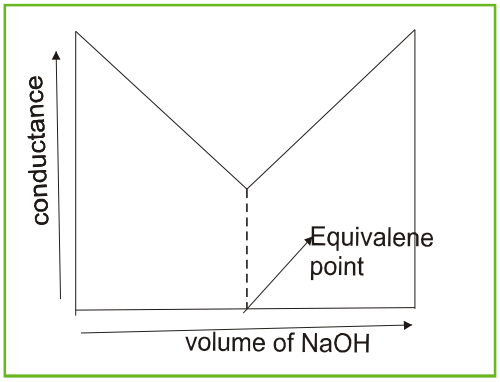
REDOX REACTIONS & ELECTROCHEMISTRY

SYNOPSIS

* **CONDUCTOMETRIC TITRATION**

The electrical conductivity of a solution serves as means of determining the end point in a chemical reaction, involved in the titration of acids and bases or precipitation. The measurment of conductance of resulting solution form an acid and base titration is used to calculate equivalence point if there is a regular change in the conductance and sharp change at equivalence point.

a. Strong acid (HCl) vs strong base (NaOH) (S_A / S_B)



When as drop of NaOH is added to a certain volume of HCl solution taken in a conducivity cell, NaOH reacts with equivalent amount of HCl.

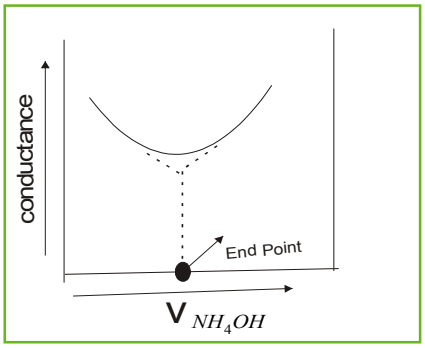
$$NaOH + HCl \rightarrow Na^+Cl^- + H_2O$$

Before NaOH is added the conductance of HCl has a high value due to the presence of highly mobile $H^{\oplus}$ ions. As NaOH is added, $H^{\oplus}$ ions combine with OH^- ions to form undissociated H_2O, and thus faster moving $H^{\oplus}$ ions are replaced by relatively slower moving $Na^{\oplus}$ ions. Hence the conductance of the solution decreases upto equivalence point. The addition of further NaOH increases the conductance due to release of fast moving $OH^{\odot}$ ions.

b. Strong acid (HCl) vs weak base $(NH_4OH)(S_A / S_B)$

On addition of NH_4OH there is replacement of fast moving $H^{\oplus}$ ions by slow moving $NH_4^{\oplus}$ ions as follows.

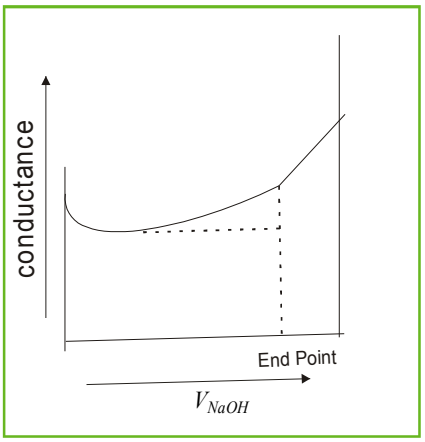
$$H^+Cl^- + NH_4^+OH^- \rightarrow NH_4^+Cl^- + H_2O$$



therefore, the conductance decreases. A slight curvature is noticed near the end point. It is due to the following reaction.

$$NH_4^+ + 2H_2O \rightleftharpoons NH_4OH + H_3O^+$$

c. **Weak acid** (CH_3COOH) **vs strong base** $(NaOH)$

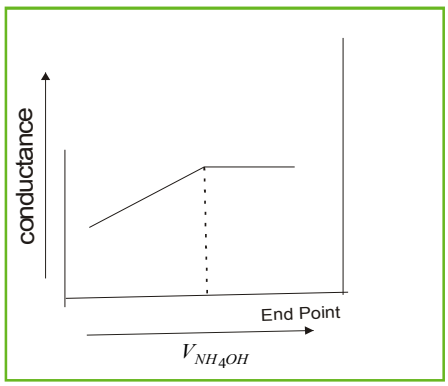


Initially the solution shows poor conductance due to feeble ionization of CH_3COOH. But soon the conductance starts increasing as the

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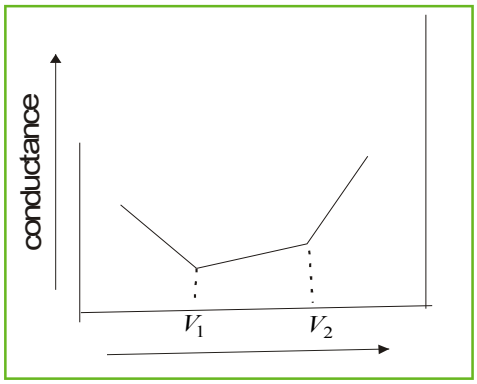
addition of NaOH neutralizes the undissociated HAc to Na^+Ac^- upto equivalence point. The graph near the equivalence point is curved due to the hydrolysis of salt NaAc.

d. Weak acid (CH_3COOH) vs Weak base $(NH_4OH)(W_A/W_B)$



After the equivalence point, conductance virtually remains the same as weak base which is being added is feebly ionized.

e. Mixture of weak and strong acids $(HCl + CH_3COOH)$ vs Strong base $(NaOH)$



In this case, strong acid is first neutralized after that weak acid starts neutralizing. Thus, we have the neutralization reaction in two stages and the curve contains two breaks.

* **CONCENTRATION CELLS**

The cells whose E°_{cell} is zero are called concentration cells. This means that the two compartments (cathode and anode) of the electrochemical cell involve same chemical species but the concentrations of the chemical species in the two compartments are different. The concentration cells are of basically two types. (a) Electrode concentration cells and (b) Electrolyte concentration cells

(a) ELECTRODE CONCENTRATION CELLS

In such cells, two similar electrodes at different concentrations/pressures are dipped in same solution with similar concentration.

Let us have an electrochemical cell represented as

Pt | H_2 (P_1 atm) | H^+ (c M) || H^+ (c M) | H_2 (P_2 atm) | Pt

For the given cell, the reactions occuring are

At cathode : $2H^+_C + 2e^- \longrightarrow H_2(P_2)$

At anode : $H_2(P_1) \longrightarrow 2H^+_A + 2e^-$

Net cell reaction : $H_2(P_1) \longrightarrow H_2(P_2)$

Since the H^+ concentration at the anode and cathode are same, so the net reaction independent of the concentration of the electrolyte. Applying Nernst equation to the net reaction gives.

$$E_{cell}(25^\circ C) = E^\circ_{H^+_C|H_2(P_2)} - E^\circ_{H^+_A|H_2(P_1)} - \frac{0.059}{2}\log\left(\frac{P_2}{P_1}\right)$$

$$E_{cell}(25^\circ C) = E^\circ_{cell} - \frac{0.059}{2}\log\left(\frac{P_2}{P_1}\right)$$

or

$$E_{cell}(25^\circ C) = -\frac{0.059}{2}\log\left(\frac{P_2}{P_1}\right)$$

(since, $E_{cell} = 0$)

$$E_{cell}(25^\circ C) = \frac{0.059}{2}\log\left(\frac{P_1}{P_2}\right)$$

The EMF of the given cell would be positive when $P_1 > P_2$ and the cell reaction would spontaneous.

An other example of the electrode concentration cell is that of an amalgam with two different concentrations of the same metal dipped in same electrolyte solution.

The cell is represented as

Hg - Pb (c_1 M) | $PbSO_4$ (c M) | Hg - Pb (c_2 M)

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The reactions for the given cell are

At cathode :

$$Pb^{2+}(c) + 2e^- \longrightarrow Pb(c_2)$$

At anode :

$$Pb(c_1) \longrightarrow Pb^{2+}(c) + 2e^-$$

Net cell reaction : $Pb(c_1) \longrightarrow Pb(c_2)$

Since, the concentration of Pb^{2+} for the two half cells is same as the electrolyte solution for the two compartments is same, so the net reaction is independent of the electrolyte concentration.

Applying Nernst equation to the net cell reaction gives

$$E_{cell}(25^\circ C) = E^\circ_{Pb^{2+}(c)|Pb(c_2)} - E^\circ_{Pb^{2+}(c)|Pb(c_1)} - \frac{0.059}{2}\log\frac{c_2}{c_1}$$

$$E_{cell}(25^\circ C) = E^\circ_{cell} - \frac{0.059}{2}\log\frac{c_2}{c_1}$$

$$E_{cell}(25^0 C) = -\frac{0.059}{2}\log\frac{c_2}{c_1}$$

(since, $E^\circ_{cell} = 0$)

$$E_{cell}(25^0 C) = \frac{0.059}{2}\log\frac{c_1}{c_2}$$

The net cell reaction would be spontaneous, when the EMF of the cell is positive, which is possible only when $c_1 > c_2$.

(b) ELECTROLYTE CONCENTRATION CELLS

In such cells, two electrodes of the same metal are dipped in solutions of metal ions of different concentrations. Let us have an electrochemical cell represented as

Pt | H_2 (P atm) | HA (c_1 M) || HB (c_2 M) | H_2 (P atm) | Pt

In such cells, HA and HB would represent strong acids, if their K_a's are not given while they would be weak acids, if their K_a's are mentioned.

For the given cell, the reactions occuring are

At cathode :

$$2H^+_c(c_2) + 2e^- \longrightarrow H_2(P)$$

At anode :

$$H_2(P) \longrightarrow 2H^+_A(c_1) + 2e^-$$

Net cell reaction : $\underset{(C_2)}{2H^+_c} \longrightarrow \underset{(C_1)}{2H^+_A}(n=2)$

The net cell reaction is independent of the pressure terms as the pressure of H_2 in the two half cells is same.

Applying Nernst equation to the net cell reaction gives

$$E_{cell}(25^\circ C) = E^\circ_{H^+_c|H_2} - E^\circ_{H^+_A|H_2} - \frac{0.059}{1}\log\frac{[H^+_A]}{[H^+_C]} =$$

$$= E^\circ_{cell} - 0.059\log\frac{c_1}{c_2}$$

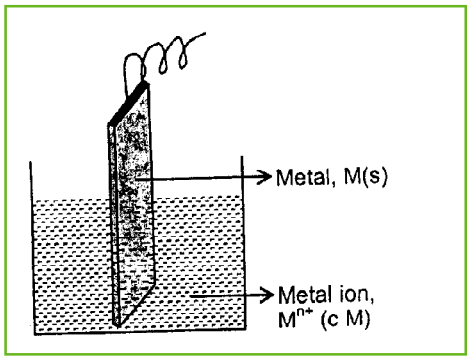
$$E_{cell}(25^\circ C) = 0.059\log\frac{c_1}{c_2} \quad (\text{since } E^\circ_{cell} = 0)$$

The net cell reaction would be feasible spontaneously only when the EMF of the cell is positive, which is possible only when concentration of H^+ in cathode compartment (c_2) is greater than the concentration of H^+ in anode compartment (c_1).

