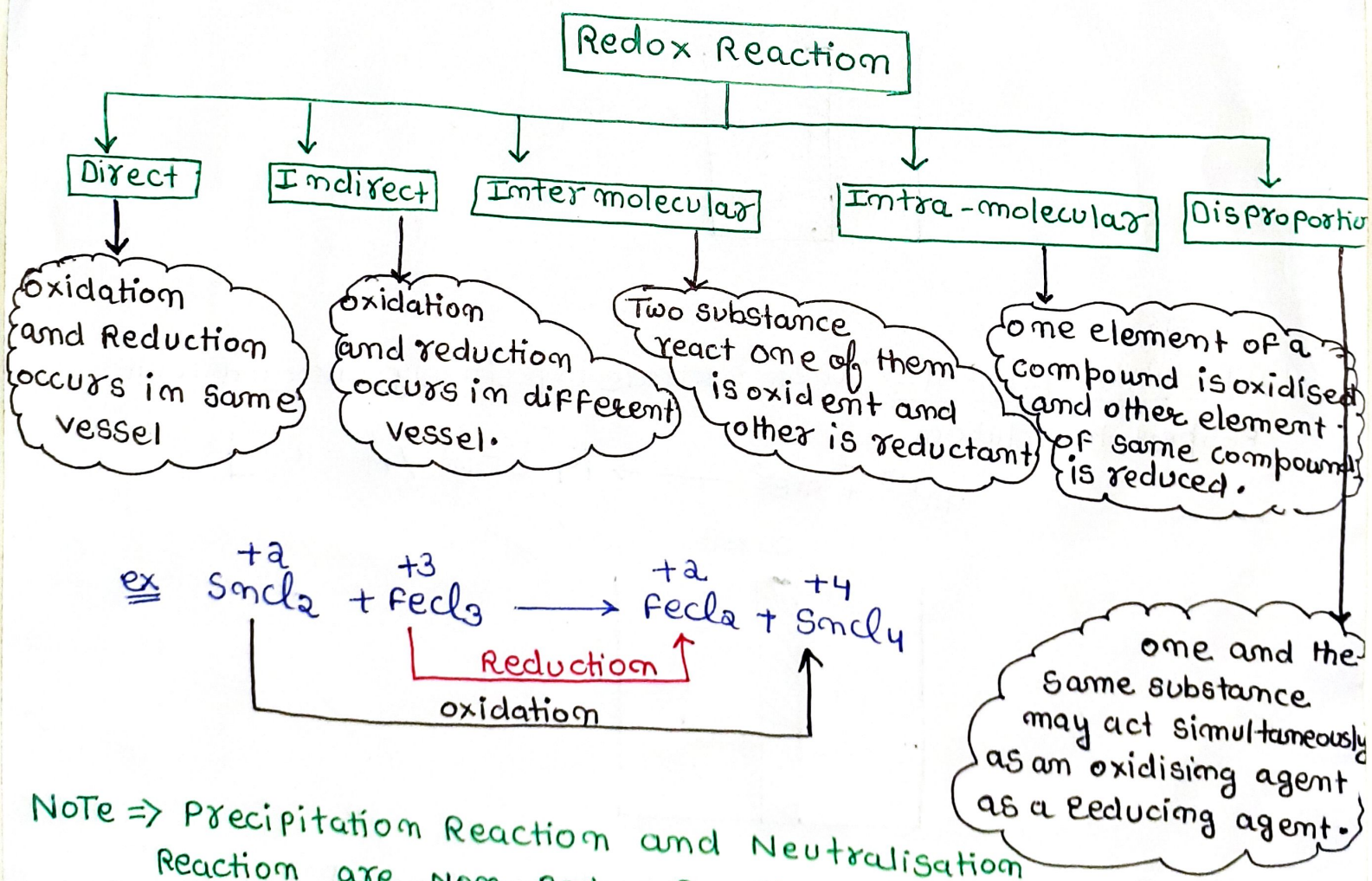


Electrochemistry

①

Redox-Reaction \Rightarrow A chemical Reaction is a process that leads to the transformation of one set of chemical substances to another substance. Classically, chemical reaction encompasses changes that strictly involve the motion of electrons in the forming and breaking of chemical bonds. The concept of electron transfer can easily explain in the Redox Reaction. In the case of ionic substance. However for covalent compound we use a new term oxidation number to explain oxidation and reduction or Redox Reaction. Redox Reactions are the chemical reactions which involve both oxidation as well as reduction simultaneously. In fact oxidation and reduction go hand in hand.



Note \Rightarrow Precipitation Reaction and Neutralisation Reaction are Non-Redox Reaction.

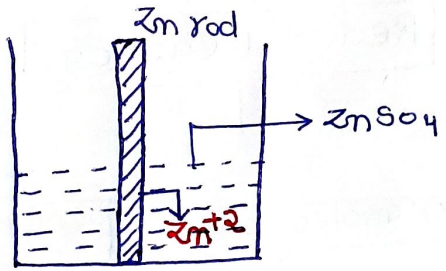
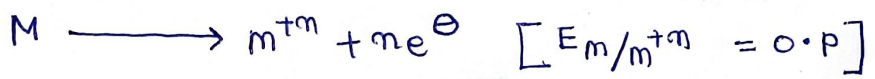
Electrode potential ⇒

when a metal is placed in a solution of its ion, the metal acquires either a positive or negative charge with respect to the solution. on account of this, a definite potential difference is developed between the metal and the solution. This potential difference is called electrode potential.

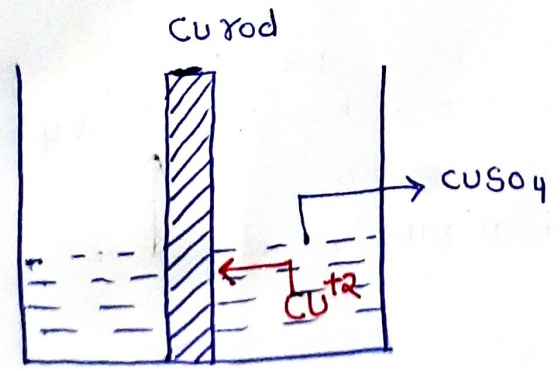
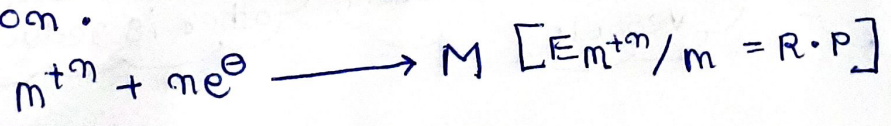
- * electrode potential is mainly depends on following factor -
 - Nature of electrode.
 - concentration of solution.
 - Temperature.

