ELECTROCHEMISTRY

“Electrochemistry is the branch of chemistry concerned with the interrelation of electrical and chemical changes that are caused by the passage of current.”

“Chemical reactions that involve the input or generation of electric currents are called electrochemical reactions.”

“A device capable of either generating electrical energy from chemical reactions or using electrical energy to cause chemical reactions is called Electrochemical cell.”

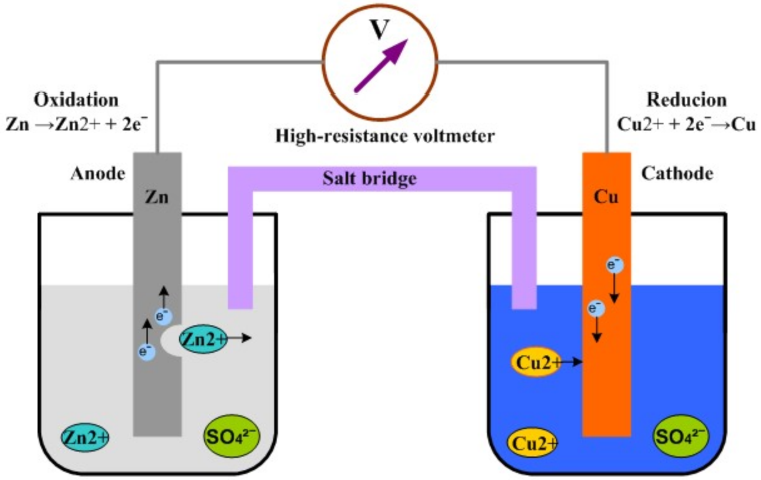
GALVANIC CELL

“A Galvanic cell is an electrochemical cell that produces electricity as result of spontaneous reaction occurring in it.”

“A Galvanic cell is a device in which the free energy of a physical or chemical process is converted in to electrical energy.”

- **It is also called as Voltaic (voltage generated) cell.**

Daniell Cell: *A Daniell cell is the best example of a galvanic cell which converts chemical energy into electrical energy. The Daniell cell consists of two electrodes of dissimilar metals, Zn and Cu; each electrode is in contact with a solution of its own ion; Zinc sulphate and copper sulphate respectively.*

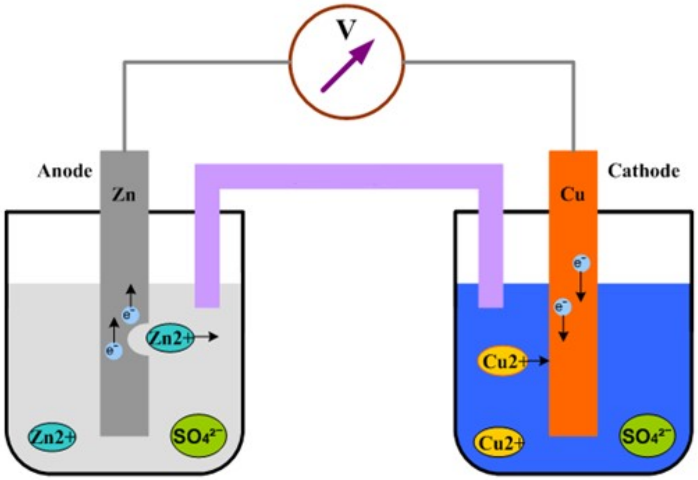


$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

Electrode: ***An electrode is a small piece of metal or other substance that is used to take an electric current to or from a source of power.***

Electrolyte: ***Electrolyte is a substance that conducts electric current as a result of dissociation into cations and anions, in a polar solvent.***

The most familiar electrolytes are acids, bases, and salts, which ionize when dissolved in solvents such as water or alcohol. Many salts, such as sodium chloride, behave as electrolytes when melted in the absence of any solvent; and some, such as silver iodide, are electrolytes even in the solid state.



Anode and Cathode: ***Anode is the electrode at which the oxidation half-reaction occurs, and the cathode is the electrode at which the reduction half-reaction occurs.***

Redox Reaction: *It is a chemical reaction in which electrons are transferred between two reactants participating in it. This transfer of electrons can be identified by observing the changes in the oxidation states of the reacting species.*

The loss of electrons and the corresponding increase in the oxidation state of a given reactant is called oxidation. The gain of electrons and the corresponding decrease in the oxidation state of a reactant is called reduction.

Electron-accepting species which tend to undergo reduction in redox reactions are called oxidizing agents. An electron-donating species which tend to undergo oxidation are called reducing agents.

At Anode (oxidation): $Zn\,(s) \longrightarrow Zn^{2+}(aq) + 2\bar{e}$

At Cathode (reduction): $Cu^{2+}(aq) + 2\bar{e} \longrightarrow Cu\,(s)$

Overall Redox Reaction: $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu\,(s)$

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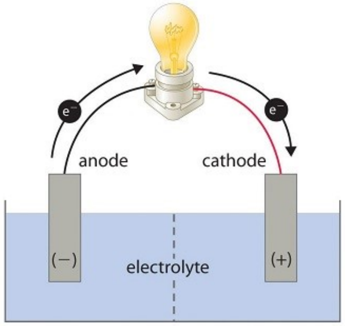
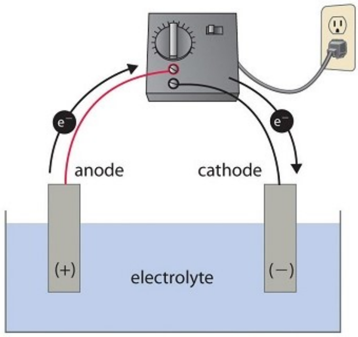
Electrochemical Cell

It is a device capable of either generating electrical energy from chemical reactions or using electrical energy to cause chemical reactions.

Galvanic Cells	Electrolytic Cells
Chemical energy is converted in to electrical energy.	Electrical energy is converted in to chemical energy.
It produces EMF.	It requires EMF.
Anode is −ve and cathode is +ve.	Anode is +ve and cathode is −ve.
Oxidation takes place at anode and reduction takes place at cathode in different containers.	Oxidation takes place at anode and reduction takes place at cathode in same container.
Discharge of ions occur only at cathode.	Discharge of ions occur at both electrodes.
Spontaneous reaction takes place.	Non-spontaneous reaction occurs.
These may be reversible cells.	These are irreversible cells.
Flow of electrons is from anode to cathode.	Electrons start at the negative terminal of the battery and flow to cathode and then enter anode through electrolytic solution.
Electrons leave the cell at anode and enter the cell at cathode.	Electrons leave the cell at anode and enter the cell at cathode.

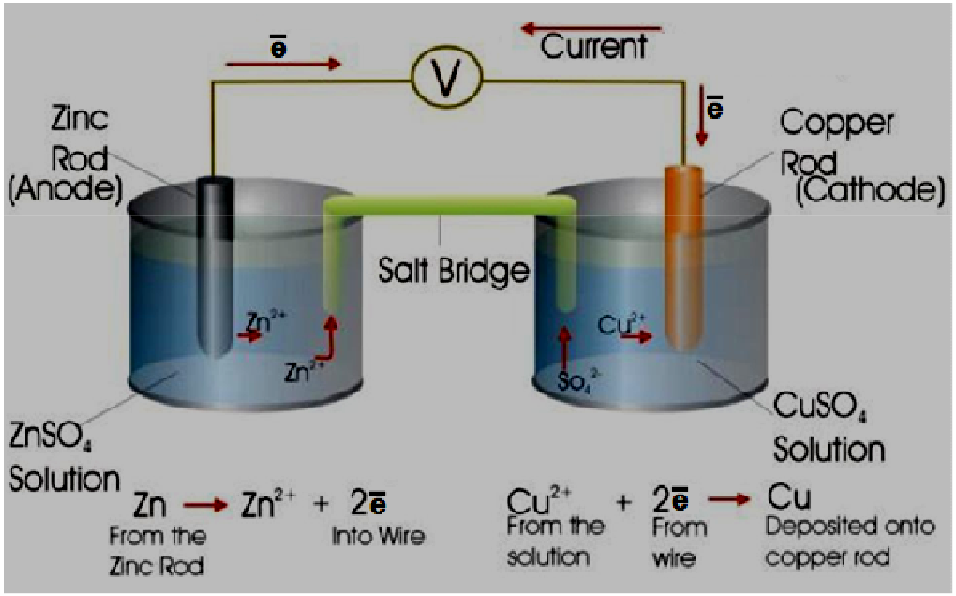


GALVANIC CELL

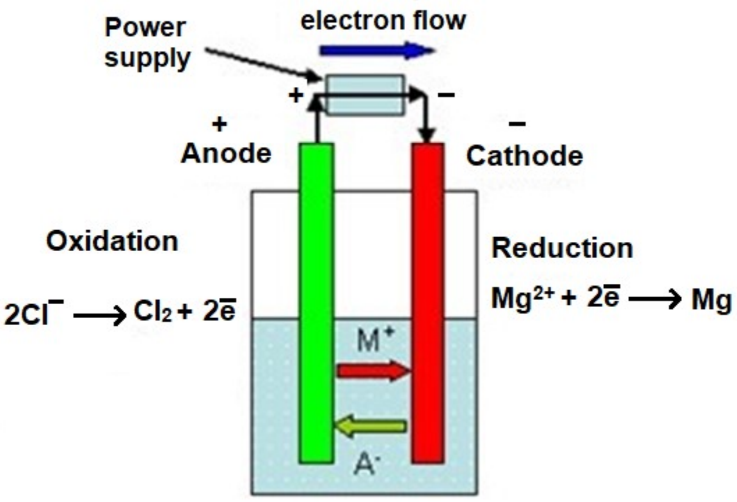


ELECTROLYTIC CELL

Galvanic Cells



Electrolytic Cells



CELL POTENTIAL

Cell Potential: *The potential difference between the two electrodes of a Galvanic cell is called the cell potential.*

Potential Difference: *It is the work done in moving a unit positive electric charge from one point to another.*

Electromotive Force (EMF): *When no current is drawn through the cell, the cell potential is called EMF.*

OR

EMF is the maximum potential difference between to electrodes of the Galvanic cell.

Electrode Potential: *When a metal is placed in a solution of its ions, the metal acquires either positive or negative charge w.r.t. the solution. A potential difference occurs between metal and solution. This is known as Electrode potential.*

Magnitude of the *Electrode Potential*

The magnitude of the *electrode potential of a metal is a measure of its relative tendency to lose or gain electrons i.e., oxidation or reduction.*

Oxidation: *Conversion of metal atoms into metal ions by the attractive force of polar water molecules.*

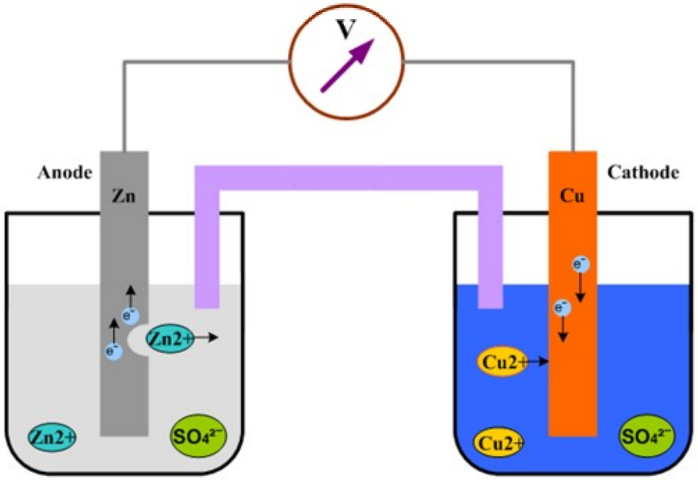
$$M \longrightarrow M^{n+} + n\bar{e}$$

The M^{n+} ions go into solution and ēs remain on the metal making it negatively charged.

The tendency of a metal to change into ions is known as *electrolytic solution pressure*.

Reduction: *Metal ions in solution gain* ēs from the electrode and leave positive charge *on the electrode. Thus metal ions start depositing on the metal surface leading to a positive charge on the metal.*

$$M^{n+} + n\bar{e} \longrightarrow M$$



In the beginning oxidation and reduction both occur with different speeds but soon an equilibrium is established.

