

ELECTRO CHEMISTRY

Introduction, conductors, conductivity, electrolysis;

Electro Chemistry deals with

- The use of electrical energy for the dissociation of chemical compounds (electrolysis)
- The use of chemical reactions for the production of electrical energy (Electro- chemical cells)
- The use of electrical energy in the study and preparation of chemical substances.
- The commercial power generating cells, namely secondary cells (batteries & fuel cells)

Electric current is considered as flow of electrons or flow of electrical charges through a conducting system.

- The Substance which allows the electric current to pass through it, is called Electrical Conductor.

The electrical conductors are of two types.

- Electronic Conductors (Metals),
- Electrolytic conductors

Electronic conductors	Electrolytic conductors
1. Conductivity is due to mobility of free electrons from negative to positive end	1. Conductivity is due to mobility of free ions towards oppositely charged electrodes
2. During conduction matter is not transferred	2. During conduction matter is transferred in the form of ions
3. Passage of current may bring only as physical changes	3. Passage of current brings in physical well as chemical changes
4. The conductivity power is high	4. The conductivity power is relatively less
5. An increase in temperature decreases conductivity due to increased thermal vibration of particles or resistance increases	5. With an increase in temperature. conductivity increases due to the increase in the degree of ionisation and increase in the mobility of ions.

CdS and CuS exhibits electronic conduction due to crystal defect.

Solutions of alkali metals in liquid ammonia are mixed conductors. They contain ammoniated cations (solvated cations) and ammoniated electrons (solvated electrons). They conduct electric current due to the mobility of ions and electrons.

2. Electronic conduction depends on

- the nature and structure of the metal
- the number of valence electrons per atom
- temperature (conductivity decreases with increase of temperature)

* Non-metals like Carbon-black, graphite, organic polymers like polyaniline, poly pyrrole, poly thiophene, poly acetylene when exposed to vapours of iodine. are electronic conductors.

* Metals and their alloys, at very low temperatures (0 to 15 K) were known to behave as superconductors.

3. Electrolytic conduction depends on

- (i) the nature of the electrolyte added
- (ii) size of the ions produced and their solvation
- (iii) the nature of the solvent and its viscosity
- (iv) concentration of the electrolyte
- (v) temperature (conductivity increases with the increase of temperature)

4. ELECTROLYTIC SOLUTION - RESISTANCE AND CONDUCTANCE :

Like electronic conductors (Metallic wires) electrolytic solutions obey ohm's law and Aqueous electrolytic solutions offer resistance like metallic wires to the flow of current.

i. **OHM'S LAW** : It states that the current (I) flowing through a conductor at a given temperature is proportional to the potential difference (V) and inversely proportional to resistance (R). Mathematically it can be expressed as $V=IR$

ii. **RESISTANCE(R)** : It is the opposition to the flow of current offered by the electrolytic solution. Its units are Ohm(Ω)

S.I base units of ohm = $(kg\ m^2)/(S^3 A^2)$

The resistance 'R' offered by the electrolytic solution, taken in a conductivity cell, is directly proportional to distance of separation. 'l' between the two parallel electrodes of the cell and inversely proportional to the area of cross-section (a) of electrode i.e, $R \propto \frac{l}{a}$ or $R = \rho \cdot \frac{l}{a}$ where ρ = specific resistance (Resistivity). It can be measured with the help of wheatstone bridge.

iii. **CONDUCTANCE (C)** :

It is the reciprocal of the electrical resistance (R) , $C = \frac{1}{R}$

It measures the ease with which the current flows through a conductor

$$C = \frac{1}{R} \Rightarrow C = \frac{1}{\rho \times \frac{l}{a}} = k \times \frac{1}{l/a} \therefore k = C \times \frac{l}{a}$$

Where C = Conductance, K=Specific conductance (Conductivity), $\frac{l}{a}$ = Constant known as cell constant. Its units are cm^{-1} (or) m^{-1} .

