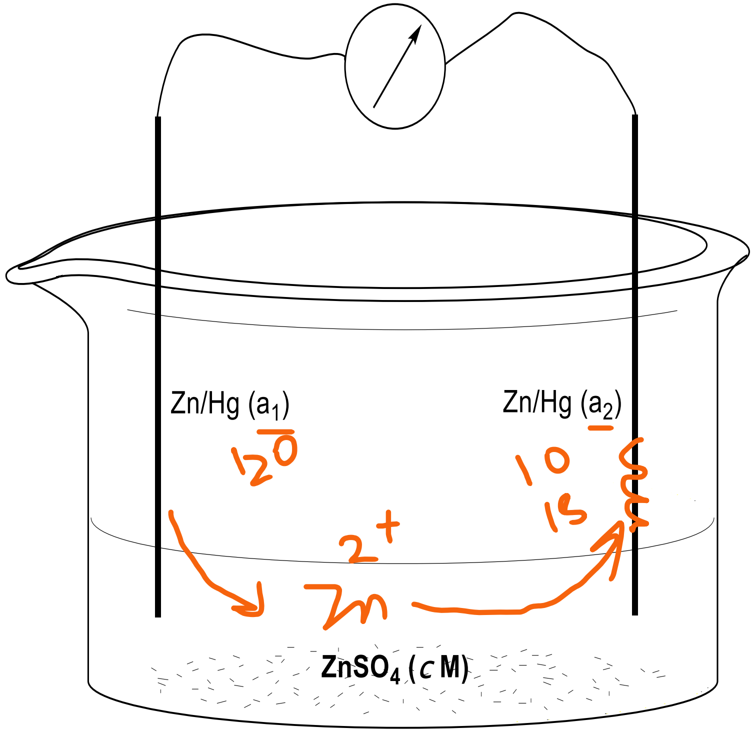
Oxidation half reaction (anode): $\text{Zn (s, } \mathbf{a_1}) \rightarrow \text{Zn}^{2+}(\text{aq, } \boldsymbol{c}\ \mathbf{M}) + 2\ e^-$

Reduction half reaction (cathode), $\text{Zn}^{2+}\ (\text{aq, } \boldsymbol{c}\ \mathbf{M}) + 2e^- \rightarrow \text{Zn (s, } \mathbf{a_2})$

The overall reaction is: $\text{Zn (s, } \mathbf{a_1}) \rightarrow \text{Zn (s, } \mathbf{a_2})$

The Nernst equation can be written as (at 25 °C):

$$E_{cell} = E^{o}_{cell} - \frac{0.0591}{n} \mathbf{log}[\frac{\mathbf{a_2}}{\mathbf{a_1}}]$$



Zn-Hg (a_1), $ZnSO_4$ (1M), Zn-Hg (a_2)

$$E_{cell} = E^{o}_{cell} - \frac{0.0591}{n}\mathbf{log}[\frac{\mathbf{a_2}}{\mathbf{a_1}}]$$

Since electrodes are of the same electrode material, $E^{o}_{cell} = 0$

Therefore, $E_{cell} = - \frac{0.0591}{n}\mathbf{log}[\frac{\mathbf{a_2}}{\mathbf{a_1}}]$ { where, $a_2 < a_1$}

If $a_2 > a_1$, then $\log(a_2/a_1) > 0$, then $E_{cell} < 0$, the cell does not work

If $a_2 < a_1$, then $\log(a_2/a_1) < 0$, then $E_{cell} > 0$, the cell works

The amalgam electrode with higher activity acts as the anode.

Q. Calculate the emf of the electrode concentration cell

$$Zn\text{-}Hg\ (c_1)\ ,\ Zn^{2+}(1M),\ Zn\text{-}Hg\ (c_2)$$

at 25 °C if c_1 = 2 g per 100 g Hg and c_2 = 1 g per 100 g Hg.

Answer: $E_{cell} = -0.0591/n \times \log \{\overset{c_2}{a_2}/\overset{c_1}{a_1}\} = -0.0591/2\ \log (1/2) = 8.8 \times 10^{-3}$ V