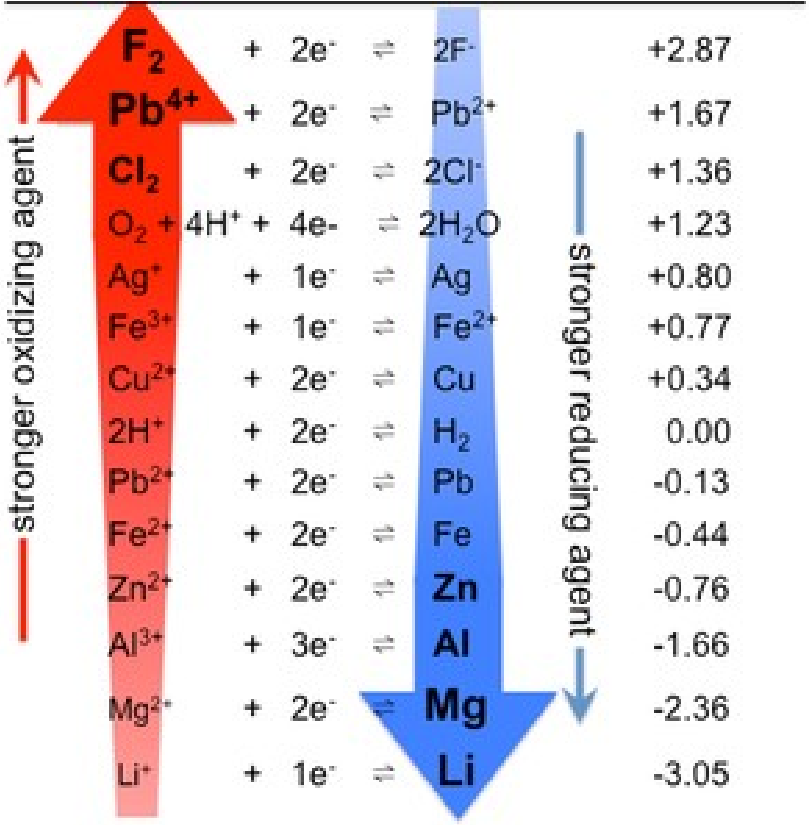
$$M \rightleftharpoons M^{n+}(aq) + n\,\bar{e}$$

In practice, one effect is greater than the other. If oxidation is greater then the electrode acquires negative charge and of reduction is greater it will acquire positive charge.

The magnitude of the *electrode potential depends on:*

1) Concentration of ions
2) *Temperature and*
3) *Nature of the electrode.*

Electrochemical Series:



Half reaction	Standard reduction potential
$F_2 + 2e^- \rightleftharpoons 2F^-$	+2.87
$Pb^{4+} + 2e^- \rightleftharpoons Pb^{2+}$	+1.67
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23
$Ag^+ + 1e^- \rightleftharpoons Ag$	+0.80
$Fe^{3+} + 1e^- \rightleftharpoons Fe^{2+}$	+0.77
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
$Pb^{2+} + 2e^- \rightleftharpoons Pb$	-0.13
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	-0.44
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	-0.76
$Al^{3+} + 3e^- \rightleftharpoons Al$	-1.66
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	-2.36
$Li^+ + 1e^- \rightleftharpoons Li$	-3.05

EMF of Galvanic Cells

When no current is drawn through the cell, the cell potential is called EMF.

OR

EMF is the maximum potential difference between to electrodes of the Galvanic cell.

$$E_{cell} = E_{Red}\,(RHS) - E_{Red}\,(LHS) \Rightarrow E_{cell} = E_{Cu^{2+}/Cu} - E_{Zn^{2+}/Zn}$$

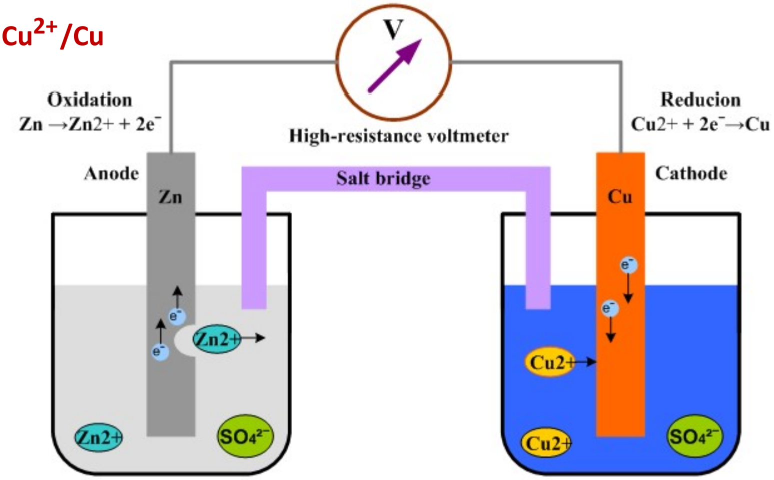
$$E_{cell} = E_{Ox}\,(LHS) + E_{Red}\,(RHS) \Rightarrow E_{cell} = E_{Zn/Zn^{2+}} + E_{Cu^{2+}/Cu}$$

$$E_{cell} = E_{Ox}\,(LHS) - E_{Ox}\,(RHS)$$

$$\Rightarrow E_{cell} = E_{Zn/Zn^{2+}} - E_{Cu/Cu^{2+}}$$

$$E_{cell} = -\,E_{Red}\,(LHS) - E_{Ox}\,(RHS)$$

$$\Rightarrow E_{cell} = -\,E_{Zn^{2+}/Zn} - E_{Cu/Cu^{2+}}$$



$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu\,(s)$$

Reversible Galvanic Cells

For a reversible Galvanic cell, the following thermodynamic conditions should be fulfilled.

1) ***If the opposing EMF is exactly equal to that of the cell itself, no current is given out by the cell and no chemical reaction takes place.***
2) ***If the opposing EMF is infinitesimally smaller than that of the cell itself, an extremely small current is given out by the cell and a correspondingly small amount of the chemical reaction takes place in the cell.***
3) ***If the opposing EMF is infinitesimally greater than that of the cell itself, an extremely small current flows through the cell in the opposite direction and a small amount of reaction also takes place in the opposite direction.***

Example: $Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$ $E^{o}_{cell} = 1.1\ V$

$E^{o}_{Zn^{2+}/Zn} = -0.76\ V$

$E^{o}_{Cu^{2+}/Cu} = +0.34\ V$

External EMF applied	E^{o}_{cell}	Direction of flow of ēs
No EMF applied	+ 1.10 V	Zn to Cu
– 1.09 V	+ 0.01 V	Same direction
– 1.10 V	+ 0.00 V	-
– 1.11 V	– 0.01 V	Reverse direction (Cu to Zn)

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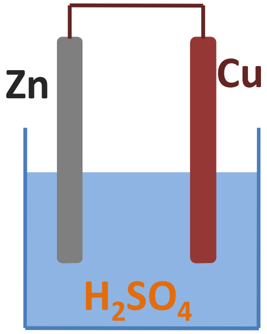
Irreversible Galvanic Cells

Cell reaction: $Zn(s) + 2H^{+}(aq) \rightleftharpoons Zn^{2+}(aq) + H_2\,(g)$

$E^{o}_{cell} = 0.76$ V *There are no Cu^{2+} ions to get reduced.*



When the external EMF is slightly smaller than that of the cell, a small current flows in the external circuit.

But if the external EMF is slightly higher than that of the cell, it results in the flow of a comparatively large current while reversibility demands a small current.

Cell reaction: $Cu(s) + 2H^{+}(aq) \rightleftharpoons Cu^{2+}(aq) + H_2\,(g)$

$E^{o}_{Zn^{2+}/Zn} = -0.76$ V

$E^{o}_{H^{+}/H_2} = 0.0$ V

$E^{o}_{Cu^{2+}/Cu} = +0.34$ V

External EMF applied	E^{o}_{cell}	Direction of flow of ēs
No EMF applied	+ 0.76 V	Zn to Cu
– 0.75 V	+ 0.01 V	Same direction
– 0.76 V	+ 0.00 V	–
– 0.77 V	– 1.11 V (– 0.77 – 0.34)	Reverse direction

When reversible current is high, the one which has less reduction potential will be reduced. *There are no Zn^{2+} ions to get reduced.*

Activity and Mean Ionic Activity

Activity is sometimes regarded as *Effective concentration*.

"At infinite dilution, activity is equal to concentration as the solution is ideal."

An electrolytic solution, even at low concentration, deviates from ideality due to interaction between the ions. Thus activity is not equal to concentration.

There is no method by which activities of individual ionic species can be determined experimentally.

Reason: It is not possible to have a solution containing only one kind of ions.

Activity and concentrations are the measures of chemical potential in a mixture.

$$\mu = \mu_o + RT\, ln a$$

$$a = m\gamma_m = c\gamma_c$$

Where, m = molality; c = molarity; γ = activity coefficient.

Mean Ionic Activity ($a_\pm$):

For an electrolyte, $$\underset{m}{M_xN_y} \rightleftharpoons xM^{z+} + yN^{z-}$$

$m_+ = xm \qquad m_- = ym$

➡ $\text{Activity, } a = a_+^{\,x}\, a_-^{\,y}$

$$\boxed{a = (a_\pm)^{x+y}}$$

$$\text{Also, } a = (\gamma_+ m_+)^x (\gamma_- m_-)^y \quad = (\gamma_+ xm)^x (\gamma_- ym)^y$$

Example:

$$Na_2SO_4 \rightleftharpoons 2Na^+ + SO_4^{2-}$$

$\text{Activity, } a = (a_\pm)^{2+1}$

$x = 2;\ y = 1$

$\text{Also, } a = x^x y^y (\gamma_\pm m)^{x+y}$

$a = (a_\pm)^3$ or $a = a_+^{\,2}\, a_-^{\,1}$

$a = 2^2 1^1 (\gamma_\pm m)^{2+1}$

➡ $a = 4\,(\gamma_\pm m)^3$

Gibbs Free Energy Change

For a cell reaction at equilibrium involving n moles of electrons, nF coulombs of electricity is produced by the cell.

The electrical work done by the cell = Amount of electricity × EMF (E_{cell})

➡ Electrical work done by the cell = nF × E_{cell}

For a Galvanic cell operating reversibly the work is done by using decrease in Gibbs free energy of the cell reaction.

$$\therefore -\Delta G = nFE_{cell}$$

➡ $\boxed{\Delta G = -nFE_{cell}}$ ➡ $\boxed{\Delta G^o = -nFE^o_{cell}}$

➡ $E_{cell} \propto \frac{(-\Delta G)}{n}$

Where, (−ΔG)/n is the Gibbs energy decrease per mole of the electrons transferred.

Thus the EMF of a cell is an intensive property whereas the Gibbs energy is an extensive property.

ΔG	E_{cell}	Cell reaction
−	+	Spontaneous
0	0	Equilibrium
+	−	Non-spontaneous

Nernst Equation

Thermodynamic derivation of the EMF of a Galvanic cell:

Consider a Reversible cell reaction,

$$aA + bB \rightleftharpoons cC + dD$$

Gibbs energy change of this reaction is given by,

$$\Delta G = (cG_C + dG_D) - (aG_A + bG_B)$$

From Thermodynamics we have,

$$G = G^o + RT\, ln a$$

➡ $G_A = G^o_A + RT\, ln a_A$ $G_C = G^o_C + RT\, ln a_C$

$G_B = G^o_B + RT\, ln a_B$ $G_D = G^o_D + RT\, ln a_D$

Where, ‘G^o’s are standard Gibbs free energies and ‘*a*’s are activities.

➡ $\Delta G = \{c(G^o_C + RT\, ln a_C) + d(G^o_D + RT\, ln a_D)\} - \{a(G^o_A + RT\, ln a_A) + b(G^o_B + RT\, ln a_B)\}$

$$\Delta G = \{(cG^o_C + dG^o_D) - (aG^o_A + bG^o_B)\} + \{(cRT\, ln a_C + dRT\, ln a_D) - (aRT\, ln a_A + bRT\, ln a_B)\}$$

$$\Delta G = \Delta G^o + RT \ln \frac{a_C^c\, a_D^d}{a_A^a\, a_B^b}$$

Where, ΔGº is standard Gibbs free energy change.