OTHER HALF CELLS

(a) METAL-METAL ION HALF-CELL

In this type of half-cell, the metal rod is dipped in a solution of the corresponding metal ion having concentration c M. The assembly is shown in figure.



Metal-metal ion half-cell

The representation of the half-cell when functions as anode can be represented as

M(s) | M^{n+} (c M)

The anodic half-cell reaction is

$M(s) \longrightarrow M^{n+}(aq) + ne^-$

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The representation of the half-cell when it functions as cathode is

M^{n+} (c M) | M (s)

The cathodic half-cell reaction is

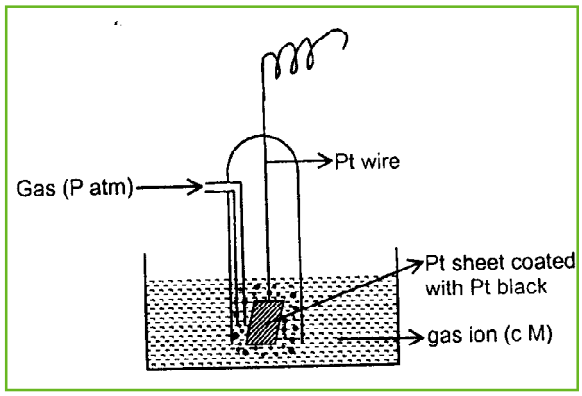
$M^{n+}(aq) + ne^- \longrightarrow M(s)$

Examples of this type of half-cell when used as cathode are Cu^{2+} | Cu, Zn^{2+} | Zn, Ag^+ | Ag, Sn^{2+} | Sn etc. The half-cells or electrodes used in Daniel cell are of the metal-metal ion type.

For such type of half-cells, very active metals cannot be used, because they react with water. For such highly reactive metals, an amalgam of the metal in mercury is used instead of pure metal.

(b) GAS-GAS ION HALF-CELL

In a gas-gas ion half-cell, a gas is bubbled into a solution of the gas ion, with a platinum rod having a sheet coated with platinum black being dipped in the gas ion solution. Platinum is used for making electrical contact because the gases are non-conducting and the platinum do not react with gas ions as it is an unreactive metal. Platinum black is used over the platinum sheet, which gives it a large surface area for the adsorption of gases. The half-cell assembly is shown in figure.



Gas-gas ion half-cell

The given half-cell when function as anode can be represented as

Pt | Gas (P atm) | Gas ion (c M).

Let us consider a hydrogen gas half-cell, functioning as anode. It is represented as

Pt | H_2 (P atm) | H^+ (c M)

and the anodic half-cell reaction is

H_2 (Pt) $\longrightarrow$ $2H^+(aq) + 2e^-$ (Pt).

The chlorine gas half-cell when functions as anode can be represented as

Pt | Cl_2 (P atm) | Cl^- (c M)

and the anodic half-cell reaction is

$2Cl^- \longrightarrow Cl_2 + 2e^-$

The oxygen gas half-cell when functions as anode can be represented as

Pt | O_2 (P atm) | OH^- (c M)

and the anodic half-cell reaction is

$$2OH^- \longrightarrow \frac{1}{2}O_2 + H_2O + 2e^-$$

The gas-gas ion half-cell when functions as cathode can be represented as

Gas ion (c M) | Gas (P atm) | Pt.

Let us consider a hydrogen half-cell, functioning as cathode. It is represented as

H^+ (c M) | H_2 (P atm) | Pt

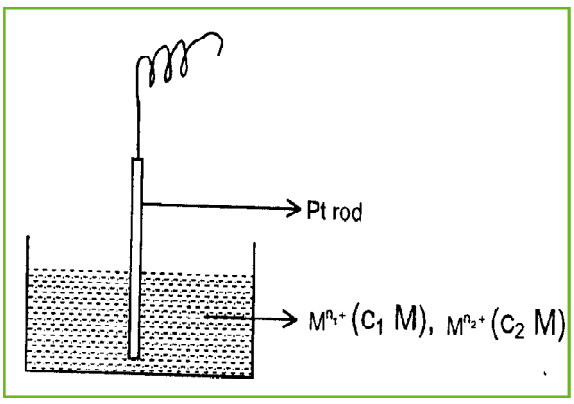
and the cathodic half-cell reaction is

$2H^+(aq) + 2e^-$ (Pt) $\longrightarrow$ H_2 (Pt).

The hydrogen electrode is called standard hydrogen electrode when the concentration of H^+ ion is 1 M and the pressure of H_2 gas is 1 atm. The standard hydrogen electrode (SHE) functions as reference electrode and is used for the measurement of standard reduction potentials of other half-cells or couples. The standard reduction potential values obtained in this manner are arranged in the decreasing order to give electrochemical series.

(c) REDOX HALF-CELL

In redox half-cell, a platinum rod is dipped in a solution containing two different oxidation states of a metal ion ($M^{n_1^+}$ and $M^{n_2^+}$, where n_2 is greater than n_1). The half-cell assembly is shown in figure.



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Redox half-cell

The given half-cell when functions as anode can be represented as

$Pt \mid M^{n_1^+}(c_1\ M),\quad M^{n_2^+}(c_2\ M)$

and the anodic half-cell reaction is

$$M^{n_1^+} \longrightarrow M^{n_2^+} + (n_2 - n_1)e^-$$

The redox half-cell when functions as cathode can be represented as

$M^{n_2^+}(c_2\ M), M^{n_1^+}(c_1\ M) \mid Pt$

and the cathodic half-cell reaction is

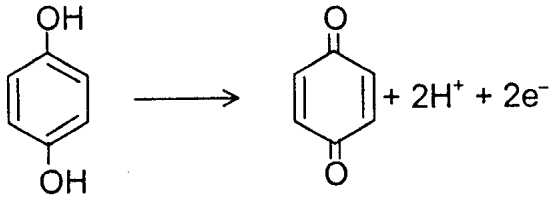
$$M^{n_2^+} + (n_2 - n_1)e^- \longrightarrow M^{n_1^+}$$

Examples of this type of half-cell when used as anode are $Pt \mid Cr^{2+}(c_1\ M), Cr^{3+}(c_2\ M)$; $Pt \mid Fe^{2+}(c_1\ M), Fe^{3+}(c_2\ M)$; $Pt \mid Sn^{2+}(c_1\ M), Sn^{4+}(c_2\ M)$ etc. In such half-cells, the oxidising and reducing agents are both metal ions.

Redox half-cell can also be made with organic molecules that can exist in two different oxidation states. A couple of hydroquinone (QH_2) and quinone (Q) forms a redox half-cell. Its representation, when it functions as anode is

$Pt \mid QH_2\ (1\ M), Q(1\ M), H^+\ (c\ M)$

and the anodic half-cell reaction is

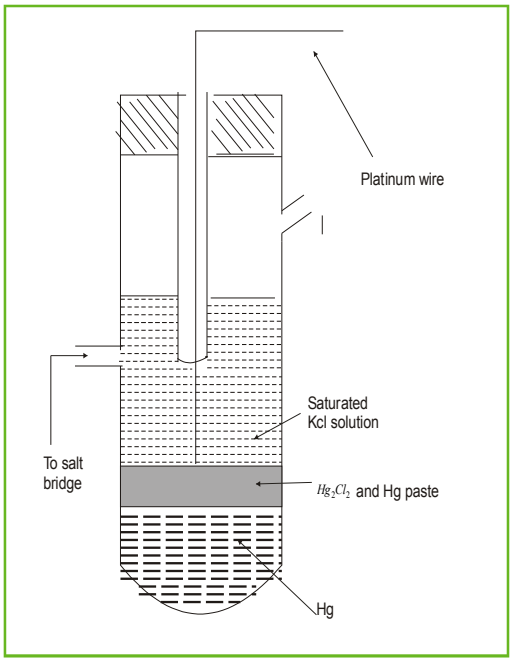


or $QH_2 \longrightarrow Q + 2H^+ + 2e^-$.

This redox electrode having organic molecules is called quinhydrone electrode because of the charged complex formed between quinone and hydroquinone.

d. Calomel electrode:

A calomel electrode consists of Hg covered with Hg_2Cl_2 (mercurous chloride) (calomel) in contact with a solution of KCl.



Electrode representation: $Hg(l)$, $Hg_2Cl_2(s) \mid Cl^{\Theta}(aq)$

Anode reaction:

$$E_{cell} = E^{\Theta}_{cell} - \frac{0.059}{2}\log\frac{1}{\left[Cl^{\Theta}\right]^2}$$

Cathode reaction:

$$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^{\Theta}(aq)$$

$$E_{cell} = E^{\Theta}_{cell} - \frac{0.059}{2}\log\left[Cl^{\Theta}\right]^2$$

Three types of calomel electrodes generally used are:

(i) Most common calomel electrode is the standard calomel electrode (SCE) is which the concentration of KCl is at its saturation (about 3.5M).

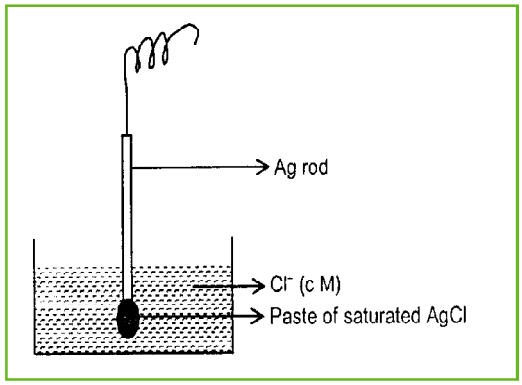
(ii) Normal calomel electrode (NCE) in which 1.0 N KCl is used $\left(E_{NCE} = 0.268V\right)$

(iii) Decinormal calomel electrode in which 0.1 N KCl is used $\left(E_{DNCE} = 0.338V\right)$.

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(e). METAL - INSOLUBLE METAL SALT - ANION HALF-CELL

Let us take an example of such a half-cell, which functions as cathode, as Cl^- (c M) | AgCl | Ag. The assembly of this half-cell is made by dipping a rod of silver coated with a paste of saturated AgCl at the bottom, in a solution of ionic electrolyte like KCl, NaCl or HCl. The cation part in the electrolyte must have standard reduction potential less than the standard reduction potential of the cation of the metal salt. The half-cell assembly is shown is figure.



