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Redox Reactions and Electrochemistry

TOPIC 1

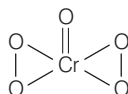
Redox Reactions

- 01** The oxidation state of Cr in CrO_5 is
[NEET (Odisha) 2019]

(a) -6 (b) +12
(c) +6 (d) +4

Ans. (c)

The structure of CrO_5 is



Oxidation state of Cr is +6 due to the presence of two peroxide linkages, which can be calculated as.

In $\text{CrO}(\text{O}_2)_2$, let the oxidation state of Cr be x

$$x + (-1)4 + (-2) = 0$$

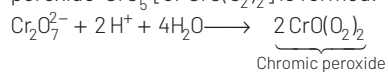
$$x - 6 = 0 \Rightarrow x = +6$$

- 02** In acidic medium, H_2O_2 changes $\text{Cr}_2\text{O}_7^{2-}$ to CrO_5 which has two $(-\text{O}-\text{O}-)$ bonds. Oxidation state of Cr in CrO_5 is
[CBSE AIPMT 2014]

(a) +5 (b) +3 (c) +6 (d) -10

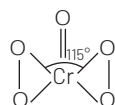
Ans. (c)

When H_2O_2 is added to an acidified solution of a dichromate $\text{Cr}_2\text{O}_7^{2-}$, a deep blue coloured complex, chromic peroxide CrO_5 [or $\text{CrO}(\text{O}_2)_2$] is formed.



[blue coloured complex]

This deep blue coloured complex has the following structure



Oxidation state of Cr in CrO_5 is +6 due to the presence of two peroxide linkages which can be calculated as

$$\begin{matrix} x & + & (-1) \times 4 & + & 1 \times (-2) \\ \text{[For Cr]} & & \text{[For O-O]} & & \text{[For O]} \end{matrix}$$

$$x - 6 = 0; \quad x = +6$$

- 03** Oxidation state of Fe in Fe_3O_4 is
[CBSE AIPMT 1999]

(a) $\frac{3}{2}$ (b) $\frac{4}{5}$ (c) $\frac{5}{4}$ (d) $\frac{8}{3}$

Ans. (d)

Oxidation state of Fe in Fe_3O_4 is calculated as

$$\begin{matrix} x & -2 \\ \text{Fe}_3 & \text{O}_4 \end{matrix}$$

$$3x + (-2 \times 4) = 0$$

$$3x = +8$$

$$x = +\frac{8}{3}$$

- 04** The oxidation state of Cr in $\text{K}_2\text{Cr}_2\text{O}_7$ is
[CBSE AIPMT 1988]

(a) +5 (b) +3 (c) +6 (d) +7

Ans. (c)

Let the oxidation state of Cr is x

$$\text{K}_2\text{Cr}_2\text{O}_7$$

$$\therefore 2(+1) + 2x + 7(-2) = 0$$

$$2 + 2x - 14 = 0$$

$$2x - 12 = 0$$

$$2x = 12$$

$$x = \frac{12}{2} = +6$$

TOPIC 2

Electrolytic Conductance, Electrolysis and Its Quantitative Aspect

- 05** The molar conductance of NaCl, HCl and CH_3COONa at infinite dilution are 126.45, 426.16 and 91.0 $\text{S cm}^2 \text{mol}^{-1}$ respectively. The molar conductance of CH_3COOH at infinite dilution is

Choose the right option for your answer. [NEET 2021]

(a) 201.28 $\text{S cm}^2 \text{mol}^{-1}$
(b) 390.71 $\text{S cm}^2 \text{mol}^{-1}$
(c) 698.28 $\text{S cm}^2 \text{mol}^{-1}$
(d) 540.48 $\text{S cm}^2 \text{mol}^{-1}$

Ans. (b)

Molar conductance of NaCl,

$$\lambda_{\text{NaCl}}^\circ = 126.45 \text{ S cm}^2 \text{mol}^{-1}$$

Molar conductance of HCl,

$$\lambda_{\text{HCl}}^\circ = 426.16 \text{ S cm}^2 \text{mol}^{-1}$$

Molar conductance of CH_3COONa ,

$$\lambda_{\text{CH}_3\text{COONa}}^\circ = 91.0 \text{ S cm}^2 \text{mol}^{-1}$$

According to Kohlrausch's law;

$$\lambda_{\text{HCl}}^\circ = \lambda_{\text{H}^+}^\circ + \lambda_{\text{Cl}^-}^\circ \quad \dots(\text{i})$$

$$\lambda_{\text{NaCl}}^\circ = \lambda_{\text{Na}^+}^\circ + \lambda_{\text{Cl}^-}^\circ \quad \dots(\text{ii})$$

$$\lambda_{\text{CH}_3\text{COONa}}^\circ = \lambda_{\text{Na}^+}^\circ + \lambda_{\text{CH}_3\text{COO}^-}^\circ \quad \dots(\text{iii})$$

$$\lambda_{\text{CH}_3\text{COOH}}^\circ = \lambda_{\text{CH}_3\text{COO}^-}^\circ + \lambda_{\text{H}^+}^\circ$$

$$\lambda_{\text{CH}_3\text{COOH}}^\circ = (\lambda_{\text{CH}_3\text{COO}^-}^\circ + \lambda_{\text{Na}^+}^\circ)$$

$$+ (\lambda_{\text{H}^+}^\circ + \lambda_{\text{Cl}^-}^\circ) - (\lambda_{\text{Na}^+}^\circ + \lambda_{\text{Cl}^-}^\circ)$$

$$\lambda_{\text{CH}_3\text{COOH}}^\circ = \lambda_{\text{CH}_3\text{COO}^-}^\circ + \lambda_{\text{HCl}}^\circ - \lambda_{\text{NaCl}}^\circ$$

$$\lambda_{\text{CH}_3\text{COOH}}^\circ = 91.0 + 426.16 - 126.45$$

$$\lambda_{\text{CH}_3\text{COO}^-}^\circ = 390.71 \text{ S cm}^2 \text{ mol}^{-1}$$

- 06** The molar conductivity of 0.007 M acetic acid is $20 \text{ S cm}^2 \text{ mol}^{-1}$. What is the dissociation constant of acetic acid? Choose the correct option.

$$[\lambda_{\text{H}^+}^\circ = 350 \text{ S cm}^2 \text{ mol}^{-1}, \lambda_{\text{CH}_3\text{COO}^-}^\circ = 50 \text{ S cm}^2 \text{ mol}^{-1}]$$

[NEET 2021]

- (a) $1.75 \times 10^{-4} \text{ mol}^{-1} \text{ L}^{-1}$
 (b) $2.50 \times 10^{-4} \text{ mol}^{-1} \text{ L}^{-1}$
 (c) $1.75 \times 10^{-5} \text{ mol}^{-1} \text{ L}^{-1}$
 (d) $2.50 \times 10^{-5} \text{ mol}^{-1} \text{ L}^{-1}$

Ans. (c)

$$\lambda_{\text{CH}_3\text{COOH}}^\circ = 20 \text{ S cm}^2 \text{ mol}^{-1}$$

Concentration of CH_3COOH , $C = 0.007 \text{ M}$

$$\lambda_{\text{H}^+}^\circ = 350 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\lambda_{\text{CH}_3\text{COO}^-}^\circ = 50 \text{ S cm}^2 \text{ mol}^{-1}$$

According to Kohlrausch's law,

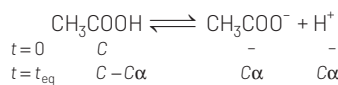
$$\lambda_{\text{CH}_3\text{COOH}}^\circ = \lambda_{\text{H}^+}^\circ + \lambda_{\text{CH}_3\text{COO}^-}^\circ$$

$$\lambda_{\text{CH}_3\text{COOH}}^\circ = 350 + 50 = 400 \text{ S cm}^2 \text{ mol}^{-1}$$

Degree of dissociation,

$$\alpha = \frac{\lambda_{\text{CH}_3\text{COOH}}^\circ}{\lambda_{\text{CH}_3\text{COO}^-}^\circ}$$

$$\alpha = \frac{20}{400} = \frac{1}{20} = 0.05 = 5 \times 10^{-2}$$



Equilibrium constant,

$$k = \frac{C^2 \alpha^2}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

$$\text{As } \alpha \ll 1; 1-\alpha \approx 1$$

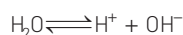
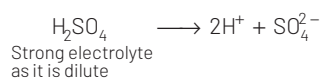
$$k = C\alpha^2 = 0.007 \times (0.05)^2 = 0.007 \times 25 \times 10^{-4} = 1.75 \times 10^{-5} \text{ mol L}^{-1}$$

- 07** On electrolysis of dilute sulphuric acid using platinum (Pt) electrode, the product obtained at anode will be **[NEET (Sep.) 2020]**

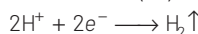
- (a) oxygen gas (b) H_2S gas
 (c) SO_2 gas (d) hydrogen gas

Ans. (a)

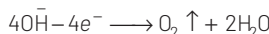
Dilute H_2SO_4 contains H_2SO_4 and H_2O and they show electrolytic dissociation as,



Reaction at cathode (Pt)



Reaction at anode (Pt)

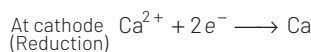
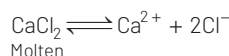


We get, O_2 gas at anode.