We have, $\Delta G = -nFE$ and $\Delta G^o = -nFE^o$

$$-nFE = -nFE^o + RT \ln \frac{a_C^c\, a_D^d}{a_A^a\, a_B^b}$$

$$\boxed{E_{cell} = E^o_{cell} - \frac{2.303\, RT}{nF} \log Q_c}$$

This is known as Nernst Equation

Equilibrium Constant

From Nernst equation we have,

$$E_{cell} = E^{o}_{cell} - \frac{2.303\ RT}{nF} \log Q_c$$

When the cell reaction is at equilibrium, $E_{cell} = 0$ and $Q_c = K_c$

➡ $0 = E^{o}_{cell} - \frac{2.303\ RT}{nF} \log K_c$ ➡ $E^{o}_{cell} = \frac{2.303\ RT}{nF} \log K_c$

Also we have, $\Delta G^{o} = -nFE^{o}_{cell}$ ➡ $\Delta G^{o} = -nF \frac{2.303\ RT}{nF} \log K_c$

➡ $\Delta G^{o} = -2.303\ RT\ \mathit{log} K_c$

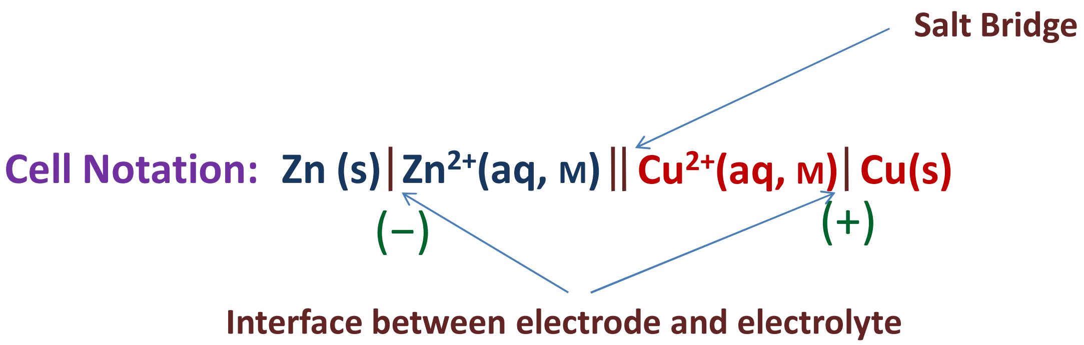
➡ $K_c = 10^{\left[\frac{-\Delta G^{o}}{2.303\ RT}\right]}$

ΔG^{o}	E^{o}_{cell}	K_c	Cell reaction
–	+	>1	Spontaneous
0	0	1	Equilibrium
+	–	<1	Non-spontaneous

Cell Notation

For the reaction,

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$



Salt Bridge

Cell Notation: $Zn(s) | Zn^{2+}(aq, M) || Cu^{2+}(aq, M) | Cu(s)$

(−) (+)

Interface between electrode and electrolyte

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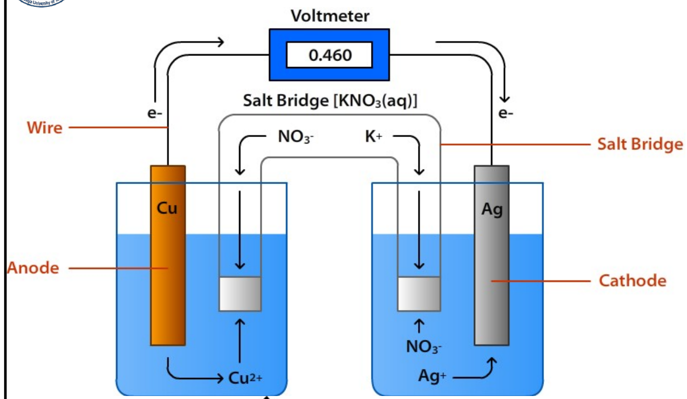
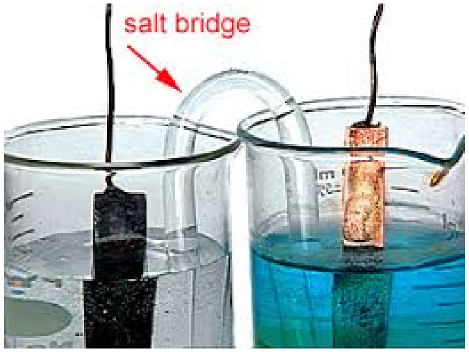
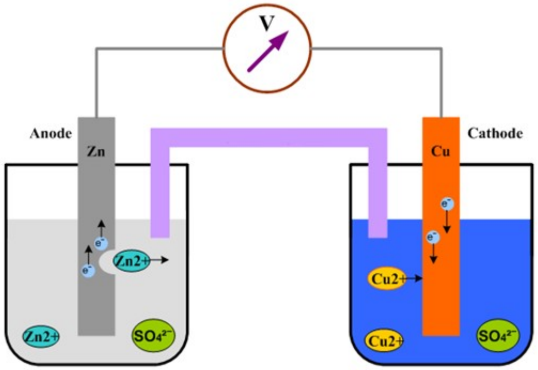
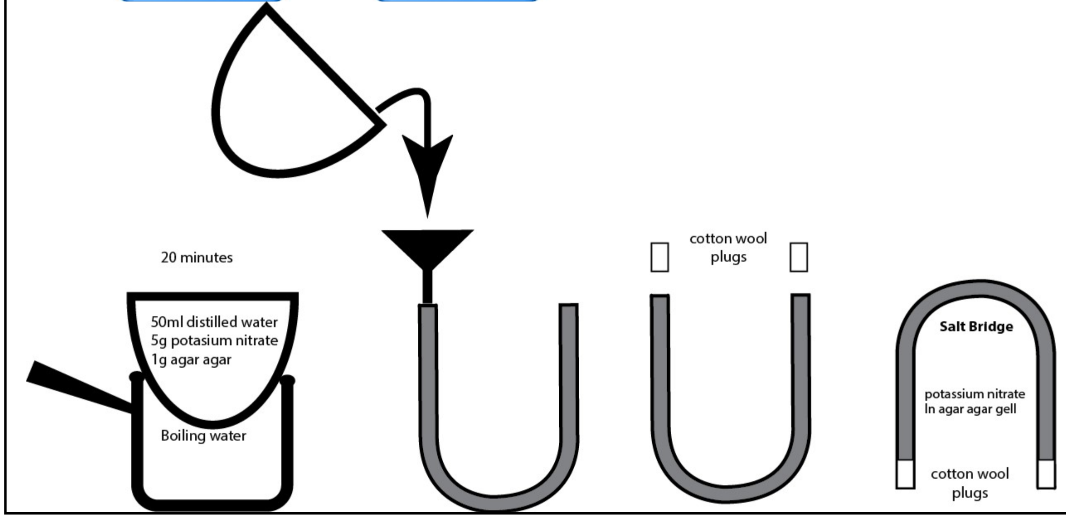
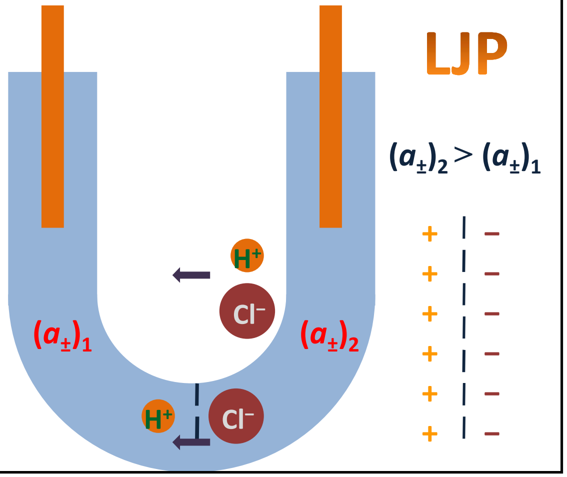
SALT BRIDGE





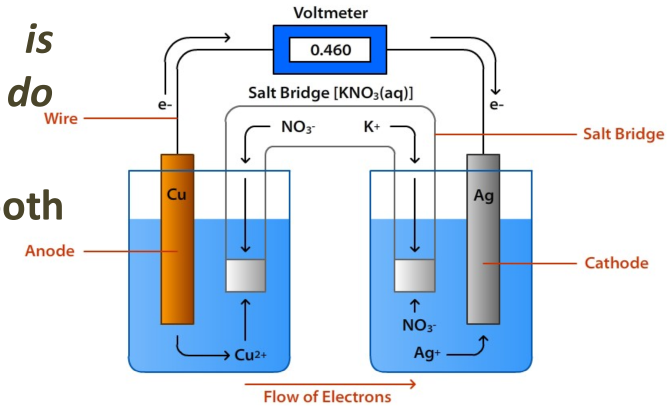


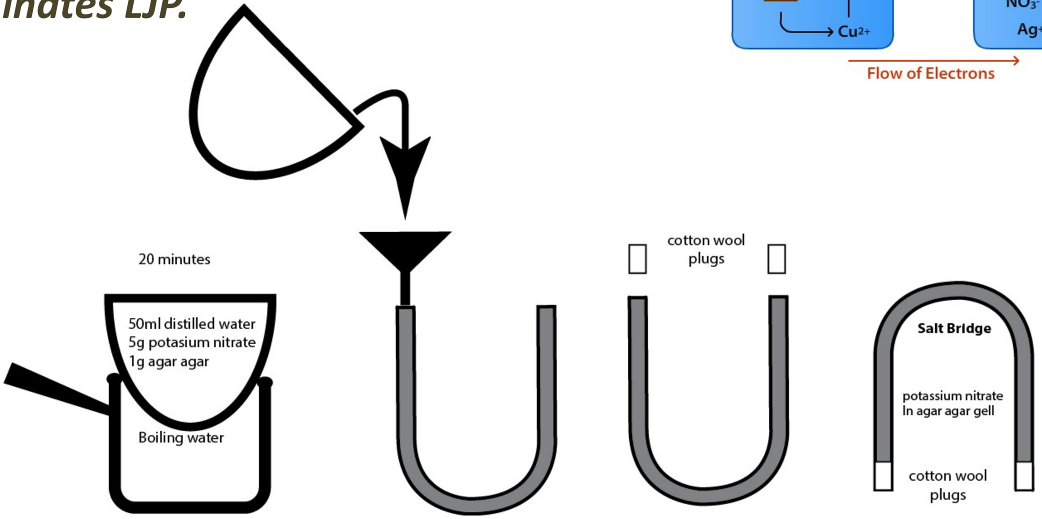


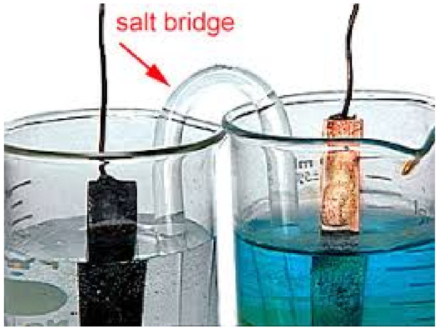


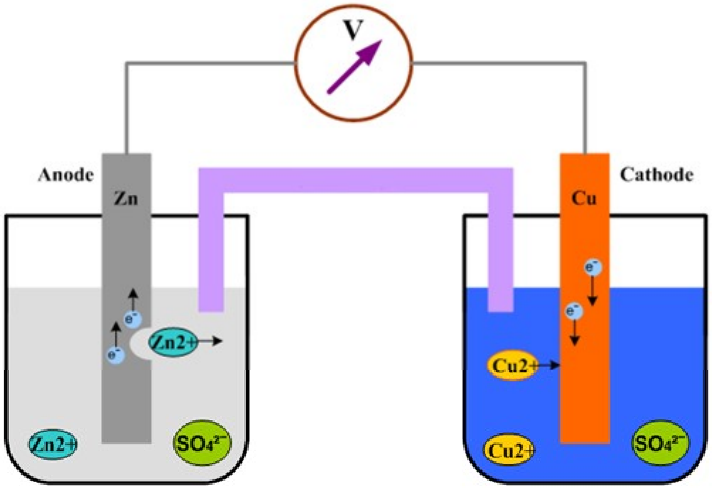
SALT BRIDGE

- ***The electrical circuit of the cell is completed and the workings of the cell do not get disturbed.***
- **It maintains electrical neutrality of both the electrolytes.**
- ***It eliminates LJP.***








V
Anode
Zn
Cathode
Cu
e⁻
e⁻
Zn2+
Zn2+
SO4²⁻
e⁻
e⁻
Cu2+
Cu2+
SO4²⁻

Liquid Junction Potential

“The potential which is generated at the junction of two electrolytic solutions because of the difference in the speeds of ions moving across the boundary is called liquid junction potential.”

LJP in Concentration Cells: When two same electrolytic solutions of different activities are brought together, a potential difference develops at the junction of the two electrolytes, known as LJP.