S.I unit of conductance = Siemens (S) or 'mho '

iv. **SPECIFIC RESISTANCE (OR) RESISTIVITY (ρ) :**

The resistance in ohm of a conductor having length of 1cm and area of cross - section is called resistivity (or) "The resistance offered by 1 solution of an electrolytic solution" is called resistivity ().

Its units are ohm - cm

S.I unit : ohm - metre

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

v. **MEASUREMENT OF CONDUCTIVITY OF IONIC SOLUTIONS:**

Resistance of ionic solution is measured by using conductivity cell.

Conductivity cell consists of two platinum electrodes coated with platinum black, whose area of cross section equal to 'a' and are separated by distance 'l'

Resistance of solution is determined by the equation. $R = \rho \frac{\ell}{a} = \frac{\ell}{ka}$

The quantity $\frac{1}{a}$ is called cell constant denoted by the symbol, G^* . It depends on
Distance between the electrodes & Area of cross sections

The cell constant is determined by measuring the resistance of the cell containing a solution whose conductivity is already known.

vi. SPECIFIC, MOLAR AND EQUIVALENT CONDUTANCE

The conductance (or) the current conducting capacity of an electrolytic solution can be expressed as

- Specific conductance (k),
- Molar conductance (μ),
- Equivalent conductance (Λ)

a) **SPECIFIC CONDUCTANCE (k)** : It is the conductance of the solution enclosed between two parallel electrodes of unit area of cross section separated by a unit distance. (or) The conductance of the electrolyte in the solution of volume of 1cm^3 (CGS units) (or) The conductance of the electrolyte in the solution of volume of 1m^3 (SI units)

$$k = C \times \frac{\ell}{a}$$

If Cell constant = 1 then $k = C$

The conductivity of solutions of different electrolytes in the same solvent and at a given temperature differs due to

- Charge and size of the ions in which they dissociate.
- The concentrations of ions (or) ease with which the ions move under a potential gradient.

b) **Molar Conductance (μ)** :

The conductance of a volume of solution containing 1 gram molecular weight of the electrolyte placed between two parallel electrodes separated by a distance of unit length of 1 centimeter (in CGS system) or 1 meter (in SI system) is called molar conductance.

Relation between specific conductance (k) & molar conductance (μ), of an electrolytic solutions, is as follows

$$\mu = \frac{k \times 1000}{\text{molarity}}$$

Units of molar conductance are $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ in CGS system and $\text{S m}^2 \text{mol}^{-1}$ in SI system.

c) **Equivalent conductance (Λ)** :- The conductance of a volume of solution containing 1 gram equivalent of the electrolyte placed between two parallel electrodes separated by unit length of 1 centimeter (in CGS units) (or) 1 meter (in SI units) is called equivalent conductance.

$$\text{Relation between 'k' and } (\Lambda) \text{ is } \Lambda = \frac{k \times 1000}{\text{normality}}$$

Units of equivalent conductance are $\text{ohm}^{-1} \text{cm}^2 \text{eq}^{-1}$ in CGS system and $\text{Sm}^2 \text{eq}^{-1}$ in SI system.

$$\text{If 'k' is given in SI units, then } \mu = \frac{k}{1000M} \text{ and } \Lambda = \frac{k}{1000N}.$$

For a given solution, $\mu \times \text{Molarity} = \Lambda \times \text{Normality}$

Note: An electrolytic solution whose molarity is equal to its normality has the same value for molar conductance (μ) & equivalent conductance

Eg: KCl solution, NaCl solution, HCl, NaOH etc

Vii. Factors Effecting Molar and Equivalent conductances:

1. Nature of electrolyte i.e, strong (or) weak
2. Nature of the solvent
3. Viscosity of solvent
4. Temperature
5. Concentration of electrolyte
6. Size of the ions produced & their solvation