Metal-insoluble metal salt-anion half-cell

The cathodic half-cell reaction is

$$AgCl(s) \rightleftharpoons Ag^+ + Cl^- \quad ...(i)$$

$$Ag^+ + e^- \longrightarrow Ag(s) \quad ...(ii)$$

Net half-cell reaction:

$$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^- \quad ...(iii)$$

Applying Nernst equation to the net half-cell reaction, gives

$$E_{Cl^-|AgCl|Ag} = E^o_{Cl^-|AgCl|Ag} - \frac{RT}{F}\ln[Cl^-] \quad ...(i)$$

(AgCl and Ag not appear in the expression as they are pure solids).

Now, if we are given $E^o_{Ag^+|Ag}$, concentration of Cl^- and K_{sp} of AgCl, how can we calculate the half-cell potential $\left(E_{Cl^-|AgCl|Ag}\right)$ for the reaction, $AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-$. In Nernst equation, can $E^o_{Ag^+|Ag}$, be replaced for $E^o_{Cl^-|AgCl|Ag}$. Let us see

$$AgCl(s) \rightleftharpoons Ag^+ + Cl^-;$$

$$\Delta G^o_1 = -RT \ln K_{sp}$$

$$Ag^+ + e^- \longrightarrow Ag(s);$$

$$\Delta G^o_2 = -FE^o_{Ag^+|Ag}$$

$$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-;$$

$$\Delta G^o_3 = -FE^o_{Cl^-|AgCl|Ag}$$

It is evident that ΔG^o_2 is not equal to ΔG^o_3 as ΔG^o_1 is not zero. Thus, $E^o_{Ag^+|Ag}$, is not equal to $E^o_{Cl^-|AgCl|Ag}$ and we cannot replace $E^o_{Cl^-|AgCl|Ag}$ by $E^o_{Ag^+|Ag}$.

But using Hess's law; we can calculate $E^o_{Cl^-|AgCl|Ag}$ as

$$\Delta G^o_1 + \Delta G^o_2 = \Delta G^o_3$$

$$-RT\ln K_{sp} - FE^o_{Ag^+|Ag} = -FE^o_{Cl^-|AgCl|Ag}$$

Dividing this equal by - F,

$$\frac{RT}{F}\ln K_{sp} + E^o_{Ag^+|Ag} = E^o_{Cl^-|AgCl|Ag}$$

Substituting the value of $E^o_{Cl^-|AgCl|Ag}$ in equation (i) gives

$$\therefore E_{Cl^-|AgCl|Ag} = E^o_{Ag^+|Ag} + \frac{RT}{F}\ln K_{sp} - \frac{RT}{F}\ln[Cl^-]$$

$$E_{Cl^-|AgCl|Ag} = E^o_{Ag^+|Ag} - \frac{RT}{F}\ln\frac{[Cl^-]}{K_{sp}}$$

Since, $E^o_{Ag^+|Ag}$, concentation of Cl^- and K_{sp} of AgCl are given, the reduction potential $\left(E_{Cl^-|AgCl|Ag}\right)$ for the reaction, $AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-$ can be calculated

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* **APPLICATIONS OF EMF MEASUREMENTS**
(Determination of Solubility of a Sparingly soluble salt, pH of solution etc.)
Electromotive Force

Potential difference is the difference in electric potential (electrical pressure) between two points. You measure this quantity in volts. The volt, V, is the SI unit of potential difference.

The electrical work expended in moving a charge though a conductor is

Electrical work = charge × potential difference

Corresponding SI units for the terms in this equation are

Joules = coulombs × volts

The Faraday constant, F is the magnitude of charge on one mole of electrons; it equals 9.65×10^4 C (96,500 coulombs). The faraday is a unit of charge equal to 9.65×10^4C. In moving this quantity of charge (one faraday of charge) from one electrode to another, the numerical value of the work done by a voltaic cell is the product of the faraday constant F times the potential difference between the electrodes. The work w is the negative of this, because the voltaic cell loses energy as itdoes work on the surroundings.

w = – F × potential difference.

In the normal operation of a voltaic cell, the potential difference (voltage) across the electrodes is less than the maximum possible voltage of the cell. One reason for this is that it takes energy or work to drive a current through the cell itself. The decrease in cell voltage as current is drawn reflects this energy expenditure within the cell; and the greater the current, the lower the voltage. Thus, the cell voltage has its maximum value only when no current flows. The situation is analogous to measuring the difference between the pressure of water in a faucet and that of the outside atmosphere. The maximum potential difference between the electrodes of a voltaic cell is referred to as the electromotive force (emf) of the cell, or E_{cell}.

We can now write an expression for the maximum work obtainable from a voltaic cell. Let n be the number of electrons transferred in the overall cell equation. The maximum electrical work of a voltaic cell for molar amounts of reactants (according to the cell equation as written) is

$W_{max} = -nFE_{cell}$

Here E_{cell} is the cell emf, and F is the Faraday constant, 9.65×10^4C

* **Thermodynamics of the Cells**

The e.m.f. of the cell is related to free energy by equation(1) i.e.

$$\Delta G = -nFE \quad \ldots(1)$$

$$\text{Now} \left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S$$

$$\text{So} \left(\frac{\partial \Delta G}{\partial T}\right)_P = -nF\left(\frac{\partial E}{\partial T}\right)_P = -\Delta S$$

$$\text{or } \Delta S = nF\left(\frac{\partial E}{\partial T}\right)_P \quad \ldots(2)$$

The enthalpy of the cell reaction will be

…(3)

The thermodynamic quantities of the cell reaction can be calculated by equations (1), (2) and (3) provided one knows the emf of cell and its dependence on temperature.

The heat effects in the system can be calculated as follows. If the process is irreversible (i.e. by mixing the reactants together), heat flow to the system can be given by the reaction $\Delta H = Q_P$. If the process is reversible the heat flow to system is given by $Q_P = T\Delta S$.

Condition of Equilibrium ($E_{cell} = 0.0V$)

When $E_{cell} = 0.0V$, i.e., no potential difference is obtained between the terminals of cell (battery), the cell reaction in such a state is said to be in equilibrium. So in such cases,

When $E_{cell} = Q = K_{eq}$ = equilibrium constant.

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{n}\log Q$$

$$0.0 = E^\circ_{cell} - \frac{0.059}{n}\log K_{eq}$$

$$E^\circ_{cell} = \frac{0.059}{n}\log K_{eq}$$

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Solubility Product

The solubility product of sparingly soluble salt MX can be discussed in terms of the equilibrium of the kind

$$MX_{(s)} \rightleftharpoons M^{+}_{(aq)} + X^{-}_{(aq)}$$

Since the activity of the pure solid is always unity, the equilibrium constant of the solubility product can be written.

$$K_{sp} = a_{M^+} a_{x^-} \quad \ldots(1)$$

When the solubility of the salt is very small, the solution is ideal and thus $a_1 = c_1$ of ions. The equation (1) can be written as

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_{M^+} a_{X^{-1}}}{a_{MX}}$$

Under equilibrium conditions the emf of the cell will be zero i.e., E = 0 and also the activity of pure solid is unity. Further the above equation at 25°C can be written as

$$\log K_{sp} = \frac{E^0 . n}{0.0591} \quad \ldots(2)$$

The solubility product thus can be calculated from the standard emf of one cell, formed in such a way that the final reaction is the type given above

LEVEL - IV

SINGLE ANSWER QUESTIONS

1. **For the reaction, $4Al(s) + 3O_2(g) + 6H_2O + 4OH^- \longrightarrow 4[Al(OH)_4]^-$; $E^\circ_{cell} = 2.73V$. If $\Delta G^\circ_f(OH^-) = -157 kJ mol^{-1}$ and $\Delta G^\circ_f(H_2O) = -237.2 kJ mol^{-1}$, determine $\Delta G^\circ_f(Al(OH)_4^-)$.**

(A) 1.30×10^3 kJ mol^{-1}
(B) -1.30×10^3 kJ mol^{-1}
(C) 3.30×10^3 kJ mol^{-1}
(D) -3.30×10^3 kJ mol^{-1}

2. **Calculate the EMF of the electrode concentration cell**
Hg-Zn (c_1 M) | Zn^{2+} (c M) | Hg-Zn (c_2 M) at 25°C, if the concentration of the zinc amalgam are 2 g per 100 g of mercury and 1 g per 100 g of mercury in anode and cathode half-cell respectively.

(A) 6.8×10^{-2} V (B) 8.8×10^{-3} V
(C) 5.7×10^{-2} V (D) 7.8×10^{-3} V

3. **The emf of a cell corresponding to the reaction,**

$$Zn + 2H^+(aq) \rightarrow Zn^{2+}(0.1M) + H_2(g)1atm$$

is 0.28 volt at $25^0 C$. Calculate the pH of the solution at the hydrogen electrode $E^0_{Zn^{2+}/Zn} = -0.76$ volt and $E^0_{H^+/H_2} = 0$

(A) 7.62 (B) 8.62 (C) 7.5 (D) 9.62

4. **The electrical resistance of a column of 0.05 mol L^{-1} NaOH solution of diameter 1 cm and length 50 cm is 5.55×10^3 Ω. Its resistivity, conductivity and molar conductivity.**

(A) 87.135 Ω, 0.01148 S cm^{-1}, 229.6 S cm^2 mol^{-1}
(B) 77.123 Ω, 0.241 S cm^{-1},119.5 S cm^2 mol^{-1}
(C) 92.29 Ω, 0.124 S cm^{-1}, 272.3 S cm^2 mol^{-1}
(D) 83.92 Ω, 0.1192 S cm^{-1},220.3 S cm^2 mol^{-1}

5. **A silver electrode is immersed in saturated $Ag_2SO_4(aq)$. The potential difference between silver and the standard hydrogen electrode is found to be 0.711 V. Calculate $K_{sp}(Ag_2SO_4)$.**

$$\left[\text{Given } E^0_{Ag^+/Ag} = 0.799V\right]$$

(A) 1.7×10^{-5} (B) 1.7×10^{-4}
(C) 2.7×10^{-5} (D) 2.7×10^{-4}

6. **The specific conductivity of $AgCl(aq)$ at $25^0 C$ is 1.26×10^{-6} and ionic conductivity of $Ag^+(aq)$ and $Cl^-(aq)$ at infinite dilution are $62 S cm^2 mol^{-1}$ and $76 S cm^2 mol^{-1}$ respectively. Then the solubility product of AgCl at $25^0 C$**

(A) 8.3×10^{-11} (B) 8.3×10^{-10}
(C) 9.3×10^{-10} (D) 9.3×10^{-11}

7. **The equivalent conductance of 0.10 N solution of $MgCl_2$ is 97.1 mho cm^2 equi^{-1} at 25°C. a cell with electrode that are 1.5 cm^2 in surface area and 0.5 cm apart is filled with 0.1 N $MgCl_2$ solution. How much current will flow when potential difference between the electrodes is 5 volt.**

(A)0.1432 ampere (B) 0.214 ampere
(C) 0.321 ampere (D) 0.1456 ampere

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8. **An aqueous solution containing Na^+, Sn^{2+}, Cl^- & SO_4^{2-} ions, all at unit concentration, is electrolysed between a silver anode and a platinum cathode. What changes occur at the electrodes when current is passed through the cell ? Given :** $E^\circ_{Ag^+|Ag} = 0.799\ V$

$E^\circ_{Sn^{2+}|Sn} = -0.14\ V, E^\circ_{Cl_2|Cl^-} = 1.36\ V, E^\circ_{S_2O_8^{2-}|SO_4^{2-}} = 2V, E^\circ_{Sn^{4+}|Sn^{2+}} = 0.13\ V$

(A) Sn^{2+} is reduced and Cl^- is oxidized.
(B) Ag is oxidized and Sn^{2+} is reduced.
(C) Sn^{2+} is reduced and Sn^{2+} is oxidized.
(D) H^+ is reduced and Sn^{2+} is oxidized.