Example:

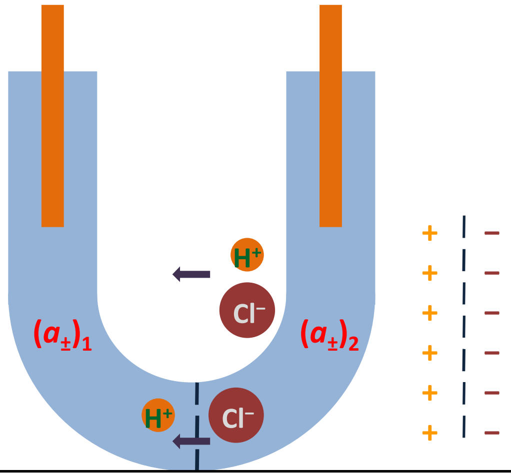
Assuming **$(a_\pm)_2 > (a_\pm)_1$,** HCl will diffuse from side II to side I. As the mobility of H$^+$ ions is greater than Cl$^-$ ions, H$^+$ shall diffuse more rapidly than Cl$^-$ from side II to side I.

Thus an electrical double layer will be formed at the junction. It produces potential difference, making side I solution more positive which sloes the faster moving of H$^+$ ions and speeds up Cl$^-$ ions until the two rates become equal across the double layer.

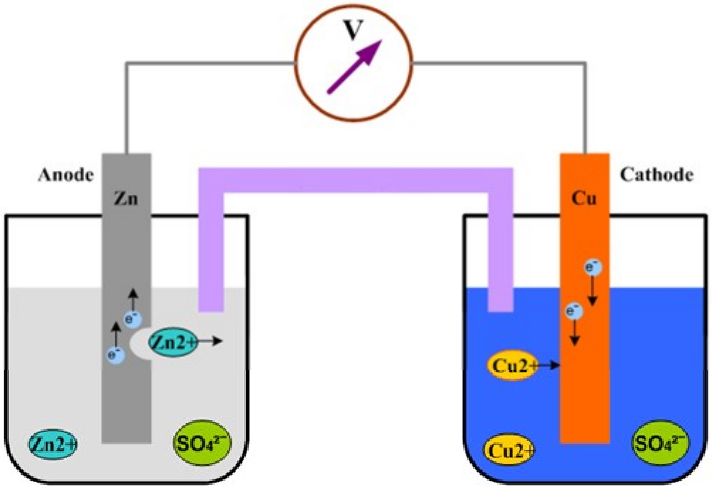
When stationary state is reached, the potential difference between two electrolytes at the boundary is known as ***liquid junction potential or diffusion potential.***

Side I	Side II
HCl	HCl
$(a_\pm)_1$	$(a_\pm)_2$

$(a_\pm)_2 > (a_\pm)_1$



LJP in Chemical Cells:



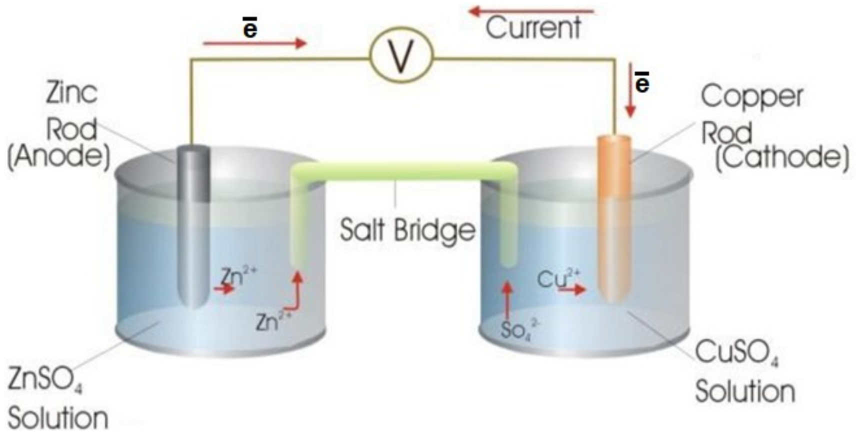
Chemical Cells vs Concentration Cells

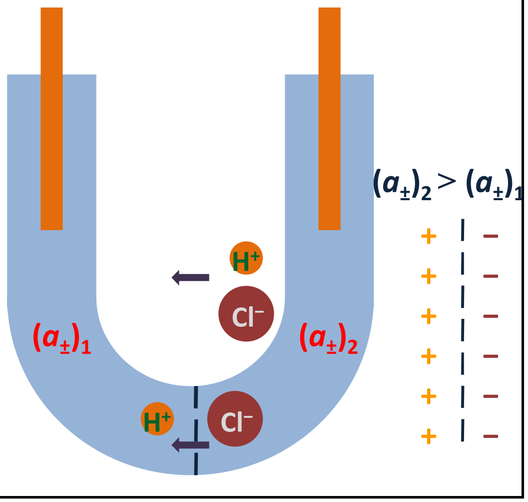
The EMF of the **chemical cells** arises due to the presence of two different half cells with two different electrolytes.

Example: Daniell Cell

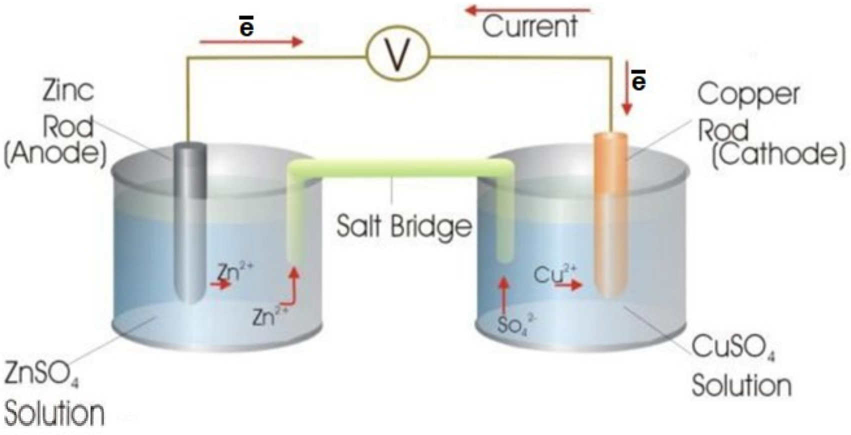
However a chemical cell may contain only one electrolyte.

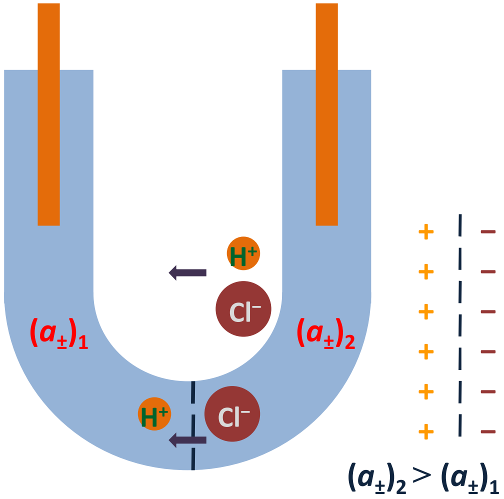
In **concentration cells**, the EMF arises not due to any chemical reaction but due to the transfer of matter from one half cell to the other because of the difference in concentrations of the species involved.



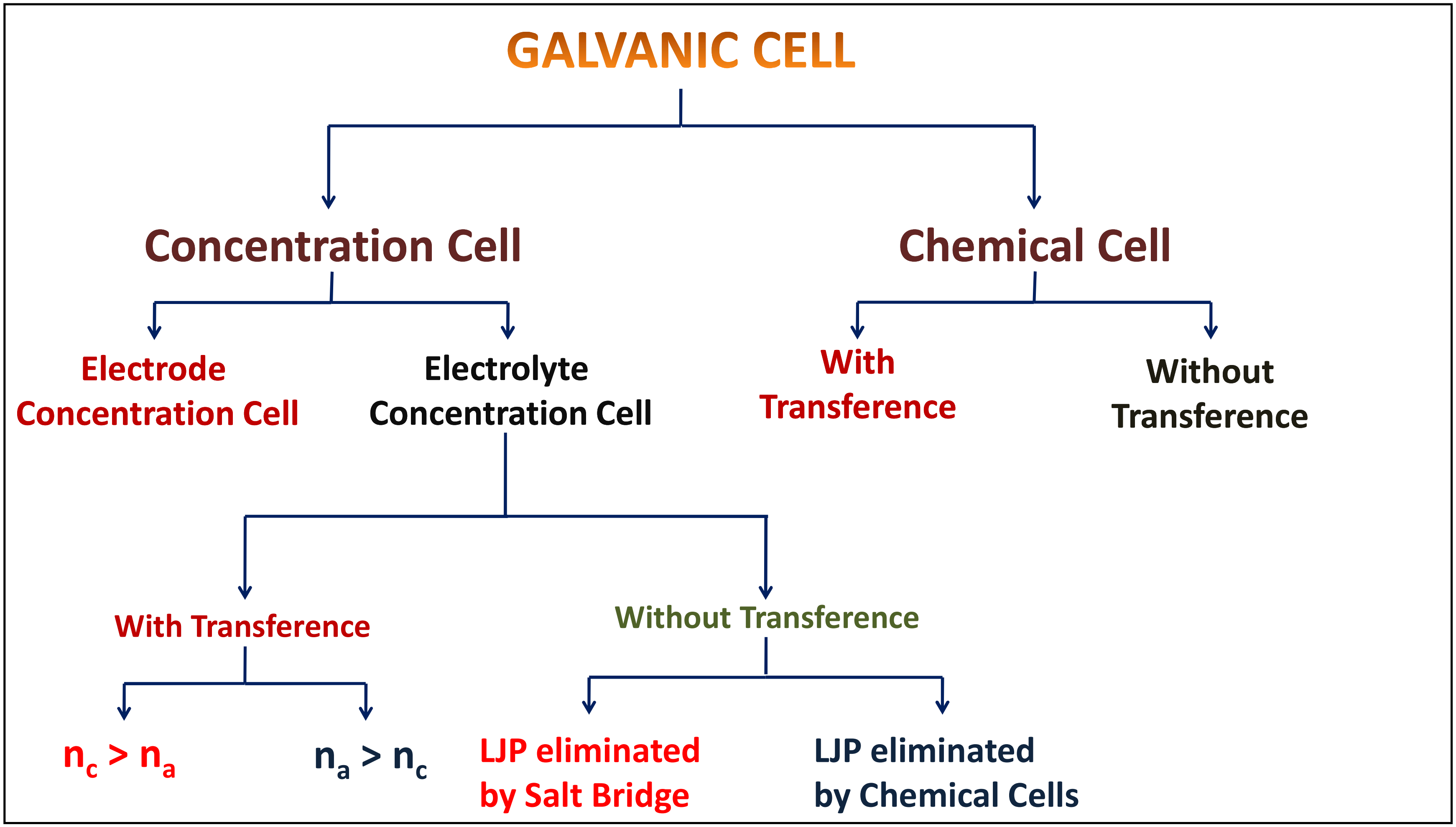


Chemical Cells	Concentration cells
Two half cells are chemically different.	Two half cells are chemically same.
Two half cells are reversible w.r.t different ions.	Two half cells or the cell is reversible w.r.t single ion.
E_{cell} conatains $E^o_{cell.}$	The E_{cell} expression does not contain the term E^o_{cell}.
$E^o_{cell} \neq 0$	$E^o_{cell} = 0$
There is an overall cell reaction.	There is no overall cell reaction. But, reactions take place at half cells.
Example: $Zn\ (s) \vert Zn^{2+}(aq, M) \Vert Cu^{2+}(aq, M) \vert Cu(s)$ $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu\ (s)$	$Cu\ (s) \vert CuSO_4\ (a_1) \Vert CuSO_4\ (a_2) \vert Cu(s)$ The over all cell reaction: $Cu^{2+}(a_2) \longrightarrow Cu^{2+}(a_1)$


ē
Current
V
ē
Zinc
Rod
(Anode)
Copper
Rod
(Cathode)
Salt Bridge
Zn²⁺
Zn²⁺
Cu²⁺
SO₄²⁻
ZnSO₄
Solution
CuSO₄
Solution


H⁺
Cl⁻
H⁺
Cl⁻
(a±)1
(a±)2
+ −

$(a_{\pm})_2 > (a_{\pm})_1$



GALVANIC CELL

- Concentration Cell
  - Electrode Concentration Cell
  - Electrolyte Concentration Cell
    - With Transference
      - $n_c > n_a$
      - $n_a > n_c$
    - Without Transference
      - LJP eliminated by Salt Bridge
      - LJP eliminated by Chemical Cells
- Chemical Cell
  - With Transference
  - Without Transference

Concentration Cells

Electrode Concentration Cells

In these cells, two like electrodes at different concentrations are dipped in same solution.