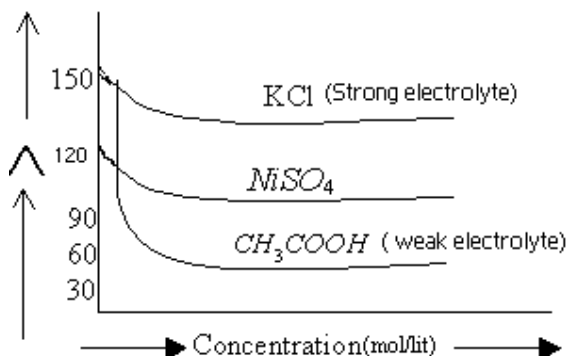
Viii. Variation of Conductance with concentration:

a) specific conductance of a solution increases with increase in the ionic concentration of the solution (no. of ions per unit volume increases) But equivalent and molar conductance decrease with increase in concentration (decrease in ionic mobility and increase in interionic attractions)

b) The specific conductance (k) or conductivity at any specified concentration of an electrolyte depends on the nature of the electrolyte.

Strong electrolytes show high conductance while weak electrolytes show low conductance at any given concentration.

The variation of equivalent conductance (or) molar conductance (Λ) with the concentration of the electrolyte is generally expressed graphically, as follows



It indicates that the variation of Λ with concentration depends to a great extent on the type of the electrolyte rather than on the actual chemical nature of it.

Thus equivalent conductance (or) molar conductance of electrolytic solution increases with decrease in concentration.

For strong uni-univalent electrolytes (Eg. KCl), the decrease in Λ with increase in concentration is not very large.

If electrolyte is not uni-univalent electrolyte then decrease in Λ with concentration is more marked as the valency of the ions increases. They behave in an intermediate manner.

Eg; NiSO_4 (Bi-Bivalent), BaCl_2 (Bi-Univalent)

Weak electrolytes [CH_3COOH , NH_4OH] exhibit an apparently different behaviour as they are not ionised completely.

Effect of Dilution :

- (1) With dilution " Λ " as well as " k " of both weak & strong electrolytes increases.
- (2) Specific conductivity (k) decreases with dilution because of decrease in no. of ions per l.c of electrolyte.
- (3) The molar (or) equivalent conductance of an electrolyte at infinite dilution (or) zero concentration is known as limiting molar conductance (or) limiting equivalent conductance [Λ°]
- (4) Λ° value for any strong electrolyte is calculated by graphically but for weak electrolyte it is determined by Kohlrausch's law.

5. The magnitude of increase in molar conductance for weak electrolyte is much larger than that for a strong electrolyte because strong electrolytes are almost completely ionised in all concentration and increase in μ (or) Λ with dilution is only due to decrease in interionic attractions.

EFFECT OF TEMPERATURE:

The conductivity of all electrolytes increases with increase in temperature

CONDUCTANCE RATIO: The ratio of the equivalent conductance at any concentration (Λ_c) to that at infinite dilution [Λ_o] is called conductance ratio[α] .

$$\alpha = \frac{\Lambda_c}{\Lambda_o} \quad \text{or} \quad \alpha = \frac{\mu_c}{\mu_o}$$

For weak electrolytes, α = degree of ionisation.

α is high for 0.01 M CH_3COOH solution when compared to that of 0.1 M CH_3COOH , because Λ_c is high in case of 0.01 M

IX: DEBYE - HUCKEL - ONSAGER EQUATION:

In the case of weak electrolytes like CH_3COOH , NH_4OH , α is known as degree of dissociation (or) degree of ionisation of electrolyte.