- 08** The number of Faradays (F) required to produce 20 g of calcium from molten CaCl_2 (Atomic mass of $\text{Ca} = 40 \text{ g mol}^{-1}$) is **[NEET (Sep.) 2020]**

- (a) 2 (b) 3 (c) 4 (d) 1

Ans. (d)



According to Faraday's first law,

Charge passed in Faraday = Gram equivalent of product

$$= \frac{\text{Given mass}}{\text{Atomic mass}} \times \text{no. of } \text{e}^- \text{ released}$$

$$= \frac{20}{40} \times 2 = 1 \text{ F}$$

So, one Faraday (F) is required for the process.

- 09** Which of the following reactions are disproportionation reaction?

- (i) $2\text{Cu}^+ \longrightarrow \text{Cu}^{2+} + \text{Cu}^0$
 (ii) $3\text{MnO}_4^{2-} + 4\text{H}^+ \longrightarrow 2\text{MnO}_4^- + \text{MnO}_2 + 2\text{H}_2\text{O}$
 (iii) $2\text{KMnO}_4 \xrightarrow{\Delta} \text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2$
 (iv) $2\text{MnO}_4^- + 3\text{Mn}^{2+} + 2\text{H}_2\text{O} \longrightarrow 5\text{MnO}_2 + 4\text{H}^+$

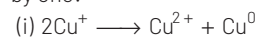
Select the correct option from the following. **[NEET (National) 2019]**

- (a) (i), (ii) and (iii)
 (b) (i), (iii) and (iv)
 (c) (i) and (iv) only
 (d) (i) and (ii) only

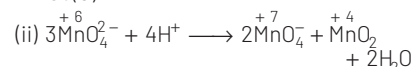
Ans. (d)

The reaction in which the same species is simultaneously oxidised and reduced are called disproportionation reactions.

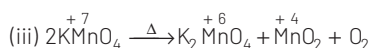
Let us, consider the given reaction one by one:



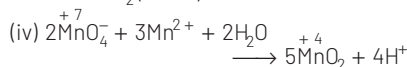
The above reaction is a disproportionation reaction as $\text{Cu}(+1)$ is oxidised to $\text{Cu}(+2)$ and reduced to $\text{Cu}(0)$.



The above reaction is a disproportionation reaction as $\text{Mn}(+6)$ is oxidised to $\text{MnO}_4^- (\text{Mn}^{+7})$ and reduced to $\text{MnO}_2 (\text{Mn}^{+4})$.



The above reaction is not a disproportionation reaction as $\text{Mn}(+7)$ is only reduced to $\text{K}_2\text{MnO}_4 (\text{Mn}^{+6})$ and $\text{MnO}_2 (\text{Mn}^{+4})$.



The above reaction is not a disproportionation reaction as $\text{Mn}(+7)$ is only reduced to $\text{MnO}_2 (+4)$. Hence, option (d) is correct.

- 10** Following limiting molar conductivities are given as

$$\lambda_{\text{m}}^\circ (\text{H}_2\text{SO}_4) = x \text{ S cm}^2 \text{ mol}^{-1}$$

$$\lambda_{\text{m}}^\circ (\text{K}_2\text{SO}_4) = y \text{ S cm}^2 \text{ mol}^{-1}$$

$$\lambda_{\text{m}}^\circ (\text{CH}_3\text{COOK}) = z \text{ S cm}^2 \text{ mol}^{-1}$$

$$\lambda_{\text{m}}^\circ (\text{in S cm}^2 \text{ mol}^{-1}) \text{ for } \text{CH}_3\text{COOH}$$

will be

[NEET (Odisha) 2019]

- (a) $x - y + 2z$ (b) $x + y - z$
 (c) $x - y + z$ (d) $\frac{(x-y)}{2} + z$

Ans. (d)

Key Idea According to Kohlrausch's law,

$$\lambda_{\text{m}}^\circ \text{ for } \text{A}_x\text{B}_y = x\lambda_{(\text{A})^{y+}}^\circ + y\lambda_{(\text{B})^{x-}}^\circ$$

where, λ_{m}° = limiting molar conductivity of electrolyte and $\lambda_{(\text{A})^{y+}}^\circ$ and $\lambda_{(\text{B})^{x-}}^\circ$ are the limiting molar conductivities of cation (A^{y+}) and anion (B^{x-}), respectively.

Given

$$\lambda_{\text{m}}^\circ (\text{H}_2\text{SO}_4) = 2\lambda_{\text{H}^+}^\circ + \lambda_{\text{SO}_4^{2-}}^\circ = x \text{ S cm}^2 \text{ mol}^{-1} \dots (i)$$

$$\lambda_{\text{m}}^\circ (\text{K}_2\text{SO}_4) = 2\lambda_{\text{K}^+}^\circ + \lambda_{\text{SO}_4^{2-}}^\circ = y \text{ S cm}^2 \text{ mol}^{-1} \dots (ii)$$

$$\lambda_{\text{m}}^\circ (\text{CH}_3\text{COOK}) = \lambda_{\text{CH}_3\text{COO}^-}^\circ + \lambda_{\text{K}^+}^\circ = z \text{ S cm}^2 \text{ mol}^{-1} \dots (iii)$$

To find : $\lambda_{\text{m}}^\circ (\text{CH}_3\text{COOH}) = \lambda_{\text{CH}_3\text{COO}^-}^\circ + \lambda_{\text{H}^+}^\circ$
 The above equation can be obtained by

$$\text{Eq. (iii)} + \frac{\text{Eq. (i)}}{2} - \frac{\text{Eq. (ii)}}{2}$$

$$\begin{aligned}\therefore \lambda_{m(\text{CH}_3\text{COOH})}^{\circ} &= \lambda_{m(\text{CH}_3\text{COOK})}^{\circ} + \frac{\lambda_{m(\text{H}_2\text{SO}_4)}^{\circ}}{2} \\ &\quad - \frac{\lambda_{m(\text{K}_2\text{SO}_4)}^{\circ}}{2} \\ &= \left(z + \frac{x}{2} - \frac{y}{2} \right) \text{S cm}^2 \text{ mol}^{-1} \\ &= \left(\frac{x-y}{2} + z \right) \text{S cm}^2 \text{ mol}^{-1}\end{aligned}$$

- 11** The molar conductivity of a 0.5 mol/dm³ solution of AgNO₃ with electrolytic conductivity of 5.76 × 10⁻³ S cm⁻¹ at 298 K is
[CBSE AIPMT 2016, Phase II]

- (a) 2.88 S cm²/mol
(b) 11.52 S cm²/mol
(c) 0.086 S cm²/mol
(d) 28.8 S cm²/mol

Ans. (b)

Key Idea The relation between molar conductivity (λ_m) and electrolytic conductivity (κ) is given as

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

where, M is molarity of solution.

Given, concentration of solution,

$$M = 0.5 \text{ mol / dm}^3$$

Electrolytic conductivity,

$$\kappa = 5.76 \times 10^{-3} \text{ S cm}^{-1}$$

Temperature, $T = 298 \text{ K}$

\therefore Molar conductivity,

$$\begin{aligned}\lambda_m &= \frac{\kappa \times 1000}{M} \\ &= \frac{5.76 \times 10^{-3} \times 1000}{0.5} \\ &= 11.52 \text{ S cm}^2/\text{mol}\end{aligned}$$

- 12** During the electrolysis of molten sodium chloride, the time required to produce 0.10 mol of chlorine gas using a current of 3 amperes is
[CBSE AIPMT 2016, Phase II]

- (a) 55 minutes (b) 110 minutes
(c) 220 minutes (d) 330 minutes

Ans. (b)

Key Idea This problem is based on Faraday's first law of electrolysis which states that when an electric current is passed through an electrolytic solution, the amount of substance (w), deposited at the electrode, is proportional to the electric charge (q) passed through the electrolytic solution.