1. Amalgam Concentration Cell:

Consider two different electrodes made with amalgams of Zn-Hg having Zn with activities a_1 and a_2 respectively and are in contact with $ZnSO_4$ solution.

$$\begin{array}{ccc} (E_1)_{Red} & & (E_2)_{Red} \\ Zn - Hg & |\ ZnSO_4\ sol^n\ | & Zn - Hg \\ (a_1) & & (a_2) \\ \text{Anode } (-) & & \text{Cathode } (+) \end{array}$$

Electrodic Reactions:

At Anode: $Zn\ (a_1) \rightleftharpoons Zn^{2+} + 2\bar{e}$ **(Oxidation)**

At Cathode: $Zn^{2+} + 2\bar{e} \rightleftharpoons Zn\ (a_2)$ **(Reduction)**

Cell process: $Zn\ (a_1) \rightleftharpoons Zn\ (a_2)$

The net result is the transfer of Zn from anode to cathode ($a_1 > a_2$) and activity of Zn^{2+} is same in both half cells.

$$E_{cell} = E_{Red}\,(RHS) - E_{Red}\,(LHS) = E_2 - E_1$$

$$Zn^{2+} + 2\bar{e} \rightleftharpoons Zn\,(a_2) \qquad Zn^{2+} + 2\bar{e} \rightleftharpoons Zn\,(a_1)$$

$$E_{cell} = \left\{E^{o}_{Zn^{2+}/Zn} - \frac{RT}{2F}\, ln\, \frac{(a_{Zn})_R}{a_{Zn^{2+}}}\right\} - \left\{E^{o}_{Zn^{2+}/Zn} - \frac{RT}{2F}\, ln\, \frac{(a_{Zn})_L}{a_{Zn^{2+}}}\right\}$$

$$E_{cell} = -\frac{RT}{2F}\, ln\, (a_{Zn})_R + \frac{RT}{2F}\, ln\, (a_{Zn})_L$$

$$E_{cell} = \frac{RT}{2F}\, ln\, \frac{(a_{Zn})_L}{(a_{Zn})_R}$$

$$\boxed{\therefore E_{cell} = \frac{RT}{2F}\, ln\, \frac{a_1}{a_2}}$$

As $a_1 > a_2$, E_{cell} = positive. Since $ZnSO_4$ is the only electrolyte, the amalgam cell is without transference.

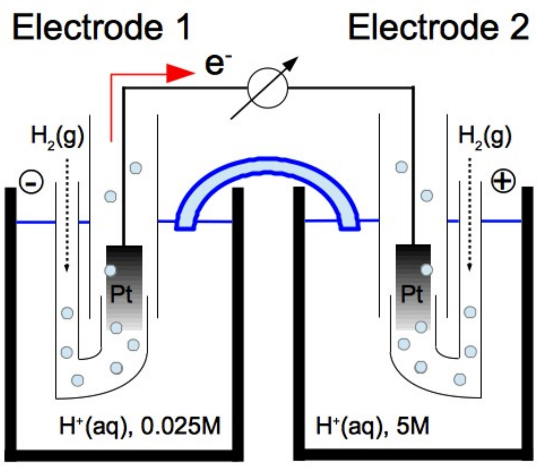
2. Gas Concentration Cell:

Two hydrogen electrodes at different pressures p_1 and p_2 immersed in the same solution of H^+ ions constitute a electrode –concentration cell.

$(E_1)_{Red}$ $(E_2)_{Red}$

Pt; $H_2\,(p_1)$|Sol^n of H+ ions (say HCl sol^n) |$H_2\,(p_1)$; Pt

Anode (–)



Electrodic processes:

At Anode: $\frac{1}{2} H_2\,(p_1) \rightleftharpoons H^+ + \bar{e}$ **(Oxidation)**

At Cathode: $H^+ + \bar{e} \rightleftharpoons \frac{1}{2} H_2\,(p_2)$ **(Reduction)**

Overall reaction: $\frac{1}{2} H_2\,(p_1) \rightleftharpoons \frac{1}{2} H_2\,(p_2)$

Activity of H^+ ions is same in both the half cells. If E_1 and E_2 are the reduction potentials of the anode and the cathode respectively.

$$E_{cell} = E_2 - E_1$$

$$H^+ + \bar{e} \rightleftharpoons \tfrac{1}{2} H_2\,(p_2) \qquad H^+ + \bar{e} \rightleftharpoons \tfrac{1}{2} H_2\,(p_1)$$

➡ $$E_{cell} = \left\{E^{o}_{H^+/H_2} - \frac{RT}{F}\, ln \frac{(a_{H_2})_R^{1/2}}{a_{H^+}}\right\} - \left\{E^{o}_{H^+/H_2} - \frac{RT}{F}\, ln \frac{(a_{H_2})_L^{1/2}}{a_{H^+}}\right\}$$

$$E_{cell} = \frac{RT}{F}\, ln \frac{(a_{H_2})_L^{1/2}}{(a_{H_2})_R^{1/2}}$$

As, $a_{H_2} \propto p_{H_2}$

$$\boxed{E_{cell} = \frac{RT}{2F}\, ln \frac{p_1}{p_2}}$$

As $p_1 > p_2$, E_{cell} = positive. This cell is without transference as there is only one liquid, HCl.

H_2 flows from high pressure to lower pressure side i.e., p_1 to p_2.

➡ **Anode to cathode.**

Electrolyte Concentration Cell Without Transference

The two liquids of the two half cells have different concentration values and the EMF of the cell arises because of this difference. The two electrodes in the half cells are of the same concentration.

1. LJP Eliminated by Salt Bridge

(a) Electrodes Reversible *w.r.t.* Cations:

$(E_1)_{Red}$ $(E_2)_{Red}$

$$\text{Pt; } H_2 \,|\, \text{HCl sol}^n \,||\, \text{HCl sol}^n \,|\, H_2 \text{; Pt}$$

1 atm $(a_\pm)_1$ $(a_\pm)_2$ 1 atm

Anode (–) Cathode (+)

The two half cells are separated by a salt bridge to eliminate the LJP.

$a_\pm$ is the mean activity of HCl.

Electrodic Reactions:

At Anode: $\frac{1}{2} H_2 \rightleftharpoons H_L^+ + \bar{e}$ **(Oxidation)**

At Cathode: $H_R^+ + \bar{e} \rightleftharpoons \frac{1}{2} H_2$ **(Reduction)**

Overall reaction: $H_R^+ \rightleftharpoons H_L^+$

Thus the net result is flow of H+ ions from the cathode to anode.

Mass transfer is not through salt bridge. Change occurs in electrode content.

$$E_{cell} = E_2 - E_1$$

$H_R^+ + \bar{e} \rightleftharpoons \frac{1}{2} H_2$ $\qquad$ $H_L^+ + \bar{e} \rightleftharpoons \frac{1}{2} H_2$

➡ $$E_{cell} = \left\{E^o_{H^+/H_2} - \frac{RT}{F}\, ln \frac{(a_{H_2})_R^{1/2}}{(a_{H^+})_R}\right\} - \left\{E^o_{H^+/H_2} - \frac{RT}{F}\, ln \frac{(a_{H_2})_L^{1/2}}{(a_{H^+})_L}\right\}$$

$$E_{cell} = \frac{RT}{F}\, ln \frac{(a_{H^+})_R}{(a_{H^+})_L}$$

We have, $a_{HCl} = a_{H^+} \cdot a_{Cl^-}$ ➡ $a_{\pm} = \sqrt{a_{H^+} \cdot a_{Cl^-}}$

Assume that , $a_{H^+} = a_{Cl^-}$ $\quad \therefore a_{\pm} = a_{H_+} = a_{Cl_-}$

➡ $$\frac{(a_{\pm})_2}{(a_{\pm})_1} = \frac{(a_{H^+})_R}{(a_{H+})_L} = \frac{(a_{Cl^-})_R}{(a_{Cl_-})_L}$$ ➡ $$\boxed{E_{cell} = \frac{RT}{F}\, ln \frac{(a_{\pm})_2}{(a_{\pm})_1}}$$

If $(a_{\pm})_2 > (a_{\pm})_1,$ E_{cell} = positive.

The right electrode will reduce more than the left electrode, causing electrons to flow from the anode to the cathode in the external circuit.

(b) Electrodes Reversible *w.r.t.* Anions:

Consider the cell reversible w.r.t anions:

$$\begin{array}{ccc} (E_1)_{Red} & & (E_2)_{Red} \\ Ag(s)\,|AgCl\,(s)\,|\,HCl\ sol^n\,||\,HCl\ sol^n\,|\,AgCl\,(s)\,|\,Ag(s) \end{array}$$

Anode (−) $(a_\pm)_1$ $(a_\pm)_2$ Cathode (+)

Electrodic Reactions:

At Anode: $Ag + Cl^-_L \rightleftharpoons AgCl + \bar{e}$ **(Oxidation)**

At Cathode: $AgCl + \bar{e} \rightleftharpoons Ag + Cl^-_R$ **(Reduction)**

Overall reaction: $Cl^-_L \rightleftharpoons Cl^-_R$

This shows that Cl⁻ ions flow from anode to cathode, i.e., from higher concentration to lower concentration. $(a_\pm)_1 > (a_\pm)_2$

$$E_{cell} = E_2 - E_1$$

$$AgCl + \bar{e} \rightleftharpoons Ag + Cl^-_R \qquad AgCl + \bar{e} \rightleftharpoons Ag + Cl^-_L$$

$$E_{cell} = \left\{ E^o_{AgCl,\,Cl^-} - \frac{RT}{1F} \ln \frac{a_{Ag}\,(a_{Cl^-})_R}{a_{AgCl}} \right\} - \left\{ E^o_{AgCl,\,Cl^-} - \frac{RT}{1F} \ln \frac{a_{Ag}\,(a_{Cl^-})_L}{a_{AgCl}} \right\}$$

$$= \left\{ E^o_{AgCl/Cl^-} - \frac{RT}{F} \ln (a_{Cl^-})_R \right\} - \left\{ E^o_{AgCl/Cl^-} - \frac{RT}{F} \ln (a_{Cl^-})_L \right\}$$

$$E_{cell} = \frac{RT}{F} \ln \frac{(a_{Cl^-})_L}{(a_{Cl^-})_R}$$

Assume, $\dfrac{(a_{Cl^-})_R}{(a_{Cl^-})_L} = \dfrac{(a_\pm)_1}{(a_\pm)_2}$

$$\boxed{E_{cell} = \frac{RT}{F} \ln \frac{(a_\pm)_1}{(a_\pm)_2}}$$

If $(a_\pm)_1 > (a_\pm)_2$, E_{cell} = positive.

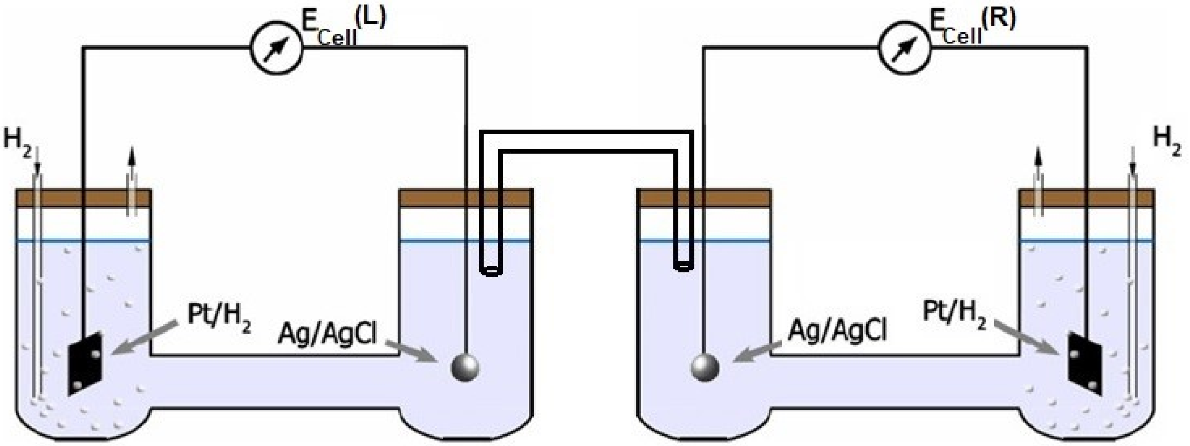
2. LJP Eliminated by Chemical Cells

A concentration cell without transference may also be possible to construct by combining two chemical cells without transference in opposition in such a way that the LJP is eliminated.