* Electrode potential are two types ⇒

(a) oxidation potential ⇒ when electrode is negatively charged with respect to solution. [greater the o.p greater will be tendency to oxidised]



(b) Reduction potential ⇒ when electrode is positively charged with respect to solution.



[greater the R.P greater will be the tendency to get reduced.]

Reference - electrode \Rightarrow

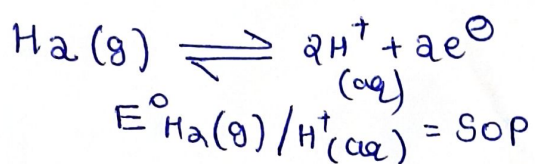
(3)

- * The potential of a single electrode cannot be determined but the potential difference between two electrodes can be accurately measured using a reference electrode.
- * An electrode is chosen as a reference with respect to which all other electrodes are valued.
- * There are two types of reference electrode.

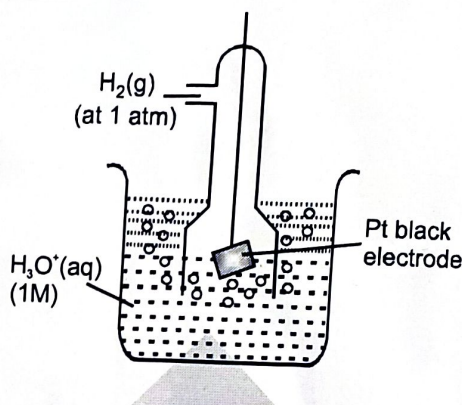
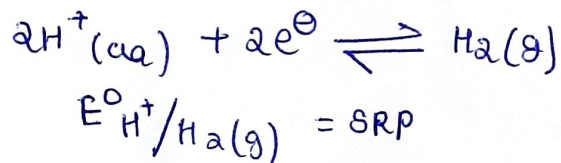
(a) Primary - reference electrode \Rightarrow Standard Hydrogen electrode [S.H.E]

* Representation: $\text{Pt}, \text{H}_2(\text{g}) | \text{H}^+(\text{aq})$

* when acts as anode



* when acts as cathode



* For SHE electrode potential is arbitrarily assumed to be zero at all temperature.

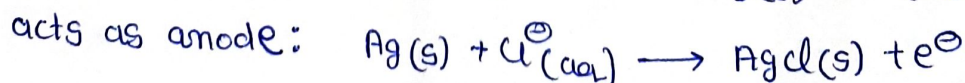
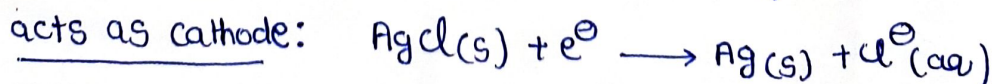
$$\text{SOP} = -\text{SRP} = 0 \text{ for SHE}$$

* To calculate standard potential of any other electrode a cell is coupled with Standard Hydrogen electrode (S.H.E) and its potential is measured that gives the value of electrode potential of that electrode.

(b) Secondary reference - electrode \Rightarrow

(i) silver-silver electrode \Rightarrow

Representation: $\text{Pt}/\text{Ag}-\text{AgCl}(\text{s})/\text{KCl}(\text{aq})$



(ii) Calomel ~~Silver-silver~~ chloride electrode $\Rightarrow [Hg_2Cl_2]$ (4)

Representation: $Pt/Hg - Hg_2Cl_2(s) / KCl(aq)$

when acts as cathode $\frac{1}{2} Hg_2Cl_2(s) + e^- \rightarrow Hg + Cl^-(aq)$

when acts as anode: $Hg + Cl^-(aq) \rightarrow \frac{1}{2} Hg_2Cl_2(s) + e^-$

Electrochemical - SERIES \Rightarrow Arrangement of elements on the basis of their SRP values is known as ECS.

Table 3.1: Standard Electrode Potentials at 298 K

Ions are present as aqueous species and H_2O as liquid; gases and solids are shown by g and s.