The formula used in the problem is

$$w = \frac{Eit}{96500} \quad \dots(i)$$

where, E = gram-equivalent mass of Cl^-

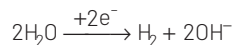
i = current, t = time, $it = q$

Given, $w = 0.10 \text{ mol} = (0.10 \times 71) \text{ g}$,

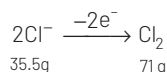
$i = 3 \text{ A}$, $E = 35.5$

The following reactions occurred,

At cathode :



At anode :



Putting all values in expression (i) we get

$$(0.10 \times 71) = \frac{35.5}{96500} \times 3 \times t$$

or $t = 6433 \text{ s}$

or $t = 107.22 \text{ min}$

$$\approx 110 \text{ min} \quad \left[1 \text{ s} = \frac{1}{60} \text{ min} \right]$$

- 13** The number of electrons delivered at the cathode during electrolysis by a current of 1 ampere in 60 seconds is (charge on electron = $1.60 \times 10^{-19} \text{ C}$)
[CBSE AIPMT 2016, Phase II]

- (a) 6×10^{23} (b) 6×10^{20}
(c) 3.75×10^{20} (d) 7.48×10^{23}

Ans. (c)

From Faraday's first law of electrolysis,

$$\frac{w}{E} = \frac{it}{96500} \quad \dots(i)$$

Given, $i = 1 \text{ A}$; $t = 60 \text{ s}$

Putting these values in Eq. (i), we get

$$\frac{w}{E} = \frac{1 \times 60}{96500}$$

$$\text{or } \frac{w}{E} = \frac{6}{9650}$$

= Number of mole of electrons

\therefore Number of electrons

$$\begin{aligned}&= \frac{6}{9650} \times 6.022 \times 10^{23} \\ &= 3.75 \times 10^{20}\end{aligned}$$

- 14** Aqueous solution of which of the following compounds is the best conductor of electric current?
[CBSE AIPMT 2015]

- (a) Acetic acid, $\text{C}_2\text{H}_4\text{O}_2$
(b) Hydrochloric acid, HCl
(c) Ammonia, NH_3
(d) Fructose, $\text{C}_6\text{H}_{12}\text{O}_6$

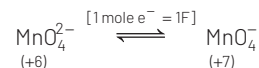
Ans. (b)

Since, HCl is strong acid and dissociates completely. Hence, it conducts electricity best in its aqueous solution.

- 15** When 0.1 mole of MnO_4^{2-} is oxidised, the quantity of electricity required to completely oxidise MnO_4^{2-} to MnO_4^- is
[CBSE AIPMT 2014]

- (a) 96500 C (b) $2 \times 96500 \text{ C}$
(c) 9650 C (d) 96.50 C

Ans. (c)



As per the equation, for 1 mole of MnO_4^{2-} , 1 F of electricity is required. Thus, for 0.1 mole of MnO_4^{2-} , 0.1 F of electricity is required.

Since, $1 \text{ F} = 96500 \text{ C}$

$\therefore 0.1 \text{ F} = 0.1 \times 96500 \text{ C} = 9650 \text{ C}$

Hence, 9650 C of electricity is required to completely oxidise MnO_4^{2-} to MnO_4^- .

- 16** The weight of silver (at. wt. = 108) displaced by a quantity of electricity which displaces 5600 mL of O_2 at STP will be
[CBSE AIPMT 2014]

- (a) 5.4 g (b) 10.8 g
(c) 54.0 g (d) 108.0 g

Ans. (d)

Since, 22400 mL volume is occupied by 1 mole of O_2 at STP.

Thus, 5600 mL O_2 means

$$= \frac{5600}{22400} \text{ mol } \text{O}_2 = \frac{1}{4} \text{ mol } \text{O}_2$$

$$\therefore \text{Weight of } \text{O}_2 = \frac{1}{4} \times 32 = 8 \text{ g}$$

According to problem,

Equivalents of Ag = Equivalents of O_2

$$= \frac{\text{Weight of Ag}}{\text{Equivalent weight of Ag}}$$

$$= \frac{W_{\text{O}_2}}{\text{Equivalent weight of } \text{O}_2}$$

$$\frac{W_{\text{Ag}}}{M_{\text{Ag}}} = \frac{W_{\text{O}_2}}{M_{\text{O}_2}}$$

1 4

$$\therefore \frac{W_{\text{Ag}}}{108} \times 1 = \frac{8}{32} \times 4$$

$$\Rightarrow \frac{W_{\text{Ag}}}{108} = 1 \quad [\because 2\text{H}_2\text{O} \longrightarrow \text{O}_2 + 4\text{H}^+ + 4e^-]$$

- 17** At 25°C molar conductance of 0.1 molar aqueous solution of ammonium hydroxide is $9.54 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ and at infinite dilution its molar conductance is

$238 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. The degree of ionisation of ammonium hydroxide at the same concentration and temperature is [NEET 2013]

- (a) 2.080 % (b) 20.800 %
(c) 4.008 % (d) 40.800 %

Ans. (c)

Given, molar conductance at 0.1 M concentration,

$$\lambda_c = 9.54 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$$

Molar conductance at infinite dilution,

$$\lambda_c^\infty = 238 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$$

We know that, degree of ionisation,

$$\alpha = \frac{\lambda_c}{\lambda_c^\infty} \times 100$$

$$= \frac{9.54}{238} \times 100 = 4.008\%$$

18 Limiting molar conductivity of NH_4OH

(i.e. $\Lambda_m(\text{NH}_4\text{OH})$) is equal to

[CBSE AIPMT 2012]

- (a) $\Lambda_m^\circ(\text{NH}_4\text{Cl}) + \Lambda_m^\circ(\text{NaCl}) - \Lambda_m^\circ(\text{NaOH})$
(b) $\Lambda_m^\circ(\text{NaOH}) + \Lambda_m^\circ(\text{NaCl}) - \Lambda_m^\circ(\text{NH}_4\text{Cl})$
(c) $\Lambda_m^\circ(\text{NH}_4\text{OH}) + \Lambda_m^\circ(\text{NH}_4\text{Cl}) - \Lambda_m^\circ(\text{HCl})$
(d) $\Lambda_m^\circ(\text{NH}_4\text{Cl}) + \Lambda_m^\circ(\text{NaOH}) - \Lambda_m^\circ(\text{NaCl})$

Ans. (d)

According to Kohlrausch's law, limiting molar conductivity of NH_4OH

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

19 An increase in equivalent conductance of a strong electrolyte with dilution is mainly due to [CBSE AIPMT 2010]

- (a) increase in ionic mobility of ions
(b) 100% ionisation of electrolyte at normal dilution
(c) increase in both, i.e. number of ions and ionic mobility of ions
(d) increase in number of ions

Ans. (a)

Key Idea $\lambda_{eq} = \kappa \times V = \frac{\kappa \times 1000}{\text{Normality}}$

On dilution, the number of current carrying particles per cm^3 decreases but the volume of solution increases.

Consequently, the ionic mobility increases, which in turn increases the equivalent conductance of strong electrolyte.

20 The equivalent conductance of $\frac{M}{32}$

solution of a weak monobasic acid is 8.0 mho cm^2 and at infinite dilution is 400 mho cm^2 . The dissociation constant of this acid is [CBSE AIPMT 2009]

- (a) 1.25×10^{-5} (b) 1.25×10^{-6}
(c) 6.25×10^{-4} (d) 1.25×10^{-4}

Ans. (a)

Degree of dissociation, $\alpha = \frac{\Lambda_c}{\Lambda^\infty}$

where, Λ_c and Λ^∞ are equivalent conductances at a given concentration and at infinite dilution respectively.

$$\Rightarrow \alpha = \frac{8.0}{400} = 2 \times 10^{-2}$$

From Ostwald's dilution law (for weak monobasic acid),

$$K_c = \frac{C\alpha^2}{(1-\alpha)}$$

or
$$= C\alpha^2 \quad (\because 1 \gg \alpha)$$

$$= \frac{1}{32} (2 \times 10^{-2})^2$$

$$= 1.25 \times 10^{-5}$$

21 Al_2O_3 is reduced by electrolysis at low potentials and high currents. If $4.0 \times 10^4 \text{ A}$ of current is passed through molten Al_2O_3 for 6 h, what mass of aluminium is produced? (Assume 100% current efficiency, atomic mass of $\text{Al} = 27 \text{ g mol}^{-1}$) [CBSE AIPMT 2009]

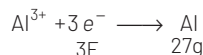
- (a) $9.0 \times 10^3 \text{ g}$ (b) $8.1 \times 10^4 \text{ g}$
(c) $2.4 \times 10^5 \text{ g}$ (d) $1.3 \times 10^4 \text{ g}$

Ans. (b)

Al_2O_3 ionises as,



At cathode



\therefore Mass of aluminium deposited by 3 F of electricity = 27 g

\therefore Mass of aluminium deposited by

$$4.0 \times 10^4 \times 6 \times 3600 \text{ C of electricity}$$

$$= \frac{27 \times 4.0 \times 10^4 \times 6 \times 3600}{3F} \text{ g}$$

$$= \frac{27 \times 4.0 \times 10^4 \times 6 \times 3600}{3 \times 96500} \text{ g}$$

$$= 8.1 \times 10^4 \text{ g}$$

22 Kohlrausch's law states that at [CBSE AIPMT 2008]

- (a) infinite dilution, each ion makes definite contribution to equivalent conductance of an electrolyte, whatever be the nature of the other ion of the electrolyte
(b) infinite dilution, each ion makes definite contribution to equivalent conductance of an electrolyte depending on the nature of the other ion of the electrolyte
(c) infinite dilution, each ion makes definite contribution to conductance of an electrolyte, whatever be the nature of the other ion of the electrolyte
(d) infinite dilution, each ion makes definite contribution to equivalent conductance of an electrolyte, whatever be the nature of the other ion of the electrolyte

Ans. (d)

Kohlrausch's law states that "the equivalent conductance of an electrolyte at infinite dilution is equal to the sum of the equivalent conductances of the component ions."

$$\lambda_\infty = \lambda_a + \lambda_c$$

where, λ_a = equivalent conductance of the anion

λ_c = equivalent conductance of the cation

Each ion has the same constant ionic conductance at a fixed temperature, no matter of which electrolyte it forms a part.

