Electrochemistry

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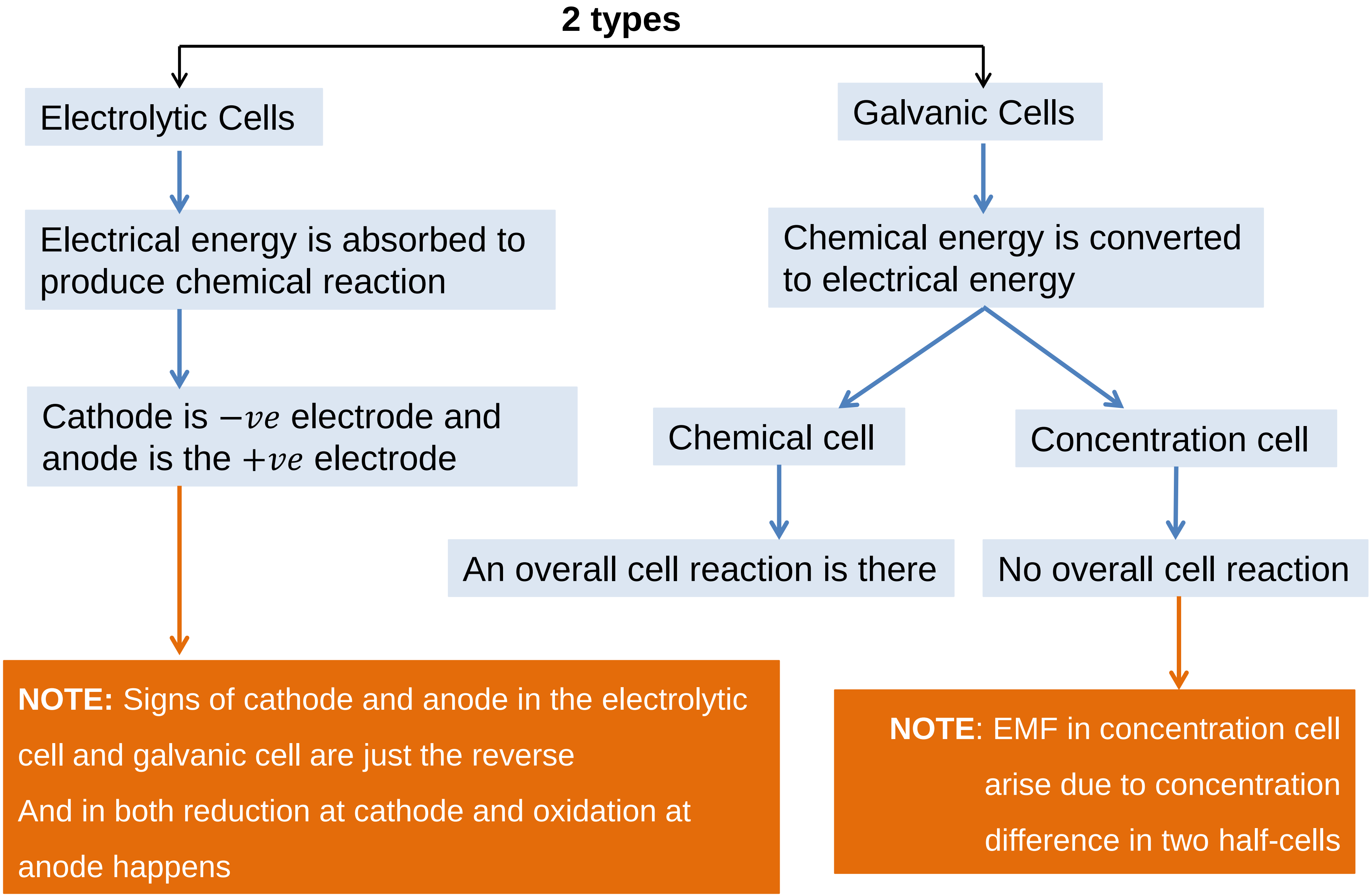
By
Nitesh Jain (B.tech, IIT Bombay)

Electrochemical Cells



2 types

Electrolytic Cells

Electrical energy is absorbed to produce chemical reaction

Cathode is $-ve$ electrode and anode is the $+ve$ electrode

NOTE: Signs of cathode and anode in the electrolytic cell and galvanic cell are just the reverse