The equivalent conductance at large dilution (or) at very low concentration is known as equivalent conductance at infinite dilution (Λ_∞) or Zero concentration (Λ_o)

The equivalent conductance of an electrolytic solution at any concentration (C) is related to (Λ_o) for a solution is given by the following Debye-Huckel - onsagar equation.

$$\Lambda_c = \Lambda_o - \left[\frac{82.4}{(DT)^{1/2}} + \frac{8.2 \times 10^5}{(DT)^{3/2}} \Lambda_o \right] \sqrt{C} \quad \text{Where}$$

D = Dielectric constant of water

T = Temperature in kelvin scale

Λ_c = Equivalent conductance at conc 'c'

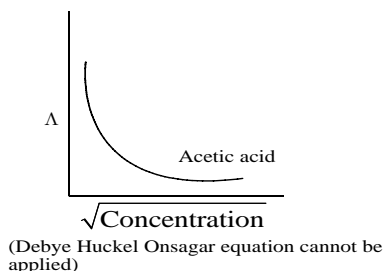
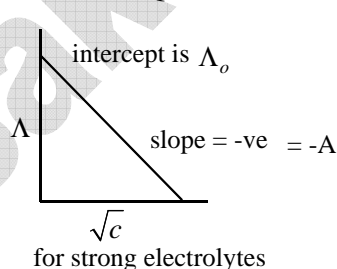
(Λ_o) = equivalent conductance at almost zero concentration or infinite dilution.

η = viscosity co-efficient of solvent.

In short form this equation is represented as $\Lambda_c = \Lambda_o - b\sqrt{C}$

Where b is constant and depends on the nature of the solvent and temperature.

VARIATION OF EQUIVALENT CONDUCTANCE WITH \sqrt{c} IS a straight line with negative slope.



At infinite dilution c tends to be zero . $\therefore \Lambda_c = \Lambda_o$

(Λ_o) Can be determined by extrapolating the graph to zero concentration. This is not applicable for weak electrolytes

Basing on k (specific conductance) value, electrolytes are of two types.

1) weak electrolytes: These have low 'k' value

Eg : weak acids, weak bases.

2) Strong electrolytes: These have high 'k' value

Eg : strong Acids, strong Bases, Salt solutions.

The conductance of an electrolyte is due to its ionisation.

The ionisation extent reaches maximum for weak electrolytes as dilution reaches maximum

X; Kohlrausch's law:

“The equivalent conductance at infinite dilution (Λ_{∞}) of an electrolyte is equal to the algebraic sum of equivalent conductances (or) mobilities of anion (Λ_0^-) and cation (Λ_0^+) of the electrolyte at infinite dilution”

$$\Lambda_0(\text{electrolyte}) = \Lambda_0^+ + \Lambda_0^- (\text{ions}) \text{ and } \Lambda_{\text{eq}}^{\circ} = \frac{1}{n^+} \Lambda_c^{\circ} + \frac{1}{n^-} \Lambda_a^{\circ}$$

e.g. (i) $\Lambda_{\text{KCl}}^{\circ} = \Lambda_{\text{K}^+}^{\circ} + \Lambda_{\text{Cl}^-}^{\circ}$

(ii) $\Lambda_{\text{CaCl}_2}^{\circ} = \frac{1}{2} \Lambda_{\text{Ca}^{++}}^{\circ} + \Lambda_{\text{Cl}^-}^{\circ}$

(iii) $\Lambda_{\text{Fe}_2(\text{SO}_4)_3}^{\circ} = \frac{1}{3} \Lambda_{\text{Fe}^{3+}}^{\circ} + \frac{1}{2} \Lambda_{\text{SO}_4^{2-}}^{\circ}$

where n^+ and n^- are charge on each ion furnished by electrolyte. This law is valid at any dilution but is applied only at infinite dilution. Whereas “molar conductivity of an electrolyte at infinite dilution is the sum of the ionic conductivities of the cations and the anions each multiplied by the number of ions present in one formula unit of electrolyte” e.g. A_xB_y

$$\Lambda_M^{\circ} = x \times \lambda_A^{\circ} y^+ + y \times \lambda_B^{\circ} x^-$$

e.g ; $\Lambda_{\text{Fe}_2(\text{SO}_4)_3}^{\circ} = 2\Lambda_{\text{Fe}^{3+}}^{\circ} + 3\Lambda_{\text{SO}_4^{2-}}^{\circ}$