(a) Extreme Electrodes Reversible *w.r.t.* Cations:

$$\begin{array}{cc} (E_1)_{Red} \quad (E_2)_{Red} & (E'_1)_{Red} \quad (E'_2)_{Red} \\ Pt;\ H_2(g) \,|\, HCl\ sol^n \,|\, AgCl\,(s) \,|\, \overbrace{Ag(s) \quad\quad Ag(s)} \,|\, AgCl\,(s) \,|\, HCl\ sol^n \,|\, H_2\,;\ Pt & \sqcap \ \text{OR} \ || \\ (1\ atm) \quad (a_\pm)_1 & (a_\pm)_2 \quad (1\ atm) \end{array}$$

Chemical cell Left **Chemical cell Right**



The two extreme electrodes are reversible *w.r.t.* H⁺ ions while the inner electrode are reversible *w.r.t.* the Cl⁻ ions.

Electrodic Reactions:

	Left side cell	**Right side cell**	
At Anode:	$\frac{1}{2} H_2 \rightleftharpoons H_L^+ + \bar{e}$	$Ag + Cl_R^- \rightleftharpoons AgCl + \bar{e}$	**(Oxidation)**
At Cathode:	$AgCl + \bar{e} \rightleftharpoons Ag + Cl_L^-$	$H_R^+ + \bar{e} \rightleftharpoons \frac{1}{2} H_2$	**(Reduction)**
Overall reaction:	$H_R^+ + Cl_R^- \rightleftharpoons H_L^+ + Cl_L^-$		

$$E_{cell} = E_{cell}\,(L) + E_{cell}\,(R)$$

$$\Rightarrow E_{cell} = (E_2 - E_1)_L + (E_2' - E_1')_R$$

$$E_{cell} = \left[\left\{E^o_{AgCl/Cl^-} - \frac{RT}{F} ln\,(a_{Cl^-})_L\right\} - \left\{E^o_{H^+/H_2} - \frac{RT}{F}\,ln\,\frac{1}{(a_{H^+})_L}\right\}\right]$$

$$+\left[\left\{E^o_{H^+/H_2} - \frac{RT}{F}\,ln\,\frac{1}{(a_{H^+})_R}\right\} - E^o_{AgCl/Cl^-} - \frac{RT}{F} ln\,(a_{Cl^-})_R\right]$$

$$AgCl + \bar{e} \rightleftharpoons Ag + Cl^-_L$$

$$H_L^+ + \bar{e} \rightleftharpoons ½\, H_2$$

$$H_R^+ + \bar{e} \rightleftharpoons ½\, H_2$$

$$AgCl + \bar{e} \rightleftharpoons Ag + Cl^-_R$$

$$\Rightarrow\ E_{cell} = \frac{RT}{F}\,ln\,\frac{(a_{H^+})_R\,(a_{Cl^-})_R}{(a_{H^+})_L\,(a_{Cl^-})_L}$$

We have, $a_{HCl} = a_{H^+} \,.\, a_{Cl^-}$ ➡ $E_{cell} = \frac{RT}{F}\,ln\,\frac{(a_{HCl})_R}{(a_{HCl})_L}$

Also, $a_\pm = \sqrt{a_{H^+} \,.\, a_{Cl^-}}$ Assume that , $a_{H^+} = a_{Cl^-}$ ➡ $a_{HCl} = (a_\pm)^2$

$$\Rightarrow\ E_{cell} = \frac{RT}{F}\,ln\,\frac{(a_\pm)_2^2}{(a_\pm)_1^2}$$

$$\boxed{\therefore\ E_{cell} = \frac{2RT}{F}\,ln\,\frac{(a_\pm)_2}{(a_\pm)_1}}$$

(b) Extreme Electrodes Reversible *w.r.t.* Anions:

$$\underset{}{Ag(s)} \;|\; \overset{(E_1)_{Red}}{AgCl(s)} \;|\; \underset{(a_\pm)_1}{\overset{(E_2)_{Red}}{HCl\ soln^n}} \;|\; \underset{(1\ atm)}{H_2;\ Pt} \qquad \underset{(1\ atm)}{Pt;\ H_2(g)} \;|\; \underset{(a_\pm)_2}{\overset{(E'_1)_{Red}}{HCl\ soln^n}} \;|\; \overset{(E'_2)_{Red}}{AgCl(s)} \;|\; Ag(s)$$

Chemical cell Left **Chemical cell Right**

The two extreme electrodes are reversible w.r.t. Cl^- ions while the inner electrode are reversible w.r.t. the H^+ ions.

$$E_{cell} = E_{cell}(L) + E_{cell}(R) \Rightarrow E_{cell} = (E_2 - E_1)_L + (E'_2 - E'_1)_R$$

Electrodic Reactions:

	Left side cell	Right side cell	
At Anode:	$Ag + Cl_L^- \rightleftharpoons AgCl + \bar{e}$	$\frac{1}{2} H_2 \rightleftharpoons H_R^+ + \bar{e}$	**(Oxidation)**
At Cathode:	$H_L^+ + \bar{e} \rightleftharpoons \frac{1}{2} H_2$	$AgCl + \bar{e} \rightleftharpoons Ag + Cl_R^-$	**(Reduction)**

Overall reaction:

$$H_L^+ + Cl_L^- \rightleftharpoons H_R^+ + Cl_R^-$$

$$E_{cell} = \left[\left\{E^{o}_{H^{+}/H_2} - \frac{RT}{F}\ln\frac{1}{(a_{H^{+}})_L}\right\} - \left\{E^{o}_{AgCl/Cl^{-}} - \frac{RT}{F}\ln(a_{Cl^{-}})_L\right\}\right]$$

$$+\left[\left\{E^{o}_{AgCl/Cl^{-}} - \frac{RT}{F}\ln(a_{Cl^{-}})_R\right\} - \left\{E^{o}_{H^{+}/H_2} - \frac{RT}{F}\ln\frac{1}{(a_{H^{+}})_R}\right\}\right]$$

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

$$AgCl + \bar{e} \rightleftharpoons Ag + Cl_L^{-}$$

$$AgCl + \bar{e} \rightleftharpoons Ag + Cl_R^{-}$$

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

➡ $$E_{cell} = \frac{RT}{F}\ln\frac{(a_{H^{+}})_L(a_{Cl^{-}})_L}{(a_{H^{+}})_R(a_{Cl^{-}})_R}$$

➡ $$E_{cell} = \frac{RT}{F}\ln\frac{(a_{HCl})_L}{(a_{HCl})_R}$$

➡ $$E_{cell} = \frac{RT}{F}\ln\frac{(a_{\pm})_1^2}{(a_{\pm})_2^2}$$

$$\boxed{\therefore E_{cell} = \frac{2RT}{F}\ln\frac{(a_{\pm})_1}{(a_{\pm})_2}}$$

1. LJP Eliminated by Salt Bridge

(a) Electrodes Reversible *w.r.t.* Cations: $$E_{cell} = \frac{RT}{F} \ln \frac{(a_{\pm})_2}{(a_{\pm})_1}$$

(b) Electrodes Reversible *w.r.t.* Anions: $$E_{cell} = \frac{RT}{F} \ln \frac{(a_{\pm})_1}{(a_{\pm})_2}$$

2. LJP Eliminated by Chemical Cells

(a) Extreme Electrodes Reversible *w.r.t.* Cations: $$E_{cell} = \frac{2RT}{F} \ln \frac{(a_{\pm})_2}{(a_{\pm})_1}$$

(b) Extreme Electrodes Reversible *w.r.t.* Anions: $$E_{cell} = \frac{2RT}{F} \ln \frac{(a_{\pm})_1}{(a_{\pm})_2}$$

E_{cell} (LJP Eliminated by chemical cells) = 2 × E_{cell} (LJP Eliminated by salt bridge)

In electrode concentration cells, mass transfer is from anode to cathode.

In electrolyte concentration cells:

When cell is reversible *w.r.t.* cations mass transfer is from cathode to anode.

When cell is reversible *w.r.t.* anions mass transfer is from anode to cathode.

LJP of a Concentration Cell Reversible *w.r.t.* Cations

Consider a concentration cell with transference

$$\underset{\text{1 atm}}{\text{Pt; H}_2} \,|\, \underset{(a_\pm)_1}{\text{HCl sol}^n} \,\vdots\, \underset{(a_\pm)_2}{\text{HCl sol}^n} \,|\, \underset{\text{1 atm}}{\text{H}_2\text{; Pt}}$$

Anode (–) Cathode (+)

$\vdots$ ➡ The cell with transference

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

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

$$H_R^+ \rightleftharpoons H_L^+$$

The cell is reversible w.r.t. the H⁺ ions.

As $(a_\pm)_2 > (a_\pm)_1$, the net cell process, ignoring LJP is: $H^+ (II) \longrightarrow H^+ (I)$

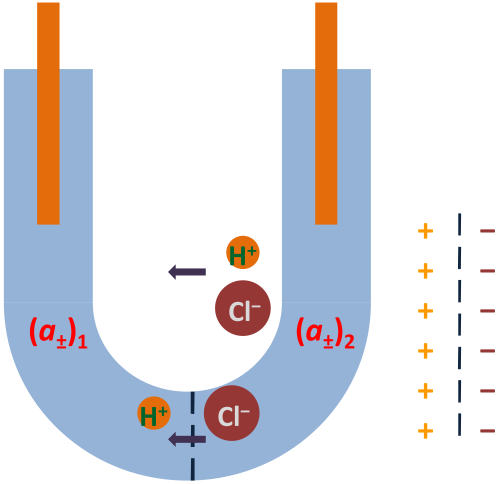
To obtain an expression for LJP, consider only the phenomenon at the junction of the two solutions. Due to the difference in ionic mobilities of H^+ and Cl^-, there develops a LJP when these ions cross the boundary.

$$u_{H^+} > u_{Cl^-}$$

➡ $t_{H^+} > t_{Cl^-}$ (Transport number)

Thus t_{H^+} fraction of the current is carried by the H^+ ions and t_{Cl^-} fraction of the current is carried by the Cl^- ions

Suppose 1F of electricity (t=1) passes across the liquid junction. This will cause a transfer of n_c moles of H^+ ions from side II to side I and n_a moles of Cl^- from side I to side II.



$$n_c\, H^+ (II) \longrightarrow n_c\, H^+ (I)$$

$$n_a\, Cl^- (I) \longrightarrow n_a\, Cl^- (II)$$

Total transfer: $n_c\, H^+(II) + n_a\, Cl^-(I) \longrightarrow n_c\, H^+(I) + n_a\, Cl^-(II)$

∴ The free energy change at the boundary would be,

$$\Delta G = \Delta G^o + RT\, ln \frac{(a_{H^+})_I^{n_c} (a_{Cl^-})_{II}^{n_a}}{(a_{H^+})_{II}^{n_c} (a_{Cl^-})_I^{n_a}}$$

Now, supposing the liquid junction to be like a mini cell within a cell across which are present two HCl solutions of different concentrations, as in a concentration cell, we have **$E^o_{L.J.} = 0$.**

$$\Rightarrow \Delta G^o = -\, nFE^o = 0$$

n is equivalent to transport number.