And in both reduction at cathode and oxidation at anode happens

Galvanic Cells

Chemical energy is converted to electrical energy

Chemical cell

An overall cell reaction is there

Concentration cell

No overall cell reaction

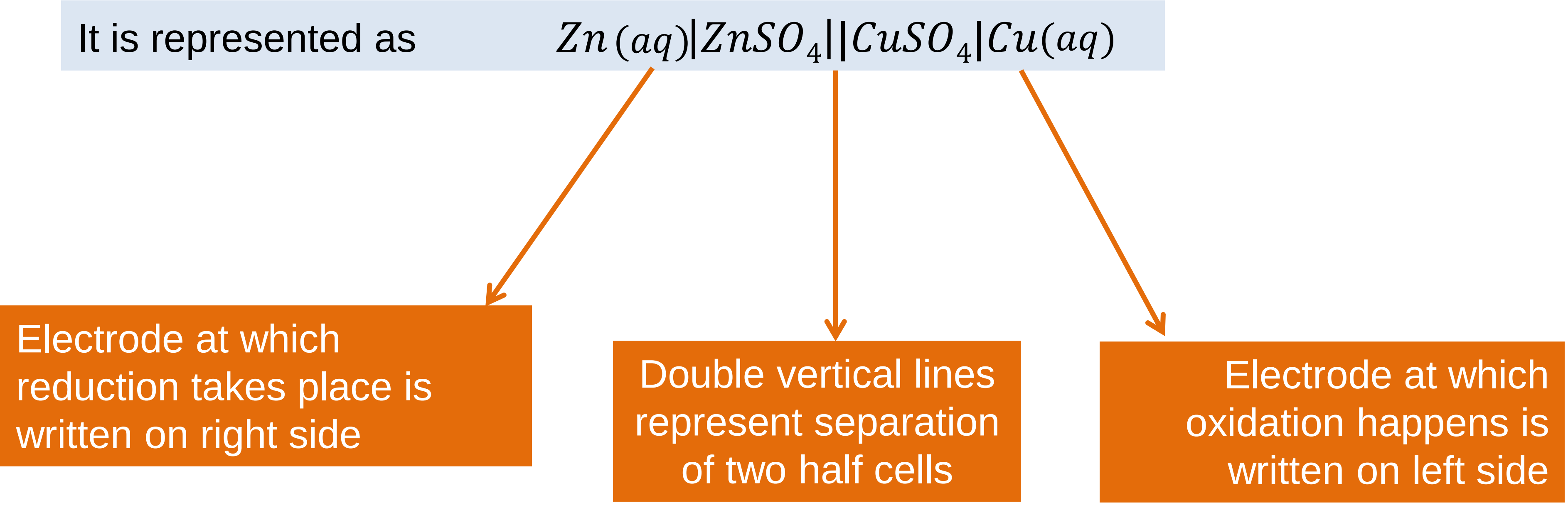
NOTE: EMF in concentration cell arise due to concentration difference in two half-cells

Representation of Chemical Cell

An overall cell reaction is there

For example: $Zn \rightleftharpoons Zn^{2+} + 2e^-$; (Oxidation) At anode

$Cu^{2+} + 2e^- \rightleftharpoons Cu$; (Reduction) At cathode



It is represented as $Zn\,(aq)|ZnSO_4||CuSO_4|Cu(aq)$

Electrode at which reduction takes place is written on right side

Double vertical lines represent separation of two half cells

Electrode at which oxidation happens is written on left side

Work Done by a Galvanic Cell

The electrical work done in moving a charge through conductor

Electrical work (W) $=$ **charge (q)** $\times$ **potential difference (V)**

(joules) (coulombs) (volts)

When **96500** Coulombs OR **1 Faraday (F)** of charge is moved from one electrode to another.

$$\mathbf{W} = \mathbf{F} \times \mathbf{V}$$

NOTE: Electrical work is usually expressed in energy units of watts times time i.e. $1\,J = 1\,W.s$

Watt is unit of **electrical Power** i.e. rate of energy expenditure

Maximum work done by cell

$W = q.V$

Note that W_{max} is when V is maximum

$$\boldsymbol{W_{max} = -n.F.Ecell}$$

n equals the number of electrons in either half–cell reaction

Note that if number of electrons are different in the half-cells, then their LCM is taken to get n

Overall $\Delta E°$ for a series of Half-Cells

$$A^{3+} + e^{-} \rightarrow A^{2+}, \qquad E_1° = +0.77\ V$$

$$A^{2+} + 2e^{-} \rightarrow A, \qquad E_2° = -0.44\ V$$

$$\therefore\ \boldsymbol{E°(A^{3+} + 3e^{-} \rightarrow} A) \neq (\mathbf{0.77 - 0.44})\boldsymbol{V}$$