Reaction (Oxidised form + ne^-)	\rightarrow Reduced form)	E^\ominus/V
$F_2(g) + 2e^-$	$\rightarrow 2F^-$	2.87
$Co^{3+} + e^-$	$\rightarrow Co^{2+}$	1.81
$H_2O_2 + 2H^+ + 2e^-$	$\rightarrow 2H_2O$	1.78
$MnO_4^- + 8H^+ + 5e^-$	$\rightarrow Mn^{2+} + 4H_2O$	1.51
$Au^{3+} + 3e^-$	$\rightarrow Au(s)$	1.40
$Cl_2(g) + 2e^-$	$\rightarrow 2Cl^-$	1.36
$Cr_2O_7^{2-} + 14H^+ + 6e^-$	$\rightarrow 2Cr^{3+} + 7H_2O$	1.33
$O_2(g) + 4H^+ + 4e^-$	$\rightarrow 2H_2O$	1.23
$MnO_2(s) + 4H^+ + 2e^-$	$\rightarrow Mn^{2+} + 2H_2O$	1.23
$Br_2 + 2e^-$	$\rightarrow 2Br^-$	1.09
$NO_3^- + 4H^+ + 3e^-$	$\rightarrow NO(g) + 2H_2O$	0.97
$2Hg^{2+} + 2e^-$	$\rightarrow Hg_2^{2+}$	0.92
$Ag^+ + e^-$	$\rightarrow Ag(s)$	0.80
$Fe^{3+} + e^-$	$\rightarrow Fe^{2+}$	0.77
$O_2(g) + 2H^+ + 2e^-$	$\rightarrow H_2O_2$	0.68
$I_2 + 2e^-$	$\rightarrow 2I^-$	0.54
$Cu^+ + e^-$	$\rightarrow Cu(s)$	0.52
$Cu^{2+} + 2e^-$	$\rightarrow Cu(s)$	0.34
$AgCl(s) + e^-$	$\rightarrow Ag(s) + Cl^-$	0.22
$AgBr(s) + e^-$	$\rightarrow Ag(s) + Br^-$	0.10
$2H^+ + 2e^-$	$\rightarrow H_2(g)$	0.00
$Pb^{2+} + 2e^-$	$\rightarrow Pb(s)$	-0.13
$Sn^{2+} + 2e^-$	$\rightarrow Sn(s)$	-0.14
$Ni^{2+} + 2e^-$	$\rightarrow Ni(s)$	-0.25
$Fe^{2+} + 2e^-$	$\rightarrow Fe(s)$	-0.44
$Cr^{3+} + 3e^-$	$\rightarrow Cr(s)$	-0.74
$Zn^{2+} + 2e^-$	$\rightarrow Zn(s)$	-0.76
$2H_2O + 2e^-$	$\rightarrow H_2(g) + 2OH^-(aq)$	-0.83
$Al^{3+} + 3e^-$	$\rightarrow Al(s)$	-1.66
$Mg^{2+} + 2e^-$	$\rightarrow Mg(s)$	-2.36
$Na^+ + e^-$	$\rightarrow Na(s)$	-2.71
$Ca^{2+} + 2e^-$	$\rightarrow Ca(s)$	-2.87
$K^+ + e^-$	$\rightarrow K(s)$	-2.93
$Li^+ + e^-$	$\rightarrow Li(s)$	-3.05

1. A negative E^\ominus means that the redox couple is a stronger reducing agent than the H^+/H_2 couple.
2. A positive E^\ominus means that the redox couple is a weaker reducing agent than the H^+/H_2 couple.

Application of Electrochemical series \Rightarrow

(5)

(i) oxidising and reducing power \Rightarrow

$$\text{oxidising power} \propto \text{SRP} \propto \frac{1}{\text{SOP}}$$

$$\text{Reducing power} \propto \text{SOP} \propto \frac{1}{\text{SRP}}$$

(ii) Reactivity of metals \Rightarrow

$$\text{Reactivity of metals} \propto \text{SOP} \propto \frac{1}{\text{SRP}}$$

- * In ECS reactivity of metals decreases from Top to Bottom.
- * Li is most reactive metal.

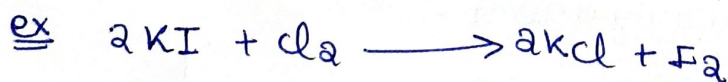
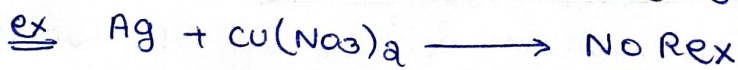
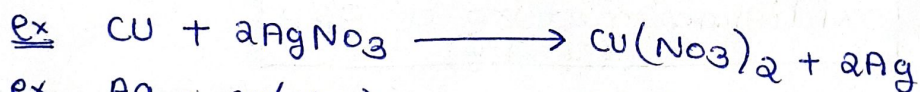
(iii) Reactivity of non-metals \Rightarrow

$$\text{Reactivity of non-metals} \propto \text{SRP} \propto \frac{1}{\text{SOP}}$$

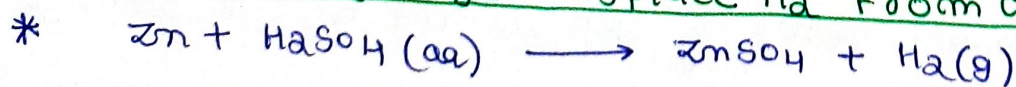
- * In ECS reactivity of non-metal increases from Top to Bottom
- * F_2 is more reactive non-metal.

(iv) Displacement reaction in solution \Rightarrow

- * More reactive metal / non-metal displace less reactive metal / non-metal in their solution.



(v) metal above hydrogen displace H_2 from dilute acid solution \Rightarrow



Q give the ~~de~~ⁱⁿcreasing order of Reducing nature -

metals	E_{SRP}°
(A) —————	-1.2V
(B) —————	+0.5V
(C) —————	-1.5V
(D) —————	+0.2V

Solⁿ

Reducing nature \propto SOP $\propto \frac{1}{SRP}$

So from data $C > A > D > B$

- Q
- (i) $A^{+2} + 2e^{\ominus} \longrightarrow A$ $E_{Red}^{\circ} = -2.3V$
 - (ii) $B^{+2} + 2e^{\ominus} \longrightarrow B$ $E_{Red}^{\circ} = -1.5V$
 - (iii) $X_a + 2e^{\ominus} \longrightarrow 2X^{\ominus}$ $E_{Red}^{\circ} = 0.5V$
 - (iv) $Y_2 + 2e^{\ominus} \longrightarrow 2Y^{\ominus}$ $E_{Red}^{\circ} = 0.8V$

Q.1 which one is act as strongest oxidising agent?

- (a) A^{+2} (b) B^{+2} (c) X_a (d) Y_2

Q.2 which one is act as ~~re~~ strongest Reducing agent?

- (a) A^{+2} (b) B (c) X_a (d) A

Solⁿ

(i) oxidising nature \propto SRP
(capacity)

So Y_2 has maximum value of SRP so act as strongest oxidising agent.

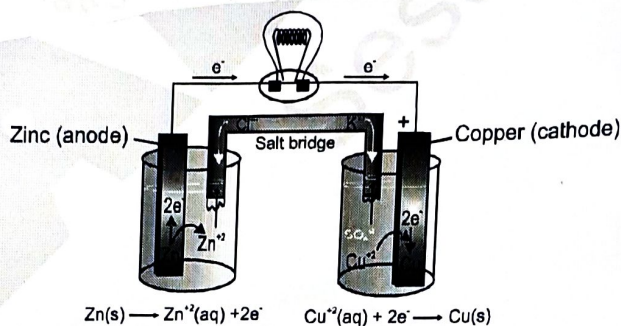
(ii) Reducing nature \propto SOP $\propto \frac{1}{SRP}$
(capacity)

So A has minimum value of SRP so act as strongest Reducing agent

Galvanic - cell \Rightarrow

(7)

- * It has two half-cells, each having a beaker containing a metal strip that dips in its aqueous salt solution.
- * The metal strips are called electrodes and are connected by conducting wire.
- * Two solutions are connected by a salt bridge.