23 4.5 g of aluminium (atomic mass 27u) is deposited at cathode from Al^{3+} solution by a certain quantity of electric charge. The volume of hydrogen produced at STP from H^+ ions in solution by the same quantity of electric charge will be [CBSE AIPMT 2005]

- (a) 44.8 L (b) 22.4 L (c) 11.2 L (d) 5.6 L

Ans. (d)

From second law of Faraday

$$\frac{m_{\text{Al}}}{m_{\text{H}}} = \frac{E_{\text{Al}}}{E_{\text{H}}}$$

$$\frac{4.5}{m_{\text{H}}} = \frac{27/3}{1}$$

or $m_{\text{H}} = 0.5 \text{ g}$

\therefore Volume of 2 g H_2 at STP = 22.4 L

\therefore Volume of 0.5 g H_2 at STP

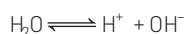
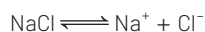
$$= \frac{22.4 \times 0.5}{2} \text{ L} = 5.6 \text{ L}$$

24 In electrolysis of NaCl when Pt electrode is taken then H_2 is liberated at cathode while with Hg cathode it forms sodium amalgam because [CBSE AIPMT 2002]

- (a) Hg is more inert than Pt
(b) more voltage is required to reduce H^+ at Hg than at Pt
(c) Na is dissolved in Hg while it does not dissolved in Pt
(d) concentration of H^+ ions is larger when Pt electrode is taken

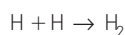
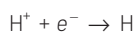
Ans. (b)

Sodium chloride in water dissociates as

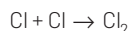
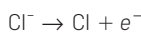


When electric current is passed through this solution using platinum electrodes, Na^+ and H^+ move towards cathode whereas Cl^- and OH^- ions move towards anode.

At cathode



At anode



If mercury is used as cathode, H^+ ions are not discharged at mercury cathode because mercury has a high hydrogen over voltage. Na^+ ions are discharged at cathode in preference of H^+ ions yielding sodium, which dissolves in mercury to form sodium amalgam.

25 Cell reaction is spontaneous when [CBSE AIPMT 2000]

- (a) E_{red}° is negative (b) E_{red}° is positive
(c) ΔG° is negative (d) ΔG° is positive

Ans. (c)

When the value of ΔG° is negative, the cell reaction is spontaneous.

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

where, n = number of electrons take part

F = Faraday constant

E° = EMF of the cell

Thus, for a spontaneous reaction, the EMF of the cell must be positive.

26 The equivalent conductances of Ba^{2+} and Cl^- are 127 and $76 \Omega^{-1} \text{ cm}^{-1} \text{ eq}^{-1}$ respectively at infinite dilution. The equivalent conductance of $BaCl_2$ at infinite dilution will be [CBSE AIPMT 2000]
(a) 139.52 (b) 203 (c) 279 (d) 101.5

Ans. (a)

The equivalent conductance of $BaCl_2$ at infinite dilution,

$$\begin{aligned}\lambda_\infty \text{ of } BaCl_2 &= \frac{1}{2} \lambda_\infty \text{ of } Ba^{2+} + \lambda_\infty \text{ of } Cl^- \\ &= \frac{127}{2} + 76 = 139.5\end{aligned}$$

27 The specific conductance of a 0.1 N KCl solution at 23°C is $0.012 \Omega^{-1} \text{ cm}^{-1}$. The resistance of cell containing the solution at the same temperature was found to be 55Ω . The cell constant will be [CBSE AIPMT 1999]

- (a) 0.142 cm^{-1}
(b) 0.66 cm^{-1}
(c) 0.918 cm^{-1}
(d) 1.12 cm^{-1}

Ans. (b)

Specific conductivity,

$$k = 0.012 \Omega^{-1} \text{ cm}^{-1};$$

Resistance = 55Ω

$$k = \frac{1}{\text{resistance}} \times \frac{l}{a} \left[G = \frac{1}{R} \right]$$

$$\frac{l}{a} = \text{cell constant}$$

$$\frac{l}{a} = 55 \times 0.012 = 0.66 \text{ cm}^{-1}$$

28 Equivalent conductance of NaCl, HCl and C_2H_5COONa at infinite dilution are 126.45, 426.16 and $91 \Omega^{-1} \text{ cm}^2$, respectively. The equivalent conductance of C_2H_5COOH is [CBSE AIPMT 1997]

- (a) $201.28 \Omega^{-1} \text{ cm}^2$
(b) $390.71 \Omega^{-1} \text{ cm}^2$
(c) $698.28 \Omega^{-1} \text{ cm}^2$
(d) $540.48 \Omega^{-1} \text{ cm}^2$

Ans. (b)

By Kohlrausch's law

$$\lambda_\infty \text{ for NaCl} = \lambda_{Na^+} + \lambda_{Cl^-} \quad \dots(i)$$

$$\lambda_\infty \text{ for HCl} = \lambda_{H^+} + \lambda_{Cl^-} \quad \dots(ii)$$

$$\lambda_\infty \text{ for } C_2H_5COONa = \lambda_{Na^+} + \lambda_{C_2H_5COO^-} \quad \dots(iii)$$

So, λ_∞ for C_2H_5COOH can be obtained by adding Eqs. (ii) and (iii) and then subtracting Eq. (i)

$$\begin{aligned}&= \lambda_\infty \text{ of } C_2H_5COONa + \lambda_\infty \text{ of HCl} \\ &\quad - \lambda_\infty \text{ for NaCl} \\ &= (91 + 426.16 - 126.45) \Omega^{-1} \text{ cm}^2 \\ &= 390.71 \Omega^{-1} \text{ cm}^2\end{aligned}$$

29 A 5A current is passed through a solution of zinc sulphate for 40 min. The amount of zinc deposited at the cathode is

[CBSE AIPMT 1996]

- (a) 40.65 g (b) 0.4065 g
(c) 4.065 g (d) 65.04 g

Ans. (c)

Current, $I = 5 \text{ A}$

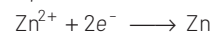
time, $t = 40 \text{ min} = 40 \times 60 = 2400 \text{ s}$

Amount of electricity passed

$$Q = It$$

$$Q = 5 \times 2400$$

$$Q = 12000 \text{ C.}$$



$$n = 2e^-$$

From Faraday first law

$$W = ZIt$$

Z = equivalent mass

[65.39 = mass of zinc]

$$= \frac{\text{Mass}}{e^- \times F} = \frac{65.39}{2 \times 96500} \text{ g of zinc}$$

therefore, 12000 C charge will deposit

$$= \frac{65.39 \times 12000}{2 \times 96500}$$

$$= 4.065 \text{ g of zinc}$$

TOPIC 3

Electronium Series, Electrode Potential and Emf

30 Identify the reaction from following having top position in EMF series (Standard reduction potential) according to their electrode potential at 298 K.

[NEET (Oct.) 2020]

- (a) $Mg^{2+} + 2e^- \longrightarrow Mg(s)$
(b) $Fe^{2+} + 2e^- \longrightarrow Fe(s)$
(c) $Au^{3+} + 2e^- \longrightarrow Au(s)$
(d) $K^+ + 1e^- \longrightarrow K(s)$

Ans. (c)

Let us consider the segment of EMF series (standard reduction potential) of the given reduction half-cell reactions:

Reduction half reaction	E/V at 298K
(a) $Mg^{2+} + 2e^- \longrightarrow Mg$	- 2.36
(b) $Fe^{2+} + 2e^- \longrightarrow Fe$	- 0.44
(c) $Au^{3+} + 3e^- \longrightarrow Au$	+ 1.40
(d) $K^+ + e^- \longrightarrow K$	- 2.93

Hence, option (c) is correct.