NOTE: Ionic conductance is more for hydrated Cs^+ than hydrated Li^+

APPLICATIONS:

i) Determination of Λ_0 for weak electrolytes

Eg : NH_4OH is a weak electrolyte its Λ_0 is calculated as

$$\Lambda_0(\text{NH}_4\text{OH}) = \Lambda_0(\text{NH}_4\text{Cl}) + \Lambda_0(\text{NaOH}) - \Lambda_0(\text{NaCl})$$

ii) Degree of ionisation of weak electrolyte (α) = $\frac{\mu_c}{\mu_0} = \frac{\Lambda_c}{\Lambda_0}$

μ_c = molar conductivity at given concentration

Λ_c = equivalent conductivity at given concentration

μ_0 = limiting molar conductivity

Λ_0 = limiting equivalent conductivity Dissociation constant of weak electrolyte

$$K = c\alpha^2$$

iii) $\mu_m^0 = \Lambda_{\text{eq}}^0 \times \frac{\text{molecular weight}}{\text{equivalent weight}}$

iv) Solubility of sparingly soluble salts, $\mu = \frac{k_{\text{salt}} \times 1000}{\text{solubility}}$ (or) $S_{\text{in moles/lit}} = \frac{k_{\text{salt}} \times 1000}{\mu}$

K_{salt} = specific conductance of sparingly soluble salt

Solubility product of salt can be calculated from solubility. $k_{\text{salt}} = k_{\text{solution}} - k_{\text{solvent}}$

K_{solution} = Specific conductance of saturated solution

K_{solvent} = Specific conductance of solvent

v) Ionic mobilities can be calculated as :

$$\text{Ionic mobility } \mu = \frac{\text{speed of the ion}}{\text{potential gradient}}, \mu_+ = \frac{\lambda_+}{F} = \frac{\lambda_+}{96,500}, \mu_- = \frac{\lambda_-}{F} = \frac{\lambda_-}{96,500}$$

vi) Calculation of dissociation constant of weak electrolytes. $K = \frac{C\alpha^2}{1-\alpha}$

XI: Electrolyte: A substance, that is, in the molten state (fused state) or in the dissolved state (in water or any other solvent) containing ions and is functioning as an electrically conducting medium is called an electrolyte.

i. Non Electrolyte: The substance which does not conduct electricity either in its molten state or in aqueous solution is called a non-electrolyte.

Sugar Solution, glucose solution, urea in water, organic solvents, non polar covalent substances, are non electrolytes. Pure water is a poor conductor of electricity.

ii. Strong ElectrolyteS:

Electrolytes, which ionize almost completely at moderate dilutions and have high conductivity are called Strong Electrolytes.

Mineral acids (HCl, H₂SO₄, HNO₃), alkali and alkaline earth metallic hydroxides and most of the salts are strong electrolytes in aqueous solution.

iii. Weak Electrolytes: Electrolytes, which ionize partially and have low conductivity are called Weak Electrolytes.

Most of the organic acids, bases and salts like CH₃COONH₄, HgCl₂, BaSO₄, NH₄OH, H₃BO₃ are weak electrolytes.