Salt - Bridge and its function \Rightarrow Salt bridge is inverted U-tube containing solution of inert electrolyte with agar-agar or gelatin to convert into semi solid form.

- ① Ions of inert electrolyte do not involve in any chemical change.
- ② The electrolyte in salt bridge should be such that speed of its anion is nearly equal to speed of its cation ex KCl, KNO₃

Function \Rightarrow ① it connects the solution of two half cell to complete the circuit.

- ② it maintains the electrical neutrality of the solution in order to give continuous flow or generation of current.
- ③ if the salt bridge is removed then voltage drops to zero.
- ④ it prevents the liquid-liquid junction potential. The potential difference which arises between two solutions when they brought in contact with each other.

Concept of EMF of cell \Rightarrow

(8)

Electron flow from anode to cathode in external circuit due to a pushing effect called or electromotive force.

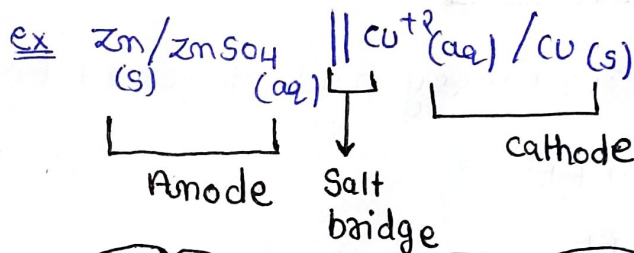
unit \Rightarrow volt

Standard Electrode potential $\rightarrow E_{\text{cell}}^{\circ} = \overset{\text{Standard}}{\text{Reduction potential of cathode}} - \overset{\text{Standard}}{\text{Reduction potential of anode}}$

Standard Electrode potential $\rightarrow E_{\text{cell}}^{\circ} = \overset{\text{Standard}}{\text{Reduction potential of cathode}} + \overset{\text{Standard}}{\text{oxidation potential of anode}}$

Sign convention of EMF \Rightarrow

EMF of cell should be positive otherwise it will not be feasible in the given direction.



Trick \Rightarrow ① A B C
 [Anode] [Bridge] [Cathode]
 ② L O A N
 [Left side] [Oxidation] [Anode] [Negative]

Q For the cell reaction $2\text{Ce}^{4+} + \text{Co} \longrightarrow 2\text{Ce}^{3+} + \text{Co}^{2+}$
 E_{cell}° is 1.89V. if $E_{\text{Co}^{2+}/\text{Co}}^{\circ}$ is -0.28V, what is the value of $E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^{\circ}$?

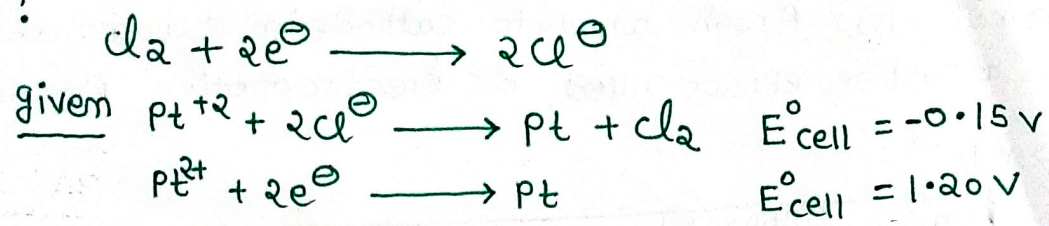
Solⁿ

$$E_{\text{cell}}^{\circ} = E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^{\circ} - E_{\text{Co}^{2+}/\text{Co}}^{\circ}$$

$$1.89 = E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^{\circ} - (-0.28)$$

$$E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^{\circ} = 1.61\text{V}$$

Q Determine the standard reduction potential for the Half Reaction?



Solⁿ

$$E^\circ_{\text{cell}} = 1.20 \text{ V} - (-0.15)$$

$$= 1.20 + 0.15$$

$$= 1.35 \text{ V}$$

Nernst equation =>

Nernst derived a relation between cell potential and concentration of Reaction Quotient.

$$\Delta G = \Delta G^\circ + RT \ln Q \quad \text{--- (1)}$$

where ΔG and ΔG° are free energy and standard free energy change

$$\therefore \Delta G^\circ = -nFE^\circ$$

$$\Delta G = -nFE$$

Thus from eq (1) we get $-nFE = -nFE^\circ + RT \ln Q$

At 25°C above equation may be written as

$$E = E^\circ - \frac{0.0591}{n} \log Q$$

[n = number of moles of electrons involved in process]

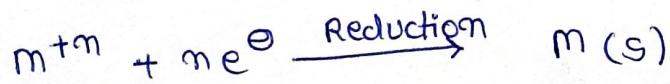
$aA + bB \longrightarrow cC + dD$, the EMF can be calculated as

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n} \log_{10} \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Application of Nernst equation \Rightarrow

(10)

(i) Calculation of electrode potential (E_{RP} or E_{op}) \Rightarrow



$$E_{RP} = E_{RP}^{\circ} - \frac{0.0591}{n} \log \frac{[M]}{[M^{+n}]}$$

$$E_{RP} = E_{RP}^{\circ} - \frac{0.0591}{n} \log \frac{1}{[M^{+n}]}$$

"if $[M^{+n}]$ increases, then E_{RP} increases."