- 31** The standard electrode potential (E^\ominus) values of Al^{3+}/Al , Ag^+/Ag , K^+/K and Cr^{3+}/Cr are -1.66 V , 0.80 V , 2.93 V and -0.74 V , respectively. The correct decreasing order of reducing power of the metal is
[NEET (Odisha) 2019]

- (a) $\text{Ag} > \text{Cr} > \text{Al} > \text{K}$
(b) $\text{K} > \text{Al} > \text{Cr} > \text{Ag}$
(c) $\text{K} > \text{Al} > \text{Ag} > \text{Cr}$
(d) $\text{Al} > \text{K} > \text{Ag} > \text{Cr}$

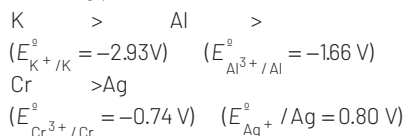
Ans. (b)

More negative the value of standard reduction potential, higher is the reduction power.

i.e. Reducing power

$$\propto \frac{1}{\text{standard reduction potential}}$$

Thus, the correct decreasing order of reducing power of the metal is



- 32** For the cell reaction,
 $2\text{Fe}^{3+}(\text{aq}) + 2\text{I}^-(\text{aq}) \longrightarrow 2\text{Fe}^{2+}(\text{aq}) + \text{I}_2(\text{aq})$
 $E_{\text{cell}}^\ominus = 0.24\text{ V}$ at 298 K . The standard Gibbs energy ($\Delta_r G^\ominus$) of the cell reaction is
[Given that Faraday constant $F = 96500\text{ C mol}^{-1}$]
[NEET (National) 2019]

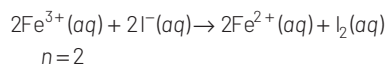
- (a) $-23.16\text{ kJ mol}^{-1}$ (b) 46.32 kJ mol^{-1}
(c) 23.16 kJ mol^{-1} (d) $-46.32\text{ kJ mol}^{-1}$

Ans. (d)

The relation between E_{cell}^\ominus and $\Delta_r G^\ominus$ is as follows:

$$\Delta_r G^\ominus = -nFE_{\text{cell}}^\ominus$$

For the cell reaction,



Given, $F = 96500\text{ C mol}^{-1}$, $E_{\text{cell}}^\ominus = 0.24\text{ V}$

Now, we know that $\Delta_r G^\ominus = -nFE_{\text{cell}}^\ominus$

On substituting the given values in above equation we get

$$\begin{aligned} \Delta_r G^\ominus &= -2\text{ mol} \times 96500\text{ C mol}^{-1} \times 0.24\text{ J mol}^{-1} \\ &= -46320\text{ J mol}^{-1} \\ &= -46.32\text{ kJ mol}^{-1} \end{aligned}$$

Hence, option (d) is correct.

- 33** In the electrochemical cell $\text{Zn}|\text{ZnSO}_4(0.01\text{ M})||\text{CuSO}_4(1.0\text{ M})|\text{Cu}$, the emf of this Daniel cell is E_1 . When the concentration ZnSO_4 is changed to 1.0 M and that of CuSO_4 changed to 0.01 M , the emf changes to E_2 . From the followings, which one is the relationship between E_1 and E_2 ?
(Given, $\frac{RT}{F} = 0.059$)
[NEET 2017, 2003]

- (a) $E_1 = E_2$ (b) $E_1 < E_2$
(c) $E_1 > E_2$ (d) $E_2 = 0 \neq E_1$

Ans. (c)

Thinking process Calculate the value of E_{cell} i.e. E_1 and E_2 by substituting the respective given values in the Nernst equation,

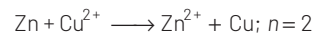
$$E_{\text{cell}} = E^\ominus - \frac{0.059}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

Compare the calculated values of E_1 and E_2 and find the correct relation.

For the electrochemical cells,



Cell reaction :



$$E_1 = E^\ominus - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

$$= E^\ominus - \frac{0.059}{2} \log \frac{0.01}{1}$$

$$E_1 = E^\ominus - \frac{0.059}{2} \log \frac{1}{100} = (E^\ominus + 0.059)$$

For cell, $\text{Zn}|\text{ZnSO}_4(1\text{ M})||\text{CuSO}_4(0.01\text{ M})|\text{Cu}$

$$E_2 = E^\ominus - \frac{0.059}{2} \log \frac{1}{0.01}$$

$$E_2 = E^\ominus - \frac{0.059}{2} \log 100$$

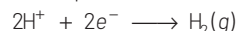
$$\therefore (E^\ominus - 0.059) \Rightarrow E_1 > E_2$$

- 34** The pressure of H_2 required to make the potential of H_2 -electrode zero in pure water at 298 K is
[CBSE AIPMT 2016, Phase I]

- (a) 10^{-12} atm (b) 10^{-10} atm
(c) 10^{-4} atm (d) 10^{-14} atm

Ans. (d)

From the question, we have an equation



According to Nernst equation,

$$E = E^\ominus - \frac{0.0591}{2} \log \frac{P_{\text{H}_2}}{[\text{H}^+]^2}$$

$$= 0 - \frac{0.0591}{2} \log \frac{P_{\text{H}_2}}{(10^{-7})^2}$$

$$[\because [\text{H}^+] = 10^{-7}]$$

\therefore For potential of H_2 electrode to be zero, P_{H_2} should be equal to $[\text{H}^+]^2$, i.e. 10^{-14} atm .

$$\therefore \log \frac{10^{-14}}{(10^{-7})^2} = 0$$

- 35** If the E_{cell}^\ominus for a given reaction has a negative value, which of the following gives correct relationships for the values of ΔG^\ominus and K_{eq} ?
[CBSE AIPMT 2016, Phase II, 2011]

- (a) $\Delta G^\ominus > 0$; $K_{\text{eq}} < 1$ (b) $\Delta G^\ominus > 0$; $K_{\text{eq}} > 1$
(c) $\Delta G^\ominus < 0$; $K_{\text{eq}} > 1$ (d) $\Delta G^\ominus < 0$; $K_{\text{eq}} < 1$

Ans. (a)

Given, $E_{\text{cell}}^\ominus = -ve$

The relation between ΔG^\ominus and E_{cell}^\ominus is given as

$$\Delta G^\ominus = -nF E_{\text{cell}}^\ominus \quad \dots (i)$$

If E_{cell}^\ominus is negative, so ΔG^\ominus comes out to be positive. Again, relation between ΔG^\ominus and K_{eq} is given as

$$\Delta G^\ominus = -2.303 nRT \log K_{\text{eq}} \quad \dots (ii)$$

From Eq. (i) we get that ΔG^\ominus is positive.

Now, if ΔG^\ominus is positive then K_{eq} comes out to be negative from eq (ii).

i.e. $\Delta G^\ominus > 1$ and $K_{\text{eq}} < 1$

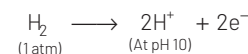
Short trick As E_{cell}^\ominus is negative so reaction is non-spontaneous or you can say reaction is moving in backward direction. For non-spontaneous reaction, ΔG^\ominus is always positive and K_{eq} is always less than 1.

- 36** A hydrogen gas electrode is made by dipping platinum wire in a solution of HCl of $\text{pH} = 10$ and by passing hydrogen gas around the platinum wire at 1 atm pressure. The oxidation potential of electrode would be
[NEET 2013]

- (a) 0.059 V (b) 0.59 V
(c) 0.118 V (d) 1.18 V

Ans. (b)

For hydrogen electrode, oxidation half reaction is



If $\text{pH} = 10$

$$[\text{H}^+] = 1 \times 10^{-\text{pH}} = 1 \times 10^{-10}$$

From Nernst equation,

$$E_{\text{cell}} = E_{\text{cell}}^\ominus - \frac{0.0591}{2} \log \frac{[\text{H}^+]^2}{P_{\text{H}_2}}$$

For hydrogen electrode, $E_{\text{cell}}^\ominus = 0$

$$E_{\text{cell}} = -\frac{0.0591}{2} \log \frac{(10^{-10})^2}{1}$$

$$= +\frac{0.0591 \times 2}{2} \log \frac{1}{10^{-10}}$$

$$= 0.0591 \log 10^{10}$$

$$= 0.0591 \times 10$$

$$= 0.591 \text{ V}$$

- 37** Standard electrode potential of three metals X, Y and Z are -1.2V, +0.5V and -3.0V respectively. The reducing power of these metals will be [CBSE AIPMT 2011]

- (a) $Y > X > Z$ (b) $Z > X > Y$
 (c) $X > Y > Z$ (d) $Y > Z > X$

Ans. (b)

$$E_X^\circ = -1.2 \text{ V},$$

$$E_Y^\circ = +0.5 \text{ V},$$

$$E_Z^\circ = -3.0 \text{ V},$$

$$\therefore Z > X > Y$$

[\therefore higher the reduction potential, lesser the reducing power.]