9. **A galvanic cell consists of two hydrogen electrodes. One is in a** $1.0\,M\ H^+$ **solution and other in a solution of unknown pH. The cell potential is 0.025V. The unknown pH is**
(A) 0.52 (B) 0.62 (C) 0.42 (D) 0.82

10. **100 mL of a buffer of 1 M** NH_3 **and 1 M** NH_4^+ **are placed in two voltaic cells separately. A current of 1.5 A is passed through both cells for 20 minutes. If electrolysis of water only takes place,**

$2H_2O + O_2 + 4e^- \longrightarrow 4OH^-$ (R.H.S.)

$2H_2O \longrightarrow 4H^+ + O_2 + 4e^-$ (L.H.S.)

then the pH of the
(A) half-cell on L.H.S. will increase
(B) half-cell on R.H.S. will increase
(C) Both the half-cells will increase
(D) Both the half-cells will decrease

11. **An acidic solution of Cu^{2+} salt containing 0.4 g of Cu^{2+} is electrolysed until all the copper is deposited. The electrolysis is continued for seven more minutes with the volume of solution kept at 100 ml and the current at 1.2 amp. Find the volume of gases evolved at NTP during the entire electrolysis.**
(A) 78.20 ml, 99.78 ml
(B) 58.48 ml, 78.20 ml
(C) 99.23ml, 58.46 ml
(D) 78.20 ml, 58.48 ml

12. **Copper sulphate solution (250 ml) was electrolysed using a platinum anode and a copper cathode. A constant current of 2 mA was passed for 16 minutes . It was found that after electrolysis, the absorbance of the solution was reduced to 50% of its original value. Find the concentration of copper sulphate in the solution to begin with.**
(A) 7.95×10^{-5} M (B) 6.23×10^{-4} M
(C) 0.25×10^{-6} M (D) 5.32×10^{-5} M

13. **Use the Standard Reduction Potentials given below to calculate** K_f **for** $Zn(NH_3)_4^{2+}$ **at** $25^0 C$ **.**

$Zn^{2+}(aq) + 4NH_3(aq) \rightleftharpoons Zn(NH_3)_4^{2+}(aq)$

$Zn(NH_3)_4^{2+} + 2e^- \rightleftharpoons Zn(s) + 4NH_3(aq);\quad E^0 = -1.04V$

$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s);\quad E^0 = -0.76V$

(A) 6×10^{18} (B) 3×10^{9}
(C) 2×10^{6} (D) 3×10^{-9}

14. **The charge required for the oxidation of one mole** Mn_3O_4 **into** MnO_4^{2-} **in presence of alkaline medium is**
(A) 5 × 96500 C (B) 96500 C
(C) 10 × 96500 C (D) 2 × 96500 C

15. **The equilibrium constant for the reaction Sr(s) + Mg^{+2} (aq) → Sr^{+2} (aq) + Mg(s) is 2.69×10^{12} at 25°C. The E° for a cell made up of the Sr/Sr^{+2} and Mg^{+2}/Mg half cells**
(A) 0.3667 V (B) 0.7346 V
(C) 0.1836 V (D) 0.1349 V

16. **For the fuel cell reaction $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$;** $\Delta_f H^\circ_{298}(H_2O, l) = -285.5$ **kJ/mol**

What is ΔS°_{298} **for the given fuel cell reaction?**
Given: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$
E° = 1.23 V
(A) – 0.322 J/K (B) – 0.635 kJ/K
(C) 3.51 kJ/K (D) – 0.322 kJ/K

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17. **Equivalent conductance of 0.1 M HA(weak acid) solution is 10 $Scm^2 equivalent^{-1}$ and that at infinite dilution is 200 $S\ cm^2\ equivalent^{-1}$ Hence pH of HA solution is**
(A) 1.3 (B) 1.7 (C) 2.3 (D) 3.7

18. **The dissociation constant of n-butyric acid is 1.6×10^{-5} and the molar conductivity at infinite dilution is $380 \times 10^{-4}\ Sm^2mol^{-1}$. The specific conductance of the 0.01 M acid solution is**
(A) $1.52 \times 10^{-5}\ Sm^{-1}$
(B) $1.52 \times 10^{-2}\ Sm^{-1}$
(C) $1.52 \times 10^{-3}\ Sm^{-1}$
(D) $1.52 \times 10^{-4}\ S_m^{-1}$

19. **The conductivity of a saturated solution of Ag_3PO_4 is $9 \times 10^{-6}\ S\ m^{-1}$ and its equivalent conductance is $1.50 \times 10^{-4}\ S \times m^2$ $equivalent^{-1}$. The K_{sp} of Ag_3PO_4 is**
(A) 4.32×10^{-18} (B) 1.8×10^{-9}
(C) 8.64×10^{-13} (D) 4.32×10^{-13}

20. **In the Hall's process, aluminum is produced by the electrolysis of molten Al_2O_3 by the following reactions. How many seconds would it take to produce enough aluminum by the Hall's process to make a case of 24 cans of aluminum soft-drink, if each can uses 5.0 g of Al, a current of 9650 amp is employed, and the current efficiency of the cell is 90.0%:**
(A) 203.2 (B) 148.14
(C) 333 (D) 6.17

21. **How much electricity in terms of Faraday is required to produce 20g of Ca from molten $CaCl_2$?**
(A) 1.5 (B) 2 (C) 1 (D) 4

22. **For a cell reaction**
$2H_2(g)+O_2(g) \rightarrow 2H_2O(l)\ \Delta_r S^0_{298} = -0.32 kJ/K.$
What is the value of
$\Delta_f H^0_{298}(H_2O,l)$? **Given :**
$O_2(g)+4H^+(aq)+4e^- \rightarrow 2H_2O(l); E^0 = 1.23V$
(A) $-285.07\ kJ/mol$
(B) $-570.14 kJ/mol$
(C) $285.07 kJ/mol$
(D) $+570.14 KJ/mol$

23. **Determine the potential of the following cell:**
$Pt\left|H_2(g,0.1bar)\right|$
$H^+(aq,10^{-3}M)\left|MnO_4^-(aq,0.1M)\right.$
$Mn^{2+}(aq,0.01M), H^+(aq,0.01M)\,Pt$
Give : $E^0_{MnO^-_4 Mn^{2+}} = 1.51V$
(A) $1.54V$ (B) $1.48V$
(C) $1.84V$ (D) $1.68V$

24. **The chlorate ion can disproportionate in basic solution according to reaction,**
$2ClO_3^- \rightleftharpoons ClO_2^- + ClO_4^-$
What is the equilibrium concentration of perchlorate ions from a solution initially at 0.1 M in chlorate ions at 298 K?
Given :
$E^0_{ClO_4^- ClO_3^-} = 0.36V\ and\ E^0_{ClO_3^-|ClO_2^-} = 0.33V\ at\ 298K$
(A) 0.019M (B) 0.024 M
(C) 0.1 M (D) 0.19 M

25. **Given the cell :**
$Cd(s)\left|Cd(OH)_2\right|(s)\left|NaOH(aq,0.01M)\right|$
$H_2(g,1bar)\,Pt(s)\left|\right.$
with
$E_{cell} = 0.0V.\ If\ E^0_{Cd^{2+}|Cd} = -0.39V, then\ K_{sp}\ of\ Cd(OH_2)\ is:$
(A) 0.1 (B) 10^{-13} (C) 10^{-15} (D) 10^{-18}

26. **Caluculate the e.m.f. (in V) of the cell :**
$Pt\left|H_2(g)\right|BOH(aq)\left|HA(aq)\right|H_2(g)\left|Pt;\right.$
$0.1bar \quad 0.1M \qquad 0.1M \qquad 1bar$
Given : $K_a(HA) = 10^{-7}, K_b(BOH) = 10^{-5}$
(A) 0.39 V (B) 0.36 V
(C) 0.93 V (D) $0.63V$

27. **Given the following molar conductivities at ,**
$25^0C,\ HCl, 426\Omega^{-1}\ cm^2mol^{-1};$
$NaCl, 126\Omega^{-1}cm^2mol^{-1}$
NaC **(sodium crotonate),** $83\Omega^{-1}cm^2mol^{-1}$.
What is the ionization constant of crotonic acid? If the conductivity of a 0.001 M crotonic acid solution is $3.83 \times 10^{-5}\Omega^{-1}cm^{-1}$?
(A) 10^{-5} (B) 1.11×10^{-5}
(C) 1.11×10^{-4} (D) 0.01

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28. **The conductivity of $0.001M$ Na_2SO_4 solution is $2.6\times10^{-4}\ Scm^{-1}$ and increases to $7.0\times x10^{-4}\ Scm^{-1}$, when the solution is saturated with $CaSO_4$, The molar conductivities of Na^+ and Ca^{2+} are 50 and 120 Scm^2mol^{-1}, respectively, Neglect conductivity of used water. What is the solubility product of $CaSO_4$?**

(A) 4×10^{-6} (B) 1.57×10^{-3}
(C) 4×10^{-4} (D) 2.46×10^{-6}

29. **Use the following E^0 for the electrode potentials, calculate ΔG^0 in kJ for the indicated reaction:**

$$5Ce^{4+}(aq)+Mn^{2+}(aq)+4H_2O(l)$$
$$\rightarrow 5Ce^{3+}(aq)+MnO_4^-(aq)+8H^+(aq)$$
$$MnO_4^-(aq)+8H^+(aq)+5e^-$$
$$\rightarrow Mn^{2+}(aq)+4H_2O(l);\ E^0=+1.51V$$
$$Ce^{+4}+e^-\rightarrow Ce^{+3}\ E^0=+1.61V$$

(A) –9.65 (B) –24.3
(C) –48.25 (D) –35.2

30. **Assuming that hydrogen behaves as an ideal gas, calculate EMF of the cell at 25^0C when $P_1=640mm$ and $P_2=425mm$**

$$Pt\,|\,H_2(P_1)\,|\,HCl\,|\,H_2(P_2)\,|\,Pt$$

(A) 0.005 V (B) 0.004 V
(C) 0.003 V (D) 0.002 V

31. **The emf of the cell: $H_2(g)$ |Buffer||Normal calomel electrode is 0.6885 V at 25^0C, when barometric pressure is 760 mm. What is the pH of the buffer solution?** $E_{calomel}=0.28V$

(A) 9.92 (B) 7.92 (C) 8.92 (D) 6.92

MULTI ANSWER QUESTIONS

32. **Electrode potential data are given below**

$Fe^{3+}(aq)+e^-\longrightarrow Fe^{2+}(aq);\ E^o=+0.77V$

$Al^{3+}(aq)+3e^-\longrightarrow Al(s);\ E^o=-1.66V$

$Br_2(aq)+2e^-\longrightarrow Br^-(aq);\ E^o=+1.08V$

Based on the given data which statement/s is/are true?