(ii) Calculation of electrode potential and pH of Hydrogen electrode \Rightarrow



$$E_{RP} = E_{RP}^{\circ} - \frac{0.0591}{2} \log \frac{P_{H_2}}{[H^{+}]^2}$$

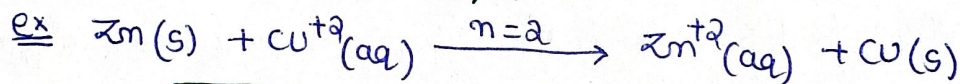
$$\because E_{RP}^{\circ} = 0, \quad E_{RP} = E_{RP}^{\circ} - \frac{0.0591}{2} \log \frac{1}{[H^{+}]^2} \quad \left[\begin{array}{l} P_{H_2} = 1 \text{ atm} \\ E_{RP}^{\circ} = 0 \end{array} \right]$$

$$E_{RP} = 0.0591 \log [H^{+}]$$

$$E_{RP} = -0.0591 \text{ pH}$$

$$E_{op} = +0.0591 \text{ pH}$$

(iii) Calculation of EMF of cell (E_{cell}) \Rightarrow



$$E_{cell} = E_{cell}^{\circ} - \frac{0.0591}{2} \log \frac{[Zn^{+2}]}{[Cu^{+2}]} \quad \left[\begin{array}{l} \text{if } [Cu^{+2}] \uparrow, E_{cell} \uparrow \\ \text{if } [Zn^{+2}] \uparrow, E_{cell} \downarrow \end{array} \right]$$

(iv) Calculation of equilibrium constant (K_{eq}) and ΔG° \Rightarrow
From Nernst equation

$$E_{cell} = E_{cell}^{\circ} - \frac{0.0591}{n} \log \frac{[P]}{[R]}$$

$$\text{At equilibrium } E_{cell} = 0 \text{ and } \frac{[P]}{[R]} = K_{eq}$$

$$E_{cell}^{\circ} = \frac{0.0591}{n} \log K_{eq}$$

$$E_{cell}^{\circ} = \frac{2.303 RT}{nF} \log K_{eq}$$

$$nFE_{cell}^{\circ} = 2.303 RT \log K_{eq}$$

$$\Delta G^{\circ} = -2.303 RT \log K_{eq}$$

Q Calculate E° and E for the cell $\text{Sm}/\text{Sm}^{2+}(1\text{M}) \parallel \text{Pb}^{2+}(10^{-3}\text{M})/\text{Pb}$
 $E^\circ(\text{Sm}^{2+}/\text{Sm}) = -0.14\text{V}$, $E^\circ(\text{Pb}^{2+}/\text{Pb}) = -0.13\text{V}$. is cell representation correct?

Solⁿ

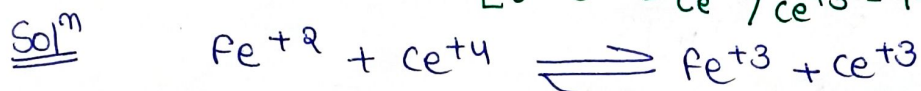
$$E^\circ_{\text{cell}} = E^\circ(\text{Pb}^{2+}/\text{Pb}) - E^\circ(\text{Sm}^{2+}/\text{Sm}) = -0.13 - (-0.14)$$

$$= +0.01\text{V}$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{2} \log \frac{[\text{Sm}^{2+}]}{[\text{Pb}^{2+}]}$$

$$= 0.01 - \frac{0.0591}{2} \log \left[\frac{1}{10^{-3}} \right] = -0.078\text{V} \quad [\text{cell with no work}]$$

Q Calculate the equilibrium constant for the reaction $\text{Fe}^{2+} + \text{Ce}^{4+} \rightleftharpoons \text{Fe}^{3+} + \text{Ce}^{3+}$ [given $E^\circ(\text{Ce}^{4+}/\text{Ce}^{3+}) = 1.44\text{V}$, $E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) = 0.68\text{V}$]

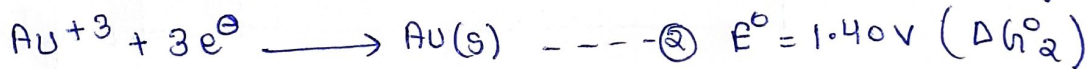
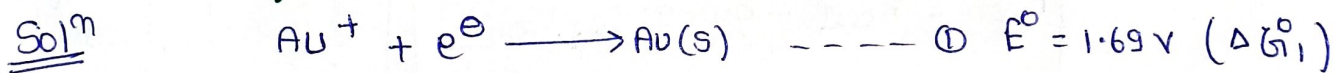


$$E^\circ_{\text{cell}} = 1.44 - 0.68 = 0.76\text{V}$$

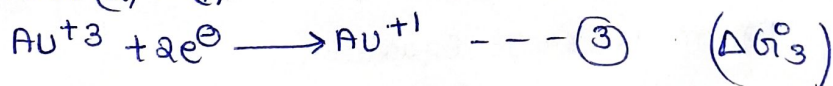
$$0.76\text{V} = \frac{0.06}{1} \log K_c$$

$$K_c = 4.64 \times 10^{12}$$

Q If $E^\circ(\text{Au}^+/\text{Au})$ is 1.69V and $E^\circ(\text{Au}^{3+}/\text{Au})$ is 1.40V then $E^\circ(\text{Au}^{3+}/\text{Au}^+)$ will be?



From (2) - (1)



$$\Delta G^\circ_3 = \Delta G^\circ_2 - \Delta G^\circ_1$$

$$-2 \times F \times E^\circ = -3 \times F \times 1.40 + 1 \times 1.69 \times F$$

$$E^\circ = 1.255\text{V}$$

Note \Rightarrow (i) ~~work~~ Let ' m ' Faraday charge be taken out of a cell of EMF ' E ' then work done by the cell will be calculated as

$$\text{work} = \text{charge} \times \text{potential} = mF \times E$$

(ii) work done by cell = Decrease in free energy

$$-\Delta G = mFE$$

$$W_{\text{max}} = +mFE^\circ \quad [E^\circ = \text{standard EMF of cell}]$$

Q The standard EMF of cell is 1.1V, calculate the EMF of a Daniel cell when the concentration of $ZnSO_4$ and $CuSO_4$ are 0.001 M and 0.1 M respectively?