Note that Potentials are not thermodynamic functions and may not be added directly

Free energy change ($\Delta G°$)$= -nFE°$

Note that $\Delta G°$ is thermodynamic function and can be added

$$\therefore\ \Delta G° = \Delta G_1° + \Delta G_2°$$

$$\Rightarrow \frac{-3F}{E°} = \frac{-F}{E_1°} - \frac{2F}{E_2°}$$

Half-Cell Potential

Tendency to lose electrons i.e. get oxidized is called **Oxidation Potential**

Tendency to gain electrons i.e. get reduced is called **Reduction Potential**

Note that since any half-cell reaction can be written as reversible process

For a single cell: $E_{ox} = -E_{red}$

Example: For electrode $Cu/CuSO_4(1M)$

$$E_{red}\ i.e.\ E^{\circ}{}_{Cu^{2+},Cu} = +0.34V$$

$$\therefore E_{ox}\ i.e.\ E^{\circ}{}_{Cu,Cu^{2+}} = -0.34V$$

Note that half-cell potentials are generally taken in **reduction terms**

Measurement of Half-Cell Potential

Note that Half-Cell potentials cannot be directly determined as there is no way of isolating a single half-cell reaction

Electrode potential (E) is determined by coupling it with a standard hydrogen electrode

E of a standard hydrogen electrode ($\boldsymbol{SHE}$) is assumed as $0\ V$ at $\mathbf{25}$℃

SHE is Represented as $P_t, H_2(1atm), HCL$ $([H^+] = 1M)$

IUPAC Sign Convention

When a half-cell reaction involves reduction → E_{red} is positive

Example: $M^{n+} + ne^- \rightarrow M, \quad Ered$

When a half-cell reaction involves oxidation → $Eoxd$ is negative

Example: $M \rightarrow M^{0+} + ne^-$ E_{oxd}

Note that $E_{red} + E_{oxd} = 0$, for the same metal M in example above

Standard Electrode Potential (E°)

For Half Cell: $M|M^{n+}(aq)$

$$\boldsymbol{M \rightleftharpoons M^{n+} + ne^-}$$

If $[M^{n+}] = 1M$ at $25^\circ\mathrm{C}$

Potential of half cell is termed E°

Example:

$$2X^+ + 2e^- \rightleftharpoons X_2, \qquad E^\circ$$

$$X^+ + e^- \rightleftharpoons \frac{1}{2}X_2, \qquad E^\circ$$

Note that E° is an intensive property; it is same whichever way the reaction is written as shown in example

Electrochemical Series ($IUPAC$ Convention)

When $E°_{\text{red}}$ values of different half cells are arranged **in decreasing order**

This arrangement of $E°$ is known as **electrochemical series**

Example:

$$\boldsymbol{F^2|F^- > Hg^{2+}|Hg > Fe^{3+}|Fe^{2+} > Sn^{4+}|Sn^{2+} > Cu^{2+}|Cu^+ > Sn^{2+}|Sn > Ni^{2+}|Ni > Zn^{2+}|Zn}$$

Note that higher the $E°_{red}$ for an electrode, more will be its tendency to get reduced

EMF of Galvanic Cell

Since Galvanic Cells are formed by coupling two half cells

$\boldsymbol{E°_{Cell}}$ = reduction potential of right hand electrode $(R.H.E)$

– reduction potential of Left hand electrode $(L.H.E)$

Example: $Zn|Zn^{2+}(1M)||Cu^{2+}(1M)|Cu$

$\mathrm{L.H.E}$ $\mathrm{R.H.E}$

Given: $E_{Zn^{2+},Zn} = -0.76V$ and $E_{Cu^{2+},Cu} = 0.34V$ (Reduction Potentials)

$$E°_{Cell} = (0.34)V - (-0.76)V = 1.1V$$

Note that for a given half cell, potential may be in $-ve$ or $+ve$ sign, but the EMF of cell should always be positive

Concentration Cell

No resultant chemical reaction,

But **EMF** arises due to concentration difference between half cells

$$(C_2 - C_1 = \Delta C)$$

$$E_{Cell} = \frac{2.303RT}{n.F} \log \frac{C_2}{C_1}$$

Note that: There is no $E°_{Cell}$ as $E°$ of two half cells are same AND get cancelled

n is the number of electrons exchanged, in oxidation and reduction processes

Nernst Equation

Relates the EMF of Cell AND concentrations of species involved

For the general cell reaction: $aA + bB \rightleftharpoons cC + dD$

$$E_{cell} = E° - \frac{2.303R.T}{nF} log\left(\frac{[C]^c.[D]^d}{[A]^a.[B]^b}\right)$$