➡ $$\Delta G = RT\, ln \frac{(a_{H^+})_{I}^{n_c}(a_{Cl^-})_{II}^{n_a}}{(a_{H^+})_{II}^{n_c}(a_{Cl^-})_{I}^{n_a}}$$

➡ $$\Delta G = n_c RT\, ln \frac{(a_{H^+})_{I}}{(a_{H^+})_{II}} + n_a RT\, ln \frac{(a_{Cl^-})_{II}}{(a_{Cl^-})_{I}}$$

Considering the approximation, $\frac{(a_{\pm})_1}{(a_{\pm})_2} = \frac{(a_{H^+})_{I}}{(a_{H^+})_{II}} = \frac{(a_{Cl^-})_{I}}{(a_{Cl^-})_{II}}$

➡ $$\Delta G = (n_a - n_c)\, RT\, ln \frac{(a_{\pm})_2}{(a_{\pm})_1}$$

1F electricity = charge of one mole electrons ➡ **n = 1**

➡ $$\Delta G = -FE_{LJP}$$

➡ $$-FE_{LJ} = (n_a - n_c)\, RT\, ln \frac{(a_{\pm})_2}{(a_{\pm})_1}$$

➡ $$\boxed{E_{LJ} = (n_c - n_a)\frac{RT}{F}\, ln \frac{(a_{\pm})_2}{(a_{\pm})_1}}$$

Also, $n_c = \frac{u_c}{u_c + u_a}$ and $n_a = \frac{u_a}{u_c + u_a}$

$$E_{LJ} = \frac{u_c - u_a}{u_c + u_a} \frac{RT}{F} ln \frac{(a_\pm)_2}{(a_\pm)_1}$$

These equations are applicable when $n_c > n_a$ or $u_c > u_a$

If, $n_a > n_c$ or $u_a > u_c$

$$E_{LJ} = (n_a - n_c) \frac{RT}{F} ln \frac{(a_\pm)_2}{(a_\pm)_1}$$

and

$$E_{LJ} = \frac{u_a - u_c}{u_c + u_a} \frac{RT}{F} ln \frac{(a_\pm)_2}{(a_\pm)_1}$$

LJP of a Concentration Cell Reversible *w.r.t.* Anions

Consider a concentration cell with transference

$$\mathrm{Ag(s)\,|\,AgCl\,(s)\,|\,HCl\ sol^{n}\ \vdots\ HCl\ sol^{n}\,|\,AgCl\,(s)\,|\,Ag(s)}$$

$(a_{\pm})_1$ $(a_{\pm})_2$

Anode (–) Cathode (+)

$$\mathrm{Ag} + \mathrm{Cl}^{-}_{L} \rightleftharpoons \mathrm{AgCl} + \bar{e}$$

$$\mathrm{AgCl} + \bar{e} \rightleftharpoons \mathrm{Ag} + \mathrm{Cl}^{-}_{R}$$

$$\mathrm{Cl}^{-}_{L} \rightleftharpoons \mathrm{Cl}^{-}_{R}$$

The cell is reversible w.r.t. the Cl^- *ions.*

In this cell, $(a_{\pm})_1 > (a_{\pm})_2$, the net cell process, ignoring LJP is: $\mathrm{Cl^-\,(I)} \longrightarrow \mathrm{Cl^-\,(II)}$

Now, consider only the phenomenon at the junction of the two liquids to derive an expression for liquid junction potential.

$$u_{H^+} > u_{Cl^-}$$

➡ $t_{H^+} > t_{Cl^-}$

or $n_{H^+} > n_{Cl^-}$

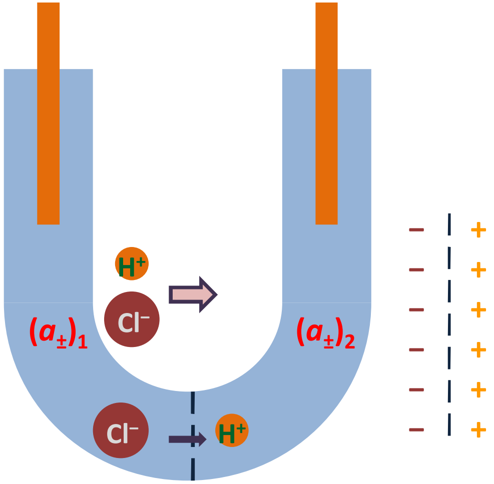
Suppose 1F of electricity (t=1) passes across the liquid junction.

This will cause a transfer of n_c moles of H^+ ions from side I to side II and n_a moles of Cl^- from side II to side I.

$$n_c\, H^+\,(I) \longrightarrow n_c\, H^+\,(II)$$

$$n_a\, Cl^-\,(II) \longrightarrow n_a\, Cl^-\,(I)$$

Total transfer: $n_c\, H^+(I) + n_a\, Cl^-(II) \longrightarrow n_c\, H^+(II) + n_a\, Cl^-(I)$



∴ The free energy change at the boundary would be:

$$\Delta G = RT\, ln \frac{(a_{H^+})_{II}^{n_c}(a_{Cl^-})_{I}^{n_a}}{(a_{H^+})_{I}^{n_c}(a_{Cl^-})_{II}^{n_a}}$$

$$\Rightarrow \Delta G = n_c RT\, ln \frac{(a_{H^+})_{II}}{(a_{H^+})_{I}} + n_a RT\, ln \frac{(a_{Cl^-})_{I}}{(a_{Cl^-})_{II}}$$

$$\Rightarrow \Delta G = -n_c RT\, ln \frac{(a_{H^+})_{I}}{(a_{H^+})_{II}} + n_a RT\, ln \frac{(a_{Cl^-})_{I}}{(a_{Cl^-})_{II}}$$

Taking the approximation, $\dfrac{(a_{\pm})_1}{(a_{\pm})_2} = \dfrac{(a_{H^+})_{I}}{(a_{H^+})_{II}} = \dfrac{(a_{Cl^-})_{I}}{(a_{Cl^-})_{II}}$

➡ $\Delta G = (n_a - n_c)\, RT\, ln \dfrac{(a_{\pm})_1}{(a_{\pm})_2}$

➡ $-FE_{LJ} = (n_a - n_c)\, RT\, ln \dfrac{(a_{\pm})_1}{(a_{\pm})_2}$

➡ $\boxed{E_{LJ} = (n_c - n_a) \dfrac{RT}{F}\, ln \dfrac{(a_{\pm})_1}{(a_{\pm})_2}}$

➡ $\boxed{E_{LJ} = (n_a - n_c) \dfrac{RT}{F}\, ln \dfrac{(a_{\pm})_1}{(a_{\pm})_2}}$

In terms of mobilities; for $n_c > n_a$ ➡ $\boxed{E_{LJ} = \dfrac{u_c - u_a}{u_c + u_a} \dfrac{RT}{F}\, ln \dfrac{(a_{\pm})_1}{(a_{\pm})_2}}$

For $n_a > n_c$ ➡ $\boxed{E_{LJ} = \dfrac{u_a - u_c}{u_c + u_a} \dfrac{RT}{F}\, ln \dfrac{(a_{\pm})_1}{(a_{\pm})_2}}$

When $n_a = n_c$ ➡ $E_{LJ} = 0$

Electrolyte Concentration Cell With Transference

If E_{WOT} and E_{WT} denotes emfs of the cells without and with transference respectively,

$$E_{WT} = E_{WOT} \pm E_{LJ}$$

LJP develops due to the difference in the transport numbers of the cations and anions.

$$\text{If, } n_c = n_a \Rightarrow u_c = u_a \Rightarrow E_{LJ} = 0$$

EMF of an Electrolyte Concentration Cell With Transference

when, $n_c > n_a$ $u_c > u_a$

(a) Cell Reversible *w.r.t.* Cations:

$$\underset{\text{1 atm}}{\mathrm{Pt;\,H_2}}\,\Big|\,\underset{(a_\pm)_1}{\mathrm{HCl\ sol^n}}\,\vdots\,\underset{(a_\pm)_2}{\mathrm{HCl\ sol^n}}\,\Big|\,\underset{\text{1 atm}}{\mathrm{H_2\,;\,Pt}}$$

Anode (−) **Cathode (+)**

The cell is reversible w.r.t. the H^+ ions.

The EMF of the cell without considering LJP is: $E_{WOT} = \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1}$

As $n_{H^+} > n_{Cl^-}$ and $(a_\pm)_2 > (a_\pm)_1$, the H^+ ions move faster than Cl^- ions from right to left cell. Consequently, the dilute solution side (anode) of the junction will be positive, which will therefore oppose the direction of the current cell.

∴ EMF of the cell with transference, $E_{WT} = E_{WOT} - E_{LJ}$

$-$ | $+$ Polarity of the cell

$(a_\pm)_1$ HCl $\longleftarrow$ HCl $(a_\pm)_2$ $(a_\pm)_2 > (a_\pm)_1$

$+$ | $-$ Charge developed due to LJP

$$\therefore E_{WT} = \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1} - (n_c - n_a)\frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1}$$

$$\Rightarrow E_{WT} = (1 - n_c + n_a)\frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1}$$

As $(n_a + n_c) = 1$ $\Rightarrow$ $E_{WT} = (n_a - n_c + n_a - n_c)\frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1}$

$$\boxed{\therefore E_{WT} = 2n_a \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1}}$$

Thus E_{WT} increases when n_a increases for the cells reversible *w.r.t.* cations.

(b) Cell Reversible *w.r.t.* Anions:

$$\mathrm{Ag(s)}\,|\,\mathrm{AgCl\,(s)}\,|\,\underset{(a_\pm)_1}{\mathrm{HCl\ sol^n}}\ \vdots\ \underset{(a_\pm)_2}{\mathrm{HCl\ sol^n}}\,|\,\mathrm{AgCl\,(s)}\,|\,\mathrm{Ag(s)}$$

Anode (–) Cathode (+)

The cell is reversible w.r.t. the Cl^- ions.

The EMF of the cell without considering LJP is: $E_{WOT} = \frac{RT}{F} \ln \frac{(a_\pm)_1}{(a_\pm)_2}$ $(a_\pm)_1 > (a_\pm)_2$

As $n_{H^+} > n_{Cl^-}$ and $(a_\pm)_1 > (a_\pm)_2$, the H^+ ions move faster than Cl^- ions from left to right cell. Consequently, the dilute solution side (cathode) of the junction will be positive, which will therefore favour the direction of the current cell.

∴ EMF of the cell with transference, $E_{WT} = E_{WOT} + E_{LJ}$

– | + **Polarity of the cell**

$(a_\pm)_1$ HCl → HCl $(a_\pm)_2$ $(a_\pm)_1 > (a_\pm)_2$

+ | – **Charge developed due to LJP**

$$\therefore E_{WT} = \frac{RT}{F} \, ln \frac{(a_{\pm})_1}{(a_{\pm})_2} + (n_c - n_a) \frac{RT}{F} \, ln \frac{(a_{\pm})_1}{(a_{\pm})_2}$$

$$\Rightarrow E_{WT} = (1 + n_c - n_a) \frac{RT}{F} \, ln \frac{(a_{\pm})_1}{(a_{\pm})_2}$$

As $(n_a + n_c) = 1$ $\Rightarrow$ $E_{WT} = (n_a + n_c + n_c - n_a) \frac{RT}{F} \, ln \frac{(a_{\pm})_1}{(a_{\pm})_2}$

$$\boxed{\therefore E_{WT} = 2n_c \frac{RT}{F} \, ln \frac{(a_{\pm})_1}{(a_{\pm})_2}}$$

Thus E_{WT} increases when n_c increases for the cells reversible *w.r.t.* anions.

EMF of an Electrolyte Concentration Cell With Transference

when, $n_a > n_c$ $u_a > u_c$

(a) Cell Reversible *w.r.t.* Cations:

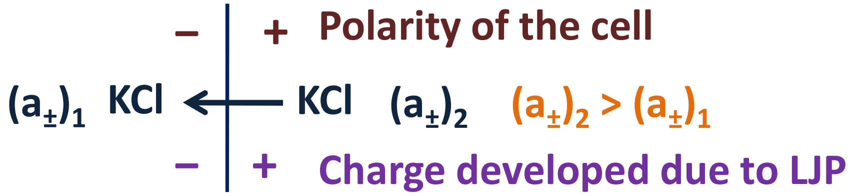
Using an electrolyte such as KCl, $AgNO_3$ or $CuSO_4$ in which , $n_a > n_c$ $u_a > u_c$.

The cell is reversible w.r.t. cations and **$(a_\pm)_2 > (a_\pm)_1$**. Anions are faster than cations and the transfer of electrolyte takes place from the cathode to anode side. Thus, the anode side electrolyte will be negative which will favour the direction of the current of the cell.