- 38** The electrode potentials for $\text{Cu}^{2+}(\text{aq}) + e^- \longrightarrow \text{Cu}^+(\text{aq})$ and $\text{Cu}^+(\text{aq}) + e^- \longrightarrow \text{Cu}(\text{s})$ are +0.15 V and +0.50 V respectively. The value of $E_{\text{Cu}^{2+}/\text{Cu}}^\circ$ will be [CBSE AIPMT 2011]
- (a) 0.325 V (b) 0.650 V
 (c) 0.150 V (d) 0.500 V

Ans. (a)

$$\text{Cu}^{2+} + e^- \longrightarrow \text{Cu}^+,$$

$$E_1^\circ = 0.15 \text{ V}, \Delta G_1^\circ = -n_1 E_1^\circ F$$

$$\text{Cu}^+ + e^- \longrightarrow \text{Cu}, E_2^\circ = 0.50 \text{ V},$$

$$\Delta G_2^\circ = -n_2 E_2^\circ F$$

$$\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}, E^\circ = ?,$$

$$\Delta G^\circ = -nE^\circ F$$

$$\Delta G^\circ = \Delta G_1^\circ + \Delta G_2^\circ$$

$$-nE^\circ F = -n_1 E_1^\circ F - n_2 E_2^\circ F$$

or $-2E^\circ F = -1F \times 0.15 + (-1F \times 0.50)$

or $-2E^\circ F = -0.15F - 0.50F$

or $-2FE^\circ = -F(0.15 + 0.50)$

$$\therefore E^\circ = \frac{0.65}{2} = 0.325 \text{ V}$$

- 39** Standard electrode potential for $\text{Sn}^{4+}/\text{Sn}^{2+}$ couple is +0.15 V and that for the Cr^{3+}/Cr couple is -0.74. These two couples in their standard state are connected to make a cell. The cell potential will be [CBSE AIPMT 2011]

- (a) +0.89 V (b) +0.18 V
 (c) +1.83 V (d) +1.199 V

Ans. (a)

$$E_{\text{Sn}^{4+}/\text{Sn}^{2+}}^\circ = +0.15 \text{ V}$$

$$E_{\text{Cr}^{3+}/\text{Cr}}^\circ = -0.74 \text{ V}$$

$$E_{\text{cell}}^\circ = E_{\text{cathode(RP)}}^\circ - E_{\text{anode(RP)}}^\circ$$

$$= 0.15 - (-0.74)$$

$$= +0.89 \text{ V}$$

- 40** For the reduction of silver ions with copper metal, the standard cell potential was found to be +0.46 V at 25°C. The value of standard Gibbs energy, ΔG° will be ($F = 96500 \text{ C mol}^{-1}$) [CBSE AIPMT 2010]

- (a) -89.0 kJ (b) -89.0 J
 (c) -44.5 kJ (d) -98.0 kJ

Ans. (a)

We know that, standard Gibbs energy,

$$\Delta G^\circ = -nFE_{\text{cell}}^\circ$$

For the cell reaction,

$$2\text{Ag}^+ + \text{Cu} \longrightarrow \text{Cu}^{2+} + 2\text{Ag}$$

$$\Delta E_{\text{cell}}^\circ = +0.46 \text{ V}$$

$$\Delta G^\circ = -nFE_{\text{cell}}^\circ$$

$$n = 2$$

$$\Delta G^\circ = -2 \times 96500 \times 0.46$$

$$= -88780 \text{ J}$$

$$= -88.7 \text{ kJ} \approx -89.0 \text{ kJ}$$

- 41** Given,

- (i) $\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu},$
 $E^\circ = 0.337 \text{ V}$
 (ii) $\text{Cu}^{2+} + e^- \longrightarrow \text{Cu}^+,$
 $E^\circ = 0.153 \text{ V}$

Electrode potential, E° for the reaction,

$$\text{Cu}^+ + e^- \longrightarrow \text{Cu}, \text{ will be}$$

[CBSE AIPMT 2009]

(a) 0.52 V (b) 0.90 V
 (c) 0.30 V (d) 0.38 V

Ans. (a)

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

For reaction,

$$\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}, \quad \dots (i)$$

$$\Delta G^\circ = -2 \times F \times 0.337$$

For reaction, $\text{Cu}^+ \longrightarrow \text{Cu}^{2+} + e^-, \quad \dots (ii)$

$$\Delta G^\circ = -1 \times F \times (-0.153)$$

$$= +0.153 F$$

Adding Eqs. (i) and (ii), we get

$$\text{Cu}^+ + e^- \longrightarrow \text{Cu}, \Delta G^\circ = -0.521 F$$

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

$$\therefore -0.521 F = -nFE^\circ$$

$$\therefore E^\circ = 0.52 \text{ V}$$

- 42** Standard free energies of formation (in kJ/mol) at 298 K are -237.2, -394.4 and -8.2 for $\text{H}_2\text{O}(l)$, $\text{CO}_2(g)$ and pentane (g), respectively. The value of E_{cell}° for the pentane-oxygen fuel cell is [CBSE AIPMT 2008]

- (a) 1.968 V (b) 2.0968 V
 (c) 1.0968 V (d) 0.0968 V

Ans. (c)

$$\Delta G \text{ of } \text{H}_2\text{O}(l) = -237.2 \text{ kJ/mol}$$

$$\Delta G \text{ of } \text{CO}_2(g) = -394.4 \text{ kJ/mol}$$

$$\Delta G \text{ of pentane (g)} = -8.2 \text{ kJ/mol}$$

In pentane-oxygen fuel cell following reaction takes place

$$\text{C}_5\text{H}_{12} + 10\text{H}_2\text{O}(l) \longrightarrow 5\text{CO}_2 + 32\text{H}^+ + 32e^-$$

$$8\text{O}_2 + 32\text{H}^+ + 32e^- \longrightarrow 16\text{H}_2\text{O}(l)$$

$$\text{C}_5\text{H}_{12} + 8\text{O}_2 \longrightarrow 5\text{CO}_2 + 6\text{H}_2\text{O}(l), E^\circ = ?$$

$$\Delta G_{\text{reaction}} = \Sigma \Delta G_{\text{product}} - \Sigma \Delta G_{\text{reactant}}$$

$$= 5 \times \Delta G_{(\text{CO}_2)} + 6 \Delta G_{(\text{H}_2\text{O})} - [\Delta G_{(\text{C}_5\text{H}_{12})} + 8 \times \Delta G_{\text{O}_2}]$$

$$= 5 \times (-394.4) + 6 \times (-237.2) - (-8.2 + 0)$$

$$= -1972 - 1423.2 + 8.2$$

$$= -3387 \text{ kJ/mol}$$

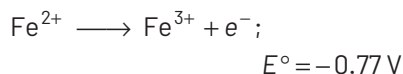
$$= -3387 \times 10^3 \text{ J/mol}$$

$$\Delta G = -nFE_{\text{cell}}^\circ$$

$$-3387 \times 10^3 = -32 \times 96500 \times E_{\text{cell}}^\circ$$

$$E_{\text{cell}}^\circ = \frac{-3387 \times 10^3}{-32 \times 96500} = 1.0968 \text{ V}$$

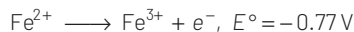
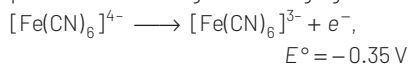
- 43** On the basis of the following E° values, the strongest oxidising agent is [CBSE AIPMT 2008]
- $$[\text{Fe}(\text{CN})_6]^{4-} \rightarrow [\text{Fe}(\text{CN})_6]^{3-} + e^-;$$
- $$E^\circ = -0.35 \text{ V}$$



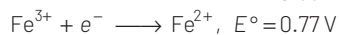
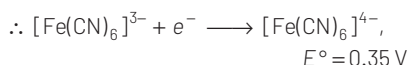
- (a) $[\text{Fe}(\text{CN})_6]^{4-}$ (b) Fe^{2+}
(c) Fe^{3+} (d) $[\text{Fe}(\text{CN})_6]^{3-}$

Ans. (c)

Substance which have higher reduction potential are stronger oxidising agent.

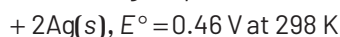
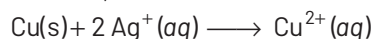


$$\therefore E^{\circ}_{\text{oxi}} = -E^{\circ}_{\text{red}}$$



Hence, Fe^{3+} has maximum tendency to reduced, so it is the strongest oxidising agent.