Solⁿ

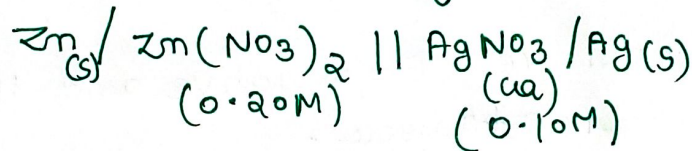


$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{2} \log \frac{[Zn^{+2}]}{[Cu^{+2}]}$$

$$= 1.1 - \frac{0.0591}{2} \log \frac{10^{-3}}{10^{-1}}$$

$$E_{cell} = 1.159 V$$

Q For Zn and Ag the standard potential is 0.76V, -0.8V respectively, calculate the EMF of cell



Solⁿ

$$E^{\circ}_{cell} = E^{\circ}_C - E^{\circ}_A$$

$$= E^{\circ}_{(Ag)} - E^{\circ}_{(Zn)}$$

$$= 0.80 - (-0.76)$$

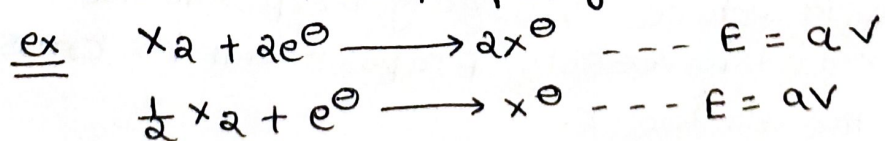
$$E^{\circ}_{cell} = 1.56 V$$

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n} \log \frac{[Anode]^x}{[Cathode]^y}$$

$$E_{cell} = 1.56 - \frac{0.0591}{2} \log_{10} \frac{0.20}{(0.1)^2}$$

$$E_{cell} = 1.52 V$$

NOTE \Rightarrow There is no change in electrode potential by multiplying any digit number, because electrode potential is an intensive property.



② The value of electrode potential does not depend on size of electrode and amount of solution, but depends on concentration of solution.

Relationship b/w ΔG and Electrode Potential \Rightarrow

Faraday charge is taken out from a cell of emf (E), then electrical work done by the cell may be calculated as
work done = nFE

From thermodynamics we know that decrease in Gibbs Free energy of a system is a measure of reversible or maximum obtainable work by the system.

$$\therefore \Delta G = -nFE$$

$$\Delta G^\circ = -nFE^\circ \quad \text{--- (1)}$$

(1) From thermodynamics we know $\Delta G = -ve$ for spontaneous process. Thus from eq (1) it is clear that the EMF should be +ve for a cell process to be feasible.

(2) when $\Delta G = \text{positive}$, $E = \text{negative}$ and the cell process will be non-spontaneous.

Reaction	ΔG	E
Spontaneous	-	+
Non-spontaneous	+	-
Equilibrium	0	0

Conductance \Rightarrow

* Both metallic and electrolytic conductors obey Ohm's Law.

$$\text{i.e. } V = IR$$

where $V = \text{Potential difference}$

$I = \text{Current}$

$R = \text{Resistance}$

* We know, Resistance is directly proportional to length of conductor and inversely proportional to cross-sectional area of the conductor.

$$R \propto \frac{l}{A} \quad \text{or} \quad R = \rho \frac{l}{A} \quad [\rho = \text{specific resistance}]$$

unit of $R \Rightarrow \text{ohm}$, unit of $\rho = \text{ohm cm}$

** specific resistance is the resistance of a conductor having length of 1cm and cross sectional area of 1cm^2 .

** Reciprocal of resistance is called as conductance and reciprocal of specific resistance is called as specific conductance.

$$\frac{1}{R} = \frac{1}{\rho} \frac{A}{l}$$

or
$$C = \kappa \frac{A}{l}$$

C = conductance [ohm^{-1}]

κ = specific conductance [$\text{ohm}^{-1}\text{cm}^{-1}$]

Equivalent Conductance \Rightarrow [λ_{eq}]

Equivalent conductance is the conductance of an electrolyte solution containing 1gm equivalent of electrolyte.

$$\lambda_{eq} = \kappa \times V \quad \text{Unit} = \text{ohm}^{-1}\text{cm}^2\text{eq}^{-1}$$

* usually concentration of electrolyte solution is expressed as C gm equivalent per liter.

$$\text{Thus } V = \frac{1000}{C}$$

{ volume having 1gm equivalent electrolyte in the solution }

$$\text{Thus } \lambda_{eq} = \kappa \times \frac{1000}{C}$$

Molar Conductance \Rightarrow [λ_m]

Molar conductance may be defined as conductance of an electrolyte solution having 1gm mole electrolyte in liter.

$$\lambda_m = \kappa \times V$$

Unit $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$

Usually concentration of electrolyte solution is expressed as "M" gm mole electrolyte per liter.

$$V = \frac{1000}{M}$$

$$\lambda_m = \kappa \times \frac{1000}{M}$$

$$\lambda_m = \lambda_{eq} \times V \cdot F$$

Factor - affecting conductance \Rightarrow (15)

(1) Inter ionic interaction \Rightarrow $\text{III} \uparrow = \text{conductance} \downarrow$
[becoz movement of ion \downarrow]

(2) Hydration \Rightarrow Hydration $\uparrow = \text{conductance} \downarrow$
[becoz movement of ion \downarrow]

(3) viscosity of medium \Rightarrow viscosity $\uparrow = \text{conductance} \downarrow$
[becoz movement of ion \downarrow]

(4) Temperature \Rightarrow $T \uparrow = \text{conductance} \uparrow$
[becoz due to increase in $T \uparrow$
 $K \cdot E \uparrow$ so the attraction force
become weak, so movement of
ion \uparrow]

(5) dilution \Rightarrow dilution $\uparrow = \text{conductance} \uparrow$ but specific \downarrow
conductance

(1) on increasing the dilution conductance increases.
For strong electrolyte on dilution inter ionic force
of attraction decreases therefore conductance increase.
For weak electrolyte with dilution degree of dissociation
(α) increases therefore conductance increases.

(2) on dilution specific conductance decreases because on
dilution number of ions in 1 mL solution decreases.

(3) on dilution equivalent and molar conductance increases
because with dilution normality or molarity decreases.