Note that: It is Valid for Complete cell or even a half-cell

$E°$ = standard emf of cell (or half cell)

n = number of electrons involved in the reaction

Note that: $\left(\frac{[C]^c.[D]^d}{[A]^c.[B]^b}\right)$ = Q (reaction Quotient)

Equilibrium Constant and Standard Free Energy Change

For a cell reaction: $aA + bB \rightleftharpoons cC + dD$

At equilibrium

$$\left(\frac{[C]^c.[D]^d}{[A]^a.[B]^b}\right) = \boldsymbol{K} \text{ (equilibrium constant)}$$

$$E_{cell} = 0$$

From Nernst Equation

$$\boldsymbol{E° = \frac{2.303RT}{n.F} logK}$$

Note that $\Delta G° = -nFE°$

$$\boldsymbol{\Delta G° = -2.303R.T.logK}$$

Note that knowing $\boldsymbol{E°}$, we can calculate $\boldsymbol{K}$ and $\Delta \boldsymbol{G}°$

Feasibility of Cell Reactions

$$\boldsymbol{\Delta G^\circ = -2.303 R.T.\log K}$$

Note that reaction is spontaneous only if $\Delta G^\circ < 0$

Spontaneity of forward reaction	ΔG°	K	E_{cell}
Spontaneous	$-ve$	> 1	$+ve$
At equilibrium	0	1	0
Non spontaneous	$+ve$	< 1	$-ve$

Note that this is steady state condition

First Law of Faraday

$$w \propto q$$

or

$$w \propto I \cdot t$$

$\boldsymbol{w}$ is amount of substance discharge at an electrode is weight in grams

$\boldsymbol{q}$ is quantity of electricity passing through electrolyte in coulombs

$$\boldsymbol{w = Z \cdot I \cdot t}$$

I is current in ampere

t is time of flow of electricity

Note : Z is constant known as electrochemical equivalent

Second Law of Faraday

$$\boldsymbol{M^{+n} + ne^{-} \rightarrow M}$$

In the reaction n electron deposits 1 M^{+n} ion at electrode

$\therefore$ 1 mole of electron deposits $\frac{1}{n}\text{moles}$ of M^{+n}

Note that (number of moles × valency) = number of equivalent

And 1 mole of electron = $N_A(6.023 \times 10^{23})$ number of electrons

1 mole of electron deposit 1 equivalent of M^{+n}

Faraday's second law states that 1 mole of electron / electricity liberates 1 equivalent of matter

Faraday's Second Law And Faradays Constant (F)

Since, 1 mole of electrons deposit 1 equivalents of matter

Charge of 1 mole electrons $= (6.023 \times 10^{23}) \times (1.6 \times 10^{-19} C)$

$= 96500\ C$

$= 26.8\ \text{ampere} - \text{hour per equivalent}$

$= 1\ \text{Faraday}$

$$\therefore \quad \mathbf{1}\boldsymbol{F} = \mathbf{96500}\ \boldsymbol{C}$$

Note that second law of Faraday states that 1 Faraday liberates 1 equivalent of matter

Number of Equivalent of Substance

Electrochemical equivalent (z) → Weight in grams of a substance liberated by $1C$ electricity

Electrochemical weight or gram equivalent weight → Weight in grams liberated by $96500C$ **OR** $1F$

From First law of faraday → $\boldsymbol{w = z \cdot q}$

$$\frac{\mathbf{w}}{\textbf{gram equivalent weight (eq. wt.)}} = \frac{\mathbf{z \cdot q}}{\textbf{eq. wt.}}$$

→ Note that number of equivalents $= \frac{z \cdot q}{eq.wt.}$

Electrochemical Equivalent (z) And Equivalent Weight (E)

$$\text{number of equivalents} = \frac{\mathrm{z}}{\mathrm{E}} \times \mathrm{q}$$

$$\boldsymbol{z = \frac{\mathrm{E}}{96500}}$$

Note that if number of equivalent $=$ 1 , then

$$q = 1F = 96500C$$

Note that for 2 substances having equivalent weight E_1 and E_2

$\frac{E_1}{E_2} = \frac{z_1}{z_2}$ $\quad (And = \frac{w_1}{w_2}$ if same amount of q is passed)

Electrolytic Conductance

$$\text{conductance} = \frac{1}{\text{resistance}}$$

Depends on

- Number of ions
- Ionic mobility
- Magnitude of charge on ions

Note that passage of current via an electrolyte involves movement of ions carrying an electric charge