XII: Mechanism of electrolysis–its application:

a) The decomposition of an electrolyte at the electrodes as a result of the passage of electric current is called electrolysis. (or) The process of decomposition of an electrolyte by passing electric current is called electrolysis.

b) The cell in which electrolysis is carried out is called electrolytic cell.

c) In an electrolytic cell, electrical energy is converted into chemical energy

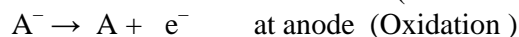
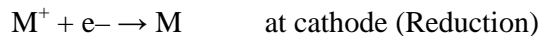
d) In the electrolytic cell, an external source of emf (battery) is used

e) The medium through which the electrons enter and leave the electrolyte is called electrode.

i. Cathode (–): It is the electrode which is connected to the –ve terminal of the battery, and through which the electrons enter the electrolyte

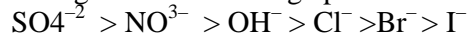
ii. Anode (+): It is the electrode, which is connected to the +ve terminal of the battery, and through which the electrons leave the electrolyte.

f) In an electrolytic cell oxidation of anions takes place at anode and reduction of cations takes place at cathode. Electrons flow from anode to cathode, but current flow from cathode to anode.

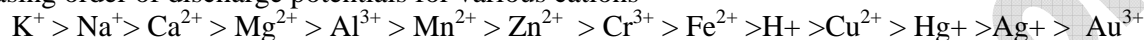


When a solution contains two (or) more anions and cations, the ion with the lower discharge potential will deposit first.

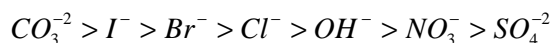
g) Decreasing order of discharge potentials for various anions



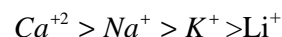
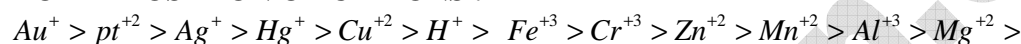
Decreasing order of discharge potentials for various cations



h) ORDER OF DEPOSITION OF ANIONS:



ORDER OF DEPOSITION OF CATIONS :



I) Electrodes which do not involve in chemical reaction during electrolysis are called inert electrodes.
Eg. Graphite, Platinum, etc

In some cases, the electrodes also may take part in the electrolysis reaction. Such electrodes are called active electrodes.

Eg: In the electrolysis of $NiCl_2$ (fused) using nickel electrodes, the anode nickel dissolves electrolytically as nickel ion.

Eg. Cu Anode in aqueous $CuSO_4$

Electrolysis of some substances and the respective products

Electrolyte used	Anode used	Anode reaction	Cathode used	Cathode reaction
Fused NaCl	Pt	$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$	Pt	$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$
Aq. NaCl	Pt	$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$	Hg	$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$
Aq. NaCl	Pt	$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$	Pt	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$
Fused NaOH	Pt	$4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^-$	Pt	$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$
Aq. NaOH	Pt	$4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^-$	Pt	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$
Aq. HCl	Pt	$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$	Pt	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$
Aq. H_2SO_4	Pt	$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{e}^- + 4\text{H}^+$	Pt	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$
50% H_2SO_4	Pt	$2\text{HSO}_4^- \rightarrow \text{H}_2\text{S}_2\text{O}_8 + 2\text{e}^-$	Pb	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$
Aq. Na_2SO_4	Pt	$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{e}^- + 4\text{H}^+$	Pt	$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$
Fused CuCl_2	Pt	$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$	Pt	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$
Aq. CuCl_2	Pt	$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$	Pt	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$
Aq. CuCl_2	Cu	$\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$	Cu	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$
Aq. CuSO_4	Pt	$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{e}^- + 4\text{H}^+$	Pt	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$
Fused MgCl_2	C	$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$	Steel	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$
Fused MgO	C	$2\text{O}^{2-} \rightarrow \text{O}_2 + 4\text{e}^-$	Fe	$\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}$
Fused NaH	Pt	$2\text{H}^- \rightarrow \text{H}_2 + 2\text{e}^-$	Pt	$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$
Aq. AgNO_3	Pt	$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{e}^- + 4\text{H}^+$	Pt	$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$
Aq. AgNO_3	Ag	$\text{Ag} \rightarrow \text{Ag}^+ + \text{e}^-$	Ag	$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$
Aq. ZnSO_4	Zn	$\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$	Zn	$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$