(16)

FARADAY'S Laws of electrolysis \Rightarrow

(1) First Law of electrolysis \Rightarrow

Amount of substance deposited at an electrode is directly proportional to amount of charge passed through the solution.

$$\omega \propto Q$$

$$\omega \propto it$$

$$\omega = zit$$

where z = electrochemical equivalent

when $Q = 1 \text{ cb}$, then $\omega = z$

Thus weight deposited by 1 cb is called electrochemical equivalent.

$$Q = It \quad \therefore \omega = zIt$$

$$1F = 96500 \text{ cb} = \text{charge of one mole } e^-$$

Let ' E ' is equivalent weight then ' E ' gm will be liberated by 96500 cb .

$$\text{So } z = \frac{E}{96500}$$

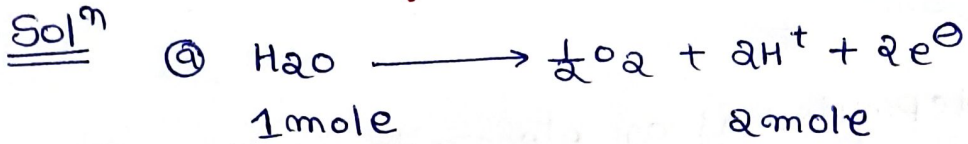
$$\omega = \frac{E}{96500} It$$

(2) Second Law of electrolysis \Rightarrow

When same amount of charge is passed through different electrolyte solution connected in series then weight of substance deposited at anode or cathode are in ratio of their equivalent weights.

$$\frac{\omega_1}{E_1} = \frac{\omega_2}{E_2}$$

Q How much electric charge is required to oxidise
 (a) 1 mole of H_2O to O_2 (b) 1 mole FeO to Fe_2O_3

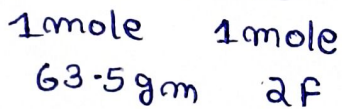
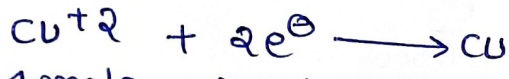
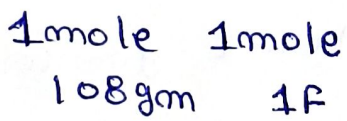
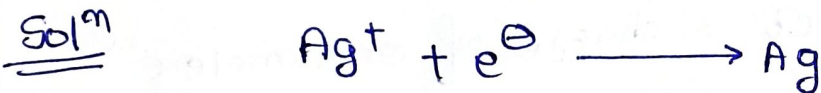


$$Q = 2F = 2 \times 96500 = 1.93 \times 10^5 \text{ cb}$$



$$Q = F = 96500 \text{ cb}$$

Q Exactly 0.4 Faraday electric charge is passed through three electrolytic cells in series, first containing AgNO_3 , second CuSO_4 , and third FeCl_3 solution, How many gram of each metal will be deposited assuming only cathodic reaction in each cell?



Hence Ag deposited = $108 \times 0.4 = 43.2 \text{ gm}$

Cu deposited = $\frac{63.5}{2} \times 0.4 = 12.7 \text{ gm}$

Fe deposited = $\frac{56}{3} \times 0.4 = 7.47 \text{ gm}$

Kohlrausch's Law \Rightarrow

(18)

* Kohlrausch determined λ_{eq} values of pairs of some strong electrolytes containing same cation say KF, KCl, NaF and $NaCl$ etc. and found that the difference in λ_{eq} values in each case remain the same

* "At infinite dilution when dissociation is complete, every ion make some definite contribution towards molar conductance of the electrolyte irrespective of the nature of the other ion which with it is associated and that the molar conductance at infinite dilution for any electrolyte is given by the sum of the contribution of two ions."

$$\lambda_{eq}^{\infty} = \lambda_c^{\infty} + \lambda_a^{\infty}$$

in terms of molar conductance

$$\lambda_{eq}^{\infty} = \frac{1}{z^{\oplus}} \lambda_m^{\infty}(c) + \frac{1}{z^{\ominus}} \lambda_m^{\infty}(a)$$

z^{\oplus}, z^{\ominus} = charge of cation and anion.

$$\lambda_m^{\infty} = a \lambda_m^{\infty}(c) + b \lambda_m^{\infty}(a)$$

a, b = stoichiometric coefficient of cation and anion

Application \Rightarrow

(1) Determination of λ_m^{∞} of a weak electrolyte \Rightarrow

In order to calculate λ_m^{∞} of a weak electrolyte say CH_3COOH , we determine experimentally λ_m^{∞} values of the following three strong electrolyte.

- A strong electrolyte containing same cation as in the test electrolyte, say HCl .
- A strong electrolyte containing same anion in the test electrolyte, say CH_3COONa .
- A strong electrolyte containing same anion of (a) and cation (b) i.e. $NaCl$.

λ_m^{∞} of CH_3COOH is then given as

$$\lambda_m^{\infty}(CH_3COOH) = \lambda_m^{\infty}(HCl) + \lambda_m^{\infty}(CH_3COONa) - \lambda_m^{\infty}(NaCl)$$

Proof

$$\lambda_m^{\infty}(HCl) = \lambda_H^{\oplus} + \lambda_{Cl}^{\ominus} \quad \text{--- (1)}$$

$$\lambda_m^{\infty}(CH_3COONa) = \lambda_{CH_3COO}^{\ominus} + \lambda_{Na}^{\oplus} \quad \text{--- (2)}$$

$$\lambda_m^{\infty}(NaCl) = \lambda_{Na}^{\oplus} + \lambda_{Cl}^{\ominus} \quad \text{--- (3)}$$

$$(1) + (2) - (3) = \lambda_{CH_3COOH}^{\infty}$$

(2) Determination of degree of dissociation $\Rightarrow [\alpha]$

$$\alpha = \frac{\text{No of molecules ionised}}{\text{total number of molecule dissolved}} = \frac{\Lambda_m^c}{\Lambda_m^\infty}$$

(3) Determination of solubility of sparingly soluble salt \Rightarrow

The specific conductivity of a saturated solution of the test electrolyte (sparingly soluble) made in conductivity water is determined by the method as described above. From this the specific conductivity of conductivity of water is deducted. Λ_m^∞ as the saturated solution of sparingly soluble salt is extremely dilute.

$$\Lambda_m^\infty = \frac{1000 \times \kappa}{S}$$

Q. 1.0 N solution of a salt surrounding two platinum electrodes 2.1 cm apart and 4.2 sq cm in area was found to offer a resistance of 50 ohm. Calculate the equivalent conductivity of the solution?
given $d = 2.1 \text{ cm}$, $a = 4.2 \text{ sq. cm}$, $R = 50 \text{ ohm}$.