(A) Fe^{2+} is stronger reducing agent than Br^-
(B) Fe^{2+} is stronger reducing agent than Al
(C) Al is stronger reducing agent than Fe^{2+}
(D) Br^- is stronger reducing agent than Al

33. **We observe blue colour if :**

(A) Cu electrode is placed in the $AgNO_3$ solution
(B) Cu electrode is placed in the $ZnSO_4$
(C) Cu electrode is placed in the dil HNO_3
(D) Cu electrode is placed in the $NiSO_4$

34. **For a strong electrolyte, equivalent conductance increases slowly with dilution and can be expressed by the relationship $\Lambda_m=\Lambda_m^0-A\sqrt{C}$. Where A is a constant. Which electrolyte(s) have same value of the constant A?**

(A) $NaCl$ (B) $CaCl_2$
(C) $ZnCl_2$ (D) $MgSO_4$

35. **Equal quantity of electricity is passed through three electrolytic cells containing aqueous solutions of $FeSO_4$, $Fe_2(SO_4)_3$ and $Fe(NO_3)_3$. Regarding the electrolytic process which of the following is/ are correct, assuming at cathode only iron is reduced.**

(A) The amount of iron deposited in three cases is equal
(B) The amount of iron deposited in $Fe_2(SO_4)_3$ and $Fe(NO_3)_3$ is equal
(C) Same gas is evolved at anode in all three electrolytic processes
(D) Amount of iron deposited in $Fe_2(SO_4)_3$ is double to that of iron deposited in case of $Fe(NO_3)_3$

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36. **Select the wrong relations**

(A) $\Delta S = \left(\frac{\partial E}{\partial T}\right)_P \times nF$

(B) $-\Delta S = \left(\frac{\partial E}{\partial T}\right)_P \times nF$

(C) $\left(\frac{\partial E}{\partial T}\right)_P = \left(\frac{\partial \Delta S}{\partial T}\right)$

(D) $\left(\frac{\partial E}{\partial T}\right)_P = \frac{\Delta H + nEF}{T}$

37. **In which of the following salt bridge is not needed**

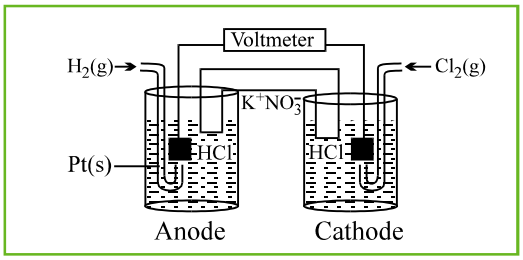
(A) $Pb \mid PbSO_{4(s)} \mid H_2SO_4 \mid PbO_{2(s)} \mid Pb$

(B) $Cd \mid CdO_{(s)} \mid KOH_{aq} \mid NiO_{2(s)} \mid Ni$

(C) $Fe_{(s)} \mid FeO_{(s)} \mid KOH_{aq}, Ni_2O_{3(s)} \mid Ni$

(D) $Zn \mid ZnSO_4 \mid CuSO_4 \mid Cu$

38. **Consider the following Galvanic cell.**



By what value the cell voltage change when concentration of ions in anodic and cathodic compartments both increased by factor of 10 at 298 K

(A) +0.0591 (B) –0.0591

(C) –0.1182 (D) 0

39. **The specific conductivity of a saturated solution of AgCl is** $3.4\times10^{-6} Scm^{-1}$ **at** 25^0C. **If** $\lambda\left(Ag^+\right) = 62.3 Scm^2 mol^{-1}$, $\lambda\left(Cl^-\right) = 67.7 Scm^2 mol^{-1}$, **solubility of AgCl at** 25^0C **is**

(A) $2.6\times10^{-5} M$ (B) $3.73\times10^{-3} g/L$

(C) $3.7\times10^{-5} M$ (D) $2.6\times10^{-3} g/L$

COMPREHENSION QUESTIONS

COMPREHENSIONS - 1

E°_{RP} **and their respective half reactions for some change are given below:**

i) $Mn^{7+}(aq) + 8H^+ + 5e \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$; $E^\circ = +1.52V$

ii) $Mn^{7+}(aq) + 4H^+ + 3e \longrightarrow MnO_2(s) + 2H_2O(l)$; $E^\circ = +2.26V$

iii) $Mn^{7+}(aq) + 2e \longrightarrow Mn^{5+}(aq)$; $E^\circ = +0.56$ V (acid med.)

iv) $Mn^{3+} + e \longrightarrow Mn^{2+}$; $E^\circ = +1.51$ V (acid med.)

v) $Mn^{4+} + e \longrightarrow Mn^{3+}$; $E^\circ = +0.95$ V (acid med.)

40. **The most stable oxidation state of Mn is:**

(A) Mn^{4+} (B) Mn^{2+} (C) Mn^{7+} (D) Mn^{6+}

41. **Which is the least stable oxidation state of Mn?**

(A) Mn^{2+} (B) Mn^{4+} (C) Mn^{7+} (D) Mn^{6+}

42 **The E° for,** $Mn^{4+} + 2e \longrightarrow Mn^{2+}$; **is equal to:**

(A) 1.23V (B) 2.46 V

(C) 0.56V (D) –0.56V

COMPREHENSIONS - II

The molar conductance of NaCl varies with the concentration as shown in the following table. and all values follows the equation $\lambda_m^C = \lambda_m^\infty - b\sqrt{C}$ **Where** λ_m^C **= molar specific conductance** λ_m^∞ **= molar specific conductance at infinite dilution**

C = molar concentration

Molar Concentration of NaCl	Molar Conductance in ohm^{-1} cm^2 mole^{-1}
4×10^{-4}	107
9×10^{-4}	97
16×10^{-4}	87

When a certain conductivity cell (C) was filled with 25×10^{-4} **(M) NaCl solution. The resistance of the cell was found to be 1000 ohm. At Infinite dilution, conductance of Cl⁻ and** SO_4^{-2} **are 80 ohm^{-1} cm^2 mole^{-1} and 160 ohm^{-1} cm^2 mole^{-1} respectively.**

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43. What is the molar conductance of NaCl at infinite dilution ?

(A) 147 $ohm^{-1}\ cm^2\ mole^{-1}$
(B) 107 $ohm^{-1}\ cm^2\ mole^{-1}$
(C) 127 $ohm^{-1}\ cm^2\ mole^{-1}$
(D) 157 $ohm^{-1}\ cm^2\ mole^{-1}$

44. What is the cell constant of the conductivity cell (C) :

(A) 0.385 cm^{-1} (B) 3.85 cm^{-1}
(C) 38.5 cm^{-1} (D) 0.1925 cm^{-1}

45. If the cell (C) is filled with 5×10^{-3} (N) Na_2SO_4 the obserbed resistance was 400 ohm. What is the molar conductance of Na_2SO_4.

(A) 19.25 $ohm^{-1}\ cm^2\ mole^{-1}$
(B) 96.25 $ohm^{-1}\ cm^2\ mole^{-1}$
(C) 385 $ohm^{-1}\ cm^2\ mole^{-1}$
(D) 192.5 $ohm^{-1}\ cm^2\ mole^{-1}$

COMPREHENSION–III

Redox reactions play a vital role in chemistry and biology. The values of standard redox potential (E°) of two half-cells reactions decide which way the reaction is expected to proceed. A simple example is a Daniell cell in which zinc goes into solution and copper gets deposited. Given below are set of half-cell reactions (acidic medium) along with their E° in V with respect to normal hydrogen electrode values.

$I_2 + 2e^- \longrightarrow 2I^-$; **E° = 0.54**

$Cl_2 + 2e^- \longrightarrow 2Cl^-$; **E° = 1.36**

$Mn^{3+} + e^- \longrightarrow Mn^{2+}$; **E° = 1.50**

$Fe^{3+} + e^- \longrightarrow Fe^{2+}$; **E° = 0.77**

$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$; **E° = 1.23**

46. Among the following, identify the correct statement

(A) Chloride ion is oxidised by O_2
(B) Fe^{2+} is oxidised by chlorine
(C) Iodide ion is oxidised by chlorine
(D) Mn^{2+} is oxidised by chlorine

47. While Fe^{3+} is stable, Mn^{3+} is not stable in acid solution because :

(A) O_2 oxidises Mn^{2+} to Mn^{3+}
(B) O_2 oxidises both Mn^{2+} and Fe^{2+}
(C) Fe^{3+} oxidizes H_2O to O_2
(D) Mn^{3+} oxidises H_2O to O_2

COMPREHENSION–IV

The concertration of potassium ions inside a biological cell is at least twenty times higher than the outside. the resulting potential difference across the cell is important in several processes such as transmission of nerve impulses and maintaining the ion balance. A simple mode for such a concentration cell involving a metal M is:

$$M_{(s)}\left|M^+_{(aq.)}0.05 molar\right|\left|M^+_{(aq.)}1\ molar\right|M_{(s)}$$

For the above electrolytic cell the magnitude of the cell potential $|E_{cell}| = 70mV$ [IIT 2010]

48. For the above cell:

a) $E_{cell} < 0; \Delta G > 0$ b) $E_{cell} > 0; \Delta G < 0$

c) $E_{cell} < 0; \Delta G^0 > 0$ d) $E_{cell} > 0; \Delta G^0 > 0$

49. If the 0.05 molar solution of M^+ is replaced by 0.0025 molar M^+ solution, then the magnitude of the ccell potential would be:

a) 35 mV b) 70 mV
c) 140 mV d) 700 mV

COMPREHENSION–V

The electrochemical cell shown below is a concentration cell.

$$M\left|M^{2+}(\text{saturated solution of a sparing soluble salt, } MX_2)\right|$$

$$\left|M^{2+}\left(0.001\ mol\ dm^{-3}\right)\right|M$$

The emf of the cell depends on the difference in concerntrations of M^{2+} ions at the two electrodes. The emf of the cell at 298 K is 0.059 V.