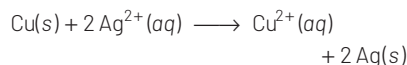
- 44** The equilibrium constant of the reaction,



is **[CBSE AIPMT 2007]**

- (a) 2.0×10^{10} (b) 4.0×10^{10}
(c) 4.0×10^{15} (d) 2.4×10^{10}

Ans. (c)



$$E^{\circ} = 0.46 \text{ V at } 298 \text{ K}$$

$$RT \ln K = nFE^{\circ}$$

$$\ln K = \frac{nFE^{\circ}}{RT}$$

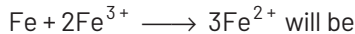
$$\ln K = \frac{2 \times 0.46}{0.0591}$$

$$K = 3.68 \times 10^{15} \approx 4 \times 10^{15}$$

- 45** $E^{\circ}_{\text{Fe}^{2+}/\text{Fe}} = -0.441 \text{ V}$ and

$$E^{\circ}_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.771 \text{ V}$$

the standard emf of the reaction

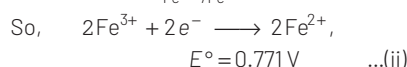
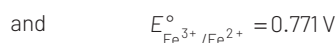
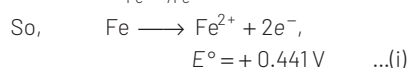


[CBSE AIPMT 2006]

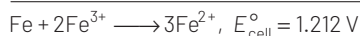
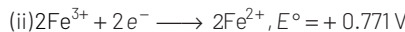
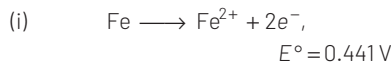
- (a) 0.111 V (b) 0.330 V
(c) 1.653 V (d) 1.212 V

Ans. (d)

$$\text{Given that } E^{\circ}_{\text{Fe}^{2+}/\text{Fe}} = -0.441 \text{ V}$$

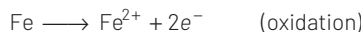


Cell reaction

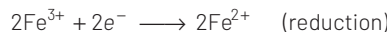


Alternative On the basis of cell reaction following half-cell reactions are written

At anode



At cathode



$$\text{So, } E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} \\ = (+0.771) - (-0.441) = +1.212 \text{ V.}$$

- 46** A hypothetical electrochemical cell is shown below



The EMF measured is + 0.20V.

The cell reaction is

[CBSE AIPMT 2006]

- (a) $\text{A} + \text{B}^{+} \rightarrow \text{A}^{+} + \text{B}$
(b) $\text{A}^{+} + \text{B} \rightarrow \text{A} + \text{B}^{+}$
(c) $\text{A}^{+} + e^{-} \rightarrow \text{A}, \text{B}^{+} + e^{-} \rightarrow \text{B}$
(d) the cell reaction cannot be predicted

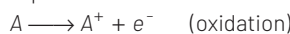
Ans. (a)

Electrochemical cell,

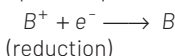


The EMF of cell is + 0.20 V. So, cell reaction is possible. The half-cell reactions are given as follows

(i) At negative pole



(ii) At positive pole



Hence, cell reaction is



- 47** The standard EMF of a galvanic cell involving cell reaction with $n=2$ is found to be 0.295 V at 25°C. The equilibrium constant of the reaction would be

$$(\text{Given } F = 96500 \text{ C mol}^{-1}, \quad R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1})$$

[CBSE AIPMT 2004]

- (a) 2.0×10^{11} (b) 4.0×10^{12}
(c) 1.0×10^2 (d) 1.0×10^{10}

Ans. (d)

By Nernst equation,

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{2.303 RT}{nF} \log_{10} K$$

At equilibrium, $E_{\text{cell}} = 0$

Given that,

$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$T = 25^{\circ} \text{C} + 273 = 298 \text{ K}$$

$$F = 96500 \text{ C and } n = 2$$

$$\therefore E^{\circ}_{\text{cell}} = \frac{2.303 \times 8.314 \times 298}{2 \times 96500} \log_{10} K \\ = \frac{0.0591}{2} \log_{10} K$$

$$\text{Given that } E^{\circ}_{\text{cell}} = 0.295 \text{ V}$$

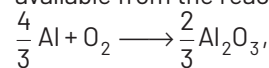
$$\therefore 0.295 = \frac{0.0591}{2} \log_{10} K$$

$$\log_{10} K = \frac{0.295 \times 2}{0.0591} = 10$$

$$\text{antilog } \log_{10} K = \text{antilog } 10$$

$$K = 1 \times 10^{10}$$

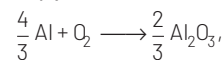
- 48** On the basis of the information available from the reaction.



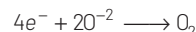
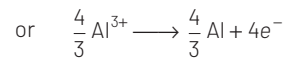
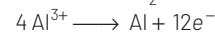
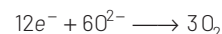
$\Delta G = -827 \text{ kJ mol}^{-1}$ of O_2 , the minimum EMF required to carry out the electrolysis of Al_2O_3 is ($F = 96500 \text{ C mol}^{-1}$) **[CBSE AIPMT 2003]**

- (a) 2.14 V (b) 4.28 V
(c) 6.42 V (d) 8.56 V

Ans. (a)



$$\Delta G = -827 \text{ kJ mol}^{-1}$$



$$\Delta G = -nEF^{\circ} \quad (n = 4)$$

$$-827 \times 10^3 \text{ J} = -4 \times E^{\circ} \times 96500$$

$$E = \frac{827 \times 10^3}{4 \times 96500}$$

$$E^{\circ} = 2.14 \text{ V}$$

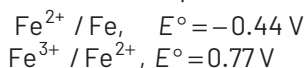
- 49** The most convenient method to protect the bottom of the ship made of iron is **[CBSE AIPMT 2001]**

- (a) coating it with red lead oxide
(b) white tin plating
(c) connecting it with Mg block
(d) connecting it with Pb block

Ans. (b)

The most convenient method to protect the bottom of ship made of iron is white tin plating which prevents the build up of barnacles.

50 Standard electrode potentials are



Fe^{2+} , Fe^{3+} and Fe block are kept together, then [CBSE AIPMT 2001]

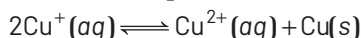
- (a) Fe^{3+} increases
 (b) Fe^{2+} decreases
 (c) $\frac{\text{Fe}^{2+}}{\text{Fe}^{3+}}$ remains unchanged
 (d) Fe^{2+} decreases

Ans. (b)

The metals have higher negative values of their electrode potential can displace metals having lower values from their salt solution.

So, Fe^{3+} decreases.

51 $\text{Cu}^+(aq)$ is unstable in solution and undergoes simultaneous oxidation and reduction according to the reaction [CBSE AIPMT 2000]



Choose the correct E° for above reaction if

$$E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.34 \text{ V}$$

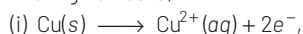
and $E^\circ_{\text{Cu}^{2+}/\text{Cu}^+} = 0.15 \text{ V}$

- (a) - 0.38 V (b) + 0.49 V (c) + 0.38 V
 (d) - 0.19 V

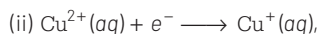
Ans. (c)

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

From given data,

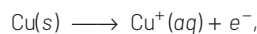


$$\Delta G_1^\circ = -2(-0.34) \times F$$



$$\Delta G_2^\circ = -1(0.15) \times F$$

On addition,



$$\Delta G_3^\circ = -1 \times E^\circ \times F$$

and $\Delta G_3^\circ = \Delta G_1^\circ + \Delta G_2^\circ$

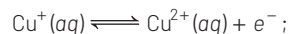
$$-n_3FE^\circ = -n_1FE_1^\circ - n_2FE_2^\circ$$

$$-E^\circ = -2(-0.34) - 1(0.15)$$

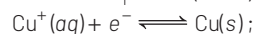
$$= (-2 \times -0.34) + (-1 \times 0.15)$$

$$-E^\circ = +0.68 - 0.15 = 0.53$$

or $E^\circ = -0.53 \text{ V}$

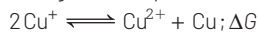


$$\Delta G_1 = -1 \times (-0.15) \times F$$



$$\Delta G_2 = -1 \times (-0.53) \times F$$

On adding above equation we get,



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

$$-nFE^\circ = 0.15F + (-0.53F)$$

$$-FE^\circ = 0.38F$$

$$E^\circ = 0.38 \text{ V}$$

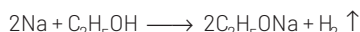
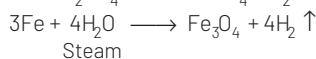
Thus, for the result reaction E° value is 0.38 V.