Sol^m

$$\text{Specific conductance } \kappa = \frac{l}{a} \cdot \frac{1}{R} = \frac{2.1}{4.2} \times \frac{1}{50} = 0.01 \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$\begin{aligned} \text{Equivalent conductivity} &= \kappa \times V \\ &= 0.01 \times 1000 \\ &= 10 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1} \end{aligned}$$

Electrolytic Conductance \Rightarrow

(20)

(a) Resistance $[R] =$ metallic and electrolytic conductors obey ohm's law according to which the resistance of a conductor is the ratio of the applied potential difference to the current flowing.

$$R = \frac{V}{I}$$

unit of $R =$ ohms

(b) Conductance $[C] \Rightarrow$ it is the property by virtue of which it favours flow of current. The conductance of a conductor is equal to reciprocal to resistance.

$$C = \frac{1}{R}$$

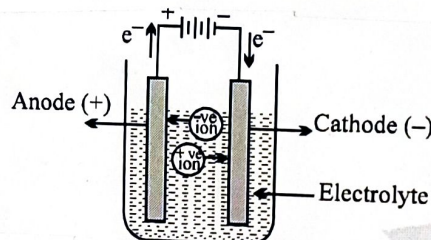
unit of $C = \text{ohm}^{-1}$ or mho or S

Qualitative aspects of electrolysis \Rightarrow An electrode product

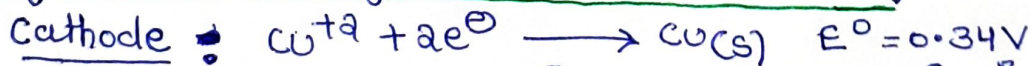
Formation depends on following:

- (i) Nature of electrolyte
- (ii) Nature of electrodes
- (iii) Concentration of electrolytic solution.

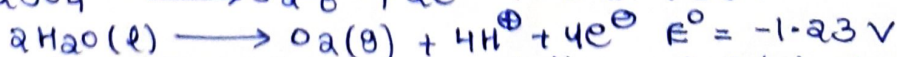
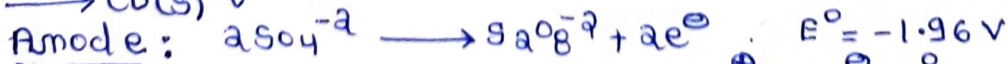
* The metal strip at which current enters is called anode, anode is positively charged in electrolytic cell. on the other hand the electrode at which current leaves is called cathode, cathode is negatively charged.



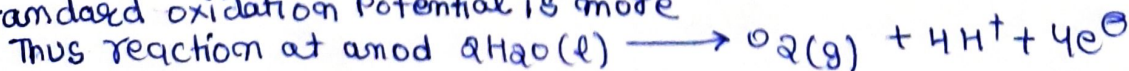
ex Electrolysis of aq CuSO_4 using inert (pt) electrode \Rightarrow



At cathode reduction of $\text{Cu}^{+2}(\text{aq})$ will be preferred over ~~reduction~~ reduction of water as its standard reduction potential is more, than that of water. Thus reaction at cathode



At anode oxidation of water is preferred over oxidation of sulphate ion as its standard oxidation potential is more



Q The equivalent conductance of sodium chloride, hydrochloric acid and sodium acetate at infinite dilution are 126.45 , 426.16 and $91.0 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$, respectively at 25°C . Calculate the equivalent conductance of acetic acid at infinite dilution?

Solⁿ

$$\lambda_{\text{CH}_3\text{COONa}}^\infty = \lambda_{\text{CH}_3\text{COO}^-}^\infty + \lambda_{\text{Na}^+}^\infty = 91.0 \quad \text{--- (1)}$$

$$\lambda_{\text{HCl}}^\infty = \lambda_{\text{H}^+}^\infty + \lambda_{\text{Cl}^-}^\infty = 426.16 \quad \text{--- (2)}$$

$$\lambda_{\text{NaCl}}^\infty = \lambda_{\text{Na}^+}^\infty + \lambda_{\text{Cl}^-}^\infty = 126.45 \quad \text{--- (3)}$$

$$\text{(1) + (2) - (3)}$$

$$= 91.0 + 426.16 - 126.45$$

$$= 390.7 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$$

Q The specific conductivity of a saturated solution of silver chloride is $2.30 \times 10^{-6} \text{ mho cm}^{-1}$ at 25°C . Calculate the solubility of silver chloride at 25°C ? if $\lambda_{\text{Ag}^+} = 61.9 \text{ cmho cm}^2 \text{ mol}^{-1}$ and $\lambda_{\text{Cl}^-} = 76.3 \text{ cmho cm}^2 \text{ mol}^{-1}$

Solⁿ

Let the solubility of AgCl be S gram mole per liter

$$\text{Dilution} = \frac{\text{L} \times \text{L} \times \text{L}}{S}$$

$$\lambda_{\text{AgCl}}^\infty = \lambda_{\text{Ag}^+}^\infty + \lambda_{\text{Cl}^-}^\infty = 61.9 + 76.3 = 138.2 \text{ cmho cm}^2 \text{ mol}^{-1}$$

$$\text{So conductivity} \times \text{dilution} = \lambda_{\text{AgCl}}^\infty = 138.2$$

$$2.30 \times 10^{-6} \times \frac{\text{L} \times \text{L} \times \text{L}}{S} = 138.2$$

$$S = \frac{2.30 \times 10^{-3}}{138.2} = 1.66 \times 10^{-5} \text{ mole per liter}$$

THANK YOU