50. The value of $\Delta G\left(kj\ mol^{-1}\right)$ for the given cell is : $\left(take\ 1F = 96500C\ mol^{-1}\right)$

a) -5.7 b) 5.7
c) 11.4 d) -11.4

51. $\left(K_{SP}; mol^3 dm^{-9}\right)$ of MX_2 at 298K based on the information available for the given concentration cell is:

$\left(take\ 2.303\times R\times 298/F = 0.059V\right)$

a) 1×10^{-15} b) 4×10^{-15}
c) 1×10^{-12} d) 4×10^{-12}

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MATRIX MATCHING QUESTIONS

52. **For the galvanic cell**

$Ag \mid Ag^{+}_{(aq)}(0.1M) \| Cd^{2+}_{(aq)}(0.1M) \mid Cd$

$(E^{o}_{Ag^{+}/Ag} = 0.80V, E^{o}_{Cd^{2+}/Cd} = -0.40V)$,

Column – I	Column – II
(A) The cell reaction	(p) –1.17V
(B) Reaction quotient	(q) –1.20V
(C) The cell potential	(r) Non-spontaneous
(D) The standard cell potential	(s) 1/10
	(t) $E^{0}_{cell} = E^{0}_{RP(cathode)} - E^{0}_{RP(anode)}$

53.

Column I (Quantities)	Column II (Factors on which dependency exist)
(A) Molar conductance	(p) Temperature
(B) emf of a cell in operation	(q) Concentration of species involved
(C) Electrode potential	(r) Nature of substance involved
(D) Standard reduction potential	(s) No. of electrons lost or gained in the reaction
	(t) dilution

54.

Column - I (Reduction process)	Column - II (Charge required)
a) 1 mole of MnO^{-}_{4} to Mn^{2+}	p) 193000C
b) 1 mole of $Cr_2O_7^{2-}$ to Cr^{3+}	q) 289500C
c) 1 mole of Sn^{4+} to Sn^{2+}	r) 482500C
d) 1 mole of Al^{3+} to Al	s) 579000C

55.

Column - I	Column - II
a) Electrochemical cell	p) $\Delta G = +ve$
b) 1 law of faraday	q) $\Delta G = -ve$
c) Electrolytic cell	r) $w = z.i.t$
d) Lead acid storage cell	s) Salt bridge
	t) Rechargeable cell

STATEMENT TYPE QUESTIONS

A) S is coreect but E is wrong
B) S is wrong but E is correct
C) Both S and E are correct and E is correct explanation of S.
D) Both S and E are correct but E is not correct explanation of S

56. **Statement :** The cathode of electrolytic cell during electrolysis of $NaCl_{(aq.)}$ on addition of little litmus showns a blue colour

Explanation : At cathod: $2H^{+} + 2e \rightarrow H_2$. The reaction at cathode give rise to an increase in pH ranging in alkaline medium and litmus showns blue colour.

57. **Statement :** $Pt_{H_2} / HCl\ at\ 25^{0}\ CE_{H} = 0$

Exaplanation : For primary reference electrode $E^{0}_{H/H^{+}} = 0$

58. **Statement :** $\left(\frac{\delta E}{\delta T}\right)_P$ is called temperature coefficient of emf.

Explanation : $\left(\frac{\delta E}{\delta T}\right)_P$ may be +ve, -ve and depends upon heat of reaction

59. **Statement :** Liquid junction potential can be eliminated by putting a salt bridge of KCl.
Explanation : The function of salt bridge is to remove liquid junction potential because the salt used has same speed of cations and anions

60. **Statement :** When acidified zinc sulphate solution is electrolysed between zinc electrodes. It is zinc that is deposited at the cathode and hydrogen evolution does not take place
Explanation : The electrode potential of zinc is more negative than hydrogen as the overvoltage for hydrogen evolution on zinc is quite large

61. **Statement :** The mobility of sodium ions is lower than that of potassium ion
Explanation : The ionic mobilities depend upon the effective radius of the ion
A) S is coreect but E is wrong
B) S is wrong but E is correct
C) Both S and E are correct and E is correct explanation of S.
D) Both S and E are correct but E is not correct explanation of S

62. **Statement :** E^{0}_{cell} is an intensive property
Explanation : $\Delta G^{0} / n$ is also intensive property

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63. **Statement :** If two half reaction with electrode potential E_1^0 *and* E_2^0 gives a third reaction then,

$\Delta G^0_3 = \Delta G_1^0 + \Delta G_2^0$

Explanation : $E^0_3 = E_1^0 + E_2^0$

INTEGER TYPE QUESTIONS

64. **Find the volume of Cl_2 at NTP produced during electrolysis of $MgCl_2$ which produces 6.6 g.Mg. (At. wt. of Mg=24.3)**

65. **The standard oxidation potential of Ni / Ni^{2+} electrode is 0.236 V. If this is combined with a hydrogen electrode in acid solution, at what pH of this solution will bbe measured e.m.f zero at $25^0 C$?**

Assume that $\left[Ni^{2+}\right] = 1M$ *and* $P_{H_2} = 1\,atm$

66. **A hydrogen electrode is dipped in a solution at $25^0 C$. The potential of cell is -0.177V. Calculate the pH of the solution.**

67. **What current is to be passed for 0.25 sec for deposition of certain weight of metal which is equal to its electrochemical equivalent?**

68. **When water is electrolysed, hydrogen and oxygen gas are produced. If 1.008 g of H_2 is liberated at cathode, calculate the mass of O_2 is formed at anod.**

KEY - LEVEL - IV

SINGLE ANSWER QUESTIONS

1. B	2. B	3. B	4. A
5. A	6. A	7. D	8. C
9. C	10. B	11. C	12. A
13. B	14. C	15. A	16.D
17. C	18. B	19.A	20. B
21.C	22.A	23. B	24.A
25.C	26.A	27.B	28.A
29.C	30.A	31.D	

MULTI ANSWER QUESTIONS

32.A,C	33. A,C
34.B,C	35.B,C
36.A,D	37. A,B,C
38. A,B	39.A,B

COMPREHENSION QUESTIONS

40.B	41. C	42. A	43. C
44. D	45. D	46.C	47.D
48. B	49. C	50. D	51. B

MATRIX MATCHING QUESTIONS

52. A- r, B-sC-p,t D-q

53. A- p,q,r,t , B-pq,r,s,t C-p,q,r,s,t D-r,s

54. a) r b) s c) p d) q

55. a)q, s b) r c) p d) t

STATEMENT TYPE QUESTIONS

56. C	57. B	58. D	59. C
60. D	61. C	62. C	63. A

INTEGER TYPE QUESTIONS

64. 6	65. 4	66. 3	67. 4
68. 8			

HINTS - LEVEL - IV

SINGLE ANSWER QUESTIONS

1. (B)The ΔG° and E°_{cell} are related by

$\Delta G^\circ = -nFE^\circ_{cell} = -$

$12 \times 96500 \times 2.73 =$

$-3.16 \times 10^3 kJ$

(since ΔG°_f of Al(s) and O_2 (g) are zero)

$\Delta G^\circ_f(Al(OH)_4^-) =$

$$\frac{-3.16 \times 10^3 + (6 \times -237.2) + (4 \times -157)}{4}$$

$$= -1.30 \times 10^3 \text{ kJ mol}^{-1}$$

2. The reactions at the two half-cells are

At cathode : $Zn^{2+}(c) + 2e^- \longrightarrow Zn(c_2)$

At anode : $Zn(c_1) \longrightarrow Zn^{2+}(c) + 2e^-$

Net cell reactgion: $Zn(c_1) \longrightarrow Zn(c_2)$

Applying Nernst equation to the net cell reaction gives

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{2}\log\frac{c_2}{c_1} =$$

$$\frac{0.059}{2}\log\frac{c_1}{c_2} (\text{since } E^\circ_{cell} = 0)$$

$$E_{cell} = \frac{0.059}{2}\log\left(\frac{2/65.4}{1/65.4}\right) = 8.8 \times 10^{-3} v$$

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3. $E^0_{Cell} = 0.76 volt$

Applying Nernst equation

$$E_{Cell} = E^0_{Cell} - \frac{0.0591}{2}\log\frac{\left[Zn^{2+}\right]\left[H_2\right]}{\left[H^+\right]^2}$$

$$\log\frac{0.1}{\left[H^+\right]^2} = \frac{2\times 0.48}{0.0591}$$

$$\log 0.1 - \log\left[H^+\right]^2 = 16.2436$$

$$2pH = 16.2436 - \log 0.1$$

$$pH = \frac{17.2436}{2} = 8.62$$

4. $A = \pi r^2 = 3.14\times 0.5^2\ cm^2$

$= 0.785\ cm^2 = 0.785\times 10^{-4} m^2$

$\ell = 50\ cm = 0.5\ m$

$$R = \frac{\rho\ell}{A} \text{ or } \rho = \frac{RA}{\ell} =$$

$$\frac{5.55\times 10^3\ \Omega\times 0.785\ cm^2}{50\ cm} =$$

$= 87.135\ \Omega cm$

$$\text{Conductivity} = \kappa = \frac{\ell}{\rho} = \left(\frac{1}{87.135}\right) S\ cm^{-1}$$

$$= \frac{0.01148\ S\ cm^{-1}\times 1000\ cm^3\ L^{-1}}{0.05\ mol\ L^{-1}} = 229.6\ S\ cm^2\ mol^{-1}$$

If we want to calculate the values of different quantities in terms of 'm' instead of 'cm'.

$$\rho = \frac{RA}{\ell} = \frac{5.55\times 10^3\Omega\times 0.785\times 10^{-4} m^2}{0.5 m} = 87.135\times 10^{-2}\Omega m$$

$$\kappa = \frac{1}{\rho} = \frac{100}{87.135}\Omega m = 1.148\ S\ m^{-1}$$

and

$$\Lambda_m = \frac{\kappa}{C} = \frac{1.148\ S\ m^{-1}}{50\ mol\ m^{-3}} =$$

$229.6\times 10^{-4}\ S\ m^2\ mol^{-1}$

5. Cell reaction $H_2 + 2Ag^+ \rightarrow 2Ag + 2H^+$

$$E = E^0 - \frac{0.0591}{n}\log_{10} Q$$

$$\text{or } 0.711 = 0.799 - \frac{0.0591}{2}\log_{10}\frac{1}{\left[Ag^+\right]^2}$$

$$\left[Ag^+\right] = 0.3243 mol L^{-1}$$

$$Ag_2SO_4 \rightleftharpoons 2Ag^+ + SO_4^{2-}$$

$$0.03243 \quad 0.016215$$

$$K_{sp} = \left[Ag^+\right]^2\left[SO_4^{2-}\right]$$

$$= \left[0.03243\right]^2\times\left(0.016215\right)$$

$$= 1.705\times 10^{-5}$$

6. $A^\infty\left(AgCl\right) = 62 + 76 = 138\ S\ cm^2\ mol^{-1}$

Since AgCl is a sparingly soluble salt, its saturated solution contain only very small amount of Ag^+ and Cl^- ions, $A^C = A^\infty$. Also concentration of Ag^+ ion or Cl^- ion in saturated solution is same as solubility(s).

$$\Rightarrow 138 = \frac{1.26\times 10^{-6}\times 1000}{S}$$

$$\left(\because A = \frac{k.1000}{C}\right)$$

$$\Rightarrow S = 9.13\times 10^{-6}$$

$$\Rightarrow K_{sp} = S^2 = 8.3\times 10^{-11}$$

7. $$\kappa = \frac{\wedge_{eq} C}{1000} = \frac{97.1\times 0.1}{1000}$$

$$= 9.71\times 10^{-3} Scm^{-1}$$

$$G = \frac{1}{R} = \kappa.\frac{A}{l}$$

$$= 9.71\times 10^{-3} Scm^{-1}\times\frac{1.5 cm^2}{0.5 cm}$$

$$= 29.13\times 10^{-3} ohm^{-1}$$

$$V = IR \Rightarrow I = \frac{V}{R} = 5\times 29.13\times 10^{-3}$$

$$= 0.1456 amperes$$

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8. At anode, either Ag can get oxidised to Ag^+ or Sn^{2+} to Sn^{4+} or Cl^- to Cl_2 or SO_4^{2-} to $S_2O_8^{2-}$. Their respective oxidation potential values are -0.799 V, -0.13 V, -1.36 V and -2 V. From these values, it is evident that Sn^{2+} would be oxidised first, followed by Ag at anode. At cathode, either Na^+ can get reduced to Na or Sn^{2+} to Sn or H^+ to H_2. The reduction potential value of Na^+ is highly negative while for Sn^{2+} | Sn is - 0.14 V and for

$$H^+ + e^- \longrightarrow \frac{1}{2}H_2$$

$\left(E_{H^+|H_2} = -0.059\log\frac{1}{10^{-7}}\right)$ -0.413 V. Thus, Sn^{2+} will get reduced at cathode followed by H^+

9. $\Rightarrow Pt, H_2 \mid H^+(?) \| H^+(1M) \mid H_2, Pt$

$$E = 0.025$$

$$= -0.059\log\frac{[H^+]}{1} = 0.059\,pH$$

$$\Rightarrow pH = 0.42$$

10. Since OH^- is produced in L.H.E., hence the pH of R.H.E. increases, whereas H^+ is produced in the L.H.E, hence the pH of L.H.E. decreases.

11. No.of equivalent of Cu^{+2}

$$\text{deposited} = \frac{0.4\times 2}{63.5} = 0.013$$

$\therefore$ Volume of O_2 liberated at anode

$= 0.013\times 5.6 \qquad = 0.07lt = 70ml$

After continuation of electrolysis for seven more minutes

Q= it $= 1.2\times 7\times 60 = 504C$

Therefore,

Volume of H_2 liberated at

cathode$= 0.00522\times 11200 = 58.46ml$

vol of O_2 liberated at anode

$= 0.00522\times 5600 = 29.23ml$

Total volume of gases liberated during the entire electrolysis

Oxygen = 70+29.23= 99.23 ml

Hydrogen $= 58.46ml$

12. charge passed $= I\times t$

$= 2\times 10^{-3}\times 16\times 60$

$= 1.92C$

$$= \frac{1.92}{96500}F$$

Total moles of copper present initially must be

$$2\times\frac{1.92}{96500}\times\frac{1}{2} = \frac{1.92}{96500}$$

$$\text{molarity} = \frac{1.92}{96500}\times\frac{1000}{250}$$

$$= 7.95\times 10^{-5}$$

13. E^0 for

$$Zn^{2+}(aq) + 4NH_3(aq) + 4NH_3(aq)$$

$$\rightleftharpoons Zn(NH_3)_4^{2+}(aq)$$

is 0.28 V

Also, RT In $K_f = nE^0F = 2\times 0.28\times 96500$

$$\Rightarrow In\ K_f = \frac{0.56\times 96500}{8.314\times 298} = 21.81$$

$$\Rightarrow K_f = 3\times 10^9$$

14. n-factor for $Mn_3O_4 \rightarrow MnO_4^{2-}$ is 10

$\therefore$ charge required is 10 F

15. $$E^0 = \frac{0.059}{2}\log\left(2.69\times 10^{12}\right)$$

16. $$\Delta G^0 = -n\,F\,E^0$$

$$\Delta S^0 = \frac{\Delta H_f^0 - \Delta G^0}{T}$$

17. $$\alpha = \frac{\wedge_C}{\wedge_{eq}} = \frac{10}{200} = \frac{1}{20} = 0.05$$

$$[H^+] = c.\alpha$$

$$= 0.1\times 0.05$$

$$= 5\times 10^{-3}$$

$\therefore pH = 2.3$

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18. $\alpha = \sqrt{\frac{K_a}{C}}$

$\sqrt{\frac{K_a}{C}} = \frac{\mu_\alpha}{\mu_C}$

$\mu_C = \frac{1000 \times \kappa}{C}$

19. $S = \frac{1000 \times \kappa}{\wedge_m}$

$K_{sp} = 27S^4$

20. No. of equivalent of aluminu, $\frac{W}{E} = \frac{I \times \eta \times t}{96500}$

$\frac{24 \times 5}{27} \times 3 = \frac{9650 \times 0.9 \times t}{96500}$

$t = 148.14 \text{sec}$

21. Eq. of Ca; $\frac{w}{E} = \frac{i \times t}{96500}$

$Ca^{2+} + 2e \rightarrow Ca$

$\therefore \; E_{Ca} = \frac{40}{2}$

or $\frac{20}{40/2} = \frac{i \times t}{96500}$

$i \times t = 1 \times 96500 = 1F$

22. We know

$2H_2(g) \rightarrow 4H^+ + 4e^-; E = 0.0V$

$\frac{O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l); E = 1.23V}{2H_2(g) + O_2(g) \rightarrow 2H_2O(l); E^0_{cell} = 1.23V}$

$\Delta G^0_{298} = -nFE^0 = -4 \times 96500 \times 1.23$

$= -474.78kJ$

$\Delta_f H^0_{298} + T.\Delta_r S^0_{298}$

$= (-474.78) + 298 \times (-0.16)$

$\Delta_f H^0_{298} = -285.07kJ/mol$

23. Anode :

$H_2(g) \rightarrow 2H^+(aq) + 2e^-; E^0 = 0.0V$

Cathode :

$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow$

$Mn^{2+}(aq) + 4H_2O(l); E^0 + 1.51V$

$E_{cell} = E_{RP(RHS)} - E_{RP(LHS)}$

$\Rightarrow \left[1.51 - \frac{0.06}{5} \log \frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}\right]$

$- \left[0 - \frac{0.06}{2} \log \frac{P_{H_2}}{[H^+]^2}\right]$

$= 1.51 - \left[\frac{0.06}{5} \log \frac{0.01}{0.1 \times (10^{-2})^8}\right]$

$+ \frac{0.06}{2} \log \left[\frac{0.1}{(10^{-3})^2}\right]$

$= 1.48V$

24. $E^0_{cell} = 0.33 - 0.36 = -0.03 \; E^0_{cell} = \frac{RT}{2F} In \, K$

$-0.03 = \frac{0.06}{2} \log K \;\; or \; K = 0.1$

$2ClO_3^- \rightleftharpoons ClO_4^- + ClO_2^-$

$0.1 - 2x \qquad x \qquad x$

$\frac{x^2}{(0.1-2x)^2} = \frac{1}{10};$

$3.16x = 0.1 - 2x$

$5.16x = 0.1$

$\Rightarrow x = 0.1/5.16 = 0.0193 \cong 1.9 \times 10^{-2}$

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25. $E_{cell} = E_{H^+|H_2} - E_{OH^-|Cd(OH)_2|Cd}$

$= E_{H^+|H_2} - E_{OH^-|Cd(OH)_2|Cd}$

$= E_{H^+|H_2} - E_{OH_{Cd^{2+}|Cd}}$

$$E_{cell} = E^0 - \frac{0.06}{2}\log\frac{\left[cd^{2+}\right]}{\left[H^+\right]^2}$$

$$E_{cell} = 0$$

$$E^0_{cell} = 0.03\log\frac{\left[cd^{2+}\right]\left[OH^-\right]^2}{K_w^2}$$

$$\log\frac{K_{sp}}{K_w^2} = \frac{0.09}{0.03} = 13$$

$$K_{sp} = 10^{13}\times\left(10^{-14}\right)^2 = 10^{-15}$$

26. $$E_{cell} = \frac{0.06}{2}\log\frac{\left[H^+\right]^2_{RHS}\left[P_{H_2}\right]_{LHS}}{\left[H^+\right]^2_{LHS}\left[P_{H_2}\right]_{RHS}} ;\because$$

$\alpha << 1$

$$\left[OH^-\right]_{LHS} = \sqrt{k_a \times C} \Rightarrow 10^{-3}$$

$$\left[H^+\right]_{LHS} = \sqrt{Ka \times C} = 10^{-11}$$

$$\left[H^+\right]_{RHS} = \sqrt{Ka \times C} = 10^{-4}$$

$$E_{cell} = \frac{0.06}{2}\log\frac{\left[10^{-4}\right]^2 \times 0.1}{\left(10^{-11}\right)^2 \times 1}$$

$Ecell = 0.39V$

27. The molar conductivity of the dissociated form of crotonic acid is

$\Lambda_m(HC) = \Lambda_m(HCl) + \Lambda_m(NaC) - \Lambda_m(NaCl)$

$= (426 + 83 - 126)\Omega^{-1}cm^2mol^{-1}$

$= 383\Omega^{-1}cm^2mol^{-1}$

The molar conductivity of HC,

$$\Lambda_m(HC) = \frac{K}{C} = \frac{383\times10^{-5}\Omega^{-1}cm^{-1}}{0.001}\times1000$$

$= 38.3\Omega^{-1}cm^2mol^{-1}$

The degree of dissocitation,

$$\alpha = \frac{\Lambda_m(HC)}{\Lambda_m(HC)} = \frac{\left(38.3\Omega^{-1}cm^2mol^{-1}\right)}{\left(383\Omega^{-1}\right)cm^2mol^{-1}} = 0.1$$

$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{\left(10^{-3}\right)(0.1)^2 = 1.11\times10^{-5}}{1-0.1}$$

28. Conductivity of $Na_2SO_4 = 2.6\times10^{-4}$

$$\Lambda_m\left(Na_2SO_4\right) = \frac{1000\times2.6\times10^{-4}}{0.001}$$

$= 260S\,cm^2mol^{-1}$

$\lambda_m\left(SO_4^{2-}\right) = \Lambda_m\left(Na_2SO_4\right) - 2\lambda_m\left(Na^+\right)$

$= 260 - 2\times50$

$= 160Scm^2mol^{-1}$

Conductivity of $CaSO_4$ solution

$= 7\times10^{-4} - 2.6\times10^{-4}$

$= 4.4\times10^{-4}\,Scm^{-1}$

$\wedge_m\left(CaSO_4\right) = \lambda_m\left(Ca^{+2}\right) + \lambda_m\left(SO_4^{2-}\right)$

$= 120 + 160$

$= 280Scm^2\,mol^{-1}$

$$S = \frac{1000\times\kappa}{\wedge_m} = \frac{1000\times4.4\times10^{-4}}{280}$$

$= 1.57\times10^{-3}\,m$

$K_{sp} = \left[Ca^{2+}\right]\left[SO_4^{2-}\right]$ total

$K_{sp} = \left(1.57\times10^{-3}\right)\left(1.57\times10^{-3} + 0.001\right)$

$K_{sp} = 4\times10^{-6}M^2$

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29. $E^0_{cell} = E^0_{RP(RHS)} - E^0_{RP(LHS)}$

$= 1.61 - 1.51 \Rightarrow 0.10V$

$\Delta G^0 = -nFE^0 \Rightarrow -5 \times 96500 \times 0.10J$

$\Delta G^0 = -48.25kJ$

30. As the cell is a concentration cell, $E^0_{cell} = 0$

Now, the cell reaction is

Left electrode:

$H_2(P_1 = 640mm) \rightleftharpoons 2H^+ + 2e^-$

Right electrode:

$: 2H^+ + 2e^- \rightleftharpoons H_2(P_2 = 425mm)$

Net cell reaction:

$H_2(P_1 mm) \rightleftharpoons H_2(P_2 mm)$

Now, from Nernst equation

$= 0 - \frac{0.059}{2}\log\frac{425}{640}$

$= 0.005V$

31. As the right electrode is normal (standard) electrode, the emf of cell may be written as

$E_{cell} = E^0_{calomel} - E_{H^+(buffer)/H_2}$

or, $0.6885 = 0.28 - E_{H^+/H_2}$

$\therefore E_{H^+/H_2} = -0.4085V$

Now, from Nernst equation,

$E_{H^+/H_2} = E^0_{H^+/H_2} - \frac{0.059}{n}\log\frac{P_{H_2}}{[H^+]^2}$

or,

$-0.4085 = 0 - \frac{0.059}{2}$

$\left(\log P_{H_2} - \log[H^+]^2\right)$

or, $0.4085 = \frac{0.059}{2}\left(\log 1 + 2P^H\right)$

$\therefore$ pH of buffer solution = 6.92

MULTI ANSWER QUESTIONS

32. Based on electrochemical series

33. Due to formation of Cu^{2+} ions in the solution

34. Conceptual

35. Conceptual

36. Conceptual

37. Conceptual

38. Conceptual

39. $A^\infty = 62.3 + 67.7 = 130 Scm^2 mol^{-1}$

$\Rightarrow \Delta^\infty = \frac{K1000}{S}$

$\Rightarrow S = \frac{3.4 \times 10^{-6} \times 1000}{130}$

$= 2.6 \times 10^{-5} molL^{-1}$

In gL^{-1} unit : solubility $= 2.6 \times 10^{-5} \times 143.5$

$= 3.7 \times 10^{-3} gL^{-1}$

40. Most -ve value of ΔG^0 correspond to most stable oxidation state

41. The three case Mn^{+7} dissociates to give Mn^{2+}, Mn^{4+} and Mn^{5+} respectively, Thus it is least stable.

42. $Mn^{+3} + e^- \rightarrow Mn^{2+};\ E^0 = 1.51V$

$Mn^{+4} + 2e^- \rightarrow Mn^{3+};\ E^0 = 0.95V$

$Mn^{4+} + 2e^- \rightarrow Mn^{2+};\ E^0 = \frac{1.51 + 0.95}{2}$

43. $\lambda_C = \lambda_\infty - b\sqrt{c}$

$\lambda_\infty = 107 + b\sqrt{4 \times 10^{-4}}$ .....(1)

$\lambda_\infty = 97 + b\sqrt{9 \times 10^{-4}}$ .....(2)

(1) and (2) $\Rightarrow b = 10^3$

from (1) $\lambda_\infty = 107 + 10^3\sqrt{4 \times 10^{-4}}$

$= 127$

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44. $\lambda_c = \lambda_\infty - b\sqrt{c}$

$= 127 - 10^3\sqrt{25\times10^{-4}}$

$= 77$

$\lambda_c == \dfrac{K\times1000}{m}$

$77 = \dfrac{K\times1000}{25\times10^{-4}}$

$K = \dfrac{77\times25\times10^{-4}}{1000} = 77\times25\times10^{-7}$

$K = \dfrac{G^*}{R}$

$G^* = KR = 77\times25\times10^{-7}\times1000$

$= 77\times25\times10^{-4} = 0.1925$

45. $\lambda = \dfrac{K\times1000}{m}$

$= \dfrac{G^*\times1000}{R\ m}$

$= \dfrac{0.1925\times1000}{400\times\left[\dfrac{5\times10^{-3}}{2}\right]}$

$= \dfrac{192.5\times2}{2000\times10^{-3}}$

$= 192.5$

COMPREHENSION QUESTIONS

COMPREHENSION- IV

48. b) It is an electrolyte concentration cell in which the electrode with concentrated electrolyte solution acts as cathode and second one as anode. for a concentration cell, applying Nernst's equation,

$$E_{cell} = \frac{0.059}{n}\log_{10}\frac{\left[M_{aq..}^{\ n+}\right]_{Cathode}}{\left[M_{aq..}^{\ n+}\right]_{anode}}$$

$$E_{cell} = \frac{0.056}{0.1}\log_{10}\frac{[1.0]}{5\times10^{-2}}$$

$= 0.076\ or\ 76mV\quad (i.e.,\ positive\ value)$

Also $\Delta G = -2FE$, because E is positive so $\Delta G < 0$.

49. c) In this case

$$E_{cell} = \frac{0.059}{1}\log_{10}\frac{[1.0]}{2.5\times10^{-3}}$$

$= 0.152V\ or \approx 140\ mV$

COMPREHENSION- V

50. $\because\ \Delta G = -2EF$

$M - 2e^- \rightarrow M^{2+}$

$\therefore n = 2$

$\Delta G = -2\times0.059\times96500 = -11,387\ J\ mol^{-1}$

$= -11.4kJ\ mol^{-1}$

51. b) For concentration cell,

$$E_{cell} = \frac{0.0591}{n}\log\frac{C_{2(RHS)}}{C_{1(LHS)}}$$

$E_{cell} = 0.059V,\ C_{2(RHS)} = 0.001$

$$0.059 = \frac{0.0591}{2}\log\frac{0.001}{C_1}$$

or

$$\frac{2\times0.059}{0.0591} = \log\frac{0.001}{C_1}\ or\ \ anti\log 2 = \frac{0.001}{C_1}$$

$$\therefore\ C_1 = \frac{0.001}{100} = 10^{-5}$$

C_1 = concentration or solubility of $M^{2+} = 10^{-5}$

$$MX_2 \rightleftharpoons \underset{S}{M^{2+}} + 2\underset{2S}{X^-}$$

$K_{SP} = S(2S)^2 = 4S^3$

$K_{SP} = 4\times\left(10^{-5}\right)^3 = 4\times10^{-15}\ mol^3dm^{-9}$

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STATEMENT TYPE QUESTIONS

56. C) Explanation is correct reason for statement

57. B) Primary reference electrode is

$$Pt_{H_2} \Big/ \begin{matrix} HCl \\ 1\,M \end{matrix} \quad \text{at } 25^0C \text{ its}, E^0 = 0$$
$1\,atm$

58. D) $\Delta H = nF\left[T\left(\frac{\delta E}{\delta T}\right)_P - E\right]$;

where $\left(\frac{\delta E}{\delta T}\right)_P$ is temperature coefficient

59. C) Explanation is correct reason for statement

60. D)These are facts

61. C) Explanation is correct reason for statement

62. C) $-\Delta G^0 = nE^0F$

$$\therefore \quad E^0 = \frac{-\Delta G^0}{nF}$$

Since ΔG is intensive property then E^0 is also intensive property

63. A) In such case E^0 are not additive

INTEGER TYPE QUESTIONS

64. At cathode $Mg^{2+} + 2e \rightarrow Mg$

At anode $2Cl^- \rightarrow Cl_2 + 2e$

$\because$ Equivalent of Mg at cathod = Equivalent of Cl_2 at anode

$$\therefore \frac{6.6}{24.3/2} = \frac{w_{Cl_2}}{35.5} \Rightarrow w_{Cl_2} = 19.28g$$

Now at NTP $PV = \frac{w}{m}RT$

$$1 \times V = \frac{19.28 \times 0.0821 \times 273}{71}$$

$$\Rightarrow \quad V = 6.08\ litre \approx 6litre$$

65. $Ni \rightarrow Ni^{2+} + 2e;\ E^0_{OP} = 0.236V$

$2H^+ + 2e \rightarrow H_2;\ \begin{matrix} E^0_{RP} = 0 \\ E^0_{cell} = 0.236V \end{matrix}$

$$E_{cell} = E^0_{cell} + \frac{0.059}{2}\log_{10}\frac{\left[H^+\right]^2}{\left[Ni^{2+}\right]}$$

$$0 = 0.236 + \frac{0.059}{2}\log_{10}\left[H^+\right]^2$$

$$-\log_{10} H^+ = 4 \quad \therefore \quad pH = 4$$

66. $E = E^0 - \frac{0.059}{n}\log\frac{1}{\left[H^+\right]}$

$$-0.177 = 0 + \frac{0.059}{1}\log\left[H^+\right]$$

$$\log\left[H^+\right] = -3$$

$$\therefore \quad pH = -\log\left[H^+\right] = 3$$

67. $w = z.i.t \quad or \quad \frac{w}{z} = i.t \qquad \left(\therefore \frac{w}{z} = 1\right)$

$$1 = i \times 0.25 \quad \Rightarrow \quad i = 4\ amp$$

68. $\because \frac{w_1}{w_2} = \frac{E_1}{E_2}$, where E_1 *and* E_2 are eq.wt. of H_2 *and* O_2 respectively

$$\therefore \frac{1.008}{w_2} = \frac{1.008}{8} \Rightarrow w_2 = 8\ g$$

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