Note that Conductance is defined as distance travelled by an ion per second

under potential difference of $1V$ per second

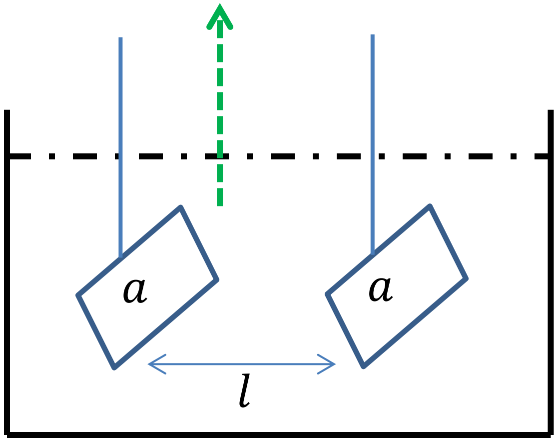
Resistance (R)

Resistance is related to the dimensions of electrolytic cell

$R \propto l$

$R \propto \frac{1}{a}$

Electrolyte is lying between 2 electrodes having area a and separated by l



$$\boldsymbol{R = \rho \frac{l}{a}}$$

ρ is known as specific resistance

Unit of R is ohm

Note that $\frac{l}{a}$ is termed as cell constant and does not change for a given cell

Specific Conductance (K)

$$\boldsymbol{K = \frac{1}{\rho}}$$

$\boldsymbol{\rho}$ is specific resistance

Unit of $\boldsymbol{K}$ is **mho per cm**

And its SI is Siemens (S) → $1\ S = ohm^{-1}$

Since, $R = \rho \frac{l}{a}$

$$\boldsymbol{K} = \frac{1}{\rho} = \frac{1}{R} \times \text{cell constant}$$

Or

$$K = \text{Conductance} \times \text{cell constant}$$

Equivalent Conductance(Λ) And Molar Conductance

$$\boldsymbol{\Lambda} = \mathbf{K} \times \textbf{volume (in ml)}$$

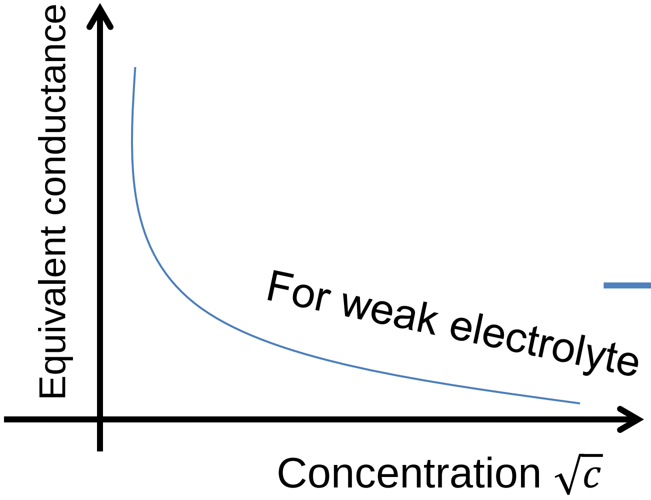
Note : V is the volume that contains 1 equivalents of the electrolyte

$$\text{molar conductance} = \mathrm{K} \times \text{volume(in ml)}$$

Note that : it is the volume that contain 1 mole of electrolyte

Unit of both equivalent and molar conductance is mho cm^2

Equivalent Conductance (Λ) At Infinite Dilution



Assuming its degree of dissociation = α

Note that on dilution concentration will decrease

$\boldsymbol{\Lambda}$ increases with increase in dilution

But after a limit it becomes constant and does not further increase

$$\textbf{Maximum value } (\boldsymbol{\Lambda}_{\infty}) = \alpha \boldsymbol{\Lambda}_c$$

$\boldsymbol{\Lambda}_c$ is equivalent conductance

Note that above expression can also be used to calculate α for a weak electrolyte

Kohlrausch's Law

At infinite dilution an ionic specie contributes a fixed value at a given temperature, towards equivalent conductance of electrolyte

Note that : it is independent of other ionic species in combination with it

This contributions are known as **equivalent ionic conductance** at ∞ dilution

$\lambda_c{}^0$ *for cation*

$\lambda_a{}^0$ *for anion*

$$\therefore\ \boldsymbol{\Lambda^0}\ \textbf{(of electrolyte at } \infty \textbf{ dilution)}\ = \boldsymbol{\lambda_c{}^0 + \lambda_a{}^0}$$