Thus, for the electrolyte, say KCl of the cell:

$$\underset{\text{Anode}\,(-)}{\mathrm{K\,(Hg)}}\;\Big|\;\underset{(a_\pm)_1}{\mathrm{KCl\ sol^n}}\;\vdots\;\underset{(a_\pm)_2}{\mathrm{KCl\ sol^n}}\;\Big|\;\underset{\text{Cathode}\,(+)}{\mathrm{K\,(Hg)}}$$

Anode (−) **Cathode (+)**



$-$ | $+$ Polarity of the cell

$(a_\pm)_1$ KCl $\longleftarrow$ KCl $(a_\pm)_2$ $(a_\pm)_2 > (a_\pm)_1$

$-$ | $+$ Charge developed due to LJP

$\therefore$ EMF of the cell with transference, $E_{WT} = E_{WOT} + E_{LJ}$

$$E_{WT} = \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1} + (n_a - n_c) \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1}$$

$$\Rightarrow E_{WT} = (1 + n_a - n_c) \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1}$$

As $(n_a + n_c) = 1$ $\Rightarrow$ $E_{WT} = (n_a - n_c + n_a - n_c) \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1}$

$$\boxed{\therefore E_{WT} = 2n_a \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1}}$$

Thus E_{WT} increases when n_a increases for the cells reversible *w.r.t.* cations.

(b) Cell Reversible *w.r.t.* Anions:

The cell is reversible w.r.t. anions and $(a_\pm)_1 > (a_\pm)_2$. Anions are faster than cations and the transfer of electrolyte takes place from the anode to cathode side. Thus, the cathode side electrolyte will be negative which will oppose the direction of the current of the cell.

− | + **Polarity of the cell**

$(a_\pm)_1$ KCl | $\longrightarrow$ KCl $(a_\pm)_2$ $\quad (a_\pm)_1 > (a_\pm)_2$

+ | − **Charge developed due to LJP**

∴ EMF of the cell with transference, $E_{WT} = E_{WOT} - E_{LJ}$

$$\therefore E_{WT} = \frac{RT}{F} \ln\frac{(a_\pm)_1}{(a_\pm)_2} - (n_a - n_c)\frac{RT}{F} \ln\frac{(a_\pm)_1}{(a_\pm)_2}$$

➡ $$E_{WT} = (1 - n_a + n_c)\frac{RT}{F} \ln\frac{(a_\pm)_1}{(a_\pm)_2}$$

As $(n_a + n_c) = 1$ ➡ $$E_{WT} = (n_a + n_c - n_a + n_c)\frac{RT}{F} \ln\frac{(a_\pm)_1}{(a_\pm)_2}$$

$$\therefore E_{WT} = 2n_c\frac{RT}{F} \ln\frac{(a_\pm)_1}{(a_\pm)_2}$$

Thus E_{WT} increases when n_c increases for the cells reversible *w.r.t.* anions.

Chemical Cell Without Transference

To construct a chemical cell without transference, i.e., with no LJP, the two half cells must be selected in such a way that one of the half cells is reversible w.r.t. cations and the other reversible w.r.t. anions of the electrolytic solution.

Example 1:

$$\underset{(1\ \text{atm})}{\text{Pt}; H_2(g)} \mid \text{HCl sol}^n \mid \text{AgCl}(s) \mid \text{Ag}(s)$$

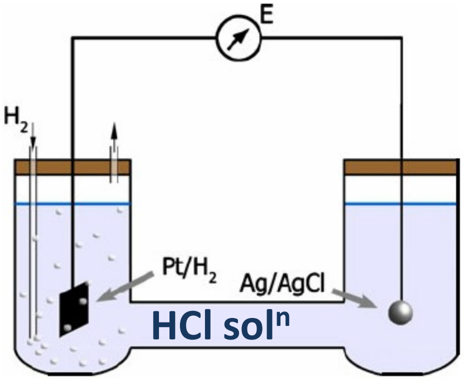
Anode (–) **Cathode (+)**

The left half cell is reversible w.r.t. H^+ ions and right half cell is reversible w.r.t. Cl^- ions. As there is only one electrolyte HCl (aq), there would be no LJP.

At Anode: $\frac{1}{2} H_2 \rightleftharpoons H^+ + \bar{e}$ (Oxidation)

At Cathode: $AgCl + \bar{e} \rightleftharpoons Ag + Cl^-$ (Reduction)

Overall reaction: $\frac{1}{2} H_2 + AgCl \rightleftharpoons H^+ + Ag + Cl^-$



$$E_{cell} = E_{Red}\,(RHS) - E_{Red}\,(LHS)$$

$$AgCl + \bar{e} \rightleftharpoons Ag + Cl^{-} \qquad H^{+} + \bar{e} \rightleftharpoons \tfrac{1}{2} H_2$$

➡ $$E_{cell} = \left\{E^{o}_{AgCl/Cl^{-}} - \frac{RT}{1F}\, ln \frac{a_{Ag}\, a_{Cl^{-}}}{a_{AgCl}}\right\} - \left\{E^{o}_{H^{+}/H_2} - \frac{RT}{1F}\, ln \frac{(a_{H_2})^{1/2}}{a_{H^{+}}}\right\}$$

$$= \left\{E^{o}_{AgCl/Cl^{-}} - \frac{RT}{F}\, ln\, a_{Cl^{-}}\right\} - \left\{E^{o}_{H^{+}/H_2} - \frac{RT}{F}\, ln \frac{1}{a_{H^{+}}}\right\}$$

As, $E^{o}_{H^{+}/H_2} = 0$ at 25 °C

➡ $$E_{cell} = E^{o}_{AgCl/Cl^{-}} - \frac{RT}{F}\, ln\, (a_{H^{+}}\, a_{Cl^{-}})$$

➡ $$\boxed{E_{cell} = E^{o}_{AgCl,\, Cl^{-}} - \frac{RT}{F}\, ln\, a_{HCl}}$$

Example 2:

$$\text{Pt; } H_2\,(g) \,|\, H_2SO_4 \text{ sol}^n \,|\, Hg_2SO_4\,(s) \,|\, Hg$$

Anode (–) **Cathode (+)**

The left half cell is reversible w.r.t. H^+ ions and right half cell is reversible w.r.t. SO_4^{2-} ions.

At Anode: $H_2 \rightleftharpoons 2H^+ + 2\bar{e}$ **(Oxidation)**

At Cathode: $Hg_2SO_4 + 2\bar{e} \rightleftharpoons 2Hg + SO_4^{2-}$ **(Reduction)**

Overall reaction: $H_2 + Hg_2SO_4 \rightleftharpoons 2H^+ + 2Hg + SO_4^{2-}$

$$E_{cell} = E_{Red}\,(RHS) - E_{Red}\,(LHS)$$

$$Hg_2SO_4 + 2\bar{e} \rightleftharpoons 2Hg + SO_4^{2-} \qquad 2H^+ + 2\bar{e} \rightleftharpoons H_2$$

➡ $$E_{cell} = \left\{E^o_{Hg_2SO_4/SO_4^{2-}} - \frac{RT}{2F}\,ln\,\frac{a_{Hg}\,a_{SO_4^{2-}}}{a_{Hg_2SO_4}}\right\} - \left\{E^o_{H^+/H_2} - \frac{RT}{2F}\,ln\,\frac{a_{H_2}}{(a_{H^+})^2}\right\}$$

$Hg_2SO_4 + 2\bar{e} \rightleftharpoons 2Hg + SO_4^{2-}$ $\qquad$ $2H^+ + 2\bar{e} \rightleftharpoons H_2$

➡ $$E_{cell} = \left\{E^o_{Hg_2SO_4/SO_4^{2-}} - \frac{RT}{2F} \ln a_{SO_4^{2-}}\right\} - \left\{E^o_{H^+/H_2} - \frac{RT}{2F} \ln \frac{1}{(a_{H^+})^2}\right\}$$

➡ $$E_{cell} = E^o_{Hg_2SO_4/SO_4^{2-}} - \frac{RT}{2F} \ln (a^2_{H^+}\, a_{SO_4^{2-}})$$

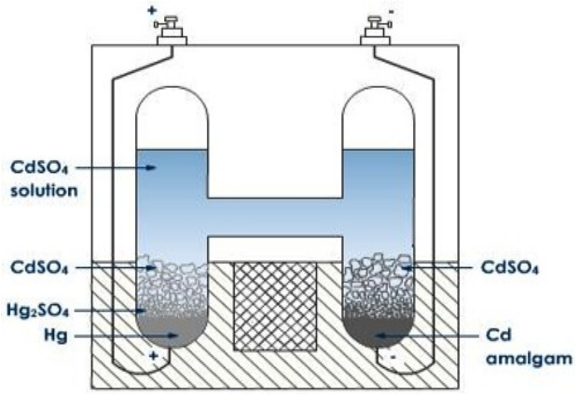
We have, $a = a_+^x\, a_-^y$

$$\boxed{\therefore\ E_{cell} = E^o_{Hg_2SO_4/SO_4^{2-}} - \frac{RT}{2F} \ln a_{H_2SO_4}}$$

Example 3:

Cd (s)| CdSO$_4$ sol^n| Hg_2SO_4 (s) | Hg

$$\boxed{E_{cell} = E^o_{cell} - \frac{RT}{2F} \ln a_{CdSO_4}}$$



Chemical Cell With Transference

$$E_{total} = E_{Red}\,(RHS) - E_{Red}\,(LHS) + E_{Junction}$$

OR

$$E_{total} = E_R + E_L + E_{Junction}$$

$E_{Junction}$ may be small. But, because of $E_{junction,}$ the exact evaluation of thermodynamic functions may not be possible.

Different types of junctions:

1) **Direct contact of electrolytes.**
2) **Salt bridge.**
3) **Flowing junction.**

The evaluation of LJP of a chemical cell is quite complicated. However, Hendorson and others derived different equations based on the speeds and concentrations of ions.

Determination of Transport Numbers

For the electrolyte concentration cell with transference reversible *w.r.t.* cations,

$$E_{WT} = 2n_a \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1}$$

And for the corresponding cell without transference,

$$E_{WOT} = \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1}$$

➡ $$\frac{E_{WT}}{E_{WOT}} = 2n_a$$

$$\boxed{\therefore n_a = \frac{E_{WT}}{2E_{WOT}}}$$

Similarly, for the electrolyte concentration cell with transference reversible *w.r.t.* anions,

$$E_{WT} = 2n_c \frac{RT}{F} \ln \frac{(a_\pm)_1}{(a_\pm)_2}$$

And for the corresponding cell without transference,

$$E_{WOT} = \frac{RT}{F} \ln \frac{(a_\pm)_1}{(a_\pm)_2}$$

➡ $$\frac{E_{WT}}{E_{WOT}} = 2n_c$$

$$\boxed{\therefore n_c = \frac{E_{WT}}{2E_{WOT}}}$$

FUEL CELLS

"Fuel cells are galvanic cells in which chemical energy of fuels is directly converted into electrical energy."

William Robert Grove observed that a small current flowed in the external circuit from the electrolytic cell immediately after removing the external power supply used for the electrolysis.

In a way an electrolytic cell had turned into a galvanic cell when the external source was withdrawn.

"A fuel cell is a galvanic cell in which the reactants are continuously supplied and products are continuously removed."

Conventional conversion of chemical energy of fuels into electrical energy is carried out by burning the fuel, using the heat energy to raise steam which is then used for spinning the turbines connected with electric generators. The efficiency of this process varies from **20 to 40%.**

Fuel cells on the other hand, **convert about 75%** of the available chemical energy into electrical energy.

$H_2 - O_2$ Fuel Cell

A common type of fuel cell is based on the combustion of H_2 to form water;

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O\ (l)$$

This is known as $H_2 - O_2$ fuel cell.

It consists of two electrodes made of porous graphite impregnated with a catalyst (Pt, Ag or a metal oxide). Inner side of graphite electrodes are in contact with an aqueous solution of KOH or NaOH. H_2 and O_2 are continuously fed into the cell under a pressure of 50 atm.

The gases diffuse into the electrode pores and so does the electrolyte solution.

Oxidation Half–cell reaction: $H_2 \longrightarrow 2H^+ + 2\bar{e}$

H^+ ions are neutralized by OH^-: $2H^+ + 2OH^- \longrightarrow 2H_2O$

The net oxidation half–cell reaction: $H_2 + 2OH^- \longrightarrow 2H_2O + 2\bar{e}$

Reduction Half–cell reaction: $O_2 + 2H_2O + 4\bar{e} \longrightarrow 4OH^-$

∴ Overall cell reaction: $2H_2(g) + O_2(g) \longrightarrow 2H_2O$

EMF of this cell = 1 volt.

The water produced vapourises off since the cell is operated at 100 ^{o}C. This can be condensed and used.

In place of KOH or NaOH; phosphoric acid can be used at 200 ^{o}C. At this temperature phosphoric acid can be polymerised to pyro phosphoric acid. Pt-Co-Cr alloy is used as catalyst.

$H_2 – O_2$ Fuel Cells in Manned Space Flights: