7 Electrolysis and Electrochemical Cells

Electrolysis: The phenomenon in which passage of current through an electrolytic cell containing molten or aqueous solution brings in chemical changes involving electronation (reduction) as well as de-electronation (oxidation) of ions or atoms is known as electrolysis.

The products formed during electrolysis depend upon:

(1) Nature of electrolyte **See Examples I to III**

(2) Conc. of electrolyte **See Examples II (A and B)**

(3) Charge density flown during electrolysis **See Examples VIII (A and B)**

(4) Nature of electrodes used–attacked or non attacked electrode. **See Examples I to VII and IX**

Anode is the electrode at which oxidation occurs.

Cathode is the electrode at which reduction occurs.

Examples:

Case I. Electrolysis of molten NaCl using Pt electrodes:

At anode: $Cl^- \longrightarrow \frac{1}{2}Cl_2 + e$

At cathode: $Na^+ + e \longrightarrow Na$

Thus, Cl_2 and Na are formed at anode and cathode respectively due to discharge of Cl^- and Na^+ at opposite electrodes.

Case II. Electrolysis of aq. NaCl using Pt electrodes:

A. Conc. NaCl(*aq.*) $NaCl \longrightarrow Na^+ + Cl^-$

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

At anode: $Cl^- \longrightarrow \frac{1}{2}Cl_2 + e$

At cathode: $H_3O^+ + e^- \longrightarrow H_2O + \frac{1}{2}H_2$

It is found experimentally that if a mixture of ions is electrolysed, certain ion gets discharged at an electrode in preference of other on the basis of preferential discharge theory. The more is the discharge potential (D.P.) of ion, lesser is its tendency to get discharged.

Discharge potential of Cl^- < Discharge potential of OH^-

Discharge potential of H_3O^+ < Discharge potential of Na^+

B. Dilute NaCl(*aq.*)

In case of very dilute solution of NaCl (*aq.*) following charges are noticed.

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

At cathode: $2H_3O^+ + 2e \longrightarrow 2H_2O + H_2$

Case III. Electrolysis of NaCl(*aq.*) using Hg as cathode:

At anode : $2Cl^- \longrightarrow Cl_2 + 2e$

At cathode: $2Na^+ + 2e \longrightarrow 2Na$

$$2Na + 2Hg \longrightarrow 2Na - Hg \text{ (amalgam)}$$

$$2Na - Hg + 2H_2O \longrightarrow 2NaOH + H_2 + 2Hg$$

The discharge potential of Na^+ <D.P. of H_3O^+ at Hg cathode.

Case IV. Electrolysis of HCl(*aq.*) using Pt electrodes:

At anode: $2Cl^- \longrightarrow Cl_2 + 2e$

At cathode: $2H_3O^+ + 2e \longrightarrow 2H_2O + H_2$

Case V. Electrolysis of $NaNO_3(aq.)$ or $Na_2SO_4(aq.)$ using Pt electrodes:

For $NaNO_3$ (*aq.*)	**For Na_2SO_4 (*aq.*)**
At anode:	
$2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e$	$2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e$
At cathode:	
$2H_3O^+ + 2e \longrightarrow 2H_2O + H_2$	$2H_3O^+ + 2e \longrightarrow 2H_2O + H_2$
D.P. of NO_3^- > D.P. of OH^-	D.P. of SO_4^{2-} > D.P. of OH^-
D.P. of Na^+ > D.P. of H_3O^+	

Case VI. Electrolysis of $CuSO_4(aq.)$ or $AgNO_3(aq.)$ using Pt electrodes:

For $CuSO_4(aq.)$	For $AgNO_3(aq.)$
At anode:	
$2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e$	$2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e$
At cathode:	
$Cu^{2+} + 2e \longrightarrow Cu$	$Ag^+ + e \longrightarrow Ag$
D.P. of Cu^{2+} > D.P. of H_3O^+	D.P. of Ag^+ > D.P. of H_3O^+

Case VII: Electrolysis of $RCOONa(aq.)$ using Pt electrodes:

At anode: $2RCOO^- \longrightarrow R - R + 2CO_2 + 2e$

At cathode: $2H_3O^+ + 2e \longrightarrow 2H_2O + H_2$

D.P. of $RCOO^-$ < D.P. of OH^-

Case VIII: Electrolysis of H_2SO_4 using Pt electrodes:

Part A. Normal current density:

$H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-}$ and $2H_2O \rightleftharpoons H_3O^+ + OH^-$

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

At cathode: $2H^+$ or $2H_3O^+ + 2e \longrightarrow 2H_2O + H_2$

$\because$ H^+ in solution exists as H_3O^+

Part B. High current density: Electrolysis of 50% H_2SO_4 using high current density gives:

At anode: $2HSO_4^- \longrightarrow H_2S_2O_8 + 2e$

At cathode: $2H^+ + 2e \longrightarrow H_2$

The distillation of $H_2S_2O_8$ with water yields H_2O_2

$$H_2S_2O_8 + H_2O \longrightarrow H_2SO_4 + H_2SO_5$$
$$H_2SO_5 + H_2O \longrightarrow H_2SO_4 + H_2O_2$$

Note : All these examples were of non attacked electrodes.

Case IX: Attacked electrodes: The electrodes which themselves take part (dissolution or deposition occurs) in electronation or de-electronation, *e.g.*, electrolysis of $CuSO_4(aq.)$ using Cu electrodes.

At cathode: $Cu^{2+} + 2e \longrightarrow Cu$

At anode: Three reactions are possible

$Cu \longrightarrow Cu^{2+} + 2e$ $\quad E° = -0.34$ V

$SO_4^{2-} \longrightarrow SO_4 + 2e$ $\quad E° = -2.0$ V

$2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e$ $\quad E° = -1.2$ V

It is clear that discharge potential of Cu^{2+} to get oxidized is lowest and thus Cu anode dissolves in preference to other process.

Thus in case of attacked electrodes:

(1) Metal dissolves at anode, *i.e.*, oxidation.

(2) Metal ions are reduced at cathode.

(3) No change in concentration of solution during electrolysis.

Note : 1. The phenomenon of electrolysis occurs only at the electrodes. Oxidation occurs at anode; reduction occurs at cathode.

2. Corrosion of metals is electrochemical phenomenon. It is defined as the process of slow oxidation of metals. *e.g.*, rusting of iron, tarnishing of silver, green deposits on copper.
3. Rusting of iron is favoured by H^+ (*i.e.*, water vapours in atmosphere), CO_2 and O_2.
4. Purest form of metal is not corroded. Strained articles of metals are easily corroded.
5. Rust is $Fe_2O_3 \cdot XH_2O$.

Faraday's laws of Electrolysis

I law: The mass, w of an ion oxidized or reduced at either electrodes during the passage of current (*i.e.*, electrolysis) is directly proportional to the quantity of charge passed through electrolyte, *i.e.*,

$$w \propto Q$$
$$\propto i\,t$$
$$w = Z\,i\,t \qquad ...(1)$$

Q is total charge passed through electrolyte
i is current strength in amperes
t is time in seconds for which current flows
Z is electrochemical equivalent, a characteristic constant for the given metal defined as the mass of ion oxidized or reduced by the passage of one coulomb charge. The unit of $Z = kg\ C^{-1}$.

Note : 1. One Faraday of charge = charge on one mole electron
= charge which discharges one g equivalent of ion
$= 1.602 \times 10^{-19} \times 6.023 \times 10^{23}$
= charge which deposits or discharges E g where, E is eq. mass
= 96514.8 C
≈ 96500 C

Thus, 96500 C discharge E g of ion

$\therefore$ 1 C discharge $\frac{E}{96500}$ g ion $= Z$

$\therefore$ By Eq. (1) $\quad w = \frac{E \cdot i \cdot t}{96500} \qquad ...(2)$

2. Also, $\quad F = N \times e \qquad ...(3)$

where, F is charge in Faraday, N is Avogadro's number, e is charge on one electron,

3. Equivalent of an ion discharged, $\left(\frac{w}{E}\right) = \frac{i \cdot t}{96500} \qquad ...(4)$

II law: The passage of same charge through different electrolytes, brings in equal equivalents of ions to be oxidized or reduced at either electrodes as the case may be

$$\frac{w}{E} = \text{constant}$$

or $\quad w \propto E \qquad ...(5)$

or $\quad \frac{w_A}{E_A} = \frac{w_B}{E_B} = \frac{w_C}{E_C} \qquad ...(6)$

Chemical cells: (i) A class of cell in which chemical energy is converted into electrical energy.

(ii) The change in free energy = Electrical work done

$$-\Delta G = nFE \quad ...(7)$$

$\Delta G = (G_{products} - G_{reactants})$ for a redox change

Nernst equation for electrode potential

$$A \rightleftharpoons A^{+n} + ne$$

$$E_{OP} = E^{\circ}_{OP} - \frac{RT}{nF}\log_e \frac{a_{\text{oxidized state}}}{a_{\text{reduced state}}} \quad ...(8)$$

and $$E_{RP} = E^{\circ}_{RP} + \frac{RT}{nF}\log_e \frac{a_{O.S.}}{a_{R.S.}} \quad ...(9)$$

Also $$E^{\circ}_{OP} = -E_{RP} \quad ...(10)$$

and $$E^{\circ}_{OP} = -E^{\circ}_{RP} \quad ...(11)$$

where, E_{OP} and E_{RP} are oxidation potential and reduction potential respectively.

E°_{OP} and E°_{RP} are standard O.P. and standard R.P. defined as equal to E_{OP} and E_{RP} respectively when, $\frac{a_{O.S.}}{a_{R.S.}} = 1$

R is molar gas constant $= 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$ (MKS system, since *E* in volt)

T is temperature in Kelvin

n is no. of electrons lost or gained during oxidation or reduction in redox change

F is one Faraday, *i.e.*, 96500 C

$a_{O.S.}$ = active mass of oxidized state in solution

$a_{R.S.}$ = active mass of reduced state in solution

Since $a = fc$ where, *f* is activity coefficient

For dilute solutions $f = 1$

$\therefore$ a = concentration in molarity

Thus, Eq. (8) may be written as

$$E_{OP} = E^{\circ}_{OP} - \frac{RT}{nF}\log_e \frac{[O.S.]}{[R.S.]} \quad ...(12)$$

$$E_{OP} = E^{\circ}_{OP} - \frac{2.303\,RT}{nF}\log_{10} \frac{[O.S.]}{[R.S.]} \quad ...(13)$$

$\because$ Numerical value of $\frac{2.303\,RT}{F} = 0.058$ at 288 K

$= 0.059$ at 298 K

$= 0.060$ at 308 K

i.e., no significant change with temperature.

By Eq. (13)

$$\therefore \quad E_{OP} = E^{\circ}_{OP} - \frac{0.059}{n}\log_{10} \frac{[O.S.]}{[R.S.]} \quad ...(14)$$

Similarly,

and $$E_{RP} = E^{\circ}_{RP} + \frac{0.059}{n}\log_{10} \frac{[O.S.]}{[R.S.]} \quad ...(15)$$

Formation of equation for different electrodes

Case I. $M \mid M^{+n}$ (*aq.*), *i.e.*, $M \rightleftharpoons M^{+n} + ne$

$$E_{OP} = E^{\circ}_{OP} - \frac{0.059}{n}\log_{10} \frac{[M^{+n}]}{[M]}$$

or $$E_{OP} = E^{\circ}_{OP} - \frac{0.059}{n}\log_{10} [M^{+n}]$$

[$\because$ *M* in solid state = unity]

and $$E_{RP} = E^{\circ}_{RP} + \frac{0.059}{n}\log_{10} [M^{+n}]$$

Case II. $Pt_{H_2} \mid H^+ (aq.)$,
(*P*)

i.e., $H_2 \rightleftharpoons 2H^+ + 2e$ or $\frac{1}{2}H_2 \rightleftharpoons H^+ + e$

For gaseous phase concentration is reported as pressure, *i.e.*, $[H_2]$ as P_{H_2}

$$E_{OP} = E^{\circ}_{OP} - \frac{0.059}{2}\log_{10} \frac{[H^+]^2}{P_{H_2}} \quad ...(16)$$

or $$E_{OP} = E^{\circ}_{OP} - \frac{0.059}{1}\log_{10} \frac{[H^+]}{(P_{H_2})^{1/2}} \quad ...(17)$$

Note : Eqs. (16) and (17) are same and thus it is evident that stoichiometry of change in half cell emf has no effect on Nernst expression.

Similarly, $$E_{RP} = E^{\circ}_{RP} + \frac{0.059}{2}\log_{10} \frac{[H^+]^2}{P_{H_2}}$$

Case III. $Pt_{Cl_2} \mid Cl^- (aq.)$ *i.e.*, $2Cl^- \rightleftharpoons Cl_2 + 2e$

$$E_{OP} = E^{\circ}_{OP} - \frac{0.059}{2}\log_{10} \frac{P_{Cl_2}}{[Cl^-]^2} \quad ...(18)$$

Similarly, $$E_{RP} = E^{\circ}_{RP} + \frac{0.059}{2}\log_{10} \frac{P_{Cl_2}}{[Cl^-]^2} \quad ...(19)$$

Formulation of equation for emf of cell

A model question: *Given that*

$A \longrightarrow A^{2+} + 2e$ $\quad E^{\circ} = +0.76$ V

$B \longrightarrow B^{2+} + 2e$ $\quad E^{\circ} = +0.44$ V

Find out

(*a*) *Anode of cell*

(*b*) *Cathode of cell*

(*c*) *Reaction at anode*

(*d*) *Reaction at cathode*

(*e*) *Redox change*

(*f*) *No. of electrons used for redox change*

(*g*) *Direction of flow of electron*

(*h*) *Direction of flow of current*

(*i*) E°_{cell}

(*j*) E_{cell}

(*k*) *Design of cell.*

Solution (1) First decide the nature of E° values given, *i.e.*, whether they are E°_{OP} or E°_{RP} by noting.

(a) Given directly, *i.e.*, mentioned as E°_{OP} or E°_{RP}

or

(b) See the change,

(i) If oxidation reaction is mentioned, then

$$E^\circ_{OP} \quad i.e., \quad E_{A/A^{2+}} \text{ then } E^\circ_{OP}$$

(ii) If reduction reaction is mentioned, then

$$E^\circ_{RP} \quad i.e., \quad E_{A^{2+}/A} \text{ then } E^\circ_{RP}$$

(2) Write E°_{OP} and E°_{RP} of both

$$E^\circ_{OP\ A/A^{2+}} = +0.76 \quad \text{then } E^\circ_{RP\ A^{2+}/A} = -0.76$$

$$E^\circ_{OP\ B/B^{2+}} = +0.44 \qquad E^\circ_{RP\ B^{2+}/B} = -0.44$$

(3) Write the process for oxidation at the electrode having more or +ve value of E°_{OP} and reduction for other.

$$A \longrightarrow A^{2+} + 2e$$

Anode of cell; cell reaction at anode

$$B^{2+} + 2e \longrightarrow B$$

Cathode of cell; cell reaction at cathode **[Ans. to a, b, c, d]**

(4) Now add these two after making electrons same on two sides.

$$A + B^{2+} = A^{2+} + B$$

This is cell reaction of redox change **[Ans. to e]**

Also no. of electrons lost or gained during process is 2. **[Ans. to f]**

Also, In a redox cell: Anode has negative polarity.
Cathode has positive polarity.

Thus, electrons flow from A to B **[Ans. to g]**

and Current flows from B to A **[Ans. to h]**

(5) $E^\circ_{cell} = E^\circ_{OP_A} + E^\circ_{RP_B}$ **[Ans. to i]**

$$= +0.76 + (-0.44) = +0.32 \text{ V}$$

Write E°_{OP} for one which show oxidation	Put a +ve sign in
Write E°_{RP} for one which show reduction	between two

Similarly, $E_{cell} = E_{OP_A} + E_{RP_B}$ **[Ans. to j]**

$$= E^\circ_{OP_A} - \frac{0.059}{2}\log_{10}[A^{2+}] + E^\circ_{RP_B} + \frac{0.059}{2}\log_{10}[B^{2+}]$$

$$= E^\circ_{OP_A} + E^\circ_{RP_B} + \frac{0.059}{2}\log_{10}\frac{[B^{2+}]}{[A^{2+}]}$$

$$E_{cell} = E^\circ_{cell} + \frac{0.059}{2}\log_{10}\frac{[B^{2+}]}{[A^{2+}]}$$

(6) For design of cell, keep electrode showing oxidation on left and other showing reduction on right. Put two vertical lines in between these two electrodes to show salt bridge in order to eliminate **liquid junction potential.**

	L.H.S.		R.H.S.
	$A\|A^{2+}$	$\|\|$	$B^{2+}\|B$
or	$A\|A(NO_3)_2$ (Anode) (– ve polarity)	$\|\|$	$B(NO_3)_2\|B$ (Cathode) (+ve polarity)

Liquid junction potential is arised due to different ionic mobility of ions.

Some applications of Nernst equation

(1) In computation of E°_{cell} and E_{cell}: See model question.

$$E^\circ_{cell} = E^\circ_{OP} + E^\circ_{RP}, \quad E_{cell} = E_{OP} + E_{RP}$$

(2) In computation of equilibrium constant: When the cell reaction is at equilibrium, the system does no net work and the cell emf is zero.

i.e., $\quad -\Delta G = nFE \quad$ or $\quad -\Delta G = 0 \qquad (\because E = 0)$

Consider the following reaction in equilibrium

$$Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu$$

At equilibrium $\quad K_C = \frac{[Zn^{2+}]}{[Cu^{2+}]}$ ...(20)

As discussed in model question,

$$E_{cell} = E^\circ_{cell} + \frac{RT}{nF}\log_e\frac{[Cu^{2+}]}{[Zn^{2+}]} \quad ...(21)$$

$\because$ Zn is oxidized and Cu^{2+} is reduced

At equilibrium $\quad E_{cell} = 0$

$\therefore$ By Eqs. (20) and (21), $\quad -E^\circ_{cell} = \frac{RT}{nF}\log_e\frac{1}{K_C}$

$$E^\circ_{cell} = \frac{RT}{nF}\log_e K_C$$

or $\quad n.F.E^\circ_{cell} = RT\log_e K_C$

or $\quad -\Delta G^\circ = RT\log_e K_C$

$$-\Delta G^\circ = 2.303\,RT\log_{10} K_C \quad ...(22)$$

where, ΔG° is change in standard free energy.

(3) Heat of reaction for cell reaction: The heat of reaction for cell reaction (ΔH) at a temperature is calculated by Gibb's Helmholtz equation.

$$\Delta G = \Delta H + T\left(\frac{\delta}{\delta T}\Delta G\right)_P$$

$\because \quad -\Delta G = nEF$

$$-nEF = \Delta H + T\left[\frac{\delta}{\delta T}(-nEF)\right]_P$$

or $\quad E = -\frac{\Delta H}{nF} + T\left(\frac{\delta E}{\delta T}\right)_P \quad ...(23)$

or $\quad \Delta H = nF\left[T\left(\frac{\delta E}{\delta T}\right)_P - E\right] \quad ...(24)$

where, $\left(\frac{\delta E}{\delta T}\right)_P$ is called temperature coefficient of emf, *i.e.*, rate of change of emf with temperature.

(4) To decide spontaniety of cell reaction: Compute E°_{cell} for the given reaction, *e.g.*,

$$A + B^{2+} \longrightarrow A^{2+} + B$$

$$\therefore \quad E^\circ_{cell} = E^\circ_{OP_A} + E^\circ_{RP_B}$$

If E°_{cell} comes to be +ve, cell reaction is spontaneous and if E°_{cell} comes to be −ve, cell reaction is not spontaneous.

(5) To evaluate solubility product: See Solved Problems

(6) To evaluate pH of solution: See Solved Problems

Relation between standard potential of metal-metal ion electrode and the corresponding metal-insoluble salt anion electrode : Ag /AgCl, Cl$^-$

Consider and electrode Ag /Ag$^+$ with reaction :

$$Ag^+ + e \longrightarrow Ag$$

The electrode potential is :

$$E_{Ag^+/Ag} = E^\circ_{Ag^+/Ag} + \frac{0.059}{1}\log[Ag^+] \quad ...(25)$$

Now suppose excess of NaCl is added in this electrolyte chamber so that all of the Ag$^+$ ions are precipitated obeying :

$$K_{sp_{AgCl}} = [Ag^+][Cl^-] \quad ...(26)$$

By Eqs. (25) and (26),

$$E_{Ag^+/Ag} = E^\circ_{Ag^+/Ag} + \frac{0.059}{1}\log\frac{K_{sp}}{[Cl^-]} \quad ...(27)$$

Now at this stage electrode can be taken as Ag/AgCl(*s*), Cl$^-$. The half reaction for this electrode is

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

The electrode potential is :

$$E_{Cl^-/AgCl/Ag} = E^\circ_{Cl^-/AgCl/Ag} + \frac{0.0591}{1}\log\frac{1}{[Cl^-]} \quad ...(28)$$

Since, both the electrodes are same, thus Eqs. (27) and (28) are identical, therefore,

$$E^\circ_{Cl^-/AgCl/Ag} + \frac{0.0591}{1}\log\frac{1}{[Cl^-]} = E^\circ_{Ag^+/Ag} + \frac{0.059}{1}\log\frac{K_{sp}}{[Cl^-]}$$

$$E^\circ_{Cl^-/AgCl/Ag} = E^\circ_{Ag^+/Ag} + \frac{0.059}{1}\log K_{sp_{AgCl}} \quad ...(29)$$

Relation for metal amalgam-metal ion half cell :

Pt electrode : $M\,(Hg) \longrightarrow M^{n+}(aq.) + ne$

$$E_{M\,(Hg)Pt/M^{n+}} = E^\circ_{M\,(Hg)Pt/M^{n+}} + \frac{0.059}{n}\log[M^{n+}] \quad ...(30)$$

Also for a cell PtM (Hg) / $M^{n+}(aq.)$ /M

$$E_{cell} = E^\circ_{M\,(Hg)Pt/M^{n+}} - E^\circ_{M^{n+}/M} \quad ...(31)$$

Relation for oxidation-reduction in half cell :

(a) Pt / Fe^{2+}, Fe^{3+}

The half cell reaction is $Fe^{3+}(aq.) + e \longrightarrow Fe^{2+}(aq.)$

$$E_{Fe^{3+}/Fe^{2+}} = E^\circ_{Fe^{3+}/Fe^{2+}} + \frac{0.059}{1}\log\frac{[Fe^{3+}]}{[Fe^{2+}]}$$

(b) Pt / H^+, MnO_4^-, Mn^{2+}

The half cell reaction is ;

$$Mn^{7+} + 5e \longrightarrow Mn^{2+}$$

or $\quad MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} 4H_2O$

$$\therefore E_{MnO_4^-/Mn^{2+}} = E^\circ_{MnO_4^-/Mn^{2+}} + \frac{0.059}{5}\log\frac{[MnO_4^-][H^+]^8}{[Mn^{2+}]}$$

Reference electrode : Normal hydrogen electrode (NHE) is used as primary reference electrode having $E^\circ_{H^+/H} = 0$, assigned arbitrarily.

$$\underset{P=1\,atm}{PtH_2\ gas}\ \Big|\ \underset{a=1}{HCl} \qquad at\ 25°C\ E° = 0$$

The other reference electrodes such as calomel electrode [$Hg_2Cl_2(s) + KCl(aq.)$], Ag—AgCl(*s*) electrode are called secondary reference electrodes.

• NUMERICAL PROBLEMS •

1. Calculate the quantity of electricity that will be required to liberate 710 g of Cl_2 gas by electrolysing a conc. solution of NaCl. What mass of NaOH and what volume of H_2 at 27° C and 1 atm. pressure is obtained during this process?
2. How many kJ of energy is expended during the passage of 1 ampere current for 100 sec under a potential of 115 V?
3. Find the charge in coulomb on 1 g ion of N^{3-}.
4. Find out the volume of gases evolved by passing 0.965 A current for 1 hr through an aqueous solution of CH_3COONa at 25° C and 1 atm.
5. A current of 0.5 A is passed through acidulated water for 30 minute. Calculate mass of H_2 and O_2 evolved. Also calculate the volume of O_2 produced at 25° C and 760 mm of Hg if the gas is :
   (a) dry (b) saturated with water vapour (aqueous tension is 23.0 mm at 25° C).
6. Calculate the volume of Cl_2 at NTP produced during electrolysis of fused $MgCl_2$ which produces 6.50 g Mg. Atomic mass of Mg = 24.3.
7. How long would it take to deposit 100 g of Al from an electrolytic cell containing Al_2O_3 using a current of 125 ampere?
8. A metal wire carries a current of 1 ampere. How many electrons pass a point in the wire in one second?
9. How long will it take for a uniform current of 6.0 ampere to deposit 78.0 g gold from a solution of $AuCl_4^-$? What mass of chlorine gas will be formed simultaneously at the anode of the electrolytic cell?
10. An ammeter and copper voltameter are connected in series in an electric circuit through which a constant direct current flows. The ammeter shows 0.525 ampere. If 0.6354 g of Cu is deposited in one hour, what is percentage error of ammeter? Atomic mass of Cu = 63.54.
11. 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 minute. It was found that after electrolysis, the absorbance of the solution was reduced to 50% of its original value. Calculate the concentration of copper sulphate in the solution to begin with.
12. Calculate the number of electrons lost or gained during electrolysis of:
   (a) 2 g Cl^- ions. (b) 1 g Zn^{2+} ions.
13. 0.35 mole of electrons were passed through three electrolyte solutions connected in series. If the solutions are of Ag^+, Cu^{2+} and Au^{3+}, calculate the amount of each metal deposited at cathode of each cell.
14. Same quantity of electricity being used to liberate iodine (at anode) and a metal (at cathode) : The mass of metal liberated at cathode is 0.617 g and the liberated iodine completely reduced by 46.3 mL of 0.124 M sodium thiosulphate solution. What is equivalent mass of metal?
15. Cd amalgam is prepared by electrolysis of a solution of $CdCl_2$ using a mercury cathode. Find how long should a current of 5 ampere is passed in order to prepare 12% Cd-Hg amalgam on a cathode of 2 g mercury? Atomic mass of Cd = 112.40.
16. 10 g fairly concentrated solution of $CuSO_4$ is electrolysed using 0.01 Faraday of electricity. Calculate:
   (a) the mass of resulting solution.
   (b) the no. of equivalents of acid or alkali in solution. Atomic mass of Cu = 63.5.
17. A test for complete removal of Cu^{2+} ions from a solution of Cu^{2+} *(aq.)* is to add NH_3 *(aq.)*. A blue colour signifies the formation of complex $[Cu(NH_3)_4]^{2+}$ having $K_f = 1.1 \times 10^{13}$ and thus confirms the presence of Cu^{2+} in solution. 250 mL of 0.1 *M* $CuSO_4$ *(aq.)* is electrolysed by passing a current of 3.512 ampere for 1368 second. After passage of this charge sufficient quantity of NH_3 *(aq.)* is added to electrolysed solution maintaining $[NH_3] = 0.10$ M. If $[Cu(NH_3)_4]^{2+}$ is detectable upto its concentration as low as 1×10^{-5}, would a blue colour be shown by the electrolysed solution on addition of NH_3?
18. A current of 3.7 ampere is passed for 6 hr between Ni electrodes in 0.5 litre of 2 M solution of $Ni(NO_3)_2$. What will be the molarity of solution at the end of electrolysis?
19. How much current is necessary to produce hydrogen gas at the rate of 1 cc per second at NTP conditions?
20. 3 ampere current was passed through an aqueous solution of an unknown salt of Pd for 1 hour. 2.977 g of Pd^{n+} was deposited at cathode. Find *n*. (Atomic mass of Pd = 106.4)
21. A Zn rod weighing 25 g was kept in 100 mL of 1 *M* $CuSO_4$ solution. After a certain time the molarity of Cu^{2+} in solution was 0.8. What was molarity of SO_4^{2-}? What was the mass of Zn rod after cleaning? (Atomic mass of Zn = 65.4)
22. Assume that impure copper contains only Fe, Au and Ag as impurities. After passage of 140 ampere for 482.5 sec. the mass of anode decreased by 22.260 g and the cathode increased in mass by 22.011 g. Calculate the

percentage of iron and percentage of copper originally present.

23. Chromium metal can be plated out from an acidic solution containing CrO_3 according to following equation,

$$CrO_3(aq.) + 6H^+ + 6e \longrightarrow Cr(s) + 3H_2O$$

Calculate:

(a) how many gram of chromium will be plated out by 24000 coulomb?

(b) how long will it take to plated out 1.5 g of Cr by using 12.5 ampere current? **(IIT 1993)**

24. In an electrolysis experiment, current was passed for 5 hour through two cells connected in series. The first cell contains a solution of gold and the second contains $CuSO_4$ solution. 9.85 g of gold was deposited in the first cell. If the oxidation no. of gold is +3, find the amount of Cu deposited on cathode in second cell. Also calculate the current strength in ampere. Atomic mass of Au = 197 and atomic mass of Cu = 63.5.

25. An electric current is passed through two solutions of (i) $AgNO_3$ and (ii) a solution of 10 g $CuSO_4 \cdot 5H_2O$ crystals in 500 mL H_2O, platinum electrodes being used in each case. After 30 minute it is found that 1.307 g Ag has been deposited. What was the conc. of Cu expressed in g of Cu per litre in solution after electrolysis?

(Atomic mass of Cu = 63.54, Ag = 108)

26. Electrolysis of a solution of $MnSO_4$ in aqueous sulphuric acid is a method for the preparation of MnO_2 as per reaction,

$$Mn^{2+}(aq.) + 2H_2O \longrightarrow MnO_2(s) + 2H^+(aq.) + H_2(g)$$

Passing a current of 27 A for 24 hours gives one kg of MnO_2. What is the value of current efficiency? Write the reaction taking place at the cathode and at the anode. **(IIT May 1997)**

27. A constant current was flown for 2 hour through a KI solution oxidising iodide ion to iodine ($2I^- \rightarrow I_2 + 2e$). At the end of experiment liberated iodine consumed 21.75 mL of 0.0831 M solution of sodium thiosulphate following the redox change

$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$. What was the average rate of current flown in ampere?

28. 50 mL of 0.1 *M* $CuSO_4$ solution is electrolysed using Pt electrodes with a current of 0.965 ampere for a period of 1 minute. Assuming that volume of solution does not change during electrolysis, calculate $[Cu^{2+}]$, $[H^+]$ and $[SO_4^{2-}]$ after electrolysis. What will be the concentration of each species if current is passed using Cu electrodes?

29. An electric current is passed through two electrolytic cells connected in series, one containing $AgNO_3(aq.)$ and other $H_2SO_4(aq.)$. What volume of O_2 measured at 25°C and 750 mm in Hg would be liberated from H_2SO_4 if:

(a) 1 mole of Ag^+ are deposited from $AgNO_3$ solution?

(b) 8×10^{22} ions of Ag^+ are deposited from $AgNO_3$ solution?

30. In a fuel cell H_2 and O_2 react to produce electricity. In the process H_2 gas is oxidized at the anode and O_2 at cathode. If 67.2 litre of H_2 at STP reacts in 15 minutes, what is average current produced? If the entire current is used for electro deposition of Cu from Cu^{2+}, how many gram of Cu are deposited?

31. A 200 W, 110V incandescent lamp is connected in series with an electrolytic cell of negligible resistance containing a solution of $ZnCl_2$. What mass of Zn will be deposited from the solution on passing current for 30 minutes? (Atomic mass of Zn = 65.4)

32. By passing a certain amount of charge through NaCl solution, 9.2 litre of Cl_2 were liberated at STP. When the same charge is passed through a nitrate solution of metal M, 7.467 g of the metal was deposited. If the specific heat of metal is 0.216 cal/g, what is formula of metal nitrate?

33. An oxide of metal (atomic mass = 112) contains 12.5% O_2 by mass. The oxide was converted into chloride by treatment with HCl and electrolysed. Calculate the amount of metal that would be deposited at cathode if a current of 0.965 ampere was passed for a period of 5 hr. What is valency of metal?

34. A current of 3 ampere was passed for 2 hour through a solution of $CuSO_4 \cdot$ 3g of Cu^{2+} ions were discharged at cathode. Calculate current efficiency. (atomic mass of Cu = 63.5)

35. An aqueous solution of NaCl on electrolysis gives $H_2(g)$, $Cl_2(g)$ and NaOH according to reaction:

$$2Cl^-(aq.) + 2H_2O \longrightarrow 2OH^-(aq.) + H_2(g) + Cl_2(g)$$

A direct current of 25 ampere with a current efficiency of 62% is passed through 20 litre of NaCl solution (20% by mass).

(a) Write down the reactions taking place at the electrodes.

(b) How long will it take to produce 1 kg of Cl_2?

(c) What will be the molarity of solution with respect to OH^-?

Assume no loss in volume due to evaporation. **(IIT 1992)**

36. A current of 1.70 A is passed through 300 mL of 0.160 M solution of $ZnSO_4$ for 230 sec. with a current efficiency of 90%. Find the molarity of Zn^{2+} after the deposition of Zn. Assume the volume of the solution remains constant during electrolysis. **(IIT 1991)**

37. 19g fused $SnCl_2$ was electrolysed using inert electrodes. 0.119 g Sn was deposited at cathode. If nothing was given out during electrolysis, calculate the ratio of mass of $SnCl_2$ and $SnCl_4$ in fused state after electrolysis (Atomic mass of Sn = 119).

38. After electrolysis of a sodium chloride solution with inert electrodes for a certain period of time, 600 mL of the 1N solution was left which was found to be NaOH. During the same time 31.80 g Cu was deposited in copper voltameter in series with the electrolytic cell. Calculate the % of NaOH obtained. (Atomic mass of Cu = 63.6).

39. Per disulphuric acid ($H_2S_2O_8$) can be prepared by electrolytic oxidation of H_2SO_4 as

$$2H_2SO_4 \rightarrow H_2S_2O_8 + 2H^+ + 2e.$$

Oxygen and hydrogen are byproducts. In such an electrolysis 9.72 litre of H_2 and 2.35 litre of O_2 were generated at STP. What is the mass of $H_2S_2O_8$ formed?

40. An acidic solution of Cu^{2+} salt containing 0.4 g of Cu^{2+} is electrolysed until all the Cu is deposited. The electrolysis is containued for seven more minutes with the volume of solution kept at 100 mL and the current at 1.2 ampere. Calculate volume of gases evolved at NTP during entire electrolysis. (Atomic mass of Cu = 63.6)

41. Calculate the quantity of electricity that would be required to reduce 12.3 g of nitrobenzene to aniline, if current efficiency is 50%. If the potential drops across the cell is 3.0 volt, how much energy will be consumed? **(IIT 1990)**

42. Calculate the quantity of electricity required to reduce 6.15 g of nitrobenzene to aniline if the current efficiency is 68 per cent. If potential drops across the cell is 7.0 volt, calculate the energy consumed in the process.

43. In the manufacture of Al, Al_2O_3 is dissolved in Na_3AlF_6 at 300 K and electrolysed between Al and carbon electrodes following the net reaction,

$$2Al_2O_3 \text{ (solution)} + 3C \longrightarrow 4Al(l) + 3CO_2(g)$$

write the reaction of each electrode. Calculate the minimum voltage required between the electrodes if the Gibbs free energy change for the above reaction is -1370 kJ mol^{-1}.

44. During the discharge of a lead storage battery, the density of sulphuric acid fell from 1.294 g mL^{-1} to 1.139 g mL^{-1}. Sulphuric acid of density 1.294 g mL^{-1} is 39% by mass and that of density 1.139 g mL^{-1} is 20% by mass. The battery holds 3.5 litre of acid and the volume practically remained constant during the discharge. Calculate the no. of ampere hour for which the battery must have been used. The charging and discharging reactions are:

$$Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2e \qquad \text{charging}$$

$$PbO_2 + 4H^+ + SO_4^{2-} + 2e \longrightarrow PbSO_4 + 2H_2O \qquad \text{discharging}$$

45. A lead storage cell is discharged which causes the H_2SO_4 electrolyte to change from a concentration of 34.6% by mass (density 1.261 g mL^{-1} at 25°C) to one of 27% by mass. The original volume of electrolyte is one litre. How many Faraday have left the anode of battery? Note the water is produced by the cell reaction as H_2SO_4 is used up. Overall reaction is:

$$Pb(s) + PbO_2 + 2H_2SO_4(l) \longrightarrow 2PbSO_4(s) + 2H_2O$$

46. The electrolytic reduction of 300 mL of 0.01 *M* nitroalkane was carried out in acidic buffer medium of pH 5.0 following the change :

$$RNO_2 + 4H_3O^+ + 4e \longrightarrow RNHOH + 5H_2O$$

If the total concentration of weak acid and its conjugate base was 0.50*M*, calculate the pH of solution after completion of reduction. K_a for weak acid is 1.8×10^{-5}.

47. Two litre solution of a buffer mixture containing 1.0 *M* NaH_2PO_4 and 1.0 *M* Na_2HPO_4 is placed in two compartments (one litre in each) of an electrolytic cell. The platinum electrodes are inserted in each compartment and 1.25 ampere current is passed for 212 minute. Assuming electrolysis of water only at each compartment. What will be pH in each compartment after passage of above charge? (pK_a for $H_2PO_4^- = 2.15$).

48. The density of copper is 8.94 g mL^{-1}. Find out the number of coulomb needed to plate an area of $10 \times 10\ cm^2$ to a thickness of 10^{-2} cm using $CuSO_4$ solution as electrolyte. (Atomic mass of Cu = 63.6)

49. How many grams of silver could be plated out on a serving tray by electrolysis of solution containing silver in +1 oxidation state for a period of 8.0 hour at a current of 8.46 ampere? What is the area of the tray if the thickness of the silver plating is 0.00254 cm? (Density of silver is 10.5 g / cm^3). **(IIT July 1997)**

50. A current of 40 microampere is passed through a solution of $AgNO_3$ for 32 minutes using Pt electrodes. A uniform single atom thick layer of Ag is deposited covering 43% cathode surface. What is the total surface area of cathode if each Ag atom covers $5.4 \times 10^{-16}\ cm^2$?

51. Calculate emf of half cells given below:

(a) Pt_{H_2} (2 atm) | HCl (a = 0.02) $\qquad E^\circ_{OP} = 0V$

(b) Fe | $FeSO_4$ (a = 0.1) $\qquad E^\circ_{OP} = 0.44\ V$

(c) Pt_{Cl_2} (10 atm) | HCl (a = 0.1) $\qquad E^\circ_{OP} = -1.36V$

52. Calculate the pH of the following half cells solutions:

(a) Pt_{H_2} | HCl $E = 0.25V$
1 atm

(b) Pt_{H_2} | H_2SO_4 $E = 0.3V$
1 atm

(c) A solution containing 4.5 mM of $Cr_2O_7^{2-}$ and 15 mM of Cr^{3+} shows a pH of 2.0. Calculate the potential of half reaction. (Standard potential of the reaction $Cr_2O_7^{2-} \rightarrow Cr^{3+}$ is 1.33 V.)

(Roorkee 2001)

53. Consider the reaction: $2Ag^+ + Cd \rightarrow 2Ag + Cd^{2+}$. The standard reduction potential of $Ag^+ - Ag$ and $Cd^{2+} - Cd$ couples are +0.80 and −0.40 volt respectively.

(a) What is the standard cell emf, $E°$?

(b) Will the total emf of the reaction be more *+ve* or *−ve*, if conc. of Cd^{2+} is 0.10*M* rather than 1*M*?

54. Calculate the values for cell

$$Zn \mid Zn^{2+}(aq.) \mid\mid Cu^{2+}(aq.) \mid Cu$$

(i) cell reaction and (ii) emf of cell if Zn^{2+} and Cu^{2+} are 1 *M* each, (iii) the minimum concentration of Cu^{2+} at which the cell reaction,

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

will be spontaneous if Zn^{2+} is 1 *M* (iv) does the displacement of $Cu^{2+}(aq.)$ by Zn goes to completion.

Given, $E^{\circ}_{RP_{Cu^{2+}/Cu}} = +0.35$ V

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

55. Two students use same stock solution of $ZnSO_4$ and a solution of $CuSO_4$. The emf of one cell is 0.03 V higher than the other. The conc. of $CuSO_4$ in the cell with higher emf value is 0.5 *M*. Find out the conc. of $CuSO_4$ in the other cell $\left(\frac{2.303\,RT}{F} = 0.06\right)$. **(IIT 2003)**

56. A graph is plotted between E_{cell} and $\log_{10}\frac{[Zn^{2+}]}{[Cu^{2+}]}$. The curve was linear with intercept on E_{cell} axis equal to 1.10 V. Calculate E_{cell} for

$$Zn \mid \underset{0.1\,M}{Zn^{2+}} \mid\mid \underset{0.01\,M}{Cu^{2+}} \mid Cu$$

57. If $NO_3^- \longrightarrow NO_2$ (acidic medium); $E° = 0.790$ V and $NO_3^- \longrightarrow NH_2OH$ (acidic medium); $E° = 0.731$ V. At what pH the above two half reactions will have same *E* values? Assume the concentrations of all the species to the unity.

58. The following electrochemical cell has been set up.

$$Pt_{(I)} \mid Fe^{3+}, Fe^{2+}\ (a = 1) \mid\mid Ce^{4+}, Ce^{3+}\ (a = 1) \mid Pt_{(II)}$$

$E^{\circ}_{Fe^{3+}/Fe^{2+}} = 0.77$ V and $E^{\circ}_{Ce^{4+}/Ce^{3+}} = 1.61$ V

If an ammeter is connected between the two platinum electrode, predict the direction of flow of current. Will the current increase or decrease with time? **(IIT 2000)**

59. 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 the solution will the measured emf be zero at 25°C? (Assume $[Ni^{2+}] = 1M$ and $P_{H_2} = 1$ atm).

60. Calculate the equilibrium constant for the reaction:

$$Fe^{2+} + Ce^{4+} \rightleftharpoons Fe^{3+} + Ce^{3+}$$

Given, $E^{\circ}_{Ce^{4+}/Ce^{3+}} = 1.44$ V and $E^{\circ}_{Fe^{3+}/Fe^{2+}} = 0.68$ V

(IIT July 1997)

61. Calculate the equilibrium constant for the reaction, $2Fe^{3+} + 3I^- \rightleftharpoons 2Fe^{2+} + I_3^-$. The standard reduction potentials in acidic conditions are 0.77 and 0.54V respectively for Fe^{3+} / Fe^{2+} and I_3^- / I^- couples.

(IIT 1998)

62. Find the equilibrium constant for the reaction:

$$In^{2+} + Cu^{2+} \longrightarrow In^{3+} + Cu^+ \text{ at 298 K}$$

Given, $E^{\circ}_{Cu^{2+}/Cu^+} = 0.15$ V, $E^{\circ}_{In^{3+}/In^+} = -0.42$ V, $E^{\circ}_{In^{2+}/In^+} = -0.40$ V **(IIT 2004)**

63. Construct a cell in which the disproportionation reaction

$$2CuCl \longrightarrow CuCl_2 + Cu$$

takes place. Also calculate the equilibrium constant for the reaction if Cu^{2+} / Cu^+ and Cu^+ / Cu are 0.153 V and 0.518V respectively.

64. Zinc granules are added in excess to 500 mL of 1*M* $Ni(NO_3)_2$ solution at 25°C until the equilibrium is reached. If $E^{\circ}_{Zn^{2+}/Zn}$ and $E^{\circ}_{Ni^{2+}/Ni}$ are −0.75 V and −0.24 V respectively, find out the $[Ni^{2+}]$ at equilibrium.

(IIT 1991)

65. The standard reduction potential for Cu^{2+} / Cu is +0.34 V. Calculate the reduction potential at pH = 14 for the above couple, K_{sp} of $Cu(OH)_2$ is 1.0×10^{-19}.

(IIT 1996)

66. The emf of cell Ag | AgI(*s*), 0.05*M KI*||0.05*M* $AgNO_3$ | Ag is 0.788 V. Calculate solubility product of AgI.

67. If it is desired to construct the following voltaic cell to have $E_{cell} = 0.0860$ V, what $[Cl^-]$ must be present in the cathodic half cell to achieve the desired emf. Given K_{sp} of AgCl and AgI are 1.8×10^{-10} and 8.5×10^{-17} respectively?

Ag(*s*) | Ag^+ [Sat. AgI (*aq.*)]||

Ag^+ (Sat. AgCl · *xM*Cl^-)| Ag(*s*)

68. The standard reduction potential of $Cu^{2+}|Cu$ and $Ag^{+}|Ag$ electrodes are 0.337V and 0.799V respectively. Construct a galvanic cell using these electrodes so that its E°_{cell} is +ve. For what $[Ag^{+}]$ will the emf of cell at 25°C be zero if $[Cu^{2+}]$ is $0.01M$? **(IIT 1990)**

69. Find the solubility product of a saturated solution of Ag_2CrO_4 in water at 298K if the emf of the cell $Ag \mid Ag^{+}$ (satd. Ag_2CrO_4 sol.)$\|Ag^{+}$ $(0.1M)|$ Ag is 0.164V at 298K. **(IIT 1998)**

70. A silver electrode is immersed in saturated $Ag_2SO_4(aq.)$. The potential difference between the silver and the standard hydrogen electrode is found to be 0.711V. Determine K_{sp} (Ag_2SO_4). Given, $E^\circ_{Ag^+/Ag} = 0.799$V. **(Roorkee 2000)**

71. The emf of the cell obtained by combining Zn and Cu electrodes of a Daniel cell with N calomel electrodes are 1.083V and −0.018V respectively at 25°C. If the potential of N calomel electrode is −0.28V, find emf of Daniel cell.

72. The standard reduction potential at 25°C for the reaction $2H_2O + 2e \longrightarrow H_2 + 2OH^-$ is −0.8277V. Calculate the equilibrium constant for the reaction $2H_2O \rightleftharpoons H_3O^+ + OH^-$ at 25°C. **(IIT 1989)**

73. An excess of liquid Hg was added to $10^{-3}\,M$ acidified solution of Fe^{3+} ions. It was found that only 5% of the ions remained as Fe^{3+} at equilibrium at 25°C. Calculate E° for $2Hg \mid Hg_2^{2+}$ at 25°C for $2Hg + 2Fe^{3+} \rightleftharpoons Hg_2^{2+} + 2Fe^{2+}$ and $E^\circ_{Fe^{2+}/Fe^{3+}} = -0.77$V. **(IIT 1995)**

74. Calculate the potential of an indicator electrode versus the standard hydrogen electrode, which originally contains $0.1\,M$ MnO_4^- and $0.8\,M$ H^+ and which was treated with Fe^{2+} necessary to reduce 90% of MnO_4^- to Mn^{2+} $E^\circ_{MnO_4^-/Mn^{2+}} = 1.51$V.

75. Calculate the minimum mass of NaOH required to be added in R.H.S. to consume all the H^+ present in R.H.S. of cell of emf +0.701V at 25°C before its use. Also report the emf of cell after addition of NaOH.

$$\text{Zn} \left| \begin{matrix} Zn^{2+} \\ 0.1M \end{matrix} \right\| \begin{matrix} \text{HCl} \\ \text{1 litre} \end{matrix} \left| \begin{matrix} \text{Pt}_{H_2}(g) \\ \text{1 atm} \end{matrix} \right.$$

$E^\circ_{Zn/Zn^{2+}} = +0.760$V

76. A zinc electrode is dipped in a $0.1M$ solution at 25°C. Assuming that salt is dissociated to 20% at this dilution, calculate the electrode potential. $E^\circ_{Zn^{2+}/Zn} = -0.76$ V.

77. A cell is containing two H electrodes. The negative electrode is in contact with a solution of $10^{-6}\,M$ H^+ ion. The emf of the cell is 0.118 volt at 25°C. Calculate $[H^+]$ at positive electrode.

78. For the galvanic cell

$$Ag \mid AgCl(s),\ \underset{0.2M}{KCl} \ \|\ \underset{0.001M}{KBr},\ AgBr(s) \mid Ag$$

Calculate the emf generated and assign correct polarity to each electrode for a spontaneous process after taking an account of cell reaction at 25°C. Given, $K_{sp\,AgCl} = 2.8 \times 10^{-10}; K_{sp\,AgBr} = 3.3 \times 10^{-13}$. **(IIT 1992)**

79. Consider the cell $Ag \mid AgBr(s)Br^- \| AgCl(s)Cl^- \mid Ag$ at 25°C. The solubility product of AgCl and AgBr are 1×10^{-10} and 5×10^{-13} respectively. For what ratio of concentration of Br^- and Cl^- ions would the emf of cell be zero?

80. Calculate E° of redox change : $Ag_2S + 2e \rightleftharpoons 2Ag + S^{2-}$ if the reaction occurs at pH = 3 and saturated with $0.1\,M$ H_2S. K_1 and K_2 for H_2S are 1×10^{-8} and 1.1×10^{-13} respectively. $K_{sp\,Ag_2S} = 2 \times 10^{-49}$ and $E^\circ_{Ag^+/Ag} = 0.8$V.

81. The pK_{sp} of AgI is 16.07. If the E° value for Ag^+ / Ag is 0.7991V, find out the E° for half reaction:

$$AgI(s) + e \longrightarrow Ag + I^-$$

82. Determine potential for the cell

$$\text{Pt} \left| \begin{matrix} Fe^{2+} \\ Fe^{3+} \end{matrix} \right\| Cr_2O_7^{2-}, Cr^{3+}, H^+ \Big| \text{Pt}$$

in which $[Fe^{2+}]$ and $[Fe^{3+}]$ are 0.5 M and 0.75 M respectively and $[Cr_2O_7^{2-}]$, $[Cr^{3+}]$ and $[H^+]$ are 2 M, 4 M and 1 M respectively.

Given, $Fe^{3+} + e \longrightarrow Fe^{2+}$ $E^\circ = 0.770$V

$$14H^+ + 6e + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

$E^\circ = 1.35$V

83. The voltage of the cell given below is −0.46 V

$$\text{Pt}_{H_2} \left| \begin{matrix} NaHSO_3 \\ 0.4M \end{matrix} \quad \begin{matrix} Na_2SO_3 \\ 6.44 \times 10^{-3}\,M \end{matrix} \right\| \begin{matrix} Zn^{2+} \\ 0.3M \end{matrix} \Big| \text{Zn}(s)$$

Also, $Zn^{2+} + 2e \longrightarrow Zn(s)$, $E^\circ = -0.763$V. Calculate the value of K_2, where $K_2 = \dfrac{[H^+][SO_3^{2-}]}{[HSO_3^-]}$.

84. What ratio of Pb^{2+} to Sn^{2+} concentration is needed to reverse the following cell reaction?

$$Sn(s) + Pb(aq.)^{2+} \rightleftharpoons Sn(aq.)^{2+} + Pb(s)$$

$E^\circ_{Sn^{2+}/Sn} = -0.136$V and $E^\circ_{Pb^{2+}/Pb} = -0.126$V

85. The Edison storage cell is represented as,

$$Fe(s)|FeO(s)|KOH(aq.)|Ni_2O_3(s)|Ni(s)$$

The half cell reactions are:

$$Ni_2O_3(s)+H_2O(l)+2e^- \longrightarrow 2NiO(s)+2OH^-; \quad E^\circ=+0.40V$$

$$FeO(s)+H_2O(l)+2e^- \longrightarrow Fe(s)+2OH^-; \quad E^\circ=-0.87V$$

(i) What is the cell reaction?

(ii) What is the cell emf? How does it depend on the concentration of KOH?

(iii) What is the maximum amount of electrical energy that can be obtained from one mole of Ni_2O_3?

(IIT 1994)

86. For the electrode reaction,

$$\underset{1M}{CH_3CHO}+2H^+ +2e \longrightarrow \underset{1M}{CH_3CH_2OH},$$

the half cell potential is $-0.197V$ at pH = 7. Calculate the half cell potential when pH = 6 and ethanol and acetaldehyde each has concentration 10^{-5} M.

87. For the cell $Mg(s)|Mg(aq.)^{2+}||Ag(aq.)^+|Ag(s)$, calculate the equilibrium constant at 25°C and the maximum work that can be obtained during operation of cell. Given,

$$E^\circ_{Mg/Mg^{2+}}=+2.37\,V \text{ and } E^\circ_{Ag^+/Ag}=+0.80\,V,$$

$R=8.314$ J

88. The standard reduction potential for the half cell

$$NO_3^-(aq.)+2H^+(aq.)+e \longrightarrow NO_2(g)+H_2O$$

is 0.78V.

(i) Calculate the reduction potential in 8 M H^+.

(ii) What will be the reduction potential of the half cell in a neutral solution? Assume all the other species to be at unit concentration. **(IIT 1993)**

89. The standard reduction potential of $E^\circ_{Bi^{3+}/Bi}$ and $E^\circ_{Cu^{2+}/Cu}$ are 0.226 V and 0.344 V respectively. A mixture of salts of Bi^{3+} and Cu^{2+} at unit concentration each is electrolysed at 25°C. To what value can $[Cu^{2+}]$ be brought down before bismuth starts to deposit during electrolysis?

90. How much is the oxidizing power of ($1M$, MnO_4^-/Mn^{2+}, $1M$) couple decreased if the H^+ concentration is decreased from $1M$ to 10^{-4} M at 25°C?

91. An alloy weighing 1.05 g of Pb — Ag was dissolved in desired amount of HNO_3 and the volume was made 350 mL. An Ag electrode was dipped in solution and E_{cell} of the cell Pt $\underset{1\,atm}{H_2}$ | $\underset{1\,M}{H^+}$ || Ag^+ | Ag was 0.503 V at 298 K. Calculate the percentage of lead in alloy. Given $E^\circ_{Ag^+/Ag}=0.80V$.

92. Calculate the emf of given cell reaction and

$$Pb(s)+Hg_2SO_4 \rightleftharpoons PbSO_4(s)+2Hg(l)$$

design the cell if both electrolytes are present in their saturated solution state. Given $E^\circ_{Pb/Pb^{2+}}$ and $E^\circ_{Hg/Hg_2^{2+}}$ are 0.126 and $-0.789V$ respectively and K_{sp} of $PbSO_4$ and Hg_2SO_4 are 2.43×10^{-8} and 1.46×10^{-6} respectively.

93. The standard reduction potential of the Ag^+/Ag electrode at 298K is 0.799V. Given that for AgI, $K_{sp}=8.7\times10^{-17}$, evaluate the potential of the Ag^+/Ag electrode in a saturated solution of AgI. Also calculate the standard reduction potential of the $I^-/AgI/Ag$ electrode. **(IIT 1994)**

94. For the reaction $Ag^+(aq.)+Cl^-(aq.) \rightleftharpoons AgCl(s)$; the ΔG° values for $Ag^+(aq.)$, $Cl^-(aq.)$ and $AgCl(s)$ are $+77, -129$ and -109 kJ mol^{-1}. Write the cell representation of above reaction and calculate E° at 298 K. Also calculate K_{sp} of AgCl at 298K.

If 6.539×10^{-2} g of metallic zinc is added to 100 mL saturated solution of AgCl, find the value of $\log_{10}\frac{[Zn^{2+}]}{[Ag^+]^2}$. How many mole of Ag will be precipitated in this reaction? Given, $E^\circ_{Zn^{2+}/Zn}=-0.76V$. **(IIT 2005)**

95. The standard potential of the following cell is 0.23 V at 15°C and 0.21 V at 35°C.

$$Pt_{H_2}(g)\,|\,HCl(aq.)\,||\,AgCl(s)\,|\,Ag(s)$$

(i) Write the cell reaction.

(ii) Calculate ΔH° and ΔS° for the cell reaction by assuming that these quantities remain unchanged in the range 15°C to 35°C.

(iii) Calculate the solubility of AgCl in water at 25°C. Given, the standard reduction potential of the $Ag^+(aq.)/Ag(s)$ couple is 0.80 V at 25°C.

(IIT 2001)

96. Show that the potentials are additive for the process in which half reactions are added to yield an overall reaction but they are not additive when added to yield a third half reaction.

97. What is the standard electrode potential for the electrode MnO_4^-/MnO_2 in solution? Given:

$$E^\circ_{MnO_4^-/Mn^{2+}}=1.51V \text{ and } E^\circ_{MnO_2/Mn^{2+}}=1.23V$$

98. The reduction potential diagram for Cu in acid solution is:

$$Cu^{2+} \xrightarrow{+0.15\text{ volt}} Cu^+ \xrightarrow{+0.50\text{ volt}} Cu$$

$$Cu^{2+} \longrightarrow Cu: \quad E^\circ = X \text{ volt}$$

Calculate X. Does Cu^+ disproportionate in solution?

99. If E_1° is standard electrode potential for Fe / Fe^{2+} and E_2° is for Fe^{2+} / Fe^{3+} and E_3° for Fe / Fe^{3+}. Derive a relation between E_1°, E_2° and E_3°.

100. The following galvanic cell was

$$Zn \left| \begin{matrix} Zn(NO_3)_2(aq.) \\ 100\ mL, 1M \end{matrix} \right\| \begin{matrix} Cu(NO_3)_2(aq.) \\ 100\ mL, 1M \end{matrix} \right|$$

operated as an electrolytic cell using Cu as anode and Zn as cathode. A current of 0.48 ampere was passed for 10 hour and then the cell was allowed to function as galvanic cell. What would be the emf of the cell at 25°C? Assume that the only electrode reactions occurring were those involving Cu / Cu^{2+} and Zn / Zn^{2+}. Given $E^\circ_{Cu^{2+}/Cu} = +0.34$ V and $E^\circ_{Zn^{2+}/Zn} = -0.76$ V.

101. A cell $Ag|Ag^+||Cu^{2+}|Cu$ initially contains 1 M Ag^+ and 1 M Cu^{2+} ions. Calculate the change in the cell potential after the passage of 9.65 A of current for 1 hour. **(IIT 1999)**

102. Estimate the cell potential of a Daniel cell having 1.0 M Zn^{2+} and originally having 1.0 M Cu^{2+} after sufficient ammonia has been added to the cathode compartment to make the NH_3 concentration 2.0 M. Given $E^\circ_{Zn/Zn^{2+}}$ and $E^\circ_{Cu/Cu^{2+}}$ are 0.76 and -0.34 V respectively. Also equilibrium constant for the $[Cu(NH_3)_4]^{2+}$ formation is 1×10^{12}.

103. Two electrochemical cells are assembled in which the following reactions occur.

$$V^{2+} + VO^{2+} + 2H^+ \longrightarrow 2V^{3+} + H_2O \quad E^\circ_{cell} = 0.616V$$

$$V^{3+} + Ag^+ + H_2O \longrightarrow VO^{2+} + 2H^+ + Ag(s) \quad E^\circ_{cell} = 0.439V$$

Calculate E° for half reaction $V^{3+} + e \rightarrow V^{2+}$. Given, $E^\circ_{Ag^+/Ag} = 0.799$ volt.

104. The emf of cell $Zn|ZnSO_4||CuSO_4|Cu$ at 25°C is 0.03V and the temperature coefficient of emf is -1.4×10^{-4} V per degree. Calculate heat of reaction for the change taking place inside the cell.

105. For the reaction,

$$H_2(g) + 2AgCl(s) + 2H_2O(l) \longrightarrow 2Ag(s) + 2H_3O^+(aq.) + 2Cl^-(aq.).$$

At 25°C, the standard free energy of formation of $AgCl(s)$, $H_2O(l)$ and $(H_3O^+ + Cl^-)(aq.)$ are -109.7, -237.2 and -368.4 kJ / mol. Calculate what will be the cell voltage if this reaction is run at 25°C and one atmosphere in a cell in which H_2 activity is unity and $H_3O^+(aq.)$ and $Cl^-(aq.)$ activities are each at 0.01M?

106. E°_{cell} for reaction,

$$4Al(s) + 3O_2(g) + 6H_2O + 4OH^- \longrightarrow 4[Al(OH)_4]^-$$

is 2.73V. If G_f° for OH^- and H_2O are -157 k J mol^{-1} and -237.2 k J mol^{-1}, determine G_f° for $[Al(OH)_4]^-$.

107. Calculate the emf of cell:

$$\begin{matrix} Pt_{H_2} \\ 1\ atm \end{matrix} \left| \begin{matrix} CH_3COOH \\ 0.1M \end{matrix} \right\| \begin{matrix} NH_4OH \\ 0.01\ M \end{matrix} \left| \begin{matrix} Pt_{H_2} \\ 1\ atm \end{matrix} \right.$$

K_a for $CH_3COOH = 1.8 \times 10^{-5}$; K_b for $NH_4OH = 1.8 \times 10^{-5}$.

108. Two weak acid solutions HA_1 and HA_2 each with the same concentration and having pK_a values 3 and 5 are placed in contact with hydrogen electrode (1 atm, 25°C) and are interconnected through a salt bridge. Find emf of cell.

109. Dissociation constant for $Ag(NH_3)_2^+$ into Ag^+ and NH_3 is 6×10^{-14}. Calculate E° for the half reaction,

$$Ag(NH_3)_2^+ + e \longrightarrow Ag + 2NH_3$$

Given, $Ag^+ + e \longrightarrow Ag$ has $E^\circ = 0.799$V.

110. The overall formation constant for the reaction of 6 mole of CN^- with cobalt (II) is 1×10^{19}. Calculate the formation constant for the reaction of 6 mole of CN^- with cobalt (II). Given that,

$$Co(CN)_6^{3-} + e \longrightarrow Co(CN)_6^{4-}; \quad E^\circ_{RP} = -0.83\ V$$

$$Co^{3+} + e \longrightarrow Co^{2+}; \quad E^\circ_{RP} = 1.82\ V$$

111. The voltage of the cell :

$$Zn(s)|\underset{0.45\ M}{Zn(CN)_4^{2-}(aq.)}, \underset{2.65 \times 10^{-3}\ M}{CN^-} || \underset{3.84 \times 10^{-4}}{Zn^{2+}} | Zn(s)$$

is $+0.099$ V. Calculate the instability constant for $Zn(CN)_4^{2-}$ if only complexation resulting is $Zn^{2+} + 4CN^- \longrightarrow Zn(CN)_4^{2-}$.

112. Calculate the equilibrium constant at 25°C for the disproportionation of 3 mole of aqueous HNO_2 to yield NO and NO_3^- ions. The E° for reduction of HNO_2 to NO is 0.99V and E° for reduction of NO_3^- to HNO_2 is 0.94V.

113. The standard electrode potential corresponding to the reaction,

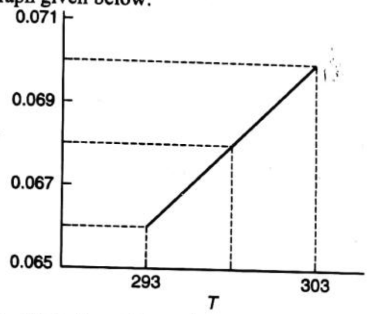
$$Au^{3+}(aq.) + 3e \longrightarrow Au(s)$$

is 1.42V. Predict if gold can be dissolved in 1M HCl solution and on passing hydrogen gas through gold salt solution, metallic gold will be precipitated or not.

114. For the cell:

$$As(s) \mid AgBr(s) \mid KBr(aq.) \mid Hg_2Br_2(s) \mid Hg(l),$$

the variation of emf with temperature is shown by the graph given below:



(a) Write the cell reaction.

(b) Calculate ΔG, ΔH and ΔS at 298K.

115. Determine the degree of hydrolysis and hydrolysis constant of aniline hydrochloride if:

$$\underset{1\,atm}{Pt.(H_2)} \mid \underset{1\,M}{H^+} \mid\mid \underset{\frac{1}{32}M}{C_6H_5NH_3Cl} \mid \underset{1\,atm}{H_2}\ Pt;\ E_{cell} = -0.188V \text{ at}$$

300K.

116. Peroxodisulphate salts (*e.g.*, $Na_2S_2O_8$) are strong oxidising agents used as bleaching agents for fats, oils and fabrics. Can oxygen gas oxidise sulphate ion to peroxide sulphate ion $S_2O_8^{2-}$ in acidic solution with $O_2(g)$ being reduced to water? Given,

$$O_2(g) + 4H^+(aq.) + 4e \longrightarrow 2H_2O;\quad E° = 1.23V$$

$$S_2O_8^{2-}(aq.) + 2e \longrightarrow 2SO_4^{2-};\ E° = 2.01V$$

117. $E°$ of some elements are given as:

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

$$MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O;\ E° = +1.52V$$

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

$$Sn^{4+} + 2e \longrightarrow Sn^{2+};\qquad E° = +0.1V$$

(a) Select the strongest reductant and oxidant in these.

(b) Select the weakest reductant and oxidant in these.

(c) Select the spontaneous reaction from the changes given below:

(i) $Sn^{4+} + 2Fe^{2+} \longrightarrow Sn^{2+} + 2Fe^{3+}$

(ii) $2Fe^{2+} + I_2 \longrightarrow 2Fe^{3+} + 2I^-$

(iii) $Sn^{4+} + 2I^- \longrightarrow Sn^{2+} + I_2$

(iv) $Sn^{2+} + I_2 \longrightarrow Sn^{4+} + 2I^-$

118. Two metals A and B have $E^°_{RP} = -0.76V$ and $+0.80V$ respectively, which will liberate H_2 from H_2SO_4?

SOLUTIONS (Numerical Problems)

1. $2Cl^- \longrightarrow Cl_2 + 2e \quad \therefore \; E_{Cl_2} = \frac{\text{Molar mass}}{2}$

$$w = \frac{E \cdot i \cdot t}{96500} = \frac{E \cdot Q}{96500}$$

$\therefore$ $$Q = \frac{96500w}{E} = \frac{96500 \times 710}{35.5} = 20\,F$$

$$Q = \mathbf{1930000\ coulomb}$$

$\because$ 1 F gives 1 g eq. or 40 g NaOH

$\therefore$ 20 F gives 20 g eq. or 40×20 g NaOH = **800 g NaOH**

$\because$ 1 F gives 1 g eq. or 1 g H_2

$\therefore$ 20 F gives 20 g eq. or 20 g H_2

from $$PV = \frac{w}{M}RT$$

$$1 \times V = \frac{20}{2} \times 0.0821 \times 300$$

$\therefore$ $$V_{H_2} = \mathbf{246.3\ litre}$$

2. Energy = charge × potential = $1 \times 100 \times 115$ = **11.5 kJ**

3. The electronic charge on $1\,N^{3-}$ is $= 3 \times 1.602 \times 10^{-19}$ C

$\therefore$ The electronic charge on 1 g eq. N^{3-}

$$= 3 \times 1.602 \times 10^{-19} \times N\,C$$

$$= 3 \times 1.602 \times 10^{-19} \times 6.023 \times 10^{23}\ C$$

$$= \mathbf{2.89 \times 10^5\ coulomb}$$

4. $2CH_3COONa(aq.) \xrightarrow{\text{Electrolysis}} \underset{\text{Anode}}{C_2H_6 + 2CO_2} + \underset{\text{Cathode}}{2NaOH + H_2}$

$$2CH_3COO^- \longrightarrow C_2H_6 + 2CO_2 + 2e$$

$$2H^+ \longrightarrow H_2 + 2e$$

$$\text{Equivalent}\left(\frac{W}{E}\right) = \frac{i \cdot t}{96500} = \frac{0.965 \times 1 \times 60 \times 60}{96500} = 0.036$$

Thus total equivalent of $C_2H_6 + CO_2 + H_2$

$$= 0.036 + 0.036 + 0.036$$

$\therefore$ Total mole of gases

$$(n) = \frac{0.036}{2} + \frac{0.036}{1} + \frac{0.036}{2} = 0.072$$

$$\left[\because E_{C_2H_6} = \frac{M}{2};\quad E_{H_2} = \frac{M}{2};\quad E_{CO_2} = \frac{M}{1}\right]$$

$\therefore$ $$V = \frac{nRT}{P} = \frac{0.072 \times 0.0821 \times 298}{1} = \mathbf{1.762\ litre}$$

5. $2H^+ + 2e \longrightarrow H_2 \qquad 4OH^- \longrightarrow 2H_2O + O_2 + 4e$

$$\because E_{H_2} = \frac{\text{Molar mass}}{2} = \frac{2}{2} = 1 \because E_{O_2} = \frac{\text{Molar mass}}{4} = \frac{32}{4} = 8$$

$$w_{H_2} = \frac{E \cdot i \cdot t}{96500} \qquad w_{O_2} = \frac{E \cdot i \cdot t}{96500}$$

$$= \frac{1 \times 0.5 \times 30 \times 60}{96500} \qquad = \frac{8 \times 0.5 \times 30 \times 60}{96500}$$

$$w_{H_2} = \mathbf{9.33 \times 10^{-3}\ g} \qquad w_{O_2} = \mathbf{7.46 \times 10^{-2}\ g}$$

(a) Using $$PV = \frac{w}{M}RT$$

$$\frac{760}{760} \times V = \frac{7.46 \times 10^{-2}}{32} \times 0.0821 \times 298$$

$\therefore$ $$V_{O_2} = \mathbf{5.7 \times 10^{-2}\ litre}$$

(b) $$P_{O_2} = P_T - P'_{H_2O} = 760 - 23 = 737\ \text{mm}$$

$\therefore$ $$\frac{737}{760} \times V = \frac{7.46 \times 10^{-2}}{32} \times 0.0821 \times 298$$

$\therefore$ $$V_{O_2} = \mathbf{5.88 \times 10^{-2}\ litre}$$

6. At cathode: $Mg^{2+} + 2e \longrightarrow Mg$

At anode: $2Cl^- \longrightarrow Cl_2 + 2e$

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

$\therefore$ $$\frac{6.5}{24.3/2} = \frac{w_{Cl_2}}{35.5}$$

$\therefore$ $$w_{Cl_2} = 18.99\,g$$

At NTP $$PV = \frac{w}{M}RT$$

$$1 \times V = \frac{18.99}{71} \times 0.0821 \times 273$$

Volume of Cl_2 = **5.99 litre**

7. $\because$ $$Al_2^{3+} + 6e \longrightarrow 2Al$$

$\therefore$ $$E_{Al} = \frac{\text{Atomic mass}}{3} = \frac{27}{3} = 9$$

Now $$w = \frac{E \cdot i \cdot t}{96500}$$

$$100 = \frac{27 \times 125 \times t}{3 \times 96500}$$

$\therefore$ $$t = \mathbf{8577.77\ second}$$

8. Total charge passed in one sec. = 1×1 = 1 coulomb ($\because Q = i \times t$)

$\because$ 1 Faraday or 96500 C current carried by $= 6.023 \times 10^{23}$ electrons

$\therefore$ 1 coulomb current carried by

$$= \frac{6.023 \times 10^{23}}{96500} = \mathbf{6.24 \times 10^{18}\ electrons}$$

9. $$AuCl_4^- + 3e \longrightarrow Au + 4Cl^-$$

$$Cl^- \longrightarrow \frac{1}{2}Cl_2 + e$$

$\therefore$ $$w_{Au} = \frac{E \cdot i \cdot t}{96500} = \frac{197 \times 6 \times t}{3 \times 96500} = 78.0$$

$\therefore$ $$t = \mathbf{19104\ sec.}$$

Also Eq. of Au = Eq. of Cl_2

$$\frac{78}{197/3} = \frac{w}{71/2}$$

$\therefore$ $$w_{Cl_2} = \mathbf{42.16\ g}$$

10. Current flown = 0.525 ampere as shown by ammeter

Actual current flown $$(i) = \frac{w}{E \times t} \times 96500$$

$$= \frac{0.6354 \times 96500}{(63.54/2) \times 60 \times 60}$$

($\because t = 60 \times 60$ sec.)

$\therefore$ $$i = 0.536\ \text{ampere}$$

Thus, error in $(i) = 0.536 - 0.525 = 0.011$

$\therefore$ % error in ammeter $= \frac{0.011 \times 100}{0.536} =$ **2.05%**

11. Equivalent of Cu^{2+} lost during electrolysis

$$= \frac{i \times t}{96500} = \frac{2 \times 10^{-3} \times 16 \times 60}{96500} = 1.989 \times 10^{-5}$$

or Mole of Cu^{2+} lost during electrolysis $= \frac{1.989 \times 10^{-5}}{2}$

This value is 50% of the initial concentration of solution

Thus, initial mole of $CuSO_4$

$$= \frac{2 \times 1.989 \times 10^{-5}}{2} = 1.989 \times 10^{-5}$$

Thus, initial concentration of $CuSO_4$

$$= \frac{1.989 \times 10^{-5} \times 1000}{250}$$

$[CuSO_4] = \mathbf{7.95 \times 10^{-5}}$ ***M***

12. (a) Eq. of Cl^- used $= \frac{2}{35.5}$ for $2Cl^- \longrightarrow Cl_2 + 2e$

$\because$ 1 eq. of an element = 1 Faraday charge

$= 6.023 \times 10^{23}$ electrons

$\therefore$ $\frac{2}{35.5}$ eq. of $Cl^- = \frac{6.023 \times 10^{23} \times 2}{35.5}$

$= \mathbf{3.39 \times 10^{22}}$ **electrons lost**

(b) Similarly, calculate for $Zn^{2+} + 2e \longrightarrow Zn$

Electrons gained $= \mathbf{1.85 \times 10^{22}}$ **electrons**

13. $\because$ 1 mole of electrons deposits 108 of Ag

$\therefore$ 0.35 mole of electrons deposits $108 \times 0.35 =$ **37.8 g Ag**

Similarly, $w_{Cu} =$ **11.113 g**, $w_{Au} =$ **22.98 g**

14. $I_2 + 2e \longrightarrow 2I^-$

$$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e \quad \left[\therefore E_{Na_2S_2O_3} = \frac{M}{1}\right]$$

Eq. of metal = Eq. of I_2 = Eq. of hypo

$$\frac{0.617}{E} = \frac{46.3 \times 0.124}{1000}$$

$\therefore$ $\boldsymbol{E = 107.47}$ **g eq^{-1}**

15. $\because$ 88 g Hg has 12 g Cd

$\therefore$ 2 g Hg require $= \frac{12 \times 2}{88}$ g Cd $= 0.273$ g Cd

$\because$ $Cd^{2+} + 2e \longrightarrow Cd$ $\left[\therefore E_{Cd} = \frac{112.40}{2}\right]$

Now, $w = \frac{E \cdot i \cdot t}{96500}$

$$0.273 = \frac{112.4 \times 5 \times t}{2 \times 96500}$$

$\therefore$ $\boldsymbol{t = 93.75}$ **second**

16. (a) **At anode:** $2H_2O \longrightarrow 4H^+ + O_2 + 4e$

At cathode: $Cu^{2+} + 2e \longrightarrow Cu$

$\therefore$ Mass loss at anode = mass of O_2 formed $= \frac{E \cdot i \cdot t}{96500}$

$$= \frac{32 \times 0.01 \times 96500}{4 \times 96500} = 0.08\,g$$

$\therefore$ Mass loss at cathode = mass of Cu formed $= \frac{E \cdot i \cdot t}{96500}$

$$= \frac{63.5 \times 0.01 \times 96500}{2 \times 96500} = 0.3175\,g$$

$\therefore$ Mass of resulting solution

= Initial mass − mass loss of O_2 − mass loss of Cu

$= 10 - 0.08 - 0.3175 =$ **9.6025 g**

(b) $\because$ 1 Faraday will produce 1 equivalent of acid or H^+

$\therefore$ 0.01 Faraday will produce $\frac{1 \times 0.01}{1}$

= 0.01 equivalent of acid

17. $Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$

$$\therefore \quad K_f = \frac{[Cu(NH_3)_4]^{2+}}{[Cu^{2+}][NH_3]^4}$$

The blue colour will be noticed upto

$[Cu(NH_3)_4]^{2+} = 1 \times 10^{-5}$.

Thus, at this stage,

$\therefore$ m mole of Cu^{2+} present $= 250 \times 0.1 = 25$

m mole of Cu^{2+} removed $= \frac{w}{E} \times \frac{1000}{2} = \frac{i \cdot t \times 1000}{96500 \times 2}$

$$= \frac{3.512 \times 1368 \times 1000}{96500 \times 2} = 24.89$$

$$\therefore \quad [Cu^{2+}]_{left} = \frac{(25 - 24.89)}{250} = 4.4 \times 10^{-4}\ M$$

Since, K_f is very high (1.1×10^{13}) thus almost whole of the $[Cu^{2+}]_{left}$ will be used to form $[Cu(NH_3)_2]^{2+}$,

or $[Cu(NH_3)_2]^{2+} = 4.4 \times 10^{-4} M > 1 \times 10^{-5} M$ detectable limit

Thus, solution **will show blue colour** as it will provide appreciable Cu^{2+} to form complex.

18. The electrolysis of $Ni(NO_3)_2$ in presence of Ni electrode will bring in following changes:

At anode: $Ni \longrightarrow Ni^{2+} + 2e$

At cathode: $Ni^{2+} + 2e \longrightarrow Ni$

$\because$ Eq. of Ni^{2+} formed = Eq. of Ni^{2+} lost

Thus, there will be no change in conc. of $Ni(NO_3)_2$ solution during electrolysis, *i.e.*, **it will remain 2 *M*.**

19. 1 Eq. or 11200 mL H_2 gas involves = 96500 coulomb

$\therefore$ 1 mL H_2 gas involves $= \frac{96500}{11200}$ coulomb

$= 8.616$ coulomb

Now time to produce 1 mL gas is 1 second and thus, 8.616 coulomb charge should be passed in one sec. to bring the change.

Therefore, $Q = i \times t$

$8.616 = i \times 1$ or $i =$ **8.616 ampere**

20. $\because$ $Pd^{n+} + ne \longrightarrow Pd$

For Pd, $\frac{w}{E} = \frac{i \times t}{96500}$

$$\frac{2.977}{106.4/n} = \frac{3 \times 1 \times 60 \times 60}{96500}$$

$\therefore$ $\boldsymbol{n = 4}$

21. $\because$ $\text{Meq.} = N \times V$

Meq. of Cu^{2+} before reaction $= 100 \times 1 \times 2 = 200$

Meq. of Cu^{2+} after reaction $= 100 \times 0.8 \times 2 = 160$

$\therefore$ Meq. of Cu^{2+} lost $= 200 - 160 = 40$

$\therefore$ Meq. of Zn lost $= 40$

$\therefore$ $\frac{w}{65.4/2} \times 1000 = 40$

$w_{Zn} = 1.308\,g$

$\therefore$ Net mass of Zn rod $= 25 - 1.308\,g =$ **23.692 g**

Also the reactions are $Zn \longrightarrow Zn^{2+} + 2e$

$Cu^{2+} + 2e \longrightarrow Cu$

$\therefore$ **No change in molarity of SO_4^{2-}**

22. The increase in mass at the cathode is due to deposition of Cu ($Cu^{2+} + 2e \rightarrow Cu$). The loss in mass of anode is due to loss of Cu and Fe because of their oxidation because only these two are active metals and will oxidise as

$Cu \longrightarrow Cu^{2+} + 2e$

$Fe \longrightarrow Fe^{2+} + 2e$

and loss of Ag and Au to fall in anode mud.

Thus, gain in mass at cathode is due to deposition of Cu $= 22.011\,g$

$\therefore$ Mole of Cu deposited at cathode $= \frac{22.011}{63.5} = 0.3466$

Equivalent of Cu and Fe dissolved at anode $= \frac{i \cdot t}{96500}$

$= \frac{140 \times 482.5}{96500} = 0.70$

$\therefore$ Mole of Cu and Fe dissolved at anode $= \frac{0.70}{2} = 0.35$

(both Cu and Fe are bivalent losing two electrons)

Mole of Fe dissolved at anode $= 0.3500 - 0.3466 = 0.0034$

$\therefore$ Mass of Fe dissolved at anode $= 0.0034 \times 56 = 0.190\,g$

Thus, anode mass loss of 22.260 g contains 22.011 g Cu, 0.190 g Fe and (Au + Ag) $= (22.260 - 22.011 - 0.190)$

$= 0.059\,g$

[$Fe \longrightarrow Fe^{2+} + 2e$; Fe^{2+} exist in solution]

$\therefore$ $\% \text{ Cu} = \frac{22.011}{22.26} \times 100 =$ **98.88%**

$\% \text{ Fe} = \frac{0.190}{22.26} \times 100 =$ **0.85%**

23. Eq. mass of Cr

$= \frac{\text{Atomic mass}}{\text{No. of electrons lost or gained by one molecule of Cr}}$

$= \frac{52}{6}$

(a) $\because$ 96500 coulomb deposit $= \frac{52}{6}$ g Cr

$\therefore$ 24000 coulomb deposit $= \frac{52}{6} \times \frac{24000}{96500}$ g Cr

= 2.1554 g of Cr

(b) Also given, $w_{Cr} = 1.5\,g$, $i = 12.5$ ampere, $t = ?$, $E_{Cr} = 52/6$

$\therefore$ $w = \frac{E \cdot i \cdot t}{96500}$

$1.5 = \frac{52 \times 12.5 \times t}{6 \times 96500}$

$\therefore$ **$t = 1336.15$ second**

24. $Au^{3+} + 3e \longrightarrow Au$

$Cu^{2+} + 2e \longrightarrow Cu$

Equivalent of gold formed = Eq. of Cu formed

$\frac{9.85}{197/3} = \frac{w_{Cu}}{63.5/2}$

$\therefore$ $w_{Cu} =$ **4.763 g**

Also $w = \frac{E \cdot i \cdot t}{96500}$

$\therefore$ $4.763 = \frac{63.5 \times i \times 5 \times 60 \times 60}{2 \times 96500}$

$\therefore$ **$i = 0.804$ ampere**

25. Eq. of Ag deposited $= \frac{1.307}{108} = 0.0121$

$\therefore$ Eq. of Cu^{2+} lost $= 0.0121$

Initial Eq. of $CuSO_4 \cdot 5H_2O = \frac{10 \times 2}{249.54} = 0.0802$

= Initial Eq. of Cu^{2+}

$\therefore$ Eq. of Cu^{2+} left $= 0.0802 - 0.0121 = 0.0681$

$\therefore$ Mass of Cu^{2+} left $= \frac{0.0681 \times 63.54}{2}$

$= 2.164$ g in 500 mL

$\therefore$ Mass of Cu^{2+} left in 1 litre $H_2O = 2.164 \times 2$

= 4.328 g / litre

26. $w = \frac{E \cdot i \cdot t}{96500}$

$\therefore$ $1000 = \frac{87 \times i \times 24 \times 60 \times 60}{2 \times 96500}$

$i = 25.6$ ampere

$\therefore$ Current efficiency $= \frac{25.6}{27} \times 100 =$ **94.8%**

Reactions

Anode : $Mn^{2+} \longrightarrow Mn^{4+} + 2e$

Cathode : $2H^+ + 2e \longrightarrow H_2$

27. $\because$ $N_{Na_2S_2O_3} = M_{Na_2S_2O_3} \times$ no. of electrons lost or gained by 1 molecule of $Na_2S_2O_3$ (*i.e.*, 1)

$\because$ $2S_2^{2+} \longrightarrow S_4^{5/2+} + 2e$

Meq. of I_2 formed = Meq. of $Na_2S_2O_3$ used

$= 21.75 \times 0.0831 \times 1 = 1.807$

or $\frac{w}{E} \times 1000 = 1.807$ or $\frac{w}{E} = \frac{1.807}{1000}$ ...(1)

Also, $\frac{w}{E} = \frac{i \cdot t}{96500}$

Thus, $\frac{1.807}{1000} = \frac{i \times 2 \times 60 \times 60}{96500}$

$\therefore$ **$i = 0.0242$ ampere**

28. Meq. of $CuSO_4 = 50 \times 0.1 \times 2 = 10$ (Meq. $= N \times V$ mL)

or Meq. of $Cu^{2+} = 10$

Anode: $2H_2O \longrightarrow 4H^+ + O_2 + 4e$

Cathode: $Cu^{2+} + 2e \longrightarrow Cu$

Now, $\frac{w}{E}=\frac{i\cdot t}{96500}$

and Equivalent of Cu^{2+} lost

$=$ Equivalent of H^+ formed $=\frac{i\cdot t}{96500}$

$=\frac{0.965\times1\times60}{96500}=6\times10^{-4}$

$\therefore$ Meq. of Cu^{2+} lost = Meq. of H^+ formed = 0.6

$\therefore$ Meq. of Cu^{2+} left in solution or Meq. of $CuSO_4$ left in solution = 10 − 0.6 = 9.4

$\therefore\quad [Cu^{2+}]=\frac{N_{Cu^{2+}}}{2}=\frac{9.4}{50\times2}=\mathbf{0.094M}$

$\left[\because N=\frac{\text{Meq.}}{\text{Volume (mL)}}\right]$

$[H^+]=\frac{N_{H^+}}{1}=\frac{0.6}{50}=\mathbf{0.012M}$

$[SO_4^{2-}]=\mathbf{0.1M}$

Since SO_4^{2-} does not take part in redox change.

Also if Cu electrodes are used, no change will be in the molarity of electrolyte, *i.e.*, 0.1*M*.

Since, the reactions are $Cu^{2+}+2e\longrightarrow Cu$

$Cu\longrightarrow Cu^{2+}+2e$

29. (a) Eq. of O_2 = Eq. of Ag

$\frac{w_{O_2}}{8}=1\quad(\because$ 1 mole Ag = 1 Eq. Ag)

$\therefore\quad w_{O_2}=8\,g$

$\because\quad T=298\,K,\ P=\frac{750}{760}$ atm.

Now $PV=\frac{w}{M}RT$

$\therefore\quad V_{O_2}=\frac{8}{32}\times\frac{0.0821\times298\times760}{750}=\mathbf{6.20\ litre}$

(b) Eq. of O_2 = Eq. of Ag $=\frac{w_{Ag}}{108}$

$=\frac{8\times10^{22}\times108}{6.023\times10^{23}\times108}=0.133$

($\because$ 6.023×10^{23} atoms or ions) = 108 g Ag

$w_{O_2}=8\times0.133=1.064\,g$

$\therefore\quad V_{O_2}=\frac{1.064\times0.0821\times298\times760}{32\times750}=\mathbf{0.824\ litre}$

30. Mole of H_2 reacting $=\frac{67.2}{22.4}=3$

$\therefore$ Eq. of H_2 used = 3 × 2 = 6

Now $\frac{w}{E}=\frac{i\cdot t}{96500};\quad 6=\frac{i\times15\times60}{96500}$

$\therefore\quad i=\mathbf{643.33\ ampere}$

Also Eq. of H_2 = Eq. of Cu formed

$\therefore$ Eq. of Cu deposited = 6

$\therefore\quad w_{Cu}=6\times\frac{63.5}{2}=190.5\,g$

Mass of Cu deposited = **190.5 g**

31. Watt = ampere × volt

$\therefore\quad$ Ampere $=\frac{200}{110}$

Now $w=\frac{E\cdot i\cdot t}{96500}$

$\therefore\quad w_{Zn}=\frac{65.4\times200\times30\times60}{2\times110\times96500}=\mathbf{1.109\ g}$

32. $\because$ Sp. heat × atomic mass = 6.4

$\therefore$ Atomic mass of metal $=\frac{6.4}{0.216}=29.63$

After electrolysis;

Eq. of metal = Eq. of Cl_2

$\therefore\quad \frac{w}{\text{atomic mass}/n}=\frac{\text{mass of }Cl_2}{\text{Eq. mass of }Cl_2}$

$\frac{7.467\times n}{29.63}=\frac{71\times9.2}{22.4\times35.5}$

$\because$ 22.4 litre of Cl_2 at STP weigh = 71 g

$\because$ Eq. mass of metal $=\frac{\text{Atomic mass}}{\text{Valency}}=\frac{29.63}{n}$

$\therefore\quad n=3.25$

$n=3\qquad(\because\ n$ is integer)

$\therefore$ **Metal nitrate is $M(NO_3)_3$.**

33. Eq. of O_2 = Eq. of metal

$\frac{12.5}{8}=\frac{87.5}{E}$

$\therefore\quad E_{metal}=\frac{87.5\times8}{12.5}=56$

$\therefore$ Valency of metal $=\frac{\text{Atomic mass}}{\text{Eq. mass}}=\frac{112}{56}=\mathbf{2}$

Now by electrolysis: $w=\frac{E\cdot i\cdot t}{96500}$

$w=\frac{56\times5\times60\times60\times0.965}{96500}=\mathbf{10.08\ g}$

34. $w_{Cu}=\frac{E\cdot i\cdot t}{96500}$

$3=\frac{63.5\times i\times2\times60\times60}{2\times96500}$

$\therefore\quad i=1.266$ ampere

Current efficiency

$=\frac{\text{Current passed actually}}{\text{Total current passed experimentally}}\times100$

$=\frac{1.266}{3}\times100=\mathbf{42.2\%}$

35. (a) **Anode:** $2Cl^-\longrightarrow Cl_2+2e$

Cathode: $2e+2H_2O\longrightarrow 2OH^-+H_2$

(b) $w=\frac{E\cdot i\cdot t}{96500}$ | $\because w_{Cl_2}=10^3$ g, $E_{Cl_2}=35.5$

$10^3=\frac{35.5\times25\times62\times t}{100\times96500}$ | $\because$ Current efficiency = 62%

$t=175374.83$ sec. | $\therefore\ i=\frac{25\times62}{100}$ ampere

$\therefore\quad t=\mathbf{48.71\ hr}$

(c) Eq. of OH^- formed = Eq. of Cl_2 formed

$$= \frac{10^3}{35.5} = 28.17$$

$\therefore$ Mole of OH^- formed = 28.17 ($\because$ monovalent)

$\therefore$ $[OH^-] = \frac{\text{mole}}{\text{Volume in litre}} = \frac{28.17}{20}$

$$= \mathbf{1.408\ mol\ litre^{-1}}$$

36. $i = \frac{1.70 \times 90}{100}$ ampere

$\therefore$ Eq. of Zn^{2+} lost $= \frac{i \cdot t}{96500}$

$$= \frac{1.70 \times 90 \times 230}{100 \times 96500} = 3.646 \times 10^{-3}$$

$\therefore$ Meq. of Zn^{2+} lost = 3.646

Initial Meq. of Zn^{2+} = $300 \times 0.160 \times 2$

$= 48 \times 2 = 96$ [$\because M \times 2 = N$ for Zn^{2+}; Meq. $= N \times V_{(\text{in mL})}$]

$\therefore$ Meq. of Zn^{2+} left in solution = 96 − 3.646 = 92.354

$\therefore$ $[ZnSO_4] = \frac{92.354}{2 \times 300} = \mathbf{0.154}\ \boldsymbol{M}$

37. Electrolysis of $SnCl_2$ yields:

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

Cathode: $Sn^{2+} + 2e \longrightarrow Sn$

Further Cl_2 formed at anode reacts with $SnCl_2$ to give $SnCl_4$

$$SnCl_2 + Cl_2 \longrightarrow SnCl_4$$

During electrolysis

Eq. of $SnCl_2$ lost = Eq. of Cl_2 formed
= Eq. of Sn formed

Eq. of Cl_2 formed $= \frac{0.119}{119/2} = 2 \times 10^{-3}$

$\therefore$ Eq. of $SnCl_4$ formed $= 2 \times 10^{-3}$

or Eq. of $SnCl_2$ lost during electrolysis $= 2 \times 10^{-3}$

Now total loss in Eq. of $SnCl_2$ during complete course = Eq. of $SnCl_2$ lost during electrolysis + Eq. of $SnCl_2$ lost during reaction with Cl_2

$$= 2 \times 10^{-3} + 2 \times 10^{-3} = 4 \times 10^{-3}$$

Initial Eq. of $SnCl_2 = \frac{19}{190/2} = 2 \times 10^{-1}$

$\therefore$ Eq. of $SnCl_2$ left in solution $= 2 \times 10^{-1} - 4 \times 10^{-3} = 0.196$

Eq. of $SnCl_4$ formed $= 2 \times 10^{-3} = 0.002$

$$\therefore \frac{\text{Mass of } SnCl_2 \text{ left}}{\text{Mass of } SnCl_4 \text{ formed}} = \frac{0.196 \times \frac{190}{2}}{0.002 \times \frac{261}{2}} = \frac{18.62}{0.261} = \mathbf{71.34}$$

38. Eq. of Cu deposited $= \frac{31.8}{63.6/2} = 1$

$\therefore$ Eq. of NaOH formed = 1

or Meq. of NaOH formed = 1000

However, 600 mL of 1*N* NaOH is formed

i.e., Experimental yield of Meq. of NaOH = 600 × 1 = 600

$\therefore$ % yield $= \frac{600}{1000} \times 100 = \mathbf{60\%}$

39. Anode reaction:

(i) $2H_2SO_4 \longrightarrow H_2S_2O_8 + 2H^+ + 2e$

(ii) $2H_2O \longrightarrow 4H^+ + O_2 + 4e$

Cathode reaction: $2H_2O + 2e \longrightarrow 2OH^- + H_2$

$\therefore$ Equivalent of $H_2S_2O_8$ + Equivalent of O_2
= Equivalent of H_2

$\because$ 22.4 litre H_2 = 1 mole = 2 Eq.

$\therefore$ 9.72 litre $H_2 = \frac{2 \times 9.72}{22.4}$ Eq. = 0.868 Eq. H_2

$\because$ 22.4 litre O_2 = 1 mole = 4 Eq.

$\therefore$ 2.35 litre $O_2 = \frac{4 \times 2.35}{22.4}$ Eq. = 0.42 Eq. O_2

$\therefore$ Eq. of $H_2S_2O_8$ = Eq. of H_2 − Eq. of O_2
= 0.868 − 0.420 = 0.448

$\therefore$ $\frac{w_{H_2S_2O_8}}{194/2} = 0.448$

$w_{H_2S_2O_8} = \frac{0.448 \times 194}{2} = \mathbf{43.456\ g}$

40. For I part of electrolysis :

Anode: $2H_2O \longrightarrow 4H^+ + O_2 + 4e$

Cathode: $Cu^{2+} + 2e \longrightarrow Cu$

$\therefore$ Eq. of O_2 formed = Eq. of Cu

$$= \frac{0.4 \times 2}{63.6} = 12.58 \times 10^{-3}$$

For II part of electrolysis : Since Cu^+ ions are discharged completely and thus further passage of current through solution will lead the following changes.

Anode: $2H_2O \longrightarrow 4H^+ + O_2 + 4e$

Cathode: $2H_2O + 2e \longrightarrow H_2 + 2OH^-$

Eq. of H_2 = Eq. of $O_2 = \frac{i \cdot t}{96500} = \frac{1.2 \times 7 \times 60}{96500} = 5.22 \times 10^{-3}$

$\therefore$ Total Eq. of O_2
$= 5.22 \times 10^{-3} + 12.58 \times 10^{-3}$
$= 17.8 \times 10^{-3}$

$\because$ 4 Eq. of O_2 at NTP
= 22.4 litre

$\therefore$ 17.8×10^{-3} Eq. O_2 at NTP
$= \frac{22.4 \times 17.8 \times 10^{-3}}{4}$ litre
= 99.68 mL

Eq. of $H_2 = 5.22 \times 10^{-3}$

$\because$ 2 Eq. of H_2 at NTP
= 22.4 litre

$\therefore$ 5.22×10^{-3} Eq. at NTP
$= \frac{22.4 \times 5.22 \times 10^{-3}}{2}$ litre
= 58.46 mL

$\therefore$ Total volume of $O_2 + H_2$ = 99.68 + 58.46 = **158.14 mL**

Note : If Cu^{2+} is as $CuCl_2$, then $\mathbf{Cl_2}$ will come out in I step and $\mathbf{H_2}$ and $\mathbf{O_2}$ in II step. Calculate their volumes.

41. $C_6H_5NO_2 + 6H^+ + 6e \longrightarrow C_6H_5NH_2 + 2H_2O$

$$N^{3+} + 6e \longrightarrow N^{3-}$$

$\therefore$ Eq. mass of nitrobenzene $= \frac{M}{6} = \frac{123}{6}$

Now $w = \frac{E \cdot i \cdot t}{96500}$

($\because$ current efficiency is 50% $\therefore i = \frac{50 i_0}{100}$)

$$12.3 = \frac{123 \times i \times t \times 50}{6 \times 100 \times 96500}$$

$\therefore \quad i \times t = \mathbf{115800\ coulomb}$

Now energy used $= Q \times V = 115800 \times 3 = \mathbf{347.4\ kJ}$

42. **[Ans. 42573.5 coulomb, 298.014 kJ]**

43. **Anode:** $2Al_2^{3+} + 12e \longrightarrow 4Al^0$

Cathode: $3C \longrightarrow 3C^{4+} + 12e$

(no. of electrons involved in change = 12)

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

$$1370 \times 10^3 = 12 \times 96500 \times E^\circ$$

$\therefore \quad E^\circ = \mathbf{1.1830\ V}$

44. Adding the charging and discharging reactions

$$Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \longrightarrow 2PbSO_4 + 2H_2O$$

$N_{H_2SO_4} = M_{H_2SO_4}$ (since $2SO_4^{2-}$ requires 2 electrons)

i.e., Normality = Molarity

Before discharge	After discharge
$M_{H_2SO_{4_I}} = \frac{39 \times 1.294 \times 1000}{98 \times 100}$	$M_{H_2SO_{4_{II}}} = \frac{20 \times 1.139 \times 1000}{98 \times 100}$
$= 5.15$	$= 2.325$
Mole of $H_2SO_4 = 5.15 \times 3.5$	Mole of $H_2SO_4 = 2.325 \times 3.5$
$= 18.025$	$= 8.1375$

$\therefore$ Mole or equivalents of H_2SO_4 used

$= 18.025 - 8.1375 = 9.8875$

$\because \quad \frac{w}{E} = \frac{i \cdot t}{96500}$

$\therefore \quad i \cdot t = 9.8875 \times 96500$

$= 954143.75$ ampere sec. $=$ **265.04 ampere hr**

45. Before electrolysis:

Volume of solution = 1 litre = 1000 mL

$\therefore$ Mass of solution $= 1000 \times 1.261 = 1261$ g

$(\because \ w = V \times d)$

$\therefore$ Mass of $H_2SO_4 = \frac{34.6 \times 1261}{100} = 436.306$ g

$\therefore$ Mass of water $= 1261 - 436.306 = 824.694$ g

After electrolysis:

Now during reaction mass of H_2O formed $= X$ g

$\therefore$ Mole of H_2O formed $= \frac{X}{18}$

$\therefore$ Mole of H_2SO_4 used $= \frac{X}{18}$

$(\because$ mole ratio of $H_2SO_4 : H_2O :: 1 : 1)$

$\therefore$ Mass of H_2SO_4 used $= \frac{98X}{18} = 5.44X$ g

$\therefore$ Mass of H_2SO_4 left $= (436.306 - 5.44X)$ g

Net mass of solution = mass of old solution + mass of H_2O formed − mass of H_2SO_4 lost

$= 1261 + X - 5.44X$

$\therefore$ % by mass of new solution $= \frac{436.306 - 5.44X}{(1261 + X - 5.44X)} = \frac{27}{100}$

$\therefore \quad X = 22.59$ g

$\therefore \quad \frac{22.59}{18}$ mole of H_2O are formed

$\because$ Mole of H_2O = Eq. of H_2O

$(\because 2H_2O$ consume 2 electrons)

Now 1 mole of H_2O formed by the passage of 1 Faraday

$\therefore \quad \frac{22.59}{18}$ mole of H_2O formed by the passage of

$= \frac{22.59}{18}$ Faraday

$=$ **1.255 Faraday**

46. Milli equivalent of $RNO_2 = 300 \times 0.01 \times 4 = 12$

$\therefore$ Milli equivalent of $[H^+]$ consumed $= 12$

or Milli equivalent of $[OH^-]$ generated $= 12$

Let a mole of weak acid and b mole of its conjugate base are present, then

$$a + b = 0.50$$

Also, $$pH = -\log K_a + \log \frac{[Salt]}{[Acid]}$$

$$5.0 = +4.7442 + \log \frac{b}{a}$$

$\therefore \quad \frac{b}{a} = 1.8$

$\therefore \quad a = 0.1786$

$b = 0.3214$

OH^- generated will increase the concentration of A^- ion

	OH^-	+ HA ⟶	H_2O	+ A^-
Meq. before reaction	12	178.6	0	321.4
Meq. after reaction	0	(178.6 − 12)		(321.4 + 12)
	0	166.6		333.4

$\therefore \quad pH = 4.7442 + \log \frac{333.4}{166.6}$

$= 4.7442 + 0.3013 = \mathbf{5.0455}$

47. **At cathode:** $2H^+ + 2e \longrightarrow H_2$

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

Equal equivalent of H^+ and OH^- will be discharged at anode and cathode respectively.

$$\frac{w}{E} = \frac{i \cdot t}{96500}$$

$$\frac{w}{E} = \frac{1.25 \times 212 \times 60}{96500} = 1.65 \times 10^{-1}\ M$$

Now for buffer mixture at anode, $[H^+]$ will increase by 1.65×10^{-1} M.

HPO_4^{2-}	$+ H^+ \rightleftharpoons$	$H_2PO_4^-$
1	0.165	1
0.835	—	1.165

$\therefore \quad pH = pKa + \log \frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$

$pH = 2.15 \log \frac{0.835}{1.165} = \mathbf{2.005}$

For buffer mixture at cathode, $[OH^-]$ will increase by 1.65×10^{-1} M.

$H_2PO_4^-$	$+ OH^- \rightleftharpoons$	$HPO_4^{2-} + H_2O$
1	0.165	1
0.835	—	1.165

$\therefore \quad pH = 2.15 + \log \frac{1.165}{0.835} = \mathbf{2.295}$

48. Volume of Cu^{2+} ion deposited on plate

(Area × thickness) $= 10 \times 10 \times 10^{-2} = 1 cm^3$

$\therefore$ Mass of Cu^{2+} deposited $= 1 \times 8.94$ g

Now
$$w = \frac{E \cdot i \cdot t}{96500}$$
$$8.94 = \frac{63.6 \times Q}{2 \times 96500}$$
$$\therefore \quad Q = \mathbf{27129.2\ coulomb}$$

49. $w_{Ag} = \frac{E \cdot i \cdot t}{96500} = \frac{107.8 \times 8.46 \times 8 \times 60 \times 60}{96500} = \mathbf{272.18\ g}$

Volume of Ag $= \frac{272.18}{10.5} = 25.92$ mL

$\therefore$ Surface area $= \frac{25.92}{0.00254} = \mathbf{1.02 \times 10^4\ cm^2}$

50. $w_{Ag} = \frac{E \cdot i \cdot t}{96500} = \frac{108 \times 40 \times 10^{-6} \times 32 \times 60}{96500} = 85.95 \times 10^{-6}$ g ...(1)

Now covered area is 43% of cathode surface. Let total area of cathode be a cm^2.

$\therefore$ Covered area $= \frac{43a}{100}$ cm^2

$\because$ 5.4×10^{-16} cm^2 is covered by one atom of Ag

$\therefore$ $\frac{43\,a}{100}$ cm^2 is covered by $= \frac{43a}{100 \times 5.4 \times 10^{-16}}$ atoms of Ag

$\therefore$ Mass of Ag atoms covering this area
$$= \frac{43a \times 108}{100 \times 5.4 \times 10^{-16} \times 6.023 \times 10^{23}} \quad ...(2)$$

By Eqs. (1) and (2), on equating, $a = \mathbf{601.65\ cm^2}$

51. (a) $H_2 \longrightarrow 2H^+ + 2e$

$$\therefore \quad E_{OP} = E^{\circ}_{OP} - \frac{0.059}{2} \log_{10} \frac{[H^+]^2}{P_{H_2}}$$
$$= 0 - \frac{0.059}{2} \log_{10} \frac{(0.02)^2}{2}$$
$$E_{OP_{H_2/H^+}} = \mathbf{+0.109\ volt}$$

(b) $Fe \longrightarrow Fe^{2+} + 2e$

$$\therefore \quad E_{OP} = E^{\circ}_{OP} - \frac{0.059}{2} \log_{10} [Fe^{2+}]$$
$$= 0.44 - \frac{0.059}{2} \log_{10} [0.1]$$
$$E_{OP_{Fe/Fe^{2+}}} = \mathbf{+0.4695\ volt}$$

(c) $2Cl^- \longrightarrow Cl_2 + 2e$

$$\therefore \quad E_{OP} = E^{\circ}_{OP} - \frac{0.059}{2} \log_{10} \frac{P_{Cl_2}}{[Cl^-]^2}$$
$$= -1.36 - \frac{0.059}{2} \log_{10} \frac{10}{(0.1)^2}$$
$$E_{OP_{Cl^-/Cl_2}} = \mathbf{-1.4485\ volt}$$

52. (a) $H_2 \longrightarrow 2H^+ + 2e$

$$\therefore \quad E_{OP_{H/H^+}} = E^{\circ}_{OP_{H/H^+}} - \frac{0.059}{2} \log_{10} \frac{[H^+]^2}{P_{H_2}}$$
$$0.25 = 0 - \frac{0.059}{2} \log_{10} \frac{[H^+]^2}{1}$$

$\therefore \quad -\log [H^+] = 4.237 \qquad \therefore \quad pH = \mathbf{4.237}$

(b) Solve accordingly: pH = **5.08**

Note: No change in calculation if any strong acid producing H^+ is given.

(c) $Cr_2O_7^{2-} + 14H^+ + 6e \longrightarrow 2Cr^{3+} + 7H_2O$

$$E = E^{\circ}_{Cr^{6+}/Cr^{3+}} + \frac{0.059}{6} \log \frac{[Cr_2O_7^{2-}][H^+]^{14}}{[Cr^{3+}]^2}$$
$$E = 1.33 + \frac{0.059}{6} \log \frac{\left[\frac{4.5}{1000}\right] \times [10^{-2}]^{14}}{\left[\frac{15}{1000}\right]^2}$$
$$= 1.33 + \frac{0.059}{6} \log 20 \times 10^{-28}$$
$$= 1.33 + \frac{0.059}{6} [\log 20 - 28 \log 10]$$
$$= 1.33 + \frac{0.059}{6} [1.3010 - 28]$$
$$= 1.33 - 0.26 = \mathbf{1.07\ V}$$

53. (a) For $2Ag^+ + Cd \longrightarrow 2Ag + Cd^{2+}$

$\because$ Ag^+ shows reduction and Cd shows oxidation:

$$\therefore \quad E^{\circ}_{cell} = E^{\circ}_{OP_{Cd/Cd^{2+}}} + E^{\circ}_{RP_{Ag^+/Ag}}$$
$$= +0.40 + 0.80$$
$$= \mathbf{1.2\ volt}$$

Given, $E^{\circ}_{RP_{Ag^+/Ag}} = +0.80$ V

$E^{\circ}_{RP_{Cd^{2+}/Cd}} = -0.40$ V

$\therefore \quad E^{\circ}_{OP_{Cd/Cd^{2+}}} = 0.40$ V

(b) Also $E_{cell} = E_{OP_{Cd}} + E_{RP_{Ag}}$
$$= E^{\circ}_{OP_{Cd/Cd^{2+}}} - \frac{0.059}{2} \log_{10} [Cd^{2+}] + E^{\circ}_{RP_{Ag^+/Ag}} + \frac{0.059}{2} \log_{10} [Ag^+]^2$$

or $E_{cell} = E^{\circ}_{OP_{Cd}} + E^{\circ}_{RP_{Ag}} + \frac{0.059}{2} \log_{10} \frac{[Ag^{2+}]}{[Cd^{2+}]}$

Thus, if $[Cd^{2+}]$ is reduced from 1M to 0.1 M, the net value of E_{cell} will increase or become **more +ve.**

Most important: For solving the problems on emf of cell, one should see E°_{OP} values for two changes and should write oxidation at the electrode having more or +ve E°_{OP} and reduction for other.

Also
$$E_{cell} = \underset{\text{(one which shows oxidation)}}{E^{\circ}_{OP}} + \underset{\text{(one which shows reduction)}}{E^{\circ}_{RP}}$$

54. (i) $\therefore$ E°_{OP} for $Cu / Cu^{2+} = -0.35$ V

E°_{OP} for $Zn / Zn^{2+} = +0.76$ V

More is E°_{OP}, more is tendency to show oxidation and thus Zn will oxidise and Cu^{2+} will reduce.

Anode: $Zn \longrightarrow Zn^{2+} + 2e$

Cathode: $Cu^{2+} + 2e \longrightarrow Cu$

Cell reaction $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$

(ii) Also $E_{cell} = E_{OP_{Zn/Zn^{2+}}} + E_{RP_{Cu^{2+}/Cu}}$

$$= E^\circ_{OP_{Zn/Zn^{2+}}} - \frac{0.059}{2}\log_{10}[Zn^{2+}] + E^\circ_{RP_{Cu^{2+}/Cu}} + \frac{0.059}{2}\log_{10}[Cu^{2+}]$$

$$= E^\circ_{OP_{Zn/Zn^{2+}}} + E^\circ_{RP_{Cu^{2+}/Cu}} + \frac{0.059}{2}\log_{10}\frac{[Cu^{2+}]}{[Zn^{2+}]}$$

$$= 0.76 + 0.35 + \frac{0.059}{2}\log_{10}\frac{1}{1}$$

E_{cell} **= 1.11 volt**

(iii) Also $E_{cell} = 1.11 + \frac{0.059}{2}\log_{10}\frac{[Cu^{2+}]}{[Zn^{2+}]}$

To make cell reaction spontaneous; $E_{cell} = +$ve

or $\frac{0.059}{2}\log_{10}\frac{[Cu^{2+}]}{[Zn^{2+}]} > -1.11$

or $\log_{10}\frac{[Cu^{2+}]}{1} > -\frac{2.22}{0.059}$

or $\log_{10}[Cu^{2+}] > -37.627$

$[Cu^{2+}] > \mathbf{2.36 \times 10^{-38}}$ ***M***

(iv) The displacement will almost go to completion.

55. Given,

Cell I : $Zn \left| \underset{C_1}{ZnSO_4} \right|\left| \underset{C_2}{CuSO_4} \right| Cu$

$$E_{cell} = E^\circ_{cell} + \frac{0.06}{2}\log\frac{[Cu^{2+}]}{[Zn^{2+}]}$$

$$E_{cell} = E^\circ_{cell} + \frac{0.06}{2}\log\frac{C_2}{C_1} \quad ...(1)$$

Cell II : $Zn \left| \underset{C_1'}{ZnSO_4} \right|\left| \underset{C_2'}{CuSO_4} \right| Cu$

$$E'_{cell} = E^\circ_{cell} + \frac{0.06}{2}\log\frac{C_2'}{C_1} \quad ...(2)$$

If $E_{cell} > E'_{cell}$, then $E_{cell} > E'_{cell} = 0.03$ V and $C_2 = 0.5\,M$

$\therefore$ By Eqs. (1) and (2) $0.03 = \frac{0.06}{2}\log\frac{0.5}{C_2'}$

or $C_2' = \mathbf{0.05}$ ***M***

56. For the given cell,

Anode: $Zn \longrightarrow Zn^{2+} + 2e$

Cathode: $Cu^{2+} + 2e \longrightarrow Cu$

and $E_{cell} = E^\circ_{cell} + \frac{0.059}{2}\log_{10}\frac{[Cu^{2+}]}{[Zn^{2+}]} \quad ...(1)$

$$y = c + mx \quad ...(2)$$

Eq. (1) represents a straight line equation like Eq. (2)

Thus, E°_{cell} = intercept = 1.10 V

Now from Eq. (1),

$$E_{cell} = 1.10 + \frac{0.059}{2}\log_{10}\frac{0.01}{0.1}$$

$$= 1.10 - 0.0295 = \mathbf{1.0705\ V}$$

57. $2H^+ + NO_3^- + e \longrightarrow NO_2 + H_2O$; $E^\circ = 0.790$ V

$7H^+ + NO_3^- + 6e \longrightarrow NH_2OH + 2H_2O$; $E^\circ = 0.731$ V

Since E_{RP} of both are same

$\therefore$ $E_{RP_{NO_3^-/NO_2}} = E_{RP_{NO_3^-/NH_2OH}}$

or $E^\circ_{RP_{NO_3^-/NO_2}} + \frac{0.059}{1}\log\frac{[H^+]^2[NO_3^-]}{[NO_2]}$

$$= E^\circ_{RP_{NO_3^-/NH_2OH}} + \frac{0.059}{6}\log\frac{[H^+]^7[NO_3^-]}{[NH_2OH]}$$

or $0.790 + \frac{0.059}{1}\log[H^+]^2 = 0.731 + \frac{0.059}{6}\log[H^+]^7$

or $0.790 + 0.118\log[H^+] = 0.731 + 0.0688\log[H^+]$

or $-\log[H^+] = \frac{0.059}{0.0492} = 1.1992$

$\therefore$ pH = **1.1992**

58. The emf of given cell $= E_{OP_{Fe^{2+}/Fe^{3+}}} + E_{RP_{Ce^{3+}/Ce^{4+}}}$

or $E_{cell} = E^\circ_{OP_{Fe^{2+}/Fe^{3+}}} - \frac{0.059}{1}\log\frac{[Fe^{3+}]}{[Fe^{2+}]} + E^\circ_{RP_{Ce^{3+}/Ce^{4+}}} + \frac{0.059}{1}\log\frac{[Ce^{4+}]}{[Ce^{3+}]}$

$$= E^\circ_{OP_{Fe^{2+}/Fe^{3+}}} E^\circ_{RP_{Ce^{4+}/Ce^{3+}}} + \frac{0.059}{1}\log\frac{[Ce^{4+}][Fe^{2+}]}{[Ce^{3+}][Fe^{3+}]}$$

$$= -0.77 + 1.61 + \frac{0.059}{1}\log 1$$

$\therefore$ $E_{cell} = 0.84$ V

Thus, $Pt_{(I)}Fe^{3+} / Fe^{2+}$ acts as anode and $Pt_{(II)}Ce^{4+} / Ce^{3+}$ acts as cathode. The electrons flow from left to right and thus current will flow from right to left. The current strength will decrease with time.

59. $Ni \longrightarrow Ni^{2+} + 2e$ $\quad E^\circ_{OP} = 0.236$ V

$2H^+ + 2e \longrightarrow H_2$ $\quad E^\circ_{RP} = 0$

$\therefore$ $E^\circ_{cell} = 0.236$

$\therefore$ $E_{cell} = E^\circ_{cell} + \frac{0.059}{2}\log_{10}\frac{[H^+]^2}{[Ni^{2+}]}$

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

or $-\log H^+ = 4$ $\therefore$ **pH = 4**

60. $E^\circ_{cell} = \frac{0.059}{1}\log_{10} K_C$

$E^\circ_{cell} = E^\circ_{OP_{Fe^{2+}/Fe^{3+}}} + E^\circ_{RP_{Ce^{4+}/Ce^{3+}}}$

$= -0.68 + 1.44 = 0.76$ V

$\therefore \quad \log_{10} K_C = \frac{0.76}{0.059} = 12.8814$

$\therefore \quad K_C = \mathbf{7.6 \times 10^{12}}$

61. For the change $2Fe^{3+} + 3I^- \rightleftharpoons 2Fe^{2+} + I_3^-$, at equilibrium, $E = 0$

$$E = E° - \frac{0.059}{2} \log_{10} K_C$$

or $$E° = \frac{0.059}{2} \log_{10} K_C$$

Also

$$E°_{cell} = E°_{RP_{Fe^{3+}/Fe^{2+}}} + E°_{OP_{I^-/I_3^-}} = 0.77 - 0.54 = 0.23 \text{ V}$$

Thus, $0.23 = \frac{0.059}{2} \log_{10} K_C \quad \therefore K_C = \mathbf{6.26 \times 10^7}$

62. Given, $In^{3+} + 2e \longrightarrow In^+; \quad E_1° = -0.42 \text{ V} \quad ...(1)$

$In^{2+} + e \longrightarrow In^+; \quad E_2° = -0.40 \text{ V} \quad ...(2)$

By subtracting Eq. (2) from Eq. (1) a third half-cell reaction can be obtained as:

$$\left[\begin{array}{l} \text{where } E_3° \times 1 \times F = E_1° \times 2 \times F - E_2° \times 1 \times F \\ \text{or} \quad E_3° = 2 \times (-0.42) - 1 \times (-0.40) \\ \quad = -0.44 \text{ V} \end{array}\right]$$

$In^{3+} + e \longrightarrow In^{2+}; \quad E_3° = -0.44 \text{ V}$

For the reactions: $Cu^{2+} + e \longrightarrow Cu^+; \quad E_4° = 0.15$

$In^{2+} \longrightarrow In^{3+} + e; \quad E_3° = +0.44$

The net redox change:

$$Cu^{2+} + In^{2+} \longrightarrow Cu^+ + In^{3+};$$

$$E°_{cell} = E_4° + E_3° = 0.15 + 0.44 = 0.59 \text{ V}$$

Also $$E°_{cell} = \frac{0.059}{1} \log K_C$$

$$0.59 = \frac{0.059}{1} \log K_C \quad \therefore K_C = \mathbf{10^{10}}$$

63. $Pt|CuCl||CuCl_2|Pt$

Anode: $Cu^+ \longrightarrow Cu^{2+} + e; \quad E°_{OP} = -0.153 \text{ V}$

Cathode: $Cu^+ + e \longrightarrow Cu; \quad E°_{RP} = 0.518 \text{ V}$

Redox: $2Cu^+ \longrightarrow Cu^{2+} + Cu$

$$E°_{cell} = E°_{OP_{Cu^+/Cu^{2+}}} + E°_{RP_{Cu^+/Cu}} = -0.153 + 0.518 = 0.365 \text{ V}$$

Also $$E° = \frac{0.059}{1} \log K_C$$

$$0.365 = \frac{0.059}{1} \log K_C \quad \therefore K_C = \mathbf{1.50 \times 10^6}$$

64. The redox change is

	Zn +	Ni^{2+} $\rightleftharpoons$	Zn^{2+} + Ni
mM before equilibrium		500	0
mM at equilibrium		*a*	$(500 - a)$

$$\therefore \quad E_{cell} = E_{OP_{Zn/Zn^{2+}}} + E_{RP_{Ni^{2+}/Ni}}$$

$$E_{cell} = E°_{Zn/Zn^{2+}} + E°_{RP_{Ni^{2+}/Ni}} + \frac{0.059}{2} \log_{10} \frac{[Ni^{2+}]}{[Zn^{2+}]}$$

At equilibrium $E_{cell} = 0$

$$\therefore \quad E°_{OP_{Zn/Zn^{2+}}} + E°_{RP_{Ni^{2+}/Ni}} = -\frac{0.059}{2} \log_{10} \frac{[Ni^{2+}]}{[Zn^{2+}]}$$

or $$0.75 + (-0.24) = -\frac{0.059}{2} \log_{10} \frac{[Ni^{2+}]}{[Zn^{2+}]}$$

$$\frac{[Ni^{2+}]}{[Zn^{2+}]} = \text{antilog}\left(-\frac{0.51 \times 2}{0.059}\right) = 5.15 \times 10^{-18}$$

$$\therefore \quad \frac{a}{500 - a} = 5.15 \times 10^{-18}$$

$$\therefore \quad a = 500 \times 5.15 \times 10^{-18}$$

$$\therefore \quad [Ni^{2+}] = \frac{mM}{V} = \frac{500 \times 5.15 \times 10^{-18}}{500} = \mathbf{5.15 \times 10^{-18}} \ M$$

65. For $Cu(OH)_2$, $\quad K_{sp} = [Cu^{2+}][OH^-]^2$

$\because \quad [H^+] = 10^{-14}$; thus $[OH^-] = 10^0 = 1$

Therefore, $$[Cu^{2+}] = \frac{K_{sp}}{[OH^-]^2} = \frac{1.0 \times 10^{-19}}{1} = 1.0 \times 10^{-19}$$

Now E_{RP} for the couple Cu^{2+}/Cu is

$$E_{RP} = E°_{RP} + \frac{0.059}{2} \log_{10} [Cu^{2+}]$$

$$= 0.34 + \frac{0.059}{2} \log_{10} [1 \times 10^{-19}] = \mathbf{-0.2205 \text{ V}}$$

66. K_{sp} of $AgI = [Ag^+][I^-] = [Ag^+][0.05] \quad ...(1)$

For given cell $E_{cell} = E_{OP_{Ag}} + E_{RP_{Ag}}$

$$= E°_{OP_{Ag/Ag^+}} - \frac{0.059}{1} \log_{10}[Ag^+]_{L.H.S.} + E°_{RP_{Ag^+/Ag}} + \frac{0.059}{1} \log_{10} [Ag^+]_{R.H.S.}$$

$$E_{cell} = \frac{0.059}{1} \log_{10} \frac{[Ag^+]_{R.H.S.}}{[Ag^+]_{L.H.S.}}$$

$$\because \quad E°_{OP_{Ag/Ag^+}} = -E°_{RP_{Ag^+/Ag}}$$

$$0.788 = \frac{0.059}{1} \log_{10} \frac{0.05}{[Ag^+]_{L.H.S.}}$$

$$\therefore \quad [Ag^+]_{L.H.S.} = 2.203 \times 10^{-15}$$

$\therefore$ By Eq. (1), $\quad K_{sp} = [2.203 \times 10^{-15}][0.05]$

$$K'_{sp_{AgI}} = \mathbf{1.10 \times 10^{-16}}$$

67. $$E_{cell} = E°_{OP_{Ag/Ag^+}} + E°_{RP_{Ag^+/Ag}} + \frac{0.059}{1} \log \frac{[Ag^+]_{R.H.S.}}{[Ag^+]_{L.H.S.}}$$

or $$0.0860 = \frac{0.059}{1} \log \frac{[Ag^+]_{R.H.S.}}{[Ag^+]_{L.H.S.}}$$

Also, $[Ag^+]_{L.H.S.}$ can be derived as

$$[Ag^+] = \sqrt{K_{sp_{AgI}}} = \sqrt{8.5 \times 10^{-17}} = 9.22 \times 10^{-9} \ M$$

$$\therefore \quad 0.0860 = \frac{0.059}{1} \log \frac{[Ag^+]_{R.H.S.}}{9.22 \times 10^{-9}}$$

or $$\frac{[Ag^+]_{R.H.S.}}{9.22 \times 10^{-9}} = 28.68$$

$$\therefore \quad [Ag^+]_{R.H.S.} = 28.68 \times 9.22 \times 10^{-9} \ M$$

Also for R.H.S.,

$$[Ag^+][Cl^-] = K_{sp_{AgCl}}$$

$\therefore$ $$[Cl^-] = \frac{K_{sp_{AgCl}}}{[Ag^+]} = \frac{1.8\times10^{-10}}{28.68\times9.22\times10^{-9}}$$

or $$[MCl^-] = \mathbf{6.8\times10^{-4}}\ \boldsymbol{M}$$

68. Given, $E^\circ_{RP_{Cu^{2+}/Cu}} = 0.337\text{ V}$ $\therefore$ $E^\circ_{OP_{Cu/Cu^{2+}}} = -0.337\text{ V}$

$E^\circ_{RP_{Ag^+/Ag}} = 0.799\text{ V}$ $\therefore$ $E^\circ_{OP_{Ag/Ag^+}} = -0.799\text{ V}$

For E°_{cell} to be +ve; oxidation of Cu and reduction of Ag^+ because

$$E^\circ_{OP_{Cu/Cu^{2+}}} > E^\circ_{OP_{Ag/Ag^+}}$$

$\therefore$ $$Cu + 2Ag^+ \longrightarrow Cu^{2+} + 2Ag$$

The cell is, $Cu\,|\,CuSO_4\,(aq.)\,||\,AgNO_3\,(aq.)\,|\,Ag$

Now, $E_{cell} = E_{OP_{Cu/Cu^{2+}}} + E_{RP_{Ag^+/Ag}}$

$$= E^\circ_{OP_{Cu/Cu^{2+}}} - \frac{0.059}{2}\log_{10}[Cu^{2+}] + E^\circ_{RP_{Ag^+/Ag}} + \frac{0.059}{2}\log_{10}[Ag^+]^2$$

$$= E^\circ_{OP_{Cu/Cu^{2+}}} + E^\circ_{RP_{Ag^+/Ag}} + \frac{0.059}{2}\log_{10}\frac{[Ag^+]^2}{[Cu^{2+}]}$$

$$= E_{cell} = -0.337 + 0.799 + \frac{0.059}{2}\log_{10}\frac{[Ag^+]^2}{[Cu^{2+}]}$$

$\because$ $E_{cell} = 0$ at $[Cu^{2+}] = 0.01M$

$\therefore$ $$0 = 0.462 + \frac{0.059}{2}\log_{10}\frac{[Ag^+]^2}{0.01}$$

$\therefore$ $$[Ag^+] = \mathbf{1.477\times10^{-9}\ mol\ litre^{-1}}$$

69. For the cell

$$Ag\,|\,Ag^+\ (Ag_2CrO_4\text{ sol. saturated})\,\Big|\Big|\,\begin{matrix}Ag^+\\0.1\,M\end{matrix}\,\Big|\,Ag;$$

$$E_{cell} = 0.164\text{ V at }298\text{ K}$$

We have $$E_{cell} = E^\circ_{OP_{Ag/Ag^+}} + E^\circ_{RP_{Ag^+/Ag}} + \frac{0.059}{1}\log_{10}\frac{[Ag^+]_{R.H.S.}}{[Ag^+]_{L.H.S.}}$$

or $$0.164 = 0 + \frac{0.059}{1}\log_{10}\frac{0.1}{[Ag^+]_{L.H.S.}}$$

$\therefore$ $[Ag^+]_{L.H.S.} = 1.66\times10^{-4}\ M$

Now K_{sp} for $Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$

$$K_{sp} = [Ag^+]^2\,[CrO_4^{2-}]$$

Since, $[Ag^+]_{L.H.S.} = 1.66\times10^{-4}\ M$

$\therefore$ $$[CrO_4^{2-}]_{L.H.S.} = \frac{1.66\times10^{-4}}{2}\ M$$

$\therefore$ $$K_{sp} = [1.66\times10^{-4}]^2\left[\frac{1.66\times10^{-4}}{2}\right]$$

$$K_{sp} = \mathbf{2.287\times10^{-12}\ mol^3\ litre^{-3}}$$

70. The given cell is $PtH_2\,\Big|\,\begin{matrix}H^+\\1\,M\end{matrix}\,\Big|\Big|\,\begin{matrix}Ag_2SO_4\,(aq.)\\\text{saturated}\end{matrix}\,\Big|\,Ag$

The reaction are, $H_2 \longrightarrow 2H^+ + 2e$

$$2Ag^+ + 2e \longrightarrow 2Ag$$

Thus, $E_{cell} = E_{OP_H} + E_{RP_{Ag}}$

$$0.711 = 0.799 + \frac{0.059}{2}\log[Ag^+]^2$$

$\therefore$ $$\log\frac{1}{[Ag^+]^2} = \frac{[0.799-0.711]\times2}{0.059} = 3$$

$\therefore$ $$[Ag^+]^2 = 10^{-3}\quad\therefore [Ag^+] = 3.2\times10^{-2}$$

Now the solubility equilibrium is,

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

$\therefore$ $$K_{sp} = (Ag^+)^2\,(SO_4^{2-})$$

$$= (3.2\times10^{-2})^2\left(\frac{3.2\times10^{-2}}{2}\right) = \mathbf{1.6\times10^{-5}}$$

[**Note :** That if $[Ag^+] = 3.2\times10^{-2}$, then

$$[SO_4^{2-}] = \frac{1}{2}\times3.2\times10^{2-}]$$

71. For Zn electrode || calomel electrode

$$E_{OP_{calomel}} = -0.28\text{ V};\quad E_{RP_{calomel}} = +0.28\text{ V}$$

$\therefore$ $$E_{cell} = E_{OP_{Zn/Zn^{2+}}} + E_{RP_{Calomel}}$$

$$1.083 = E_{OP_{Zn/Zn^{2+}}} + 0.28$$

$\therefore$ $$E_{OP_{Zn/Zn^{2+}}} = 1.083 - 0.28 = +0.803\text{ volt}$$

Now for Cu electrode || calomel electrode

$$E_{cell} = E_{OP_{Cu/Cu^{2+}}} + E_{RP\ Calomel}$$

$$-0.018 = E_{OP_{Cu/Cu^{2+}}} + E_{RP\ Calomel}$$

$\therefore$ $$E_{OP_{Cu/Cu^{2+}}} = -0.018 - 0.28 = -0.298\text{ volt}$$

Now for Zn electrode || Cu electrode, *i.e.*, Daniel cell

$$E_{cell} = E_{OP_{Zn/Zn^{2+}}} + E_{RP_{Cu^{2+}/Cu}}$$

$$= +0.803 + 0.298 = \mathbf{1.101\ volt}$$

72. Consider an electrode of H as

$$2H^+ + 2e \longrightarrow H_2;\qquad E^\circ_{RP_H} = 0$$

Given electrode is $2H_2O + 2e \longrightarrow H_2 + 2OH^-$; $E^\circ_{RP} = -0.8277\text{ V}$

$\because$ E°_{OP} for $H_2O > E^\circ_{OP}$ for H.

$\therefore$ The cell reactions are:

Anode: $H_2 + 2OH^- \longrightarrow 2H_2O + 2e$; $E^\circ_{OP} = +0.8277\text{ V}$

Cathode: $2H^+ + 2e \longrightarrow H_2$; $E^\circ_{RP} = 0$

$\therefore$ Net reaction is

$$2H^+ + 2OH^- \rightleftharpoons 2H_2O$$

and $K = \frac{[H_2O]^2}{[H^+]^2[OH^-]^2}$

Thus, for $2H_2O \rightleftharpoons [H_3O^+][OH^-]$

$K_w = [H_3O^+][OH^-]$

$\therefore \quad K = \left[\frac{1}{K_w}\right]^2 \quad ...(1)$

Also, $E_{cell} = E_{OP_{H_2O}} + E_{RP_H}$

$$= E^\circ_{OP_{H_2O}} - \frac{0.059}{2}\log_{10}\frac{[H_2O]^2}{[P_{H_2}][OH^-]^2}$$

$$+E^\circ_{RP_{H^+/H}} + \frac{0.059}{2}\log_{10}\frac{[H^+]^2}{P_{H_2}}$$

$$E_{cell} = 0.8277 + \frac{0.059}{2}\log_{10}\frac{[H^+]^2 \cdot P_{H_2} \cdot [OH^-]^2}{P_{H_2} \cdot [H_2O]^2}$$

$$E_{cell} = 0.8277 + \frac{0.059}{2}\log_{10}\frac{[H^+]^2[OH^-]^2}{[H_2O]^2}$$

$$= 0.8277 + \frac{0.059}{2}\log_{10}\frac{1}{K}$$

$$E_{cell} = 0.8277 + \frac{0.059}{2}\log_{10}[K_w]^2 \quad \text{by Eq. (1)}$$

At equilibrium, $E_{cell} = 0$

$\therefore \quad -0.8277 = 0.059\log_{10} K_w$

or $\log_{10} K_w = -\frac{0.8277}{0.059}$

or $K_w = \mathbf{9.35 \times 10^{-15}}$

73. For $2Hg + 2Fe^{3+} \rightleftharpoons Hg_2^{2+} + 2Fe^{2+}$

Before reaction	Excess	10^{-3}	0	0
After reaction	Excess	$10^{-3} \times \frac{5}{100}$	$\frac{95}{2 \times 100} \times 10^{-3}$	$\frac{95}{100} \times 10^{-3}$

For cell at equilibrium

$E_{cell} = 0 = E_{OP_{Hg/Hg_2^{2+}}} + E_{RP_{Fe^{3+}/Fe^{2+}}}$

$$0 = E^\circ_{OP_{Hg/Hg_2^{2+}}} - \frac{0.059}{2}\log_{10}[Hg_2^{2+}] + E^\circ_{RP_{Fe^{3+}/Fe^{2+}}} + \frac{0.059}{2}\log_{10}\frac{[Fe^{3+}]^2}{[Fe^{2+}]^2}$$

$$0 = E^\circ_{OP_{Hg/Hg_2^{2+}}} + 0.77 + \frac{0.059}{2}\log_{10}\frac{[Fe^{3+}]^2}{[Fe^{2+}]^2[Hg_2^{2+}]}$$

$(\because E^\circ_{OP_{Fe^{2+}/Fe^{3+}}} = -0.77\text{ V} \therefore E^\circ_{RP_{Fe^{3+}/Fe^{2+}}} = +0.77\text{ V})$

$$\text{or } E^\circ_{OP_{Hg/Hg_2^{2+}}} = -0.77 - \frac{0.059}{2}\log_{10}\frac{\left[\frac{5}{100}\times 10^{-3}\right]^2}{\left[\frac{95\times 10^{-3}}{100}\right]^2\left[\frac{95\times 10^{-3}}{2\times 100}\right]} = \mathbf{-0.792\text{ V}}$$

74. $MnO_4^- + Fe^{2+} \longrightarrow Mn^{2+} + Fe^{3+}$

Initial conc.	$0.1\,M$	
Final conc.	$\frac{0.1\times 10}{100}$	$\frac{0.1\times 90}{100}$

$E_{cell} = E_{OP_H} + E_{RP_{Mn^{2+}/MnO_4^-}} = 0 + E_{RP_{Mn^{2+}/MnO_4^-}}$

The electrode reaction is :

$MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O$ (cathode)

$$\therefore \quad E_{RP} = E^\circ_{RP_{Mn^{2+}/MnO_4^-}} + \frac{0.059}{5}\log\frac{[MnO_4^-][H^+]^8}{[Mn^{2+}]}$$

$$= 1.51 + \frac{0.059}{5}\log\frac{\frac{0.1\times 10}{100}\times(0.8)^8}{\frac{0.1\times 90}{100}}$$

$$= 1.51 - 0.099 = \mathbf{1.411\text{ V}}$$

75. For given cell $\because E^\circ_{OP_{Zn/Zn^{2+}}} > E^\circ_{OP_{H/H^+}}$

$\therefore$ Redox changes will be: $Zn \longrightarrow Zn^{2+} + 2e$

$2H^+ + 2e \longrightarrow H_2$

$E_{cell} = E_{OP_{Zn/Zn^{2+}}} + E_{RP_{H^+/H}}$

$$= E^\circ_{OP_{Zn/Zn^{2+}}} - \frac{0.059}{2}\log_{10}[Zn^{2+}] + E^\circ_{RP_{H^+/H}} + \frac{0.059}{2}\log_{10}\frac{[H^+]^2}{[P_{H_2}]}$$

$$0.701 = 0.760 + \frac{0.059}{2}\log_{10}\frac{[H^+]^2}{[Zn^{2+}]}$$

$$= 0.760 + \frac{0.059}{2}\log_{10}\frac{[H^+]^2}{[0.1]}$$

$[H^+] = 0.0316 \text{ mol litre}^{-1}$

Since, H^+ must be used by NaOH

$\therefore \quad$ Meq. of NaOH = Meq. of $[H^+]$

$\frac{w}{40} \times 1000 = 0.0316 \times 1000 \quad (\because V = 1 \text{ litre})$

$\therefore \quad w = \mathbf{1.264\text{ g}}$

After addition of NaOH to cathode solution $[H^+]$ becomes 10^{-7} since both acid and base are neutralized completely. Thus, new emf of cell,

$$E_{cell} = E^\circ_{cell} + \frac{0.059}{2}\log_{10}\frac{[H^+]^2}{(0.1)}$$

$$= 0.760 + \frac{0.059}{2}\log_{10}\frac{(10^{-7})^2}{0.1}$$

$E_{cell} = \mathbf{0.3765\text{ V}}$

76. $Zn \longrightarrow Zn^{2+} + 2e \quad E^\circ_{OP} = +0.76\text{ V}$

$[Zn^{2+}] = \left[\frac{0.1\times 20}{100}\right]$ ($\because$ Salt gives 20% of ions)

$$E_{OP_{Zn/Zn^{2+}}} = E^\circ_{OP_{Zn/Zn^{2+}}} - \frac{0.059}{2}\log_{10}[Zn^{2+}]$$

$$= +0.76 - \frac{0.059}{2}\log_{10}\left[\frac{0.1\times 20}{100}\right]$$

$E_{OP_{Zn/Zn^{2+}}} = \mathbf{0.81\text{ V}} \quad (Zn \longrightarrow Zn^{2+} + 2e)$

$\therefore \quad E_{RP_{Zn^{2+}/Zn}} = \mathbf{-0.81\text{ V}} \quad (Zn^{2+} + 2e \longrightarrow Zn)$

77. **Anode:** $H_2 \longrightarrow 2H^+ + 2e$

(negative polarity)

$$[H^+] = 10^{-6}\ M$$

Cathode: $2H^+ + 2e \longrightarrow H_2$

(positive polarity) $[H^+] \longrightarrow aM$

$$\therefore\ E_{cell} = E_{OP_{H/H^+}} + E_{RP_{H^+/H}}$$

$$= E^\circ_{OP_{H/H^+}} - \frac{0.059}{2}\log_{10}[H^+]^2_{\text{Anode}} + E^\circ_{RP_{H^+/H}} + \frac{0.059}{2}\log_{10}[H^+]^2_{\text{Cathode}}$$

$$= \frac{0.059}{2}\log_{10}\frac{[H^+]^2_{\text{Cathode}}}{[H^+]^2_{\text{Anode}}}$$

$$0.118 = \frac{0.059}{2}\log_{10}\frac{[H^+]^2_{\text{Cathode}}}{(10^{-6})^2} = \frac{0.059}{1}\log_{10}\frac{[H^+]_{\text{Cathode}}}{10^{-6}}$$

$$\therefore\ [H^+]_{\text{Cathode}} = \mathbf{10^{-4}\ M}$$

78. $$E_{cell} = E_{OP_{Ag/Ag^+}} + E_{RP_{Ag^+/Ag}}$$

L.H.S. R.H.S.

$$= E^\circ_{OP_{Ag/Ag^+}} - \frac{0.059}{1}\log_{10}[Ag^+]_{\text{L.H.S.}} + E^\circ_{RP_{Ag^+/Ag}} + \frac{0.059}{1}\log_{10}[Ag^+]_{\text{R.H.S.}}$$

$$E_{cell} = \frac{0.059}{1}\log_{10}\frac{[Ag^+]_{\text{R.H.S.}}}{[Ag^+]_{\text{L.H.S.}}} \quad ...(1)$$

Now for L.H.S. $K_{sp_{AgCl}} = 2.8\times10^{-10}$

$$\therefore\ [Ag^+][Cl^-] = 2.8\times10^{-10}$$

$$\therefore\ [Ag^+] = \frac{2.8\times10^{-10}}{[Cl^-]} = \frac{2.8\times10^{-10}}{0.2} = 1.4\times10^{-9}\ M$$

For R.H.S. $K_{sp_{AgBr}} = 3.3\times10^{-13}$

$$[Ag^+][Br^-] = 3.3\times10^{-13}$$

$$\therefore\ [Ag^+] = \frac{3.3\times10^{-13}}{[Br^-]} = \frac{3.3\times10^{-13}}{0.001} = 3.3\times10^{-10}\,M$$

$$\therefore\ \text{By Eq. (1)}\quad E_{cell} = \frac{0.059}{1}\log_{10}\frac{3.3\times10^{-10}}{1.4\times10^{-9}} = -0.037\text{ V}$$

Thus, to get E_{cell} positive, polarity of cells should be reversed.

i.e., **cell is Ag | AgBr(*s*) KBr||AgCl, KCl | Ag and $E = +0.037$ V**

0.001*M* **0.2*M***

79. Let a and b are the concentrations of Br^- and Cl^- at equilibrium when $E_{cell} = 0$.

$$\therefore\ [Ag^+]_{\text{L.H.S.}} = \frac{K_{sp_{AgBr}}}{[Br^-]} = \frac{5\times10^{-13}}{a}$$

$$[Ag^+]_{\text{R.H.S.}} = \frac{K_{sp_{AgCl}}}{[Cl^-]} = \frac{1\times10^{-10}}{b}$$

Also $$E_{cell} = E^\circ_{Ag/Ag^+} + E^\circ_{Ag^+/Ag} + \frac{0.059}{1}\log\frac{[Ag^+]_{\text{R.H.S.}}}{[Ag^+]_{\text{L.H.S.}}}$$

R.H.S. L.H.S.

$$0 = 0 + \frac{0.059}{1}\log\frac{1\times10^{-10}\times a}{5\times10^{-13}\times b}$$

$$\therefore\ \frac{a}{b} = \mathbf{\frac{1}{200}}$$

80. $$Ag_2S + 2e \longrightarrow 2Ag + S^{2-}$$

$$(Ag^{+1})_2 + 2e \longrightarrow 2Ag$$

$$\therefore\ E_{RP} = E^\circ_{RP} + \frac{0.059}{2}\log[Ag^+]^2 \quad ...(1)$$

Also $$K_1\times K_2 = \frac{[H^+]^2[S^{2-}]}{[H_2S]}$$

$$\therefore\ 1.1\times10^{-13}\times1.0\times10^{-8} = \frac{[10^{-3}]^2[S^{2-}]}{[0.1]}$$

or $$[S^{2-}] = 1.1\times10^{-16}$$

Also $$K_{sp_{Ag_2S}} = 2\times10^{-49} = [Ag^+]^2[S^{2-}]$$

$$= [Ag^+]^2[1.1\times10^{-16}]$$

$$\therefore\ [Ag^+]^2 = 1.818\times10^{-33} \quad ...(2)$$

$\therefore$ By Eqs. (1) and (2)

$$E_{RP} = 0.8 + \frac{0.059}{2}\log[1.818\times10^{-33}]$$

$$= 0.8 - 0.9658 = -0.1658\text{ V}$$

81. $Ag \longrightarrow Ag^+ + e;$ $E^\circ = -0.7991$ V

$AgI(s) + e \longrightarrow Ag + I^-;$ $E^\circ = ?$

$AgI(s) \longrightarrow Ag^+ + I^-$

$$\therefore\ E_{cell} = E^\circ_{OP_{Ag/Ag^+}} - \frac{0.059}{1}\log[Ag^+] + E^\circ_{RP_{I^-/AgI/Ag}} + \frac{0.059}{1}\log\frac{1}{[I^-]}$$

$\because\ E_{cell} = 0$ for $AgI \longrightarrow Ag^+ + I^-$

$$\therefore\ 0 = -0.7991 + E^\circ_{RP_{I^-/AgI/Ag}} + \frac{0.059}{1}\log\frac{1}{[Ag^+][I^-]}$$

$$\therefore\ E^\circ_{RP_{I^-/AgI/Ag}} = 0.7991 + \frac{0.059}{1}\log K_{sp_{AgI}}$$

$$= 0.7991 - 0.059\times16.07$$

$$= +0.7991 - 0.9481 = \mathbf{-0.1490\ V}$$

82. $\because$ $E^\circ_{OP_{Fe^{2+}/Fe^{3+}}} > E_{Cr^{3+}/Cr^{6+}}$

$\therefore$ Redox changes will be

Anode: $Fe^{2+} \longrightarrow Fe^{3+} + e$

(L.H.S.)

Cathode: $14H^+ + 6e + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$

(R.H.S.)

$$E_{cell} = E_{OP_{Fe^{2+}/Fe^{3+}}} + E_{RP_{\text{R.H.S.}}}$$

$$= E^\circ_{OP_{Fe^{2+}/Fe^{3+}}} - \frac{0.059}{6}\log_{10}\frac{[Fe^{3+}]^6}{[Fe^{2+}]^6} + E^\circ_{RP_{\text{R.H.S.}}} + \frac{0.059}{6}\log_{10}\frac{[Cr_2O_7^{2-}][H^+]^{14}}{[Cr^{3+}]^2}$$

$$= -0.770 - \frac{0.059}{1}\log_{10}\frac{0.75}{0.5} + 1.35 + \frac{0.059}{6}\log_{10}\frac{(2)\times(1)^{14}}{(4)^2}$$

$$= -0.770 - 0.0104 + 1.35 + (-0.0089) = \mathbf{+0.56\ volt}$$

83. $E_{cell} = E^\circ_{OP_H} + E^\circ_{RP_{Zn^{2+}/Zn}} + \frac{0.059}{2}\log_{10}\frac{[Zn^{2+}]}{[H^+]^2}$

$$-0.46 = 0 - 0.763 + \frac{0.059}{2}\log_{10}\frac{[0.3]}{[H^+]^2}$$

$\therefore$ $[H^+] = 4.0\times 10^{-6}$

Now $K_2 = \frac{[H^+][SO_3^{2-}]}{[HSO_3^-]}$

$\because$ $HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$

The dissociation of HSO_3^- is suppressed in presence of SO_3^{2-} due to common ion effect. Thus $[SO_3^{2-}] = 6.44\times 10^{-3}\ M$ and $[HSO_3^-] = 0.4\ M$

$\therefore$ $K_2 = \frac{4\times 10^{-6}\times 6.44\times 10^{-3}}{0.4} = \mathbf{6.44\times 10^{-8}}$

84. $E_{cell} = E_{OP_{Sn}} + E_{RP_{Pb}}$

$$= E^\circ_{OP_{Sn}} - \frac{0.059}{2}\log_{10}[Sn^{2+}] + E^\circ_{RP_{Pb}} + \frac{0.059}{2}\log_{10}[Pb^{2+}]$$

$$= E^\circ_{OP_{Sn}} + E^\circ_{RP_{Pb}} + \frac{0.059}{2}\log_{10}\frac{[Pb^{2+}]}{[Sn^{2+}]}$$

$$= 0.136 - 0.126 + \frac{0.059}{2}\log_{10}\frac{[Pb^{2+}]}{[Sn^{2+}]}$$

$$= 0.01 + \frac{0.059}{2}\log_{10}\frac{[Pb^{2+}]}{[Sn^{2+}]}$$

At equilibrium, $E_{cell} = 0$ $\therefore$ $\frac{[Pb^{2+}]}{[Sn^{2+}]} = 0.458$

Thus, till $\frac{[Pb^{2+}]}{[Sn^{2+}]} > 0.458$, cell reaction exists,

and it will be reversed when $\mathbf{\frac{[Pb^{2+}]}{[Sn^{2+}]} < 0.458}$

i.e., $E_{cell} = -\text{ve}$

85. Given, $E^\circ_{FeO/Fe} = -0.87\ V$; $\therefore$ $E^\circ_{Ni_2O_3/NiO} = +0.40\ V$

$\therefore$ $E^\circ_{Fe/FeO} = +0.87\ V$; $\therefore$ $E^\circ_{NiO/Ni_2O_3} = -0.40\ V$

Since, E°_{OP} for Fe/FeO > E°_{OP} for NiO/Ni_2O_3 and thus, redox changes are,

At anode: $Fe(s) + 2OH^- \longrightarrow FeO(s) + H_2O(l) + 2e$ (oxidation)

At cathode:

$Ni_2O_3(s) + H_2O(l) + 2e \longrightarrow 2NiO(s) + 2OH^-$ (reduction)

Redox reaction:

$$Fe(s) + Ni_2O_3(s) \longrightarrow FeO(s) + 2NiO(s)$$

(i) $E_{cell} = E^\circ_{OP_{Fe/FeO}} - \frac{0.059}{2}\log_{10}\frac{[H_2O]}{[OH^-]^2} + E^\circ_{RP_{Ni_2O_3/NiO}} + \frac{0.059}{2}\log_{10}\frac{[H_2O]}{[OH^-]^2}$

$$= E^\circ_{OP_{Fe/FeO}} + E^\circ_{RP_{Ni_2O_3/NiO}} = 0.87 + 0.40 = \mathbf{1.27\ V}$$

(ii) The E_{cell} is independent of OH^- ion concentration.

(iii) $-\Delta G^\circ = nE^\circ F = 2\times 1.27\times 96500$
$= 245110\text{J} = \mathbf{245.11\ kJ}$

86. At pH = 7: $E_{RP} = E^\circ_{RP} + \frac{0.059}{2}\log\frac{[CH_3CHO][H^+]^2}{[CH_3CH_2OH]}$

$$-0.197 = E^\circ_{RP} + \frac{0.059}{2}\log\frac{(10^{-7})^2\times 1}{1}$$

$$-0.197 = E^\circ_{RP} + \frac{0.059}{2}\times(-14)$$

$\therefore$ $E^\circ_{RP} = 0.216$

Again when pH = 6

$$E_{RP} = E^\circ_{RP} + \frac{0.059}{2}\log\frac{(10^{-6})^2\times 10^{-5}}{10^{-5}}$$

$$= 0.216 + \frac{0.059}{2}\times(-12) = 0.216 - 0.354 = \mathbf{-0.138\ V}$$

87. For the given cell, at equilibrium, the reaction is

$$Mg + 2Ag^+ \rightleftharpoons Mg^{2+} + 2Ag$$

$$E_{cell} = 0 = E_{OP_{Mg/Mg^{2+}}} + E_{RP_{Ag^+/Ag}}$$

$$0 = E^\circ_{OP_{Mg/Mg^{2+}}} - \frac{0.059}{2}\log_{10}[Mg^{2+}] + E^\circ_{RP_{Ag^+/Ag}} + \frac{0.059}{2}\log_{10}[Ag^+]^2$$

$$0 = E^\circ_{OP_{Mg/Mg^{2+}}} + E^\circ_{RP_{Ag^+/Ag}} + \frac{0.059}{2}\log_{10}\frac{[Ag^+]^2}{[Mg^{2+}]}$$

$$0 = 2.37 + 0.80 + \frac{0.059}{2}\log_{10}\frac{1}{K_C}$$

$\therefore$ $\log_{10}\frac{1}{K_C} = -107.457$

or $\log_{10}K_C = \mathbf{107.457}$

and $E^\circ_{cell} = 2.37 + 0.80 = \mathbf{3.17\ V}$

Now maximum work that can be obtained by cell is given by

$$-\Delta G^\circ = W_{max}$$

$\therefore$ $W_{max} = -\Delta G^\circ$

$$= nE^\circ F = 2\times 96500\times 3.17 = 6.118\times 10^5 \text{ joule}$$

$$= \mathbf{6.118\times 10^2\ kJ}$$

88. (i) In $8M\ H^+$ solution, conc. of all other species is unity.

$$E_{RP} = E^\circ_{RP} + \frac{0.059}{1}\log_{10}[H^+]^2$$

$$= 0.78 + 0.059\log_{10}(8)^2 = 0.78 + 0.1062$$

$$= \mathbf{0.8862\ V}$$

(ii) In case of neutral solution; concentration of $[H^+] = 10^{-7}\ M$ and conc. of all other species are unity, then

$$E_{RP} = E^\circ_{RP} + \frac{0.059}{1}\log_{10}[H^+]^2$$
$$= 0.78 + \frac{0.059}{1}\log_{10}(10^{-7})^2 = 0.78 + (-0.826)$$
$$= \mathbf{-0.046\ V}$$

89. Initially $E_{Cu^{2+}/Cu} = E^\circ_{Cu^{2+}/Cu} + \frac{0.059}{2}\log[Cu^{2+}]$

$$= 0.344 + \frac{0.059}{2}\log[1] = 0.344\ V$$
$$E_{Bi^{3+}/Bi} = 0.226 + \frac{0.059}{3}\log[Bi^{3+}]$$
$$= 0.226 + \frac{0.059}{3}\log 1 = 0.266\ V$$

Thus, passage of current would initially deposits Cu^{2+} till $E_{Cu^{2+}/Cu}$ becomes 0.266 V because then only, Bi^{3+} will be deposited.

Thus, $E_{Cu^{2+}/Cu} = E^\circ_{Cu^{2+}/Cu} + \frac{0.059}{2}\log[Cu^{2+}]$

$$0.266 = 0.344 + \frac{0.059}{2}\log[Cu^{2+}]$$

$\therefore$ $[Cu^{2+}] = \mathbf{10^{-4}}\ \boldsymbol{M}$

90. The half cell reaction is,

$$MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O$$

$$\therefore E_{MnO_4^-/Mn^{2+}} = E^\circ_{MnO_4^-/Mn^{2+}} + \frac{0.059}{5}\log_{10}\frac{[MnO_4^-][H^+]^8}{[Mn^{2+}]}$$

or $E_{RP} = E^\circ_{RP} + 0.0118\log_{10}\frac{1\times 1}{1}$

$\therefore$ $E_{RP} = E^\circ_{RP}$

If $H^+ = 10^{-4}$

Then $E_{RP} = E^\circ_{RP} + 0.0118\log_{10}\frac{1\times(10^{-4})^8}{1}$

$$E_{RP} = E^\circ_{RP} - \mathbf{0.38\ V}$$

i.e., the couple MnO_4^- / Mn^{2+} shows a decrease in its E_{RP} by 0.38 volt or an increase in its E_{OP} by 0.38 V and thus less oxidizing power.

91. The cell reactions are:

Anode: $H_2 \longrightarrow 2H^+ + 2e$

Cathode: $2Ag^+ + 2e \longrightarrow 2Ag$

Thus, $E_{cell} = E^\circ_{OP_{H_2}} + E^\circ_{RP_{Ag}} + \frac{0.059}{2}\log_{10}\frac{[Ag^+]^2 \cdot P_{H_2}}{[H^+]^2}$

or $0.503 = 0 + 0.80 + \frac{0.059}{2}\log_{10}[Ag^+]^2$

or $[Ag^+] = 9.25\times 10^{-6}\ M$

$\therefore$ Mole of Ag^+ in 350 mL $= 9.25\times 10^{-6}\times\frac{350}{1000}$

$\therefore$ Mass of Ag^+ in 350 mL $= 9.25\times 10^{-6}\times\frac{350}{1000}\times 108$

$$= 3.497\times 10^{-4}\ g$$

$\therefore$ % of Ag in 1.05 g alloy $= \frac{3.497\times 10^{-4}}{1.05}\times 100 = 0.033\%$

$\therefore$ % of lead in alloy = **99.967%**

92. E°_{OP} is more for Pb and thus,

Anode: $Pb \longrightarrow Pb^{2+} + 2e$

Cathode: $Hg_2^{2+} + 2e \longrightarrow Hg_2$

Cell is Pb | $PbSO_4$ saturated || Hg_2SO_4 saturated | Hg

Also, $E_{cell} = E^\circ_{OP_{Pb}} + E^\circ_{RP_{Hg}} + \frac{0.059}{2}\log\frac{[Hg_2^{2+}]}{[Pb^{2+}]}$

$\therefore$ $E^\circ_{OP_{Pb}} = 0.126\ V$ and $E^\circ_{RP_{Hg}} = +0.789\ V$

and for $PbSO_4 \rightleftharpoons Pb^{2+} + SO_4^{2-}$

$\therefore$ $K_{sp} = [Pb^{2+}][SO_4^{2-}] = [Pb^{2+}]^2$

or $[Pb^{2+}] = \sqrt{K_{sp}} = \sqrt{2.43\times 10^{-8}}$

For $Hg_2SO_4 \rightleftharpoons Hg_2^{2+} + SO_4^{2-}$

$$[Hg_2^{2+}] = \sqrt{K_{sp}} = \sqrt{1.46\times 10^{-6}}$$

$$\therefore E_{cell} = 0.126 + 0.789 + \frac{0.059}{2}\log\frac{\sqrt{1.46\times 10^{-6}}}{\sqrt{2.43\times 10^{-8}}} = \mathbf{0.941\ V}$$

93. $\because$ $E_{Ag^+/Ag} = E^\circ_{Ag^+/Ag} + \frac{0.059}{1}\log_{10}[Ag^+]$ ...(1)

Also, $K_{sp_{AgI}} = [Ag^+][I^-]$

$\because$ $[Ag^+] = [I^-]$ **(for a saturated solution)**

$\therefore$ $[Ag^+] = \sqrt{K_{sp_{AgI}}} = \sqrt{8.7\times 10^{-17}} = 9.32\times 10^{-9}$ ...(2)

$\therefore$ By Eq. (1), $E_{Ag^+/Ag} = 0.799 + \frac{0.059}{1}\log_{10}(9.32\times 10^{-9})$

$$= 0.799 - 0.474 = \mathbf{0.32\ V}$$

Also, $Ag \longrightarrow Ag^+ + e;$ $E^\circ_{OP} = -0.799\ V$

$$\underline{AgI(s) + e \longrightarrow Ag + I^-}$$
$$AgI \rightleftharpoons Ag^+ + I^-$$

$$\therefore E_{cell} = E^\circ_{OP_{Ag/Ag^+}} - \frac{0.059}{1}\log[Ag^+] + E^\circ_{RP_{I^-/AgI/Ag}} + \frac{0.059}{1}\log\frac{1}{[I^-]} \quad ...(3)$$

$\because$ $E_{cell} = 0$ at equilibrium, thus, from Eq. (3)

$$E^\circ_{OP_{Ag/Ag^+}} + E^\circ_{RP_{I^-/AgI/Ag}} = \frac{0.059}{1}\log[Ag^+][I^-]$$
$$= \frac{0.059}{1}\log K_{sp_{AgI}}$$
$$-0.799 + E^\circ_{RP_{I^-/AgI/Ag}} = \frac{0.059}{1}\log 8.7\times 10^{-17}$$

or $E^\circ_{RP_{I^-/AgI/Ag}} = -0.948 + 0.799 = \mathbf{-0.149\ V}$

94. $Ag(s) + \frac{1}{2}Cl_2(g) \longrightarrow AgCl(s);$ $\Delta G^\circ_1 = -109\ kJ$ ...(1)

$Ag(s) \longrightarrow Ag^+(aq.) + e;$ $\Delta G^\circ_2 = +77\ kJ$ ...(2)

$\frac{1}{2}Cl_2(g) + e \longrightarrow Cl^-(aq.);$ $\Delta G^\circ_3 = -129\ kJ$ ...(3)

By Eqs. (1) – (2) – (3),

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

$$\Delta G_4^\circ = -109 - 77 + 129 = -57 \text{ kJ}$$

$\because$ $-\Delta G^\circ = nE^\circ F$

$\therefore$ $57\times10^3 = 1\times E^\circ\times96500$ $\therefore$ $E_{cell}^\circ = 0.59$ V

The cell is Ag | AgCl(s)||Cl⁻ (aq.) || Ag⁺ (aq.) | Ag
(Anode) (Cathode)

Also, $E_{cell} = E_{OP_{Ag/AgCl/Cl^-}}^\circ - 0.059\log\frac{1}{[Cl^-]} + E_{RP_{Ag^+/Ag}}^\circ + 0.059\log[Ag^+]$

At equilibrium $E_{cell} = 0$, thus,

$$E_{Ag/AgCl/Cl^-}^\circ + E_{RP_{Ag^+/Ag}}^\circ = -0.059\log[Ag^+][Cl^-]$$

$$E_{cell}^\circ = -0.059\log K_{sp\,AgCl}$$

$\therefore$ $0.59 = -0.059\log K_{sp\,AgCl}$

or $K_{sp\,AgCl} = \mathbf{1\times10^{-10}\ M^2}$

Let solubility of AgCl be S, then

$$S = \sqrt{K_{sp}} = \sqrt{10^{-10}} = 10^{-5}\text{ M}$$

Mole of AgCl in its 100 mL saturated solution

$$= 10^{-5}\times\frac{100}{1000} = 10^{-6}$$

Mole of Zn added in it $= \frac{6.539\times10^{-2}}{65.39} = 10^{-3}$

For $Ag \longrightarrow Ag^+ + e$; $\Delta G^\circ = 77$ kJ

$\therefore$ $-\Delta G^\circ = nE^\circ F$

or $E_{Ag/Ag^+}^\circ = \frac{-77\times10^3}{1\times96500} = -0.80$ V

For the redox change on addition of Zn to AgCl saturated solution

$$Zn \longrightarrow Zn^{2+} + 2e \qquad E_{OP}^\circ = +0.76\text{ V}$$
$$2Ag^+ + 2e \longrightarrow 2Ag \qquad E_{RP}^\circ = +0.80\text{ V}$$
$$Zn + 2Ag^+ \longrightarrow Zn^{2+} + 2Ag \qquad E_{cell}^\circ = 1.56\text{ V}$$

Also, $E_{cell} = E_{cell}^\circ + \frac{0.059}{2}\log\frac{[Ag^+]^2}{[Zn^{2+}]}$

At equilibrium, $E_{cell} = 0$

$\therefore$ $E_{cell}^\circ = \frac{0.059}{2}\log\frac{[Zn^{2+}]}{[Ag^+]^2}$

$\therefore$ $\log\frac{[Zn^{2+}]}{[Ag^+]^2} = \frac{1.56\times2}{0.059} = \mathbf{52.88}$

and $K_C = \frac{[Zn^{2+}]}{[Ag^+]^2} = 7.61\times10^{52}$

Since, K_C is appreciably high, thus, nearly whole of Ag^+ is converted to Ag. Thus, mole of Ag formed = mole of Ag^+ in 100 mL solution $= 10^{-6}$. Note that Zn is in excess.

95. $Pt_{H_2}(g)|HCl(aq.)||AgCl(s)|Ag(s)$

(i) $\frac{1}{2}H_2 \longrightarrow H^+ + e$ (Anode)

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

$\frac{1}{2}H_2 + AgCl \longrightarrow H^+ + Ag + Cl^-$

(ii) $-\Delta G^\circ = nE^\circ F = 1\times0.23\times96500 = 22195$ J (at 15° C)

$-\Delta G^\circ = nE^\circ F = 1\times0.21\times96500 = 20265$ J (at 35° C)

Also, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$\therefore$ $-22195 = \Delta H^\circ - 288\times\Delta S^\circ$

$-20265 = \Delta H^\circ - 308\times\Delta S^\circ$

$+ \quad - \quad +$

$\therefore$ $\Delta S^\circ = -96.50$ J

Also, $-22195 = \Delta H^\circ - 288\times(-96.5) = -49987$ J

$\therefore$ $\Delta H^\circ = -49.987$ kJ

(iii) Consider the following reaction at $AgCl(s)Cl^- / Ag$ electrodes

$E_{cell} = 0$ at equilibrium

Also, $E_{RP_{Cl^-/AgCl/Ag}}^\circ + E_{OP_H}^\circ = 0.22$ at 25° C

$\therefore$ $E_{RP_{Cl^-/AgCl/Ag}}^\circ = 0.22$ at 25° C

Also, $E_{Cl^-/AgCl/Ag}^\circ = E_{Ag^+/Ag}^\circ + 0.059\log K_{sp_{AgCl}}$

or $0.22 = 0.80 + 0.059\log K_{sp\,AgCl}$

$\therefore$ $K_{sp_{AgCl}} = 1.47\times10^{-10}$

$\therefore$ Solubility of AgCl $= \sqrt{K_{sp}} = \sqrt{1.47\times10^{-10}}$

$= \mathbf{1.21\times10^{-5}\ mol\ litre^{-1}}$

96. When two half reactions are added to give an overall reaction, the no. of mole of electrons involved in each half reaction and overall reaction are necessarily the same, *e.g.*,

$M_1 \longrightarrow M_1^{n_1+} + n_1e$; $\qquad -\Delta G_1^\circ = n_1E_1^\circ F$

$M_2^{n_2+} + n_2e \longrightarrow M_2$; $\qquad -\Delta G_2^\circ = n_2E_2^\circ F$

$M_1 + M_2^{n_2+} \longrightarrow M_1^{n_1+} + M_2$; $\qquad -\Delta G_3^\circ = n_3E_3^\circ F$

$\therefore$ $\Delta G_3^\circ = \Delta G_1^\circ + \Delta G_2^\circ$

$n_3E_3^\circ F = n_1E_1^\circ F + n_2E_2^\circ F$

or $E_3^\circ = \frac{n_1E_1^\circ + n_2E_2^\circ}{n_3}$

Since, $n_1 = n_2 = n_3$

$\therefore$ $E_3^\circ = E_1^\circ + E_2^\circ$

Also, when two half reactions are added to give a third reaction then $n_1 \neq n_2 \neq n_3$, *e.g.*,

$M_1 \longrightarrow M_1^{n_1+} + n_1e$ $\qquad -\Delta G_1^\circ = n_1E_1^\circ F$

$M_1^{n_1+} \longrightarrow M_1^{n_2+} + (n_2 - n_1)e$ $\qquad -\Delta G_2^\circ = (n_2 - n_1)E_2^\circ F$

$M_1 \longrightarrow M_1^{n_2+} + n_2e$ $\qquad -\Delta G_3^\circ = n_2E_3^\circ F$

$\therefore$ $\Delta G_3^\circ = \Delta G_1^\circ + \Delta G_2^\circ$

$n_2E_3^\circ F = n_1E_1^\circ F + (n_2 - n_1)E_2^\circ F$

$\therefore$ $E_3^\circ = \frac{n_1E_1^\circ + n_2E_2^\circ - n_1E_2^\circ}{n_2}$

97. $MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O$; $E_1^\circ = 1.51\,V$ ...(1)

$\therefore \quad \Delta G_1^\circ = -5 \times 1.51 \times F = -7.55\,F$

$MnO_2 + 4H^+ + 2e \longrightarrow Mn^{2+} + 2H_2O$; $E_2^\circ = 1.23\,V$ ...(2)

$\therefore \quad \Delta G_2^\circ = -2 \times 1.23 \times F = -2.46\,F$

Subtracting Eqs. (2) from (1),

$MnO_4^- + 4H^+ + 3e \longrightarrow 2H_2O + MnO_2$; $E_3^\circ = ?$

or $\quad \Delta G_3^\circ = -n_3 E_3^\circ F$

$\therefore \quad \Delta G_3^\circ = \Delta G_1^\circ - \Delta G_2^\circ$

$-3E_3^\circ F = -7.55F + 2.46F$

$\therefore \quad E_3^\circ = \frac{-5.09}{-3} = $ **1.70 volt**

98. Given, $Cu^{2+} + e \longrightarrow Cu^+$; $E_1^\circ = 0.15\,V$; ΔG_1° ...(1)

$Cu^+ + e \longrightarrow Cu$; $E_2^\circ = 0.5\,V$; ΔG_2° ...(2)

$Cu^{2+} + 2e \longrightarrow Cu$; $E_3^\circ = ?$; ΔG_3° ...(3)

For Eq. (1), $+\Delta G_1^\circ = -nE_1^\circ F = -1 \times 0.15 \times F = -0.15F$

For Eq. (2), $+\Delta G_2^\circ = -nE_2^\circ F = -1 \times 0.5 \times F = -0.5F$

$\therefore$ Adding $\quad \Delta G_1^\circ + \Delta G_2^\circ = \Delta G_3^\circ$

$-0.15F + (-0.5F) = \Delta G_3^\circ$

$\Delta G_3^\circ = -0.65F$

$\therefore \quad -nE_3^\circ F = -0.65F$

or $\quad E_3^\circ = \frac{-0.65F}{-2F} = 0.325$ volt

$\therefore \quad X = $ **+0.325 volt**

Now for disproportionation,

$Cu^+ \longrightarrow Cu^{2+} + e$; E_{OP}°

$Cu^+ + e \longrightarrow Cu$; E_{RP}°

$2Cu^+ \longrightarrow Cu^{2+} + Cu$ ...(4)

$\therefore \quad E_{cell}^\circ = E_{OP_{Cu^+/Cu^{2+}}}^\circ + E_{RP_{Cu^+/Cu}}^\circ$

$= -0.15 + 0.5 = $ **+0.35 V**

Since, E° of Eq. (4) is +ve and thus the reaction is feasible. In other words disproportionation of Cu^+ takes place, *i.e.*, Cu^+ acts as reductant and oxidant both.

99. $Fe \longrightarrow Fe^{2+} + 2e$; $\quad -\Delta G_1^\circ = 2E_1^\circ F$ ...(1)

$Fe^{2+} \longrightarrow Fe^{3+} + e$; $\quad -\Delta G_2^\circ = E_2^\circ F$ ...(2)

$Fe \longrightarrow Fe^{3+} + 3e$; $\quad -\Delta G_3^\circ = 3E_3^\circ F$ ...(3)

Subtracting Eqs. (1) from (3),

$Fe \longrightarrow Fe^{3+} + 3e$; $\quad -\Delta G_3^\circ = 3E_3^\circ F$

$Fe \longrightarrow Fe^{2+} + 2e$; $\quad -\Delta G_1^\circ = 2E_1^\circ F$

$- \quad - \quad - \quad + \quad -$

$Fe^{2+} \longrightarrow Fe^{3+} + e$, $\quad -\Delta G_3^\circ + \Delta G_1^\circ = 3E_3^\circ F - 2E_1^\circ F$ ...(4)

Comparing Eqs. (2) and (4),

$-\Delta G_2^\circ = -\Delta G_3^\circ + \Delta G_1^\circ = 3E_3^\circ F - 2E_1^\circ F$

$+E_2^\circ F = 3E_3^\circ F - 2E_1^\circ F$

$\therefore \quad E_3^\circ \, \frac{2E_1^\circ + E_2^\circ}{3}$ or $3E_3^\circ = 2E_1^\circ + E_2^\circ$

100. During electrolysis some Zn^{2+} will discharge and some Cu^{2+} will pass in solution

Thus, $\quad \frac{w}{E} = \frac{0.48 \times 10 \times 60 \times 60}{96500} = 0.18$

or Mole of Cu^{2+} formed = Mole of Zn^{2+} deposited = 0.09

or *m* mole of Cu^{2+} formed = *m* mole of Zn^{2+} deposited = 90

$\therefore \quad$ *m* mole of Zn^{2+} left $= 100 \times 1 - 90 = 10$

m mole of Cu^{2+} left $= 100 \times 1 + 90 = 190$

Both are present in 100 mL solution of each

Now

$$E_{cell} = E_{OP_{Zn/Zn^{2+}}}^\circ + E_{RP_{Cu^{2+}/Cu}}^\circ + \frac{0.059}{2}\log_{10}\frac{[Cu^{2+}]}{[Zn^{2+}]}$$

$$= 0.76 + 0.34 + \frac{0.059}{2}\log_{10}\frac{190}{10}$$

$E_{cell} =$ **1.137 V**

101. Note that given cell will not work as electrochemical cell since $E_{OP_{Cu}}^\circ > E_{OP_{Ag}}^\circ$. The equation for electrochemical cell will be:

$Cu \longrightarrow Cu^{2+} + 2e$

$2Ag^+ + 2e \longrightarrow 2Ag$

Thus, emf of cell $Cu|Cu^{2+}||Ag^+|Ag$ will be

$$E_{cell} = E_{OP_{Cu}}^\circ + E_{RP_{Ag}}^\circ + \frac{0.059}{2}\log_{10}\frac{[Ag^+]^2}{[Cu^{2+}]}$$

$\because \quad [Ag^+] = 1M$ and $[Cu^{2+}] = 1M$

$\therefore \quad E_{cell} = E_{cell}^\circ + \frac{0.059}{2}\log_{10}\frac{1}{1}$

$E_{cell} = E_{cell}^\circ \quad$ (where $E_{cell}^\circ = E_{OP_{Cu}}^\circ + E_{RP_{Ag}}^\circ$)

After the passage of 9.65 ampere for 1 hr, *i.e.*, $9.65 \times 60 \times 60$ coulomb charge, during which the cell reaction is reversed thus, Cu^{2+} are discharged from solution and Ag metal passes to ionic state. The reaction during passage of current are:

$Cu^{2+} + 2e \longrightarrow Cu$

$2Ag \longrightarrow 2Ag^+ + 2e$

Ag^+ ions formed $= \frac{9.65 \times 60 \times 60}{96500}$ eq $= 0.36$ eq $= 0.36$ mol

Cu^{2+} ions discharged $= \frac{9.65 \times 60 \times 60}{96500}$ eq

$= 0.36$ eq $= 0.18$ mol

Thus, $\quad [Ag^+]_{left} = 1 + 0.36 = 1.36\,M$

$[Cu^{2+}]_{left} = 1 - 0.18 = 0.82\,M$

Thus, $\quad$ new cell is $Cu \left| \begin{matrix} Cu^{2+} \\ 0.82\,M \end{matrix} \right|\left| \begin{matrix} Ag^+ \\ 1.36\,M \end{matrix} \right| Ag$

Thus, $\quad E_{cell} = E_{cell}^\circ + \frac{0.059}{2}\log_{10}\frac{(1.36)^2}{(0.82)}$

$= E_{cell}^\circ + 0.010$ volt

Thus, E_{cell} increases by **0.010 V**

102. $Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$

$\therefore \quad K_f = 1\times 10^{12} = \dfrac{[Cu(NH_3)_4]^{2+}}{[Cu^{2+}][NH_3]^4} = \dfrac{1.0}{x(2.0)^4}$

$\therefore \quad x = 6.25\times 10^{-14}$ M

Note that due to high value of K_f almost all of the Cu^{2+} ions are converted to $Cu(NH_3)_4^{2+}$ ion

Now

$$E_{cell} = E^\circ_{OP_{Zn/Zn^{2+}}} + E^\circ_{RP_{Cu^{2+}/Cu}} + \frac{0.059}{2}\log_{10}\frac{Cu^{2+}}{Zn^{2+}}$$

$$= 0.76 + 0.34 + \frac{0.059}{2}\log_{10}\left[\frac{6.25\times 10^{-14}}{1}\right]$$

E_{cell} = **0.71 V**

103. For I cell, half reactions are;

$$V^{2+} \longrightarrow V^{3+} + e$$
$$e + V^{4+} \longrightarrow V^{3+}$$
$$V^{2+} + V^{4+} \longrightarrow 2V^{3+} \quad ...(A)$$

$\therefore \quad E^\circ_{cell} = E^\circ_{V^{2+}/V^{3+}_{OP}} + E_{V^{4+}/V^{3+}_{RP}} \quad ...(1)$

For II cell, half reactions are;

$$V^{3+} \longrightarrow V^{4+} + e$$
$$Ag^+ + e \longrightarrow Ag(s)$$
$$V^{3+} + Ag^+ \longrightarrow V^{4+} + Ag(s) \quad ...(B)$$

$\therefore \quad E^\circ_{cell} = E^\circ_{V^{3+}/V^{4+}_{OP}} + E^\circ_{Ag^+/Ag_{RP}} \quad ...(2)$

$\therefore \quad 0.439 = E^\circ_{V^{3+}/V^{4+}_{OP}} + 0.799$

or $E^\circ_{V^{3+}/V^{4+}_{OP}} = -0.360$ V or $E^\circ_{V^{4+}/V^{3+}_{RP}} = +0.360$ V

On substituting this value in Eq. (1),

$E^\circ_{cell} = E_{V^{2+}/V^{3+}_{OP}} + 0.360$

$\because \quad E^\circ_{cell} = 0.616$ V

$\because \quad 0.616 = E_{V^{2+}/V^{3+}_{OP}} + 0.360$

or $\quad E^\circ_{V^{2+}/V^{3+}_{OP}} = \mathbf{0.256\ V}$ or $E_{V^{3+}/V^{2+}_{RP}} = \mathbf{-0.256}$

104. According to Gibbs-Helmholtz equation, heat of reaction ΔH, given as,

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

$T = 273 + 25 = 298$ K, $n = 2$, $F = 96500$ C, $E = +0.03$ V

and $\quad \left(\dfrac{\delta E}{\delta T}\right)_P = -1.4\times 10^{-4}$ V/K

$\therefore \Delta H = 2\times 96500[298\times(-1.4\times 10^{-4}) - 0.03]$

$= -13842$ joule $=$ **−13.842 kJ mol⁻¹**

105. For $H_2(g) + 2AgCl(s) + 2H_2O(l) \longrightarrow 2Ag(s) + 2H_3O^+(aq.) + 2Cl^-(aq.)$

$\Delta G^\circ_{Reaction} = G^\circ_{Products} - G^\circ_{Reactants}$

$= 2G^\circ_{Ag}(s) + 2G^\circ_{(H_3O^+ + Cl^-)} - G^\circ_{H_2} - 2G^\circ_{AgCl}(s) - 2G^\circ_{H_2O}$

$= 0 + 2\times(-368.4) - 0 - 2\times(-109.7) - 2\times(-237.2)$

$= -43.0$ kJ

($\because$ G° of pure element = 0, *i.e.*, $G^\circ_{Ag} = 0$ and $G^\circ_{H_2} = 0$)

Now $\quad \Delta G^\circ = -nE^\circ F$

$-43\times 10^3 = -2\times E^\circ \times 96500$

$E^\circ = 0.2228$ volt

Further $E = E^\circ + \dfrac{0.059}{2}\log_{10}\dfrac{[AgCl(s)]^2 P_{H_2}}{[Ag(s)]^2[H_3O^+]^2[Cl^-]^2}$

$\because$ [Solid] = 1

$\therefore \quad E = E^\circ + \dfrac{0.059}{2}\log_{10}\dfrac{P_{H_2}}{[H_3O^+]^2[Cl^-]^2}$

$= 0.2228 + \dfrac{0.059}{2}\log_{10}\dfrac{1}{(0.01)^2(0.01)^2}$

= **0.458 volt**

106. For given cell reaction,

$\Delta G^\circ = -nE^\circ F$

$\therefore \quad \Delta G^\circ = -12\times 2.73\times 96500$ J

$= -3.1613\times 10^3$ kJ

$$\left[\begin{array}{l} n = 12 \because 4Al^\circ \longrightarrow 4Al^{3+} + 12e \\ 3O_2^\circ + 12e \longrightarrow 6O^{2-} \end{array}\right]$$

Now for given reaction,

$\Delta G^\circ = 4\times G^\circ_f[Al(OH)_4]^- - 6\times G^\circ_f[H_2O] - 4\times G^\circ_f[OH^-]$

(Also note that G°_f for elements is zero)

$-3.1613\times 10^3 = 4\times G^\circ_f[Al(OH)_4]^- - 6\times(-237.2) - 4\times(-157)$

$\therefore \quad G^\circ_f[Al(OH)_4]^-$ = **1303 kJ mol⁻¹**

107. At L.H.S.:

From $\quad CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$[H^+] = C\times\alpha = C\sqrt{\left(\dfrac{K_a}{C}\right)} = \sqrt{(K_a\cdot C)}$

$= \sqrt{(1.8\times 10^{-5}\times 0.1)} = 1.342\times 10^{-3}$ mol litre⁻¹

At R.H.S.: From $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$[OH^-] = C\times\alpha = C\sqrt{\left(\dfrac{K_b}{C}\right)}$

$= \sqrt{(K_b\cdot C)} = \sqrt{(1.8\times 10^{-5}\times 0.01)}$

$= 0.424\times 10^{-3}$ mol litre⁻¹

$\therefore \quad [H^+] = \dfrac{10^{-14}}{0.424\times 10^{-3}} = 2.359\times 10^{-11}$ mol litre⁻¹

Note : See chapter 13 of ionic equilibria for dissociation of weak acids and weak bases.

Now for cell $\frac{1}{2}H_2 \longrightarrow H^+ + e$ At anode, *i.e.*, L.H.S.

$H^+ + e \longrightarrow \frac{1}{2}H_2$ At cathode, *i.e.*, R.H.S.

$$E_{cell} = E_{OP_{H/H^+}} + E_{RP_{H^+/H}}$$

$$= E^\circ_{OP_{H/H^+}} - \frac{0.059}{1}\log_{10}\frac{[H^+]_{L.H.S.}}{[P_{H_2}]^{1/2}} + E^\circ_{RP_{H^+/H}} + \frac{0.059}{1}\log_{10}\frac{[H^+]_{R.H.S.}}{[P_{H_2}]^{1/2}}$$

$$= \frac{0.059}{1}\log_{10}\frac{[H^+]_{R.H.S.}}{[H^+]_{L.H.S.}} \quad (\because P_{H_2} = 1\,\text{atm on both sides})$$

$$= \frac{0.059}{1}\log_{10}\frac{2.359\times10^{-11}}{1.342\times10^{-3}} = \mathbf{-0.4575\ volt}$$

108. The cell is demonstrated as,

$$\text{Pt } H_2\ (1\text{atm})\,|\,HA_2\,||\,HA_1\,|\,(H_2)(1\text{atm})\text{ Pt}$$

At L.H.S. : $E_{H/H^+} = E^\circ_{OP_{H/H^+}} - \frac{0.059}{1}\log_{10}[H^+]_2$

$\because$ $-\log H^+ = pH$

$\therefore$ $E_{H/H^+} = E^\circ_{OP_{H/H^+}} + 0.059\,(pH)_2$

At R.H.S.: $E_{H^+/H} = E^\circ_{RP_{H^+/H}} + \frac{0.059}{1}\log_{10}[H^+]_1$

$\therefore$ $E_{H^+/H} = E^\circ_{RP_{H^+/H}} - 0.059\,(pH)_1$

For Acid HA_1, $HA_1 \rightleftharpoons H^+ + A_1^-$

$$[H^+] = C\cdot\alpha = \sqrt{K_a\cdot C}$$

$\therefore$ $(pH)_1 = \frac{1}{2}pK_{a_1} - \frac{1}{2}\log_{10} C$

Similarly, $(pH)_2 = \frac{1}{2}pK_{a_2} - \frac{1}{2}\log_{10} C$ $(\because C$ are same)

$\therefore$ $E_{cell} = E_{OP_{H/H^+\text{ for II}}} + E_{RP_{H^+/H\text{ for I}}}$

$$= 0.059\left[\frac{1}{2}pK_{a_2} - \frac{1}{2}pK_{a_1}\right]$$

$$= \frac{0.059}{2}[5-3] = \mathbf{+0.059\ V}$$

109. Use $Ag \longrightarrow Ag^+ + e;$ $E^\circ_{OP} = -0.799\ V$

$Ag(NH_3)_2^+ + e \longrightarrow Ag + 2NH_3;$ $E^\circ_{RP} = ?$

$\therefore$ $Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3$

and $E_{cell} = E^\circ_{cell} + \frac{0.059}{1}\log_{10}\frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2}$

Also, $E_{cell} = 0$

and $E^\circ_{cell} = E^\circ_{OP_{Ag/Ag^+}} + E^\circ_{RP_{Ag(NH_3)_2^+/Ag}}$

$\therefore$ $E^\circ_{cell} = \frac{0.059}{1}\log_{10} K_C$

$$= \frac{0.059}{1}\log_{10} 6\times10^{-14} = -0.780\ V$$

$\therefore$ $E^\circ_{Ag(NH_3)_2^+/Ag} = -0.780 + 0.799 = \mathbf{+0.019\ V}$

110. Use $Co(CN)_6^{4-} \longrightarrow Co(CN)_6^{3-} + e,$ $E^\circ_{OP} = +0.83\,V$

$Co^{3+} + e \longrightarrow Co^{2+};$ $E^\circ_{RP} = 1.82\,V$

$$Co(CN)_6^{4-} + Co^{3+} \rightleftharpoons Co^{2+} + Co(CN)_6^{3-}$$

and $E_{cell} = E^\circ_{cell} + \frac{0.059}{1}\log_{10}\frac{[Co^{3+}][Co(CN)_6^{4-}]}{[Co^{2+}][Co(CN)_6^{3-}]}$

or $E_{cell} = E^\circ_{cell} + \frac{0.059}{1}\log_{10}\frac{[Co^{3+}][Co(CN)_6^{4-}][CN^-]^6}{[Co^{2+}][Co(CN)_6^{3-}][CN^-]^6}$

Also, $6CN^- + Co^{2+} \rightleftharpoons Co(CN)_6^{4-}$

and $K_{f_1} = \frac{[Co(CN)_6^{4-}]}{[Co^{2+}][CN^-]^6}$

and $6CN^- + Co^{3+} \rightleftharpoons Co(CN)_6^{3-}$

and $K_{f_2} = \frac{[Co(CN)_6^{3-}]}{[Co^{3+}][CN^-]^6}$

$\therefore$ $E_{cell} = E^\circ_{cell} + \frac{0.059}{1}\log_{10}\frac{K_{f_1}}{K_{f_2}}$

$0 = 0.83 + 1.82 + \frac{0.059}{1}\log_{10}\frac{10^{19}}{K_{f_2}}$ (At equilibrium $E_{cell} = 0$)

$\therefore$ $\frac{K_{f_2}}{10^{19}} = 8.23\times10^{44}$ $\therefore$ $K_{f_2} = \mathbf{8.23\times10^{63}}$

111. $Zn \longrightarrow Zn^{2+} + 2e$

$Zn^{2+} + 2e \longrightarrow Zn$

$\therefore$ $E_{cell} = E^\circ_{OP_{Zn}} - \frac{0.059}{2}\log[Zn^{2+}]_{L.H.S.} + E^\circ_{RP_{Zn}} + \frac{0.059}{2}\log[Zn^{2+}]_{R.H.S.}$

$$0.099 = \frac{0.059}{2}\log\frac{3.84\times10^{-4}}{[Zn^{2+}]_{L.H.S.}}$$

Also, $[Zn^{2+}]_{L.H.S.} = 1.69\times10^{-7}$

$$K_{inst.} = \frac{[Zn^{2+}][CN^-]^4}{[Zn(CN)_4]^{2-}}$$

for $[Zn(CN)_4]^{2-} \rightleftharpoons Zn^{2+} + 4CN^-$

$$= \frac{\mathbf{1.69\times10^{-7}\times(2.65\times10^{-3})^4}}{\mathbf{0.45}}$$

$$K_{inst.} = \mathbf{1.85\times10^{-17}}$$

112. $N^{3+} \longrightarrow N^{5+} + 2e;$ $E^\circ = -0.94\ V$

$2N^{3+} + 2e \longrightarrow 2N^{2+};$ $E^\circ = 0.99\ V$

or $3N^{3+} \longrightarrow 2N^{2+} + N^{5+}$

$\therefore$ $E^\circ_{cell} = E^\circ_{OP_{HNO_2/NO_3^-}} + E^\circ_{RP_{HNO_2/NO}}$

$$E^\circ_{cell} = -0.94 + 0.99 = 0.05$$

Also, $E^\circ_{cell} = \frac{0.059}{2}\log K_c$

$$0.05 = \frac{0.059}{2}\log K_c$$

$\therefore$ $K_c = \mathbf{49.53}$

113. Given, $Au^{3+}(aq.) + 3e \longrightarrow Au(s);$

$E^\circ_{RP} = 1.42\ V$ and $E^\circ_{OP} = -1.42\ V$

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

$E^\circ_{RP} = 0.0\ V$ and $E^\circ_{OP} = 0$

More is E°_{OP} more is the tendency for oxidation, thus in case of above two half reactions.

$$\frac{3}{2}H_2 \longrightarrow 3H^+ + 3e$$
$$Au^{3+} + 3e \longrightarrow Au$$
$$\frac{3}{2}H_2 + Au^{3+} \longrightarrow Au + 3H^+$$
$$E^\circ = E^\circ_{OP_H} + E^\circ_{RP_{Au}} = \mathbf{1.42\ V}$$

Thus H_2 will reduce Au^{3+} to Au (E°_{cell} = + ve) but HCl will not dissolve Au (E°_{cell} = −ve for reverse reaction).

114. Cathode : $Hg_2Br_2(s) + 2e \longrightarrow 2Hg(l) + 2Br^-(aq.)$

Anode : $2Ag(s) + 2Br^- \longrightarrow 2AgBr(s) + 2e$

Cell reaction: $Hg_2Br_2(s) + 2Ag(s) \longrightarrow 2Hg(l) + 2AgBr(s)$

Also, $\left(\frac{\partial E}{\partial T}\right)_P = \frac{0.070 - 0.066}{10} = 0.0004$

$$\Delta G = -nFE = -2\times 96500\times 0.068$$
$$= \mathbf{-13124\ J = -13.124\ kJ}$$
$$\Delta H = -nF\left[E - T\left(\frac{\partial E}{\partial T}\right)_P\right]$$
$$= -2\times 96500[0.068 - 298\times 0.0004]$$
$$= \mathbf{9881.6\ J = 9.882\ kJ}$$

Also, $\Delta S = nF\left(\frac{\partial E}{\partial T}\right)_P = 2\times 96500\times 0.0004 = \mathbf{77.2\ J}$

115.
$$\frac{1}{2}H_2 \longrightarrow H^+ + e$$
$$H^+ + e \longrightarrow \frac{1}{2}H_2$$

$\therefore$ $E_{cell} = E_{OP_{H_2/H^+}} - \frac{0.059}{1}\log[H^+] + E^\circ_{RP_{H^+/H_2}} + \frac{0.059}{1}\log[H^+]$

$$-0.188 = 0 + 0 + \frac{0.059}{1}\log[H^+]$$

$\therefore$ $[H^+] = 6.51\times 10^{-4}\ M$

Now $C_6H_4NH_3^+ + H_2O \rightleftharpoons C_6H_5NH_2 + H_3O^+$

$\therefore$ $[H^+] = c\cdot h$ or $6.51\times 10^{-4} = \frac{1}{32}\times h$

$\therefore$ $h = 2.08\times 10^{-2}$

Also, $K_H = ch^2$

$$K_H = \frac{1}{32}\times(2.08\times 10^{-2})^2 = \mathbf{1.352\times 10^{-5}}$$

116. The net reaction for given change will be

$$4SO_4^{2-} + O_2 + 4H^+ \longrightarrow 2H_2O + S_2O_8^{2-}$$
$$E^\circ_{cell} = E^\circ_{OP_{SO_4^{2-}/S_2O_8^{2-}}} + E^\circ_{RP_{O_2/H_2O}}$$
$$E^\circ_{cell} = -2.01 + 1.23 = -0.78\ V$$

Since, E°_{cell} is negative and thus oxygen will not oxidise SO_4^{2-} to $S_2O_8^{2-}$.

117. (a) More or +ve is the E°_{OP} more is the tendency for oxidation. Therefore, since, maximum E°_{OP} stands for :

$$Sn^{2+} \longrightarrow Sn^{4+} + 2e; \quad E^\circ_{OP} = -0.1\ V$$

$\therefore$ Strongest reductant: $\mathbf{Sn^{2+}}$

and Weakest oxidant: $\mathbf{Sn^{4+}}$

(b) More or +ve is E°_{RP}, more is the tendency for reduction. Therefore, since maximum E°_{RP} stands for:

$$MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O; \quad E^\circ_{RP} = +1.52\ V$$

$\therefore$ Strongest oxidant: $\mathbf{MnO_4^-}$

and Weakest reductant: $\mathbf{Mn^{2+}}$

Note : Stronger is oxidant, weaker is its conjugate reductant and *vice-versa*.

(c) For (i)

$E^\circ_{cell} = E^\circ_{OP_{Fe^{2+}/Fe^{3+}}} + E^\circ_{RP_{Sn^{2+}/Sn^{3+}}} = -0.77 + 0.1$ $\quad$ $\because$ Fe^{2+} oxidises and Sn^{4+} reduces in change.

$$E^\circ_{cell} = -0.67\ V$$

E°_{cell} is negative.

(i) Is non-spontaneous change.

For (ii) $E^\circ_{cell} = E^\circ_{OP_{Fe^{2+}/Fe^{3+}}} + E^\circ_{RP_{I_2/I^-}}$
$= -0.77 + 0.54 = \mathbf{-0.23\ V}$

(ii) Is non-spontaneous change.

For (iii) $E^\circ_{cell} = E^\circ_{OP_{I^-/I_2}} + E^\circ_{RP_{Sn^{4+}/Sn^{2+}}}$
$= -0.54 + 0.1 = \mathbf{-0.44\ V}$

(iii) Is non-spontaneous change.

For (iv) $E^\circ_{cell} = E^\circ_{OP_{Sn^{2+}/Sn^{4+}}} + E^\circ_{RP_{I_2/I^-}}$
$= -0.1 + 0.54 = \mathbf{+0.44\ V}$

(iv) Is spontaneous change.

118. Given,

For A $A^{n+} + ne \longrightarrow A$ $\quad$ $E^\circ_{RP} = -0.76\ V$

For B $B^{n+} + ne \longrightarrow B$ $\quad$ $E^\circ_{RP} = +0.80\ V$

We have,

For H $H^+ + e \longrightarrow \frac{1}{2}H_2$ $\quad$ $E^\circ_{RP} = 0$

Now coupling A with H_2SO_4:

$$2A + nH_2SO_4 \longrightarrow A_2(SO_4)_n + nH_2$$
$$E^\circ_{cell} = E^\circ_{OP_A} + E^\circ_{RP_H} = +0.76 + 0.0 = +0.76\ V$$

Since, E° is +ve;

$\therefore$ Reaction $2A + nH_2SO_4 \longrightarrow A_2(SO_4)_n + nH_2$ is spontaneous, *i.e.*, **A will liberate H_2 from H_2SO_4.**

Now coupling B with H_2SO_4:

$$2B + nH_2SO_4 \longrightarrow B_2(SO_4)_n + nH_2$$
$$E^\circ_{cell} = E^\circ_{OP_B} + E^\circ_{RP_H} = -0.80 + 0 = -0.80$$

Since, E° is −ve;

$\therefore$ Reaction $2B + nH_2SO_4 \longrightarrow B_2(SO_4)_n + nH_2$ will not occur, *i.e.*, **B will not liberate H_2 from H_2SO_4.**

• SINGLE INTEGER ANSWER PROBLEMS •

1. The quantity of charge (in Faraday) required to electrolyse 54 g H_2O is ......
2. The quantity of charge (in Faraday) required to reduce 96 g Mg from molten solution of $MgCl_2$.
3. The quantity of charge (in Faraday) required to liberate 33.6 litre Cl_2 from molten NaCl.
4. On electrolysing the solution of $CH_3COONa(aq.)$ the volume ratio of gases formed at anode and cathode is ......
5. On electrolysing the solution of sodium butyrate the mole ratio of gases formed at anode and cathode is ......
6. In rusting of iron, iron is oxidised and O_2 is reduced. The no. of electrons used during reduction of O_2 are ......
7. $E°$ (in volt) of cell $A + B^{+n} \longrightarrow A^{+n} + B$ if $E^{\circ}_{A^{n+}/A} = -2.5$ V and $E_{B^{n+}/B} = +0.5$ V.
8. 9650 charge is passed through an aqueous solution of metal nitrate $M(NO_3)_x$ to obtain 2 g metal (atomic mass 80). The valence of metal is ......
9. If $-\Delta G°$ is zero for a cell, the equilibrium constant for cell reaction is ......
10. If E_1°, E_2° and E_3° are standard oxidation potentials for $Fe|Fe^{2+}$, $Fe^{2+}|Fe^{3+}$ and $Fe|Fe^{3+}$, then $E_3^{\circ} = \frac{E_2^{\circ} + 2E_1^{\circ}}{n}$. The value of n is ......
11. The no. of cells which may be constructed with different E^0_{cell} values for the reaction : $Fe + 2Fe^{3+} \longrightarrow 3Fe^{2+}$.
12. The concentration (in molarity) of $Ni(NO_3)_2$ left after passing 965 ampere current for one second through 2 M $Ni(NO_3)_2$ solution using Ni electrode.
13. The equivalent of metal discharged when 482.5 ampere is passed through its aqueous salt solution for 800 seconds.
14. $E°$ for a cell having 2 electrons involved in redox change is 0.2655 V. The equilibrium constant for the redox change is 10^a. The value of a is ......
15. The standard oxidation potential of Ni/Ni^{2+} ($Ni^{2+} = 1M$) electrode is 0.236 V. If this is combined with a hydrogen electrode ($P_{H_2} = 1$ atm) in acid solution, at what pH of the solution will the measured e.m.f. be zero at 25°C ?
16. How much of the following element will not discharge at cathode during electrolysis of their salts in aqueous medium Al, Na, Ba, Cu, Ag, Ni, Cr ?
17. Number of Faraday required to show the conversion of one mole of $Fe_2(SO_4)_3$ to $FeSO_4$.
18. The potential for the reaction : $\underset{1\,atm}{O_2(g)} + 4H^+ + 4e \longrightarrow 2H_2O$ is 1.23 V in 0.1 N strong acid solution. If potential measured in an aqueous solution is 0.994 V, the pH of solution is....
19. K_{sp} of $Cu(OH)_2$ is 1×10^{-19}. If reduction potential of Cu^{2+}/Cu couple is 0.1335 V in a solution and $E°$ for Cu^{2+}/Cu is 0.34V, the pH of solution is....
20. A solution of metal salt MA_n was electrolysed with a current of 9.65 ampere for 100 minutes. The deposition of metal was 18g at cathode. If the atomic mass of metal is 120, the value of n is.....
21. Current is passed through a cathode where the reaction is :
$$5e + MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O$$
All the permanganate ions present in 100 mL has been reduced after a current of 15 A is passed for 96.5 sec. The original millimoles of $KMnO_4$ in 100 mL solution were....
22. A current of 4.825 amperes is passed through Hg_2Cl_2 solution (Atomic mass of $Hg_2Cl_2 = 471$) for 1000 second to reduce it completely into Hg. The total mass of Hg deposited in g is....
23. An impure silver anode of 20 g and 50.8% purity made anode in refining of silver by electrolytic method. If a current of 193 ampere is passed for 10 sec, the mass of pure Ag (atomic mass 108) left at anode is....
24. The mole ratio of gases evolved at cathode and anode during electrolysis of H_2SO_4 using Pt electrodes is....
25. 3 ampere current was passed through an aqueous solution of an unknown salt AX_n for an hour. 2.977 g of A was deposited at cathode. If the atomic mass of A is 106.4, what is the value of n ?
26. A cell was prepared by using of aM $ZnSO_4$ and bM $CuSO_4$. Another cell was prepared with aM $ZnSO_4$ and 0.5 M $CuSO_4$ and this time emf of this cell was lower than 0.03V than the previous one. The value of b is....
27. The standard oxidation potential of Ni/Ni^{2+} electrode is 0.236 V. If this is connected with a hydrogen electrode in acid solution, at what pH of the solution will the measured emf be zero at 25°C. Assume $[Ni^{2+}] = 1M$ and $P_{H_2} = 1$ atm
28. For a redox cell Hg (l) |Solution A| |Solution B| Hgl. The solution A contains 0.263g/ litre mercury (I) nitrate and solution B contains 2.63 g/litre mercury (I) nitrate. If the measured emf is 0.0289 V at 18°C, what is the value of n?
29. How many faraday of charge is required to completely oxidise one mole of $Fe_2(C_2O_4)_3$?

30. E_{RP} for $M^{(x+n)+} + ne \longrightarrow M^{x+}$ are 0.115 V and 0.101 V respectively, when percentage of reduced form is 25 and 50 respectively. What is the value of n ?

31. Total charge (in coulomb) required for the oxidation of $\frac{1}{2}$ mole of Mn_3O_4 into MnO_4^{2-}.

32. A molten salt of $InCl_x$ on electrolysis using 3.20 A current for a period of 40 minute leads to the formation of 3.05 g In. If atomic mass of In is 114.8, the value of x is ....

33. A cell having two H-electrodes. The negative electrode present in acid solutions is in contact with H^+ ion having pH = 6. What should be the pH of other electrode so that cell may deliver an emf of 0.118 V at 25°C.

34. A source of light of 100 V will produce 6 kJ energy if 10 ampere current is passed for t sec. The value of t is ....

35. 4 M solution of $AgNO_3$ is electrolysed using Ag electrode. A current of 3 ampere is passed for 9.65×10^3 sec. The molarity of solution after electrolysis is ....

36. 4 M $NiSO_4$ solution is electrolysed by passing 3 ampere current for 9.65×10^3 sec using Pt electrodes. The equivalent of gas formed at anode are ....

37. An electrolysis of oxytungsten complex ion using 1.10 A for 40 minute produces 0.838 g tungsten. If atomic mass of tungsten is 184, the charge on tungsten in complex is ....

38. The charge required to deposites all Al from the electrolysis of 1 mol molten Al_2O_3.

39. The oxidation potential of a hydrogen electrode is 0.531 V. If $P_{H_2} = 1$ atm, the pH of solution will be ....

40. The emf of cell

$$\text{Pt} \mid Q, H_2 \mid Q, H^+ \parallel 1\text{ M HCl} \mid Hg_2Cl_2(s) \mid Hg(l)\ \text{Pt}$$

is –0.065 V. If E^0_{RP} of Quinhydrone electrode and standard calomel electrode are 0.699 and 0.280 V respectively, the pH of left hand compartment is ....

41. A current of 2 A is passed for 5 hour through a molten metal salt, deposits 22.2 g of metal having atomic mass 177. The oxidation state of metal in salt is ....

ANSWERS

1. Six	**2.** Eight	**3.** Three	**4.** Three	**5.** Two	**6.** Four	**7.** Three	**8.** Four	**9.** One	**10.** Three	**11.** Three	**12.** Two
13. Four	**14.** Nine	**15.** Four	**16.** Three	**17.** Two	**18.** Five	**19.** Eight	**20.** Four	**21.** Three	**22.** Five	**23.** Eight	**24.** Two
25. Four	**26.** Five	**27.** Four	**28.** Two	**29.** Six	**30.** Two	**31.** Five	**32.** Three	**33.** Four	**34.** Six	**35.** Four	**36.** Three
37. Six	**38.** Six	**39.** Nine	**40.** Six	**41.** Three							

OBJECTIVE PROBLEMS (One Answer Correct)

1. $E°$ for $Cr^{3+} + 3e \longrightarrow Cr$ and $Cr^{3+} + e \longrightarrow Cr^{2+}$ are -0.74 V and -0.40 V respectively. $E°$ for $Cr^{2+} + 2e \longrightarrow Cr$ is :
   (a) -0.91 V (b) $+0.91$ V
   (c) -1.14 V (d) $+0.34$ V
2. A cell is to be constructed to show a redox change : $Cr + 2Cr^{3+} \rightleftharpoons 3Cr^{2+}$. The number of cells with different $E°$ and 'n' but same value of $\Delta G°$ can be made: (Given, $E^{\circ}_{Cr^{3+}/Cr^{2+}} = -0.40$ V, $E^{\circ}_{Cr^{3+}/Cr} = -0.74$ V and $E^{\circ}_{Cr^{2+}/Cr} = -0.91$ V)
   (a) 1 (b) 2
   (c) 3 (d) 4
3. The solubility product of $Pb_3(AsO_4)_2$ is 4.1×10^{-36}. The $E°$ for the reaction :
   $$Pb_3(AsO_4)_{2(s)} + 6e \rightleftharpoons 3Pb_{(s)} + 2AsO_4^{3-}$$ if $E^{\circ}_{Pb^{2+}/Pb} = -0.13$ V
   (a) $+0.478$ V (b) -0.13 V
   (c) -0.478 V (d) $+0.13$ V
4. Calculate the $E°$ for the reaction $ZnY^{2-} + 2e \rightleftharpoons Zn_{(s)} + Y^{4-}$, where Y^{4-} is the completely deprotonated anion of EDTA. The formation constant for ZnY^{2-} is : 3.2×10^{16} and $E°$ for $Zn \longrightarrow Zn^{2+} + 2e$ is 0.76 V
   (a) -1.25 V (b) 0.48 V
   (c) $+0.68$ V (d) -0.27 V
5. If $Fe^{3+} + Y^{4-} \rightleftharpoons FeY^{-}$; $K_f = 1.3 \times 10^{25}$
   $Fe^{2+} + Y^{4-} \rightleftharpoons FeY^{2-}$; $K_f = 2.1 \times 10^{14}$
   and $Fe^{3+} + e \longrightarrow Fe^{2+}$; $E° = +0.77$ V
   The $E°$ for $FeY^{-} + e^{-} \longrightarrow FeY^{2-}$
   (a) 0.13 V (b) -0.636 V
   (c) $+0.636$ V (d) 1.41 V
6. A constant current was passed through a solution of $AuCl_4^-$ ion between gold electrodes. After a period of 10.0 minute the increase in mass of cathode was 1.314g. The total charged passed through solution is : (atomic mass of $AuCl_4^- = 339$)
   (a) 1.16×10^{-2} F (b) 3.5×10^{-2} F
   (c) 2×10^{-2} F (d) 4×10^{-3} F
7. Efficiency of a fuel cell is 80% and the standard heat of reaction is -300 kJ. The reaction involves two electrons in redox change. The $E°$ for the cell is :
   (a) 1.24 V (b) 2.48 V
   (c) 0 V (d) 0.62 V
8. The E_{cell} for a given cell is 1.2346 and 1.2340 V at 300 and 310 K respectively. Calculate the change in entropy during the cell reaction if the redox change involves three electrons:
   (a) -17.37 JK^{-1} (b) $+17.37$ JK^{-1}
   (c) 173.7 JK^{-1} (d) 5.79 JK^{-1}
9. A current of 3 ampere was passed for 1 hour through an electrolyte solution of A_xB_y in water. If 2.977 g of A (atomic mass 106.4) was deposited at cathode and B was a monovalent ion, the formula of electrolyte was :
   (a) AB_2 (b) AB
   (c) AB_3 (d) AB_4
10. The $E°$ for Cu^{2+}/Cu^{+}; Cu^{+}/Cu, Cu^{2+}/Cu are 0.15 V, 0.50 V and 0.325 V respectively. The redox cell showing redox reaction $2Cu^{+} \longrightarrow Cu^{2+} + Cu$ is made. The $E°$ of this cell reaction and $\Delta G°$ may be :
    (a) $E° = 0.175$ V or $E° = 0.350$ V
    (b) $n = 2$ or 1 respectively
    (c) $\Delta G° = -33.775$ kJ
    (d) all of the above
11. Total charge required to convert three mole of Mn_3O_4 to MnO_4^- in presence of alkaline medium :
    (a) 10 F (b) 20 F
    (c) 30 F (d) 40 F
12. A current of 965 ampere is passed for 1 sec through 1 litre solution of 0.02 N $NiSO_4$ using Ni electrodes. What is the new concentration of $NiSO_4$?
    (a) 0.01 N (b) 0.01 M
    (c) 0.002 M (d) 0.02 M
13. For the given cell $Pt_{D_2/D^+} || H^+ | Pt_{H_2}$ if $E^{\circ}_{D_2/D^+} = 0.003$ V, what will be ratio of D^+ and H^+ at 25°C when the reaction : $D_2 + 2H^+ \longrightarrow 2D^+ + H_2$ attains equilibrium :
    (a) 1.34 (b) 1.24
    (c) 1.124 (d) 1.45
14. What is E°_{RP} for the reaction : $Cu^{2+} + 2e \longrightarrow Cu$ in the half cell $Pt_{S^{2-}/CuS/Cu}$ if $E^{\circ}_{Cu^{2+}/Cu}$ is 0.34 V and K_{sp} of $CuS = 10^{-35}$?
    (a) 0.34 V (b) -0.6925 V
    (c) $+0.6925$ V (d) -0.66 V
15. The combustion of butane in O_2 at 1 bar and 298 K shows a decrease in free energy equal to 2.75×10^3 kJ mol^{-1} in a fuel cell. K and $E°$ of fuel cell are :
    (a) 9.55×10^{482}, 1.096 V (b) 9.55, 1.096 V
    (c) 1.023×10^{966}, 2.85 V (d) 5.5×10^{484}, 0.55 V

16. A half cell reaction : $Ag_2S_{(s)} + 2e \longrightarrow 2Ag_{(s)} + S^{2-}$ is carried out in a half cell $Pt_{Ag_2S/Ag,\ \underset{0.1M}{H_2S}}$, at $[H^+] = 10^{-3}$.
The emf of a half cell is :
[if $E^\circ_{Ag^+/Ag} = 0.80$ V, $K_{a\,H_2S} = 10^{-21}$ and K_{sp} of $Ag_2S = 10^{-49}$]
(a) −0.1735 V (b) −0.19 V
(c) +0.1735 (d) +0.19 V

17. Which one is not correct if electrolysis of $CH_3COONa\ (aq.)$ is made using Pt electrodes ?
(a) pH of solution increases
(b) Molar ratio of gases at anode and cathode is 3 : 1
(c) $[CH_3COO^-]$ in solution decreases
(d) The molar ratio of gases at anode and cathode is 2 : 1

18. The calomel electrode and Quinhydrone electrodes are reversible with respect to which ions respectively :
(a) Cl^-, H^+ (b) H^+, Cl^-
(c) Hg_2^{2+}, OH^- (d) Hg_2^{2+}, OH^+

19. EMF of Ni-Cad battery is dependent of :
(a) $Cd(OH)_2$ (b) $Ni(OH)_2$
(c) OH^- (d) none of these

20. The electrode with reaction :
$$Cr_2O_{7\,(aq.)}^{2-} + 14H^+_{(aq.)} + 6e \longrightarrow 2Cr^{3+}_{(aq.)} + 7H_2O;$$
can be represented as :
(a) $Pt \mid H^+_{(aq.)}, Cr_2O^{2-}_{7\,(aq.)}$
(b) $Pt \mid H^+_{(aq.)}, Cr_2O^{2-}_{7\,(aq.)}, Cr^{3+}_{(aq.)}$
(c) $Pt_{H_2} \mid H^+_{(aq.)}, Cr_2O_7^{2-}$
(d) $Pt_{H_2} \mid H^+_{(aq.)}, Cr_2O^{2-}_{7\,(aq.)}, Cr^{3+}_{(aq.)}$

21. For a given reaction : $M^{(X+n)} + ne \longrightarrow M^{X+}, E^\circ_{RP}$ is known along with M^{X+n} and M^{X+} ion concentrations, then:
(a) n can be evaluated
(b) X can be evaluated
(c) $(X+n)$ can be evaluated
(d) $n, X, (X+n)$ can be evaluated

22. A dilute aqueous solution of Na_2SO_4 is electrolyzed using platinum electrodes. The products at the anode and cathode are :
(a) O_2, H_2 (b) $S_2O_8^{2-}$, Na
(c) O_2, Na (d) $S_2O_8^{2-}, H_2$

23. A standard hydrogen electrode has zero electrode potential because :
(a) hydrogen is easiest to oxidise
(b) this electrode potential is assumed to be zero
(c) hydrogen atom has only one electron
(d) hydrogen is the lightest element

24. The standard reduction potentials of Cu^{2+}/Cu and Cu^{2+}/Cu^+ are 0.339 V and 0.153 V respectively. The standard electrode potential of Cu^+/Cu half cell is :
(a) 0.525 V (b) 0.827 V
(c) 0.184 V (d) 0.490 V

25. The standard reduction potential values of three metalic cations of X, Y and Z are 0.52, −3.03 and −1.18 V respectively. The order of reducing power of the corresponding metals is:
(a) $Y > Z > X$ (b) $X > Y > Z$
(c) $Z > Y > X$ (d) $Z > X > Y$

26. A gas X at 1 atm is bubbled through a solution containing a mixture of 1 MY^- and 1 MZ^- at 25°C. If the reduction potential of $Z > Y > X$, then :
(a) Y will oxidise X and not Z
(b) Y will oxidise Z and not X
(c) Y will oxidise both X and Z
(d) Y will reduce both X and Z

27. Select the incorrect statement :
(a) The electrolysis of molten CaH_2 liberates H_2 at cathode.
(b) During discharge of lead storage battery, sulphuric acid is consumed.
(c) Sulphur acts as polymerising agent in vulcanisation of rubber.
(d) Galvanisation of iron denotes coating with Zn.

28. Select the correct statement :
(a) Faraday represents 96500 coulomb per sec.
(b) Coulomb represents one ampere for 1/2 sec.
(c) Coulomb represents 1/2 ampere for 1 sec.
(d) Coulomb represents charge of one mole electron.

29. E^0_{RP} for the reaction,
$$TeO_3^{2-}\,_{1M}(aq) + 3H_2O(l) + 4e \longrightarrow Te(s) + 6OH^-(aq)$$
is − 0.57 V. Calculate the potential of pH = 12.
(a) − 0.17 V (b) − 0.21 V
(c) − 0.39 V (d) − 0.747 V

30. Calculate E_{cell} for $Cr \mid \underset{0.04M}{Cr^{3+}} \parallel \underset{1M}{Cr^{3+}} \mid Cr$:
(a) 0.028 V (b) 0.083 V
(c) 0 V (d) 0.125 V

31. Given that K_{sp} of $CuS = 10^{-35}$ and $E^0_{Cu/Cu^{2+}} = -0.34$ V. The standard oxidation potential of $Cu \mid CuS \mid S^{2-}$ half cell is ....
(a) 1.0 V (b) 0.693 V
(c) − 0.690 V (d) − 1.0 V

32. The temperature coefficient of a given cell, $\left(\frac{\partial E}{\partial T}\right)_P$ is 1.5×10^{-4} V K^{-1} at 300 K. The change in entropy of cell during the cource of reaction,

$$Pb(s) + HgCl_2(aq) \longrightarrow PbCl_2(aq) + Hg(l)$$

(a) 28.95 J/K (b) 14.47 J/K
(c) 57.9 J/K (d) 21.70 J/K

33. If $E^0_{ClO_3^-/ClO_4^-} = -0.36$ V and $E^0_{ClO_3^-/ClO_2^-} = 0.33$ V at 300 K. The equilibrium concentration of perchlorate ion (ClO_4^-) which was initially 1.0 *M* in ClO_3^- when the reaction starts to attain the equilibrium,

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

(a) 0.0236 *M* (b) 0.0190 *M*
(c) 0.123 *M* (d) 0.40 *M*

34. The reduction of NO_3^- occurs as

$$NO_3^- + 4H^+ + 3e^- \longrightarrow NO + 2H_2O; \; E° = 0.96 \text{ V}$$

The electrons are provided by Cd till that the solution originally having 0.1 *M* NO_3^- and 0.4 *M* H^+ shows that 80% of NO_3^- ions are converted to NO showing 1 bar pressure. The reduction potential of remaining solution.

(a) 0.84 V (b) 1.36 V
(c) 1.08 V (d) 1.56 V

35. 108 g solution of $AgNO_3$ is electrolysed using Pt electrodes by passing a charge of 0.1 F. The mass of resultant solution left is :

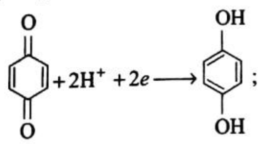
(a) 98 g (b) 107.2 g
(c) 11.6 g (d) 96.4 g

36. On the basis of reaction, $4Al + 3O_2 \longrightarrow 2Al_2O_3$; $\Delta G = -827$ kJ mol^{-1} of O_2 the minimum emf required to carry out an electrolysis of Al_2O_3 :

(a) 8.5 V (b) 2.14 V
(c) 2.83 V (d) 1.42 V

37. A Quinhydrone electrode in contact of H^+ ion is coupled with standard calomel electrode. The $E°$ of both electrodes are given as :

$$Pt \mid Q, QH_2 \mid H^+ \mid\mid 1M KCl \mid Hg_2Cl_2(s) \mid Hg(l) \mid Pt$$



$$E^0_{Q|QH_2|H^+|Pt} = +0.699 \text{ V}$$

$$\frac{1}{2}Hg_2Cl_2(s) + e \rightarrow Hg(l) + Cl^-;$$

$$E^0_{Cl^-|Hg_2Cl_2|Hg} = +0.280 \text{ V}$$

If emf of cell so obtained is – 0.124, then pH is :

(a) 5 (b) 6
(c) 7 (d) 8

38. The standard reduction potentials at 298 K for the following half reactions are given against each

$$Zn^{2+}(aq) + 2e \rightleftharpoons Zn(s) - 0.762$$
$$Cr^{+3}(aq) + 2e \rightleftharpoons Cr(s) - 0.740$$
$$2H^+(aq) + 2e \rightleftharpoons H_2(g) \; 0.000$$
$$Fe^{3+}(aq) + 2e \rightleftharpoons Fe^{2+}(aq) \; 0.770$$

which is the strongst reducing agent?

(a) Zn (*s*) (b) Cr (*s*)
(c) $H_2(g)$ (d) $Fe^{2+}(aq)$

39. Faraday's laws of electrolysis are related to the :

(a) atomic number of the reactants
(b) atomic number of the anion
(c) equivalent mass of the electrolyte
(d) speed of the cation

40. A solution containing one mole per litre of each $Cu(NO_3)_2$, $AgNO_3$, $Hg_2(NO_3)_2$ is being electrolysed by using inert electrode. The values of standard electrode potential in volts reduction potential are :

$Ag \mid Ag^+ = +0.80$, $2Hg \mid Hg_2^{++} = -0.79$
$Cu \mid Cu^{++} = +0.34$, $Mg \mid Mg^{++} = -2.37$

With increasing voltage, the sequence of deposition of metals on the cathode will be :

(a) Ag, Hg, Cu, Mg (b) Mg, Cu, Hg, Ag
(c) Ag, Hg, Cu (d) Cu, Hg, Ag

41. The electric charge for electrode deposition of one gram equivalent of a substance is :

(a) one ampere per second
(b) 96.500 coloumbs per second
(c) one ampere for one hour
(d) charge on one mole of electrons

42. The reaction,

$$\frac{1}{2}H_2(g) + AgCl(s) \longrightarrow H^+(aq) + Cl^-(aq) + Ag(s)$$

occurs in the galvanic cell :

(a) $Ag \mid AgCl(s) \mid KCl(\text{soln.}) \mid AgNO_3(\text{soln.}) \mid Ag$
(b) $Pt \mid H_2(g) \mid HCl(\text{soln.}) \mid AgNO_3(\text{soln.}) \mid Ag$
(c) $Pt \mid H_2(g) \mid HCl(\text{soln.}) \mid AgCl(s) \mid Ag$
(d) $Pt \mid H_2(g) \mid KCl(\text{soln.}) \mid AgCl(s) \mid Ag$

43. A solution of sodium sulphate in water is electrolysed using inert electrodes. The products at the cathode and anode are respectively :

(a) H_2, O_2 (b) O_2, H_2
(c) O_2, Na (d) O_2, SO_2

44. When a lead storage battery is discharged :

(a) SO_2 is evolved (b) Lead is formed
(c) $PbSO_4$ is consumed (d) H_2SO_4 is consumed

45. The standard oxidation potentials, $E°$, for the half reactions are as follows :

$$Zn \longrightarrow Zn^{2+} + 2e^-; \; E° = +0.76 \text{ V}$$
$$Fe \longrightarrow Fe^{2+} + 2e^-; \; E° = +0.41 \text{ V}$$

The EMF for the cell reaction,

$$Fe^{2+} + Zn \longrightarrow Zn^{2+} + Fe$$

(a) – 0.35 V (b) + 0.35 V
(c) + 1.17 V (d) – 1.17 V

46. If $E^{\circ}_{Cu^{2+}|Cu} = 0.34$ V and $E^{\circ}_{Cu^{2+}|Cu^{+}} = 0.15$ V than the value for disproportionation for Cu^{+} is :
(a) -0.19 V (b) -0.38 V
(c) 0.94 V (d) 0.38 V

47. For the electrochemical cell, $M|M^{+}||X^{-}|X$ $E^{\circ}_{(M^{+}/M)} = 0.44$ V and $E^{\circ}_{(X/X^{-})} = 0.33$ V. From this data one can deduce that : **(IIT 2000)**
(a) $M + X \longrightarrow M^{+} + X^{-}$ is the spontaneous reaction
(b) $M^{+} + X^{-} \longrightarrow M + X$ is the spontaneous reaction
(c) $E_{cell} = 0.77$ V (d) $E_{cell} = -0.77$ V

48. The correct relationship between Gibb's energy change in a reaction and the corresponding equilibrium constant K_c is :
(a) $\Delta G^{\circ} = RT \ln K_c$ (b) $-\Delta G^{\circ} = RT \ln K_c$
(c) $\Delta G = RT \ln K_c$ (b) $-\Delta G = RT \ln K_c$

49. Saturated solution of KNO_3 is used to make salt bridge because : **(IIT 2001)**
(a) velocity of K^{+} is greater than that of NO_3^{-}
(b) velocity of NO_3^{-} is greater than that of K^{+}
(c) velocity of both K^{+} and NO_3^{-} are nearly the same
(d) KNO_3 is highly soluble in water

50. The correct order of equivalent conductance at infinite dilution of LiCl, NaCl and KCl is : **(IIT 2001)**
(a) LiCl > NaCl > KCl (b) KCl > NaCl > LiCl
(c) NaCl > KCl > LiCl (d) LiCl > KCl > NaCl

51. Standard electrode potential data are useful for understanding the suitability of an oxidant in a redox titration. Some half cell reactions and their standard potentials are given below :

$$MnO^{-}_{4(aq.)} + 8H^{+}_{(aq.)} + 5e \longrightarrow Mn^{2+}_{(aq.)} + 4H_2O_{(l)};$$
$E^{\circ} = 1.51$ V
$$Cr_2O_7^{2-}{}_{(aq.)} + 14H^{+}_{(aq.)} + 6e \longrightarrow 2Cr^{3+}_{(aq.)} + 7H_2O_{(l)};$$
$E^{\circ} = 1.38$ V
$$Fe^{3+}_{(aq.)} + e^{-} \longrightarrow Fe^{2+}_{(aq.)}; E^{\circ} = 0.77 \text{ V}$$
$$Cl_{2(g)} + 2e^{-} \longrightarrow 2Cl^{-}_{(aq.)}; E^{\circ} = 1.40 \text{ V}$$

Identify the only incorrect statement regarding the quantitative estimation of aqueous $Fe(NO_3)_2$: (IIT 2002)
(a) MnO_4^{-} can be used in aqueous HCl
(b) $Cr_2O_7^{2-}$ can be used in aqueous HCl
(c) MnO_4^{-} can be used in aqueous H_2SO_4
(d) $Cr_2O_7^{2-}$ can be used in aqueous H_2SO_4

52. In the electrolytic cell, flow of electrons is from : **(IIT 2003)**
(a) cathode to anode in solution
(b) anode to cathode through external supply
(c) cathode to anode through internal supply
(d) anode to cathode through internal supply

53. The emf of the cell $Zn \,|\, \underset{(0.01\,M)}{Zn^{2+}} \,||\, \underset{(0.001\,M)}{Fe^{2+}} \,|\, Fe$ at 298 K is 0.2905, then the value of equilibrium constant for the cell reaction is : **(IIT 2004)**
(a) $e^{0.32/0.0295}$ (b) $10^{0.32/0.0295}$
(c) $10^{0.26/0.0295}$ (d) $10^{0.32/0.0591}$

54. The rusting of iron takes place as follows :
$$2H^{+} + 2e + 1/2O_2 \longrightarrow H_2O_{(l)}; E^{\circ} = +1.23 \text{ V}$$
$$Fe^{2+} + 2e \longrightarrow Fe_{(s)}; \quad E^{\circ} = -0.44 \text{ V}$$
The ΔG° for the net process is : **(IIT 2005)**
(a) -322 kJ mol^{-1} (b) -161 kJ mol^{-1}
(c) -152 kJ mol^{-1} (d) -76 kJ mol^{-1}

55. Electrolysis of dilute NaCl solution was carried out by passing 10 mA current. The time required to liberate 0.01 mol. of H_2 gas at the cathode is : **(IIT 2008)**
(a) 9.65×10^{4} sec (b) 19.3×10^{4} sec
(c) 28.95×10^{4} sec (d) 38.6×10^{4} sec

56. Consider the following cell reaction :
$$2Fe(s) + O_2(g) + 4H^{+} \longrightarrow 2Fe^{2+}(aq) + 2H_2O(l)$$
$E^{\circ} = 1.67$V
At $[Fe^{2+}] = 10^{3-}$ M, $P(O_2) = 0.1$ atm and pH = 3, the cell potential at 25°C is : **(IIT 2011)**
(a) 1.47 V (b) 1.77 V
(c) 1.87 V (d) 1.57 V

57. Given
$E^{\circ}_{Cr^{3+}/Cr} = -0.74$ V; $E^{\circ}_{MnO_4^{-}/Mn^{2+}} = 1.51$ V
$E^{\circ}_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33$ V; $E^{\circ}_{Cl/Cl^{-}} = 1.36$ V
Based on the data given above, the strongest oxidising agent will be : **[JEE (Main) 2013]**
(a) Mn^{2+} (b) MnO_4^{-}
(c) Cl^{-} (d) Cr^{3+}

58. Four successive members of the first row transition elements are listed below with atomic numbers. Which one of them is expected to have the highest $E^{0}_{M^{3+}/M^{2+}}$ value? **[JEE (Main) 2013]**
(a) Fe(Z=26) (b) Co(Z=27)
(c) Cr(Z=24) (d) Mn(Z=25)

SOLUTIONS (One Answer Correct)

1. (a)
$$\begin{array}{ll} Cr^{3+} + 3e \longrightarrow Cr; & -\Delta G_1^\circ = 3\times 0.74\times F \\ \underset{-}{Cr^{3+}} + e \longrightarrow \underset{-}{Cr^{2+}}; & \underset{+}{-\Delta G_2^\circ = 1\times 0.40\times F} \\ \hline Cr^{2+} + 2e \longrightarrow Cr; & -\Delta G_3^\circ = 2\times E^\circ \times F \end{array}$$
$$= (3\times 0.74 - 1\times 0.40)F = 1.82\,F$$
$$\therefore \quad E^\circ = 0.91\,V$$

2. (c) $\underset{I}{Cr|Cr^{3+}||Cr^{3+}, Cr^{2+}|Pt}$; $\underset{II}{Cr|Cr^{2+}||Cr^{3+}|Cr}$;

$\underset{III}{Cr|Cr^{2+}||Cr^{3+}, Cr^{2+}|Pt}$

(I)
$$\begin{array}{ll} Cr \longrightarrow Cr^{3+} + 3e; & E^\circ = +0.74\,V \\ 3Cr^{3+} + 3e \longrightarrow 3Cr^{2+}; & E^\circ = -0.4\,V \\ \hline Cr + 2Cr^{3+} \longrightarrow 3Cr^{2+}\ (n=3) & \end{array}$$

(II)
$$\begin{array}{ll} 3Cr \longrightarrow 3Cr^{2+} + 6e; & E^\circ = 0.91\,V \\ 2Cr^{3+} + 6e \longrightarrow 2Cr; & E^\circ = -0.74\,V \\ \hline Cr + 2Cr^{3+} \longrightarrow 3Cr^{2+}\ (n=6) & \end{array}$$

(III)
$$\begin{array}{ll} Cr \longrightarrow Cr^{2+} + 2e; & E^\circ = 0.91\,V \\ 2Cr^{3+} + 2e \longrightarrow 2Cr^{2+}; & E^\circ = -0.40\,V \\ \hline Cr + 2Cr^{3+} \longrightarrow 3Cr^{2+}\ (n=2) & \end{array}$$

$$E^\circ = 0.74 - 0.4 = 0.34\,V$$
$$-\Delta G^\circ = 3\times 0.34\times F = 1.02\,F$$
$$E^\circ = 0.91 - 0.74 = 0.17\,V$$
$$-\Delta G^\circ = 0.17\times 6\times F = 1.02\,F$$
$$E^\circ = 0.91 - 0.40 = 0.51\,V$$
$$-\Delta G^\circ = 2\times 0.51\times F = 1.02\,F$$

3. (c)
$$E^\circ_{AsO_4^{2-}|Pb_3(AsO_4)_2|Pb} = E^\circ_{Pb^{2+}/Pb} + \frac{0.059}{6}\log K_{sp}$$
$$= -0.13 + \frac{0.059}{6}\log 4.1\times 10^{-36}$$
$$= -0.13 - 0.348 = -0.478\,V$$

4. (a)
$$E^\circ_{Zn^{2+}/ZnY^{2-}/Y^{4-}} = E^\circ_{Zn^{2+}/Zn} + \frac{0.059}{2}\log K$$
$$K_f = \frac{[ZnY^{2-}]}{[Y^{4-}]} \qquad \therefore\ K = \frac{1}{K_f}$$
$$\therefore\ E^\circ_{Zn^{2+}/ZnY^{2-}/Y^{4-}} = -0.76 + \frac{0.059}{2}\log\frac{1}{3.2\times 10^{16}}$$
$$= -1.25\,V$$

5. (a) For $FeY^- + e \longrightarrow FeY^{2-}$ the change is
$$Fe^{3+} + e \longrightarrow Fe^{2+}$$
$$\therefore\quad E^\circ_{Fe^{3+}/FeY^{2-}/FeY^-} = E^\circ_{Fe^{3+}/Fe^{2+}} + \frac{0.059}{1}\log\frac{[FeY^{2-}][Fe^{3+}]}{[FeY^-][Fe^{2+}]}$$
$$= 0.77 + \frac{0.059}{1}\log\frac{2.1\times 10^{14}}{1.3\times 10^{25}} = 0.77 - 0.64 = +0.13V$$

6. (c) $Au^{3+} + 3e \longrightarrow Au$
$$\therefore\quad \frac{w}{197/3} = \frac{\text{Charge}}{96500}$$
$$\therefore\quad \text{Charge} = \frac{1.314\times 3\times F}{197} = 0.02F$$

7. (a)
$$\text{Efficiency} = \frac{\Delta G^\circ}{\Delta H^\circ} = -\frac{nE^\circ F}{\Delta H} = 80$$
$$\therefore\quad E^\circ = -\frac{80\times(-300)\times 10^3}{2\times 96500\times 100} = 1.24\,V$$

8. (a) By $\Delta S = \frac{\Delta H - \Delta G}{T}$;
$$\Delta H = -nF\left[E - T\left(\frac{\partial E}{\partial T}\right)_P\right] \quad \text{and} \quad \Delta G = -nEF$$
$$\Delta S = nF\left(\frac{\partial E}{\partial T}\right)_P = 3\times 96500\times\left(-\frac{0.0006}{10}\right)$$
$$= -17.37\,JK^{-1}$$

9. (d) $\frac{w}{E} = \frac{i\cdot t}{96500}$ $\qquad A^{Y+} + Ye \longrightarrow A$
$$\frac{2.977}{\frac{106.4}{Y}} = \frac{3\times 1\times 60\times 60}{96500}$$
$\therefore\ Y = 4\ \therefore$ electrolyte is AB_4.

10. (d) $2Cu^+ \longrightarrow Cu^{2+} + Cu$;

Cell I :	**Cell II :**
$Cu^+ \longrightarrow Cu^{2+} + e$	$Cu \longrightarrow Cu^{2+} + 2e$
$Cu^+ + e \longrightarrow Cu$	$2Cu^+ + 2e \longrightarrow 2Cu$
$2Cu^+ \longrightarrow Cu^{2+} + Cu$	$2Cu^+ \longrightarrow Cu^{2+} + Cu$
$E^\circ = -0.15 + 0.50$	$E^\circ = -0.325 + 0.50$
$= +0.35\,V$	$= +0.175\,V$
$n = 1$	$n = 2$

11. (c) $(Mn^{+8/3})_3 \longrightarrow 3Mn^{6+} + 10e$

$\therefore$ 10 Faraday charge is required for conversion of 1 mole of Mn_3O_4 to MnO_4^{2-}.

12. (b) $\frac{w}{E} = \frac{965\times 1}{96500} = 0.01$

Equivalent of $NiSO_4$ present initially $= 1\times 0.02 = 0.02$
If Ni electrodes are used no change in conc. of $NiSO_4$, *i.e.*, 0.02 N or 0.01 M.
If Pt electrodes are used then eq. of $NiSO_4$ left $= 0.01$

13. (c)
$$E_{cell} = E_{OP_{D_2}} = E_{RP_{H_2}}$$
$$= E^\circ_{OP_{D_2/D^+}} - \frac{0.059}{2}\log[D^+]^2 + E^\circ_{RP_{H^+/H_2}} + 0.059\log[H^+]^2$$
$$0 = 0.003 - \frac{0.059}{2}\log\frac{[D^+]^2}{[H^+]^2} \qquad (E^\circ_{RP_{H^+/H_2}}) = 0$$

$\therefore \quad \frac{[D^+]}{[H^+]} = 1.124$

14. (b) $E_{S^{2-}/CuS/Cu} = E^\circ_{Cu^{2+}/Cu} + \frac{0.059}{2}\log K_{sp}$ CuS

$= 0.34 + \frac{0.059}{2}\log^{10^{-35}} = -0.6925$ V

15. (a) $-\Delta G = -\Delta G^\circ = 2.75\times10^6$ J mol^{-1}

(as P = 1bar and T = 298 K)

$-\Delta G^\circ = nE^\circ F$

$\therefore \quad E^\circ = \frac{2.75\times10^6}{26\times96500}$

$$\left[\begin{array}{l} C_4H_{10} + \frac{13}{2}O_2 \longrightarrow 4CO_2 + 5H_2O \\ (C^{-5/2})_4 \longrightarrow 4C^{4+} + 26e \end{array}\right]$$

$E^\circ = 1.096$ V, Also, $E^\circ = \frac{0.059}{n}\log K_p$

$1.096 = \frac{0.059}{26}\log K_p \quad K = 9.55\times10^{482}$

16. (a) $H_2S \rightleftharpoons 2H^+ + S^{2-}$

$\therefore \quad K_a = \frac{[H^+]^2[S^{2-}]}{[H_2S]} = \frac{(10^{-3})^2\times[S^{2-}]}{0.1}$

$\therefore \quad [S^{2-}] = \frac{10^{-21}\times0.1}{10^{-6}} = 10^{-16}$,

Since, $\because \quad [Ag^+]^2[S^{2-}] = K_{sp}$

$\therefore \quad [Ag^+] = \sqrt{\frac{K_{sp}}{[S^{2-}]}} = \sqrt{\frac{10^{-49}}{10^{-16}}} = \sqrt{10^{-33}}$

$2Ag^{2+} + e \longrightarrow 2Ag$

$E_{S^{2-}/Ag_2S/Ag} = E_{Ag^+/Ag}$

$E_{S^{2-}/Ag_2S/Ag} = E^\circ_{Ag^+/Ag} + \frac{0.059}{2}\log[Ag^+]^2$

$= 0.80 + \frac{0.059}{2}\log 10^{-33} = -0.1735$ V

17. (d) Anode : $2CH_3COO^- \longrightarrow C_2H_6 + 2CO_2 + 2e$

Cathode : $2H^+ + 2e \longrightarrow H_2$

18. (a) Follow text.

19. (d) The net redox change :

$NiO_{2(s)} + Cd + 2H_2O \longrightarrow Ni(OH)_{2(s)} + Cd(OH)_{2(s)}$

20. (d) Follow text.

21. (a) $E_{RP} = E^\circ_{RP} + \frac{0.059}{n}\log\frac{[M^{x+n}]}{[M^{x+}]}$

22. (a) Anode : $2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e$

Cathode : $2H^- + 2e \longrightarrow H_2$

23. (b) It is a fact.

24. (a) $Cu^{2+} + 2e \longrightarrow Cu; \quad -\Delta G_1^\circ$

$Cu^{2+} + e \longrightarrow Cu^+; \quad -\Delta G_2^\circ$

$\quad - \quad - \qquad - \qquad +$

$\therefore \quad Cu^+ + e \longrightarrow Cu; -\Delta G_3^\circ = -\Delta G_1^\circ + \Delta G_2^\circ$

or $\quad n\times E_3^\circ F = n_1E_1^\circ F - n_2E_2^\circ F$

$E_3^\circ = \frac{n_1E_1^\circ F - n_2E_2^\circ F}{nF} = \frac{0.339\times2 - 1\times0.153}{1} = 0.525$ V

25. (a) More is E°_{RP}, more is the tendency to get reduced or more is the oxidizing power or lesser is reducing power. Thus, oxidizing power = $X^+ > Z^+ > Y^+$ reducing power = $Y > Z > X$

26. (a) $E^\circ_{RPZ/Z^-} > E^\circ_{RPY/Y^-} > E^\circ_{RPX/X^-}$.

Thus, order of oxidizing power will be $Z > Y > X$

27. (a) $2H^- \longrightarrow H_2 + 2e$; H is –ve in ionic hydrides.

28. (d) $F = N\times e, \quad 96500 = 6.023\times10^{23}\times e$

$\therefore \quad e = 1.602\times10^{-19}$

29. (c) $E_{RP} = E^\circ_{RP} + \frac{0.059}{4}\log\frac{[TeO_3^{2-}]}{[OH^-]^6}$

$[Te^{4+} + 4e \rightarrow Te$; Also pH = 12 $\therefore [OH^-] = 10^{-2}]$

$\therefore \quad E_{RP} = -0.57 + \frac{0.059}{4}\log\frac{1}{(10^{-2})^6} = -0.393$ V

30. (a) $E = \frac{0.059}{3}\log\frac{[Cr^{3+}]_{R.H.S.}}{[Cr^{3+}]_{L.H.S.}}$

$= \frac{0.059}{3}\log\frac{1}{[0.04]} = 0.028$ V

31. (b) $Cu^{2+}(aq) + 2e \longrightarrow Cu(s)$

$Cu(s) + S^{2-}(aq) \longrightarrow CuS(s) + 2e$

$Cu^{2+}(aq) + S^{2-}(aq) \longrightarrow CuS$

$E_{Cu|CuS|S^{2-}} = E_{Cu|Cu^{2+}} - \frac{0.059}{2}\log K_{SP}$

$= -0.34 - \frac{0.059}{2}\log 10^{-35}$

$= -0.34 + 1.0325 = 0.693$ V

32. (a) $\left(\frac{\partial E}{\partial T}\right)_P = \frac{\Delta S}{nF}$

$\Delta S = 1.5\times10^{-4}\times2\times96500 = 28.95$ J

33. (d) $E_{cell} = E^\circ_{OP} + E^\circ_{RP}$

$= E^\circ_{ClO_3^-|ClO_4^-} - \frac{0.059}{2}\log\frac{[ClO_4^-]}{[ClO_3^-]}$

$+ E^\circ_{ClO_3^-|ClO_2^-} + \frac{0.059}{2}\log\frac{[ClO_3^-]}{[ClO_2^-]}$

$Cl^{5+} \longrightarrow Cl^{7+} + 2e$

$2e + Cl^{5+} \longrightarrow Cl^{3+}$

E_{cell} = 0 at equilibrium. Also

$$\underset{(1-2x)}{\overset{1}{2ClO_3^-}} \rightleftharpoons \underset{x}{\overset{0}{ClO_4^-}} + \underset{x}{\overset{0}{ClO_2^-}}$$

$E_{cell} = E^\circ_{ClO_3^-|ClO_4^-} + E^\circ_{ClO_3^-|ClO_2^-}$

$+ \frac{0.059}{2}\log\frac{[ClO_3^-]^2}{[ClO_4^-][ClO_2^-]}$

$$0=-0.36+0.33+\frac{0.059}{2}\log\frac{[1-2x]^2}{x^2}$$

$$0=-0.03+0.059\log\frac{1-2x}{x}$$

$$\text{or } \log\frac{1-2x}{x}=\frac{0.03}{0.059}$$

$$\therefore\quad \frac{1-2x}{x}=0.509$$

$$\therefore\quad x=\frac{1}{2.509}=0.40\text{ M}$$

34. (a) $NO_3^- + 4H^+ + 3e \longrightarrow NO + 2H_2O$

$\underset{(0.1-x)}{0.1}\quad \underset{(0.4-0.4x)}{0.4}\quad \underset{-}{0}\quad \underset{-}{0}$

$$x=\frac{80}{100}\times 0.1=0.08$$

After reduction,

$$[NO_3^-]=0.1-0.08=0.02$$

$$[H^+]=0.4-0.32=0.08$$

$$\therefore\quad E_{RP}=E^\circ_{RP}+\frac{0.059}{3}\log\frac{[NO_3^-][H^+]^4}{[P_{NO}]}$$

$$=0.96+\frac{0.059}{3}\log\frac{0.02\times(0.08)^4}{1}$$

$$=0.96-0.12=0.84\text{ V}$$

35. (d) $Ag^+ + e \longrightarrow Ag$

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

$\therefore$ Eq. of Ag^+ lost $=0.1=$ Eq. of O_2 formed and escaped

$\therefore$ Total mass loss $=0.1\times 108+\dfrac{0.1\times 32}{4}=11.6$

$\therefore$ Mass of solution $=108-11.6=96.47$

36. (b) $\frac{4}{3}Al+O_2 \longrightarrow \frac{2}{3}Al_2O_3$; $\Delta G=-827$ kJ (Given per mole of O_2)

$\because\quad 2Al^\circ \longrightarrow (Al^{3+})_2+6e$

1 Al gives $3e$

$$\therefore\quad \frac{4}{3}Al=4e$$

Now $\quad \Delta G=-nEF$

$$-827\times 10^3=-4\times E\times 96500$$

$$\therefore\quad E=2.14\text{ V}$$

37. (a) $E_{cell}=E_{OP_{QH}}+E_{RP_{calomel}}$

$$=E^\circ_{OP_{QH}}-\frac{0.059}{2}\log[H^+]^2+E^\circ_{RP_{cal}}$$

($\because E^\circ_{RP}=E_{RP}$ for calomel)

$$=-0.699+0.059\,pH+0.280$$

$$E_{cell}=-0.419+0.059\,pH$$

$$-0.124=-0.419+0.059\,pH$$

$$pH=5$$

38. (a) E°_{OP} for Zn $=+0.762$ V (maximum in given values). More positive is E°_{OP}, more is the tendency to get itself oxidised or strong reducing agent.

39. (c) $\dfrac{w}{E}=\dfrac{i\cdot t}{96500}$ (Ist Law)

40. (c) E°_{RP} for Ag, Hg and Cu are -0.80, -0.79, -0.34. Mg^{2+} is not discharged in aqueous solution.

41. (d) 1 Faraday $=N\times e$

42. (d) None of the other cell contains salt bridge involving this reaction.

43. (a) Cathode : $2H^+ + 2e \longrightarrow H_2$

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

44. (d) $PbO_2+Pb+2H_2SO_4 \longrightarrow 2PbSO_4+2H_2O$

(Discharging reaction)

45. (b) $E^\circ_{cell}=E^\circ_{OP_{Zn}}+E^\circ_{RP_{Fe}}=0.76-0.41=0.35$ V

46. (d) $2e+Cu^{2+} \longrightarrow Cu$; $\quad \Delta G^\circ_1=-2\times 0.34\times F$

$Cu^+ \longrightarrow Cu^{2+}+e$; $\quad \Delta G^\circ_2=-1\times(-0.15)\times F$

$+ \qquad + \qquad + \qquad +$

$e+Cu^+ \longrightarrow Cu$; $\quad \Delta G^\circ_3=-1\times E^\circ_3\times F$

$$\Delta G^\circ_3=\Delta G^\circ_1+\Delta G^\circ_2=-0.68F+0.15\times F$$

$$\therefore\quad E^\circ_3=+0.53\text{ V}$$

Now, for $2Cu^+ \longrightarrow Cu+Cu^{2+}$

$$E^\circ=E^\circ_{OP_{Cu^+|Cu^{2+}}}+E^\circ_{RP_{Cu^+|Cu}}$$

$$=-0.15+0.53=+0.38\text{ V}$$

47. (b) $E_{cell}=E^\circ_{OP\,M/M^+}+E^\circ_{RP\,X/X^-}=-0.44+0.33=-0.11$ V for $M+X \longrightarrow M^++X^-$. Thus reaction is non-spontaneous. The spontaneous reaction in $M^++X^- \longrightarrow M+X$; $E^\circ=0.11$ V

48. (b) $\Delta G=\Delta G^\circ+RT\ln Q$, at eq. $\Delta G=0$ and $Q=K_c$

$$\therefore\quad -\Delta G^\circ=RT\ln K_c$$

49. (c) The salt bridge possesses the electrolyte having nearly same ionic mobilities of its cation and anion.

50. (b) Ionic mobilities depends upon size of ion. The ionic size in case of hydrated cation is $K^+_{(aq.)}<Na^+_{(aq.)}<Li^+_{(aq.)}$. Smaller is ion more is hydration and larger in size of hydrated ion.

51. (a) MnO_4^- will oxidise Cl^- ion according to equation.

$$Mn^{7+}+5e \longrightarrow Mn^{2+}$$

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

Thus, $\quad E^\circ_{cell}=E^\circ_{OPCl^-/Cl_2}+E^\circ_{RPMn^{7+}/Mn^{2+}}$

$$=-1.40+1.51=0.11\text{ V}$$

or reaction is feasible.

MnO_4^- will oxidise Fe^{2+} to Fe^{3+}

$$Mn^{7+}+5e \longrightarrow Mn^{2+}$$

$$Fe^{2+} \longrightarrow Fe^{3+} + e$$

$$E^\circ_{cell} = E^\circ_{OP\,Fe^{2+}/Fe^{3+}} + E^\circ_{RP\,Mn^{7+}/Mn^{2+}}$$

$$= -0.77 + 1.51 = 0.74\text{ V}$$

or reaction is feasible.

Thus, MnO_4^- will not oxidise only Fe^{2+} to Fe^{3+} in aqueous HCl but it will also oxidise Cl^- to Cl_2. Suitable oxidant should not oxidise Cl^- to Cl_2 and should oxidise only Fe^{2+} to Fe^{3+} in redox titration.

52. (b) Current flows from anode to cathode in external circuit of electrolytic cell and thus electrons flow from anode to cathode through external wires.

53. (b) $Zn + Fe^{2+} \longrightarrow Fe + Zn^{2+}$

$$E_{cell} = E^\circ_{cell} + \frac{0.059}{2}\log\frac{[Fe^{2+}]}{[Zn^{2+}]}$$

$$0.2905 = E^\circ_{cell} + \frac{0.059}{2}\log\frac{0.001}{0.01}$$

$$\therefore \quad E^\circ_{cell} = 0.2905 + 0.0295 = 0.32\text{ V}$$

Now $E^\circ_{cell} = \frac{0.059}{2}\log_{10} K_c$

$$0.32 = \frac{0.059}{2}\log_{10} K_c$$

$$\therefore \quad K_c = 10^{0.32/0.0295}$$

54. (a) $E^\circ_{cell} = E^\circ_{OP\,Fe} + E^\circ_{RP\,H_2O} = 0.44 + 1.23 = 1.67\text{ V}$

$$\therefore \quad \Delta G^\circ = -nE^\circ F = -2 \times 1.67 \times 96500\text{ J}$$

$$= -322.31\text{ kJ mol}^{-1}$$

55. (b) $\frac{w}{E} = \frac{i \cdot t}{96500}$

$$0.01 \times 2 = \frac{10 \times 10^{-3} \times t}{96500},$$

$t = 19.3 \times 10^4$ sec

56. (d) In the given reaction Fe is oxidised and O_2 is reduced.

$$2Fe \longrightarrow 2Fe^{2+} + 4e$$

$$4e + O_2 + 4H^+ \longrightarrow 2H_2O$$

$$\therefore E_{cell} = E^\circ_{OPFe} - \frac{0.059}{4}\log[Fe^{2+}]^2 + E^\circ_{RPO_2} + \frac{0.059}{4}\log P_{O_2} \times [H^+]^4$$

$$= E^\circ_{cell} + \frac{0.059}{4}\log\frac{P_{O_2} \times [H^+]^4}{[Fe^{2+}]^2}$$

$$= 1.67 + \frac{0.059}{4}\log\frac{0.1 \times (10^{-3})^4}{(10^{-3})^2}$$

$$= 1.67 + \frac{0.059}{4}\log 10^{-7}$$

$$= 1.67 + \frac{0.059 \times (-7)}{4}$$

$$= 1.67 - 0.103 = 1.57\text{ V}$$

57. (b) E^0_{RP} of MnO_4^- / Mn^{2+} is highest and thus MnO_4^- is easily reduced and is the strongest oxidising agent.

$$Mn^{7+} + 5e \longrightarrow Mn^{2+}$$

or $\quad MnO_4^- + 5e + 8H^+ \longrightarrow Mn^{2+} + 4H_2O$

58. (b) $E^\circ_{Mn^{3+}/Mn^{2+}} = 1.57\text{ V}$

$$E^\circ_{Fe^{3+}/Fe^{2+}} = 0.77\text{ V}$$

$$E^\circ_{Co^{3+}/Co^{2+}} = 1.97\text{ V}$$

$$E^\circ_{Cr^{3+}/Cr^{2+}} = -0.41\text{ V}$$

OBJECTIVE PROBLEMS (More Than One Answer Correct)

1. In the atmosphere of industrial smog, copper corrodes to form:
(a) basic copper carbonate
(b) copper sulphide
(c) basic copper sulphate
(d) copper oxide

2. The tarnishing of silver ornaments in atmosphere is due to :
(a) Ag_2O (b) Ag_2S
(c) Ag_2CO_3 (d) Ag_2SO_4

3. If, : $A+B \rightleftharpoons C+D; K_C = K_1$ and $E° = a$ V
$2A+2B \rightleftharpoons 2C+2D; K_C = K_2$ and $E° = b$ V
then,
(a) $a=b$ (b) $K_2 = K_1^2$
(c) $a=2b$ (d) $b=a^2$

4. Rusting of iron is catalysed by :
(a) H^+ (b) dissolved CO_2 in water
(c) O_2 (d) impurities present in Fe

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

6. Select the correct statements about NHE :
(a) $E°$ of NHE has arbitrarily assumed to be zero
(b) $E°$ of NHE is equal to zero
(c) NHE refers as $Pt_{\underset{1\ bar}{H_2 g}} \left| \underset{a=1}{H^+_{aq}} \right.$ at 25°C
(d) NHE is very susceptible to dissolved O_2, H_2S and all other reducing agents

7. In which of the following salt bridge is not needed ?
(a) $Pb|PbSO_{4(s)}|H_2SO_4|PbO_{2(s)}|Pb$
(b) $Cd|CdO_{(s)}|KOH_{aq}|NiO_{2(s)}|Ni$
(c) $Fe_{(s)}|FeO_{(s)}|KOH_{aq}, Ni_2O_{3(s)}|Ni$
(d) $Zn|ZnSO_4|CuSO_4|Cu$

8. Select the correct statements if 9.65 ampere current is passed for 1 hour through the cell $Ag|\underset{1M}{Ag^+}||\underset{1M}{Cu^{2+}}|Cu$:
(a) Ag will oxidise to Ag^+ and new $[Ag^+] = 1.36\ M$
(b) Ag^+ will reduce to Ag and new $[Ag^+] = 0.64\ M$
(c) Cu^{2+} will reduce to Cu and new $[Cu^{2+}] = 0.82\ M$
(d) Cu will oxidise to Cu^{2+} and new $[Cu^{2+}] = 0.82\ M$

9. Which of the following metals can not be obtained by the electrolysis of an aqueous solution of their salt :
(a) Ag (b) Mg
(c) Cu (d) Cr
(e) Al

10. The standard reduction potential values of three metallic cations, X, Y and Z are 0.52, – 3.03 and – 1.18 V respectively. The order of reducing power of the corresponding metals is :
(a) $Y>Z>X$ (b) $X>Y>Z$
(c) $Z>Y>X$ (d) $Z>X>Y$

11. The function of salt bridge is :
(a) to maintain electrical neutrality of two half cell solution
(b) to eliminate liquid junction potential
(c) to complete the circuit
(d) to produce current

12. In a cell $Zn|Zn^{2+}||H^+|H_2Pt$, the addition of H_2SO_4 to cathode compartment :
(a) decreases EMF
(b) increases EMF
(c) shift equilibrium to right
(d) shifts equilibrium to left

13. For the reduction of NO_3^- ion in aqueous solution, $E°$ is +0.96 V. Values of $E°$ for some metals are given below :
$V^{2+}(aq.) + 2e \longrightarrow V$; $E° = -1.19$ V
$Fe^{3+}(aq.) + 3e \longrightarrow Fe$; $E° = -0.04$ V
$Au^{3+}(aq.) + 3e \longrightarrow Au$; $E° = +1.40$ V
$Hg^{2+}(aq.) + 2e \longrightarrow Hg$; $E° = +0.86$ V
The pairs of metal that is (are) oxidised by NO_3^- in aqueous solution is (are) : **(IIT 2009)**
(a) V and Hg (b) Hg and Fe
(c) Fe and Cu (d) Fe and V

SOLUTIONS (More Than One Answer Correct)

1. (a, c) $8Cu + 6H_2O + 2SO_2 + 5O_2 \longrightarrow 2[CuSO_4 \cdot 3Cu(OH)_2]$

$2Cu + H_2O + CO_2 + O_2 \longrightarrow [CuCO_3 \cdot Cu(OH)_2]$

2. (a, b) $2Ag + \frac{1}{2}O_2 \longrightarrow Ag_2O$

$2Ag + H_2S \longrightarrow Ag_2S + H_2$

3. (a, b) $K_1 = \frac{[C][D]}{[A][B]}$ and $K_2 = \frac{[C]^2[D]^2}{[A][B]}$

Also, $E°$ is independent of stoichiometry.

4. (a,b,c,d) Follow text.

5. (a,d) $\Delta G = \Delta H - T\Delta S$ and $\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P$

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

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

Also, $-nEF = \Delta H + T \times (-nF)\left(\frac{\partial E}{\partial T}\right)_P$

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

6. (a,c,d) Follow text.

7. (a,b,c) Salt bridge is used to eliminate liquid junction potential arised due to different speed of ions present in cathodic and anodic compartments.

8. (a,c) $\frac{w}{E} = \frac{it}{96500} = \frac{9.65 \times 3600}{96500} = 0.36\,eq.$

of $Ag^+ = 0.36\,eq.$ of Cu^{2+}

$= 0.36$ mole of $Ag^+ = 0.18$ mole of Cu^{2+}

Now, Ag will oxidise to Ag^+ and Cu^{2+} will reduce to Cu.

9. (b,e) Strong electropositive metals cannot be reduced in presence of H_2O.

10. (a) Lower is $E°_{RP}$, more is $E°_{OP}$, more is the tendency to get itself oxidised and thus more is reducing power $E°_{OP}$ order in $Y > Z > X$.

11. (a,b,c)

12. (b,c) $E = E°_{cell} + \frac{0.059}{2}\log\frac{[H^+]^2}{[Zn^{2+}]}$

Anode : $Zn \longrightarrow Zn^{2+} + 2e$

Cathode: $2H^+ + 2e \longrightarrow H_2$

$Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$

On addition of H_2SO_4 to cathode compartment, $[H^+]$ increases and reaction will shift towards right.

13. (a,b,d) The oxidation of Au is not possible as $E°_{cell}$ is –ve.

(a) $E° = E°_{OP_V} + E°_{RP_{NO_3^-}} = +1.19 + 0.96 = 2.15$ V

(b) $E° = E°_{OP_{Fe}} + E°_{RP_{NO_3^-}} = +0.04 + 0.96 = 1.0$ V

(c) $E° = E°_{OP_{Au}} + E°_{RP_{NO_3^-}} = -1.40 + 0.96 = -0.44$ V

(d) $E° = E°_{OP_{Hg}} + E°_{RP_{NO_3^-}} = -0.86 + 0.96 = +0.10$ V

COMPREHENSION BASED PROBLEMS

Comprehension 1 : A current of 15 ampere is used to plate Ni from $NiSO_4$ bath. Both H_2 and Ni are formed at cathode. The current efficiency of Ni formation is 60%.
(atomic mass of Ni = 58.71)

[1] Mass of Ni is plated per hr?
(a) 9.85 g (b) 0.5596 g
(c) 16.42 g (d) 12.82 g

[2] The thickness of plating if the cathode consists of a sheet of 4 cm^2 which is coated on both sides : (The density of Ni is 8.9 g mL^{-1})
(a) 0.276 cm (b) 0.272 cm
(c) 0.316 cm (d) 0.138 cm

[3] The volume of H_2 is formed per hr at STP:
(a) 6.62 litre (b) 6.26 litre
(c) 2.51 litre (d) 5.02 litre

[4] The volume of O_2 is formed per hr at STP:
(a) 6.26 litre (b) 3.13 litre
(c) 9.39 litre (d) 2.51 litre

Comprehension 2: $E°$ values for $Fe \longrightarrow Fe^{2+} + 2e$ and $Fe \longrightarrow Fe^{3+} + 3e$ are 0.440 V and 0.036 V respectively.

[1] The number of cells showing the overall cell reaction $Fe + 2Fe^{3+} \longrightarrow 3Fe^{2+}$:
(a) 1 (b) 2
(c) 3 (d) 4

[2] $\Delta G°$ for each cell for given overall reaction in (J) is:
(a) +2.424 F (b) −2.424 F
(c) +1.616 F (d) −1.616 F

[3] $E°$ for $Fe^{3+} + e \longrightarrow Fe^{2+}$ is:
(a) +0.672 V (b) +0.772 V
(c) −0.040 (d) +0.040 V

[4] The $E°$ for $Fe \mid Fe^{2+} \parallel Fe^{3+}, Fe^{2+} \mid Pt$ is:
(a) 1.212 V (b) 0.404 V
(c) 0.808 V (d) − 0.404 V

[5] Select the correct statements:
(a) The overall reaction and $\Delta G°$ for each cell is same
(b) The E°_{cell} and 'n' values are different for each cell
(c) The $\Delta G°$ depends upon the cell reaction where as E°_{cell} depends upon the make-up of cell
(d) All of the above

Comprehension 3 : Numerical reactions involve interaction of atoms and molecules. A large number of atoms/molecules (approximately 6.023×10^{23}) are present in a few grams of any chemical compound varying with their atomic/molecular masses. To handle such large numbers conveniently, the mole concept was introduced. This concept has implications in diverse areas such as analytical chemistry, biochemistry, electrochemistry and radiochemistry. The following example illustrates a typical case, involving chemical/electrochemical reaction, which requires a clear understanding of the mole concept. A 4.0 molar aqueous solution of NaCl is prepared and 500 mL of this solution is electrolysed. This leads to the evolution of chlorine gas at one of the electrodes (atomic mass : Na = 23, Hg = 200; 1 Faraday = 96500 coulombs) **(IIT 2007)**

[1] The total number of mole of chlorine gas evolved is:
(a) 0.5 (b) 1.0
(c) 2.0 (d) 3.0

[2] If the cathode is a Hg electrode, the maximum mass (g) of amalgam formed from this solution is :
(a) 200 (b) 225
(c) 400 (d) 446

[3] The total charge (coulomb) required for complete electrolysis is :
(a) 24125 (b) 48250
(c) 96500 (d) 193000

Comprehension 4 : Redox reactions play a pivotal role in chemistry and biology. The values of standard redox potential ($E°$) of two half-cell reactions decide which way the reaction is expected to proceed. A simple example is a Daniel cell in which zinc goes into solution and copper gets deposited. Given below are a set of half-cell reactions (acidic medium) along with their $E°$ (V with respect to normal hydrogen electrode) values. Using this data obtain the correct explanations to questions given

$I_2 + 2e^- \rightarrow 2I^-$ $E° = 0.54$
$Cl_2 + 2e^- \rightarrow 2Cl^-$ $E° = 1.36$
$Mn^{3+} + e^- \rightarrow Mn^{2+}$ $E° = 1.50$
$Fe^{3+} + e^- \rightarrow Fe^{2+}$ $E° = 0.77$
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ $E° = 1.23$ **[IIT2007]**

[1] Among the following, identify the correct statement :
(a) Chloride ion is oxidised by O_2
(b) Fe^{2+} is oxidised by iodine
(c) Iodide ion is oxidised by chlorine
(d) Mn^{2+} is oxidised by chlorine

[2] 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+} to Mn^{3+} and Fe^{2+} to Fe^{3+}
(c) Fe^{3+} oxidises H_2O to O_2
(d) Mn^{3+} oxidises H_2O to O_2

[3] Sodium fusion extract, obtained from aniline, on treatment with ion (II) sulphate and H_2SO_4 in presence of air gives a Prussian blue precipitate. The blue colour is due to the formation of :
(a) $Fe_4[Fe(CN)_6]_3$ (b) $Fe_3[Fe(CN)_6]_2$
(c) $Fe_4[Fe(CN)_6]_2$ (d) $Fe_3[Fe(CN)_6]_3$

Comprehension 5: The concentration of potassium ions inside a biological cell is atleast twenty times higher than the out side. The resulting potential difference across the cell is important in several processess such as transmission of nerve impulses and maintaining the ion balance. A simple model for such a concentration cell involving a metal M is:

$$M(s) \mid M^+(aq), 0.05\text{ M} \mid\mid M^+(aq), 1\text{ M} \mid M(s)$$

For the above electrolytic cell, the magnitude of cell potential $|E_{cell}| = 70$ mV **(IIT 2010)**

[1] For the above cell :

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

[2] If the 0.05 M solution of M^+ is replaced by a 0.0025 M solution M^+, then the magnitude of cell potential will be:

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

Comprehension 6: The electrochemical cell shown below is a concentration cell.

$$M \mid M^{2+}\text{(saturated solution of a sparingly soluble salt) } MX_2) \mid\mid M^{2+}_{(0.001\text{ mol dm}^{-3})} \mid M$$

The emf of the cell depends on the difference in concentrations of M^{2+} ions at the two electrodes. The emf of the cell at 298 K is 0.059 V. **(IIT 2012)**

[1] The value of ΔG (kJ mol^{-1}) for the given cell is (take 1F $= 96500$ C mol^{-1}) :

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

[2] The solubility product (K_{sp}; mol^3 dm^{-9}) of MX_2 at 298 K based on the information available for the given concentration cell is (take $2.303 \times R \times 298/F = 0.059$ V):

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

SOLUTIONS

Comprehension 1

At cathode two reductions occur, *i.e.*, of Ni^{2+} and H^+. Since, current efficiency of Ni^{2+} is 60%.

$\therefore$ Current efficiency for H^+ is 40%.

Anode : $2OH^- \longrightarrow H_2O + 1/2O_2$

Cathode : $Ni^{2+} + 2e \longrightarrow Ni$

$2H^+ + 2e \longrightarrow H_2$

[1] (a) At cathode $\left(\frac{w}{E}\right) = \frac{i \cdot t}{96500} = \frac{15 \times 60 \times 60}{96500} = 0.5596$

or

At anode

At cathode Ni and H_2 both are formed and thus

$$w_{Ni} = \frac{0.5596 \times 60}{100} \times \frac{58.71}{2} = \mathbf{9.856\ g}$$

$$w_{H_2} = \frac{0.5596 \times 40}{100} \times \frac{2}{2} = \mathbf{0.2238\ g}$$

$\therefore V_{H_2}$ at NTP $= \frac{0.2238 \times 22.4}{2} = \mathbf{2.51\ litre}$

[2] (d) Volume on which Ni coated $= 4 \times 2 \times$ thickness $= \frac{w}{d}$

$\therefore$ Thickness $= \frac{w}{d \times 8} = \frac{9.856}{8.9 \times 8} = 0.138\,\text{cm}$

$\therefore$ Thickness $(d) = \mathbf{0.138\ cm}$

[3] (c) $w_{H_2} = 0.2238\,\text{g}$

$$V_{H_2} = \frac{0.2238 \times 22.4}{2} = \mathbf{2.51\ litre}$$

[4] (b) $w_{O_2} = 0.5596 \times 8 = 4.4768\,\text{g}$

$\therefore$ $V_{O_2} = \frac{4.4768 \times 22.4}{32} = \mathbf{3.13\ litre}$

Comprehension 2

[1] (c) [2] (b), [3] (b), [4] (a) [5] (d)

$Fe \longrightarrow Fe^{2+} + 2e;\ E^\circ_{OP} = +0.440\,V;$

$-\Delta G^\circ_1 = 2 \times 0.440 \times F$

$Fe^{3+} + 3e \longrightarrow Fe;\ E^\circ_{RP} = -0.036\,V;$

$-\Delta G^\circ_2 = 3 \times (-0.036) \times F$

$\therefore Fe^{3+} + e \longrightarrow Fe^{2+}; -1 \times E^\circ F$

$= 2 \times 0.440 \times F - 3 \times 0.036 \times F$

$= +0.772\,F$

$\therefore$ $E^\circ = \mathbf{+0.772\ V}$

Cell No. 1 : The cell is $Fe|Fe^{2+}||Fe^{3+}|Fe$

$3Fe \longrightarrow 3Fe^{2+} + 6e;$

$E^\circ_{OP} = +0.440\,V$

$2Fe^{3+} + 6e \longrightarrow 2Fe;$ $E^\circ_{RP} = -0.036\,V$

$Fe + 2Fe^{3+} \longrightarrow 3Fe^{2+};$ $E^\circ_{cell} = \mathbf{0.404\ V}$

$+\Delta G^\circ = -nE^\circ F = -6 \times 0.404\,F = \mathbf{-2.424\,F}$

Cell No. 2 : The cell is $Fe|Fe^{2+}||Fe^{3+}, Fe^{2+}|Pt$

$Fe \longrightarrow Fe^{2+} + 2e;$ $E^\circ_{OP} = +0.440\,V$

$2Fe^{3+} + 2e \longrightarrow 2Fe^{2+};$ $E^\circ_{RP} = +0.772\,V$

$Fe + 2Fe^{3+} \longrightarrow 3Fe^{2+};$ $E^\circ_{cell} = \mathbf{1.212\ V}$

$\therefore\ \Delta G^\circ = -2 \times 1.212 \times F = -2.424\,F$

Cell No. 3 : The cell is $Fe|Fe^{3+}||Fe^{3+}, Fe^{2+}|Pt$

$Fe \longrightarrow Fe^{3+} + 3e;$ $E^\circ = +0.036\,V$

$3Fe^{3+} + 3e \longrightarrow 3Fe^{2+};$ $E^\circ = 0.772\,V$

$Fe + 2Fe^{3+} \longrightarrow 3Fe^{2+};$ $E^\circ = 0.808\,V$

$\Delta G^\circ = -3 \times 0.808 \times F = \mathbf{-2.424\,F}$

Comprehension 3

[1] (b) Meq. of $Cl^- = 4 \times 500 = 2000$

$\therefore$ Eq. of $Cl^- = 2 =$ Eq. of Cl_2

$\therefore$ Mole of $Cl_2 = \mathbf{1}$ $[\because 2Cl^- \to Cl_2 + 2e]$

[2] (d) Eq. of Na $= \frac{4 \times 500}{1000} = 2$

mass of 2 [NaHg] = 2 [23 + 200] = **446 g**

[3] (d) $\frac{w}{E} = \frac{Q}{9.6500}$ $\left(\frac{w}{E} = 2\right)$

$\therefore$ Q = 2 × 96500 = 193000

Comprehension 4

[1] (c) $2I^- + Cl_2 \longrightarrow I_2 + 2Cl^-$

$\therefore\ E_{redox} = E^\circ_{RP_{Cl_2}} + E^\circ_{OP_{I_2}}$

$= 1.36 - 0.54 = \mathbf{0.82\ V}$

[2] (d) $4Mn^{3+} + 2H_2O \longrightarrow 4Mn^{2+} + O_2 + 4OH^-$

$E_{redox} = E^\circ_{RP_{Mn}} + E^\circ_{OP_{H_2O}}$

$= 1.50 - 1.23 = 0.27\,V$

$\therefore$ Reaction is possible

whereas for Fe^{3+} and H_2O

$E_{redox} = E^\circ_{RP_{Fe}} + E^\circ_{OP_{H_2O}}$

$= 0.77 - 1.23 = -0.46\,V$

Thus Fe^{3+} is not reduced by H_2O.

[3] (a)

Comprehension 5

The given cell is not electrolytic cell as reported. It is concentration cell (a type of electrochemical cell). Also E° or E may be > 0 or < 0 but ΔG is either +ve or −ve and not > 0 or < 0.

As given $|E_{cell}| = 70$ mV means + ve or − ve value

Now $E_{cell} = \underset{R.H.S.}{E_{OP}} + \underset{L.H.S.}{E_{RP}}$

$$= E^{\circ}_{OP_{M/M^+}} - \frac{0.059}{1}\log[M^+]_{\text{L.H.S.}} + E^{\circ}_{RP_{M^+/M}} + \frac{0.059}{1}\log[M^+]_{\text{R.H.S.}}$$

$$= 0.059\log\frac{[M^+]_{\text{R.H.S.}}}{[M^+]_{\text{L.H.S.}}}$$

$$= 0.059\log\frac{1}{0.05} = 0.059\times 1.30 = 0.076\text{ V} = 76\text{ mV} \simeq 70\text{ mV}$$

[1] (b) $E_{\text{cell}} = +ve$ and $\Delta G = -$ ve

[2] (c) $E_{\text{cell}} = 0.059\log\frac{1}{0.0025} = 0.059\log\frac{1}{(0.05)^2}$

$$= 0.059\times 2\times 0.76 = 0.146\text{ V} \simeq 140\text{ mV}$$

Comprehension 6

[1] (d) At anode : $M(s) \longrightarrow M^{2+}(aq.) + 2e^-$

At cathode : $M^{2+}(aq.) + 2e^- \longrightarrow M(s)$

n-factor of the cell reaction is 2.

$$\Delta G = -nFE_{cell} = -2\times 96500\times 0.059 = -113873\text{ kJ/mole}$$
$$= -11.387\text{ kJ/mole} = -11.4\text{ kJ/mol}$$

[2] (b) $M\,|\,M^{2+}$ (saturated solution of salt MX_2) $||$ M^{2+} $(0.001M)$ emf of concentration cell,

$$E_{cell} = \frac{0.059}{n}\log\frac{[M^{2+}]_{\text{R.H.S.}}}{[M^{2+}]_{\text{L.H.S.}}}$$

$$0.059 = \frac{0.059}{2}\log\frac{[0.001]}{[M^{2+}]_{\text{L.H.S.}}}$$

$$\therefore [M^{2+}]_{\text{L.H.S.}} = 10^{-5}M$$

Let solubility of salt be S mol/litre

thus $\underset{(S)}{MX_2} \longrightarrow \underset{S}{M^{2+}} + \underset{2S}{2X^-}$

$$\therefore K_{sp} = 4s^3 = 4\times(10^{-5})^3 = 4\times 10^{-15}$$

STATEMENT-EXPLANATION PROBLEMS

In each sub question given below a statement (S) and explanation (E); Choose the correct answers from the codes (a), (b), (c) and (d) given for each question:

(a) S is correct but E is wrong
(b) S is wrong but E is correct
(c) Both S and E are corect and E is correct explanation of S
(d) Both S and E are correct but E is not correct explanation of S

1. S : Anode is the electrode at which oxidation occurs and cathode is the electrode at which reduction occurs.
E : Anode and cathode in electrochemical cells and electrolyte cells have opposite polarity.

2. S : An irreversible cell is $Zn | H_2SO_4 | Ag$ showing redox change :

$$Zn \longrightarrow Zn^{2+} + 2e$$
$$2H^+ + 2e \longrightarrow H_2$$
$$\overline{Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2}$$

E : The cell on connecting through another cell having its potential slightly greater than test cell, the redox reaction becomes:

$$2Ag \longrightarrow 2Ag^+ + 2e$$
$$2H^+ + 2e \longrightarrow H_2$$
$$\overline{2Ag + H_2SO_4 \longrightarrow Ag_2SO_4 + H_2}$$

3. S : E°_{cell} is an intensive property.
E : $\frac{\Delta G^\circ}{n}$ is also an intensive property.

4. S : H_2S reacts with oxygen under standard conditions in acid medium to give H_2O and sulphur.
E : $E^\circ_{H^+/O_2/Pt} > E^\circ_{H^+/H_2S/S}$

5. S : The standard reduction potential of M^{n+}/M electrode increases with increase in activity of M^{n+} ion.
E : The standard reduction potential is given by :

$$E_{RP} = E^\circ_{RP} + \frac{0.059}{n}\log[M^{n+}]$$

6. S : The concentration cell $PtH_2 \underset{P_1}{|} HCl \underset{P_2}{|} H_2Pt$ would show spontaneous flow of current only when $P_1 > P_2$ whereas the concentration cell $PtH_2 | \underset{C_1}{HCl} || \underset{C_2}{HCl} | H_2Pt$ show spontaneous flow of current only when $C_2 > C_1$.

E : Case I : $E_{cell} = \frac{0.059}{2}\log\frac{P_2}{P_1}$

Case II : $E_{cell} = \frac{0.059}{1}\log\frac{C_1}{C_2}$

7. S : The reference electrode of silver-silver chloride is used as secondary reference electrode.
E : The electrode is reversible with respect to Cl^- ions.

8. S : Passage of charge through $CuSO_4$ (aq) solution in presence of Pt electrode increases its pH.
E : Concentration of $[OH^-]$ in solution decreases.

9. S : If two half reaction with electrode potential E°_1 and E°_2 gives a third half reaction, then

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

E : $E^\circ_3 = E^\circ_1 + E^\circ_2$

10. S : 1 Faraday is the charge that liberates 1 eq. of metal at cathode.
E : Passage of 1 Faraday charge through $aq.$ $MgCl_2$ liberates 12 g Mg at cathode.

11. S : Electrolysis involves electronation or de-electronation as a result of passage of current.
E : The species undergoes electronation at anode and other show de-electronation at cathode.

12. S : Very pure form of iron does not show rusting.
E : Rusting is catalysed by impurities present in iron and H^+ ions.

13. S : The cathode of electrolytic cell during electrolysis of NaCl (aq) on addition of little litmus shows a blue colour.
E : At cathode : $2H^+ + 2e \longrightarrow H_2$. The reaction at cathode give rise to an increase in pH ranging in alkaline medium and litmus shows blue colour.

14. S : In concentration cell neither electronation occurs at cathode nor de-electronation at anode.
E : The electrical energy is produced due to decrease in free energy during the transfer of concentration for high to low region.

15. S : In case of H^+ and Na^+ present in a solution discharge of H^+ is preferred at cathode.
E : The higher is discharge potential of ion, lesser is its tendency to get discharged.

16. S : Milliequivalent of a metal discharged at cathode during electrolysis $= \frac{i \cdot t}{96.5}$
E : This is faradays I law of electrolysis.

17. S : Pt H_2/HCl at 25°C $E^\circ_H = 0$.
E : For primary reference electrode $E^\circ_{H/H^+} = 0$.

18. S : $\left(\frac{\partial E}{\partial T}\right)_P$ is called temperature coefficient of e.m.f.

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

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

20. S : The electrolytic cells involve conversion of electrical energy into chemical energy.
    E : An increase in free energy is responsible for the flow of current.

21. S : During electrolysis of CH_3COONa the molar ratio of gases formed at anode and cathode is 2 : 1.
    E : Anode : $2CH_3COO^- \longrightarrow C_2H_6 + 2CO_2 + 2e$
    Cathode : $2H^+ + 2e \longrightarrow H_2$

22. S : Electrolysis of $CuCl_2$ (*aq*) gives 1 mole of Cu and 1 mole of Cl_2 by the passage of suitable charge.
    E : Equal equivalents of Cu and Cl_2 are formed during the passage of same charge.

23. S : A copper rod turns colourless solution of $ZnSO_4$ to light blue.
    E : Zn reduces Cu^{2+} to Cu.

24. S : Anode possesses negative polarity in electrochemical cell.
    E : Anode is the electrode which show liberation of electrons and thus electrode acquires negative charge because electrons are left on electrode.

25. S : Zinc protects the iron better than tin even after it cracks.
    E : $E^\circ_{OP_{Zn}} < E^\circ_{OP_{Fe}}$ but $E^\circ_{OP_{Sn}} > E^\circ_{OP_{Fe}}$

26. S : A dry cell becomes dead after a long time, even if it has not been used.
    E : Reaction of NH_4Cl and Zn is spontaneous one.

27. S : The anode of Daniell cell possesses negative polarity.
    E : The zinc electrode shows oxidation and thus becomes –vely charged with respect to surrounding solution.

28. S : Rusting of iron is favoured by moist air, CO_2 and O_2.
    E : Purest form of metal is not corroded.

29. S : Discharge potential of Na^+ is more than H^+.
    E : E°_{Na/Na^+} is lesser than E°_{H/H^+}.

30. S : Discharge potential of Cl^- is lesser than OH^-.
    E : $E^\circ_{Cl/Cl^-} < E^\circ_{H_2O/OH^-}$.

ANSWERS (Statement Explanation Problems)

1. (d) Both are facts.
2. (c) In reversible cell, redox change is reversed if it is connected with another cell of slightly higher e.m.f. but in test cell it is not so in this cell.
3. (c) $-\Delta G° = nE° F \quad \therefore \ E° = \frac{-\Delta G°}{nF}$. Since, ΔG is intensive property and then $E°$ is also intensive property.
4. (c) The half cell reactions gives a redox change with +ve value of $E°_{cell}$

$$2H^+ + \frac{1}{2}O_2 + 2e \longrightarrow H_2O \qquad E°_{RP} = A$$
$$H_2S \longrightarrow 2H^+ + S + 2e \qquad E°_{OP} = B$$
$$H_2S + \frac{1}{2}O_2 \longrightarrow H_2O + S$$
$$E°_{cell} = E°_{OP_{H_2S/H^+/S}} + E°_{RP_{H^+/O_2/Pt}}$$
$$E°_{cell} = +ve \qquad (\text{Given } E°_{RP_{H^+/O_2/Pt}} > E°_{RP_{H^+/H_2S/S}})$$

5. (c) Explanation is correct reason for statement.
6. (a) $H_2 \underset{P_1}{} | HCl | \underset{P_2}{H_2}$ $\qquad$ $H_2 | \underset{C_1}{HCl} \| \underset{C_2}{HCl} | H_2$

$$H_2(P_1) \longrightarrow 2H^+ + 2e \qquad H_2 \longrightarrow 2H^+(C_1) + 2e$$
$$2H^+ + 2e \longrightarrow H_2(P_2) \qquad 2H^+_{C_2} + 2e \longrightarrow H_2$$
$$H_2(P_1) \longrightarrow H_2(P_2) \qquad H^+_{C_2} \longrightarrow H^+_{C_1}$$
$$\therefore \ E_{cell} = \frac{0.059}{2}\log\frac{P_1}{P_2} \qquad E_{cell} = \frac{0.059}{2}\log\frac{C_2}{C_1}$$

if $P_1 > P_2$ $E_{cell} = +ve$ $\quad$ if $C_2 > C_1$ $\quad E_{cell} = +ve$

7. (d) Both are facts.
8. (c) Anode : $2H_2O \longrightarrow 4H^+ + O_2 + 4e$

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

Cathode : $Cu^{2+} + 2e \longrightarrow Cu$.

9. (a) In such case $E°$ are not additive.
10. (a) $MgCl_2(aq)$ shows discharge of H^+ and not of Mg^{2+}.
11. (a) Electronation (reduction) occurs at cathode and de-electronation (oxidation) occurs at anode.
12. (d) Both are facts and true.
13. (c) Explanation is correct reason for statement.
14. (b) In concentration cells no doubt oxidation occurs at anode and reduction at cathode but net redox change is zero.
15. (c) Explanation is correct reason for statement.
16. (c) Explanation is correct reason for statement.
17. (b) Primary reference electrode is $\underset{1\,atm}{PtH_2} \,|\, \underset{1M}{HCl}$ at 25°C its

$E°_H = 0$.

18. (d) $\Delta H = nF\left[T\left(\frac{\partial E}{\partial T}\right)_P - E\right]$; where $\left(\frac{\partial E}{\partial T}\right)_P$ is temperature coefficient.
19. (c) Explanation is correct reason for statement.
20. (a) In electrolytic cell, electrical energy is given to produce chemical changes.
21. (b) The molar ratio of gases at anode and cathode is 3 : 1.
22. (c) Anode : $2Cl^- \longrightarrow Cl_2 + 2e$

Cathode : $Cu^{2+} + 2e \longrightarrow Cu$

23. (b) $Zn + Cu^{2+} \longrightarrow \underset{Colourless}{Zn^{2+}} + Cu$. $CuSO_4$ solution turns light blue on addition of Zn.
24. (c) Explanation is correct reason for statement.
25. (a) $E°_{OP_{Zn}} > E°_{OP_{Fe}}; E°_{OP_{Sn}} < E°_{OP_{Fe}}$
26. (c) Explanation is correct reason for statement.
27. (c) $\underset{Electrode}{Zn} \longrightarrow \underset{Solution}{Zn^{2+}} + 2e$;

The electrons remaining on Zn electrode develops negative polarity.

28. (d) Both are correct.
29. (a) Higher is discharge potential, lesser is tendency to get discharged. In case of cation discharge potential refers for $E°_{OP}$.

$$E°_{OP\ Na/Na^+} < E°_{OP\ H/H^+}$$

30. (b) In case of anion discharge potential refers for $E°_{RP}$ and therefore $E°_{OP\ Cl^-/Cl} > E°_{OP\ OH^-/H_2O}$.

MATCHING TYPE PROBLEMS

Type I : Only One Match Is Possible

1. For a given reaction:

$$Fe + 2Fe^{2+} \longrightarrow 3Fe^{2+}$$

(A) $E_1^\circ = E^\circ_{Fe/Fe^{2+}} + E^\circ_{Fe^{3+}/Fe}$	(i) $n = 2$
(B) $E_2^\circ = E^\circ_{Fe/Fe^{2+}} + E^\circ_{Fe^{3+}/Fe^{2+}}$	(ii) $n = 3$
(C) $E_3^\circ = E^\circ_{Fe/Fe^{3+}} + E^\circ_{Fe^{3+}/Fe^{2+}}$	(iii) $n = 6$

Type II : More Than One Match Are Possible

2.

(A) Corrosion	(i) Brown deposits on Fe
(B) Rusting	(ii) Green deposits on Cu
(C) Electrolysis	(iii) Blackening of Ag coins
(D) Faraday	(iv) Electronation
	(v) De electronation
	(vi) Charge on one mole electron
	(vii) 96500 C
	(viii) Electroplating

3.

(A) Calomel electrode	1. Reversible with respect to Cl^-
(B) Ag-AgCl(s) electrode	2. Reversible with respect to H^+
(C) N.H. Electrode	3. $E^\circ = 0$
(D) PtH_2 (2 atm) H^+ (1 M)	4. E° varies with KCl molarity
	5. Secondary reference electrodes
	6. Primary reference electrode

4.

(A) $Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$	1. Reversible cell
(B) $Ag \mid Ag^+ \parallel H^+ \mid H_2$	2. Irreversible cell
(C) Lead storage Battery	3. $E^\circ_{cell} = +ve$
(D) $Cd \mid CdO(s)\ KOH(aq) \parallel NiO_2(s) \mid Ni$	4. $E^\circ_{cell} = -ve$
	5. Redox cells
	6. $n = 2$
	7. No liquid junction potential

Type III : One Match From Each List

5.

List A	List B	List C
1. Coulometry	a. Electro deposition	(i) Analysis of a gas sample
2. Eudiometry	b. Combustion in oxygen	(ii) Copper voltameter
3. Potentiometry	c. Titration	(iii) Optical rotation
4. Conductometry	d. Micellisation study	(iv) Migration of ions
5. Polarimetry	e. Optical activity	(v) Glass electrode

6. The standard reduction potential data at 25°C is given below: **[JEE (Advanced) II 2013]**

E° $(Fe^{3+}, Fe^{2+}) = +0.77\ V$;

E° $(Fe^{2+}, Fe) = -0.44\ V$

E° $(Cu^{2+}, Cu) = +0.34\ V$;

E° $(Cu^{+}, Cu) = +0.52\ V$

E° $[O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O] = +1.23\ V$;

E° $[O_2(g) + 2H_2O + 4e^- \rightarrow 4OH^-] = +0.40\ V$

E° $(Cr^{3+}, Cr) = -0.74\ V$;

E° $(Cr^{2+}, Cr) = -0.91\ V$;

Match E° of the redox pair in List I with the values given in List II and select the correct answer using the code given below the lists :

List I	List II
(P) E° (Fe^{3+}, Fe)	(1) − 0.18 V
(Q) E° $(4H_2O \rightleftharpoons 4H^+ + 4OH^-)$	(2) −0.4 V
(R) E° $(Cu^{2+} + Cu \rightarrow 2Cu^+)$	(3) − 0.04 V
(S) E° (Cr^{3+}, Cr^{2+})	(4) − 0.83 V

Codes:

	P	Q	R	S
(a)	4	1	2	3
(b)	2	3	4	1
(c)	1	2	3	4
(d)	3	4	1	2

ANSWERS

1. A—iii; B—i; C—ii
2. A—i, ii, iii, iv, v; B—i, iv, v; C—iv, v, viii; D—vi, vii
3. A—1, 4, 5; B—1, 5; C—2, 3, 6; D—2
4. A—1, 3, 5, 6; B—2, 4, 5, 6; C—1, 3, 5, 6, 7; D—1, 3, 5, 6, 7
5. 1-a-ii; 2-b-i; 3-c-v; 4-d-iv; 5-e-iii
6. (d)

$3e + Fe^{3+} \longrightarrow Fe$; $\quad \Delta G_1^\circ = -3 \times E_1^\circ \times F$

Given

$e + Fe^{3+} \longrightarrow Fe^{2+}$; $\quad 0\Delta G_2^\circ = -1 \times 0.77 \times F$

$2e + Fe^{2+} \longrightarrow Fe$; $\quad \Delta G_3^\circ = -2 \times (-0.44) \times F$

On adding last two

$Fe^{3+} + 3e \longrightarrow Fe$; $\Delta G_1^\circ = \Delta G_2^\circ + \Delta G_3^\circ$

$\therefore \quad \Delta G_1^\circ = -0.77F + 0.88F = +0.11F$

$\therefore -3E_1^\circ \times F = +0.11F$

$\therefore E_1^\circ = -0.04$

Thus P is (3)

$Cr^{3+} + e \longrightarrow Cr^{2+}$; $\quad \Delta G_1^\circ = -1 \times E_1^\circ \times F$

Given

$Cr^{3+} + 3e \longrightarrow Cr$; $\quad \Delta G_2^\circ = -3 \times (-0.74) \times F \ldots$ (i)

$Cr^{2+} + 2e \longrightarrow Cr$; $\quad \Delta G_3^\circ = -2 \times (-0.91) \times F \ldots$ (ii)

On substracting (ii) from (i)

$Cr^{3+} + e \longrightarrow Cr^{2+}$; $\quad \Delta G_1^\circ = \Delta G_2^\circ - \Delta G_3^\circ$

$\Delta G_1^\circ = +2.22F - 1.82F$

$\therefore -1 \times E_1^\circ F = -0.4F$

$E_1^\circ = -0.4V$

Thus S is (2)