52 Which one of the following pairs of substances on reaction will not evolve H_2 gas? [CBSE AIPMT 1998]

- (a) Iron and $\text{H}_2\text{SO}_4(aq)$
 (b) Iron and steam
 (c) Copper and $\text{HCl}(aq)$
 (d) Sodium and ethyl alcohol

Ans. (c)

Since copper is placed below hydrogen in the electrochemical series, thus copper does not give hydrogen with dilute acids. While all other pairs give hydrogen on reaction.



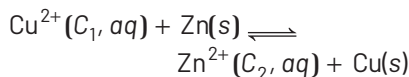
53 Without losing its concentration ZnCl_2 solution cannot be kept in contact with [CBSE AIPMT 1998]

- (a) Au (b) Al (c) Pb (d) Ag

Ans. (b)

In electrochemical series, Al is placed above Zn and all other are present below Zn. So, aluminium displaces zinc from ZnCl_2 solution. Hence, it cannot keep in contact with Al.

54 For the cell reaction,



of an electrochemical cell, the change in free energy (ΔG) at a given temperature is a function of [CBSE AIPMT 1998]

- (a) $\ln(C_1)$ (b) $\ln(C_2/C_1)$
 (c) $\ln(C_2)$ (d) $\ln(C_1 + C_2)$

Ans. (b)

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

For concentration cell, from Nernst equation,

$$E = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln \frac{C_1}{C_2}$$

$$E^\circ_{\text{cell}} = 0.00 \text{ V}$$

$$E = \frac{-RT}{nF} \ln \frac{C_2}{C_1}$$

$$E = \frac{RT}{nF} \ln \frac{C_2}{C_1}$$

$$C_2 > C_1$$

$$E = \frac{RT}{nF} \ln \frac{C_2}{C_1}$$

(R, T, n and F are constant)

therefore, E° is based upon $\ln \frac{C_2}{C_1}$

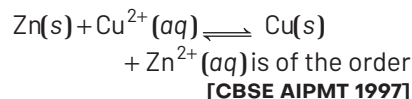
$$\Delta G = -nFE^\circ$$

$$= -nF \times \frac{RT}{nF} \ln \frac{C_2}{C_1}$$

$$= -RT \ln \frac{C_2}{C_1}$$

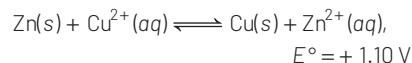
Hence, at constant temperature Gibbs free energy ΔG depends upon $\ln \frac{C_2}{C_1}$.

55 E° for the cell, $\text{Zn}|\text{Zn}^{2+}(aq)||\text{Cu}^{2+}(aq)|\text{Cu}$ is 1.10 V at 25°C . The equilibrium constant for the reaction,



- (a) 10^{-37} (b) 10^{-28} (c) 10^{18} (d) 10^{17}

Ans. (a)



$$\therefore E^\circ = \frac{0.0591}{n} \log_{10} K_{\text{eq}}$$

because at equilibrium, $E_{\text{cell}} = 0$

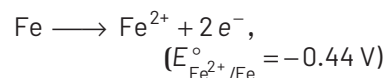
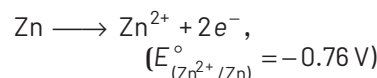
(n = number of electrons exchanged = 2)

$$1.10 = \frac{0.0591}{2} \log_{10} K_{\text{eq}}$$

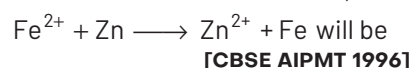
$$\frac{2.20}{0.0591} = \log_{10} K_{\text{eq}}$$

$$K_{\text{eq}} = \text{antilog } 37.225 = 1.66 \times 10^{-37}$$

56 Reduction potential for the following half-cell reactions are



The EMF for the cell reaction,



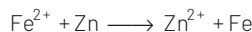
- (a) +0.32 V
(b) -0.32 V
(c) +1.20 V
(d) -1.20 V

Ans. (a)

$$E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.76 \text{ V}$$

$$E_{\text{Fe}^{2+}/\text{Fe}}^{\circ} = -0.44 \text{ V}$$

Cell reaction,



$$\begin{aligned} E_{\text{cell}}^{\circ} &= E_{\text{(cathode)}}^{\circ} - E_{\text{(anode)}}^{\circ} \\ &= -0.44 - (-0.76) \\ &= +0.32 \text{ V} \end{aligned}$$

- 57** An electrochemical cell is shown below $\text{Pt}, \text{H}_2(1\text{atm}) | \text{HCl} (0.1 \text{ M}) | \text{CH}_3\text{COOH} (0.1 \text{ M}) | \text{H}_2(1 \text{ atm}), \text{Pt}$. The EMF of the cell will not be zero, because **[CBSE AIPMT 1995]**

- (a) EMF depends on molarities of acids used
(b) pH of 0.1 M HCl and 0.1 M CH_3COOH is not same
(c) the temperature is constant
(d) acids used in two compartments are different

Ans. (b)

The EMF of the cell will not be zero because concentration of H^+ ions in two electrolytic solutions is different. Mean HCl is strong acid where, acetic acid is weak acid and gives different pH.

- 58** Standard reduction potentials at 25°C of $\text{Li}^+ / \text{Li}, \text{Ba}^{2+} / \text{Ba}, \text{Na}^+ / \text{Na}$ and $\text{Mg}^{2+} / \text{Mg}$ are -3.05, -2.90, -2.71 and -2.37 V respectively. Which one of the following is the strongest oxidising agent? **[CBSE AIPMT 1994]**

- (a) Mg^{2+}
(b) Ba^{2+}
(c) Na^+
(d) Li^+

Ans. (a)

A cation having maximum (positive) value of standard reduction potential is the strongest oxidising agent. Hence, Mg^{2+} is the strongest oxidising agent.

TOPIC 4

Arrhenius Theory, Activation Energy and Collision Theory of Biomolecular Gaseous Reaction

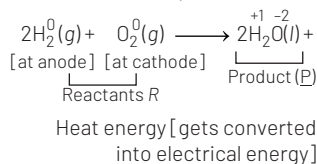
- 59** In a typical fuel cell, the reactants (R) and product (P) are

[NEET (Oct.) 2020]

- (a) $R = \text{H}_2(\text{g}), \text{O}_2(\text{g}); P = \text{H}_2\text{O}_2(\text{l})$
(b) $R = \text{H}_2(\text{g}), \text{O}_2(\text{g}); P = \text{H}_2\text{O}(\text{l})$
(c) $R = \text{H}_2(\text{g}), \text{O}_2(\text{g}), \text{Cl}_2(\text{g}); P = \text{HClO}_4(\text{aq})$
(d) $R = \text{H}_2(\text{g}), \text{N}_2(\text{g}); P = \text{NH}_3(\text{aq})$

Ans. (b)

The reaction takes place in a fuel cell is



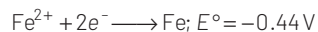
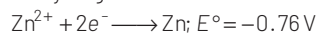
Hence, option (b) is the correct.

- 60** Zinc can be coated on iron to produce galvanised iron but the reverse is not possible. It is because **[CBSE AIPMT 2016, Phase II]**

- (a) zinc is lighter than iron
(b) zinc has lower melting point than iron
(c) zinc has lower negative electrode potential than iron
(d) zinc has higher negative electrode potential than iron

Ans. (d)

The metal with higher negative standard reduction potential, have higher tendency to get reduced.



Here, in galvanised iron, Zn has higher negative reduction potential means Zn takes electrons given by iron and itself gets reduced.

Thus, Zn works as anode and protects iron from rusting by making iron as cathode.

- 61** A device that converts energy of combustion of fuels like hydrogen and methane, directly into electrical energy is known as **[CBSE AIPMT 2015]**

- (a) fuel cell
(b) electrolytic cell
(c) dynamo
(d) Ni-Cd cell

Ans. (a)

Fuel cell is a device that converts energy of combustion of fuels like hydrogen and methane, directly into electrical energy.

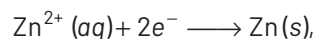
Electrolytic cell converts electrical energy into chemical energy.

Dynamo is an electrical generator that produces direct current with the use of a commutator.

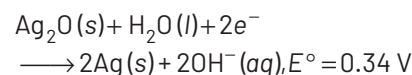
Ni-Cd cell is a type of rechargeable battery which consists of a cadmium anode and a metal grid containing NiO_2 acting as a cathode.

- 62** A button cell used in watches functions as following **[NEET 2013]**
 $\text{Zn}(\text{s}) + \text{Ag}_2\text{O}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons 2\text{Ag}(\text{s}) + \text{Zn}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq})$

If half-cell potentials are



$$E^{\circ} = -0.76 \text{ V}$$

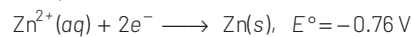


The cell potential will be

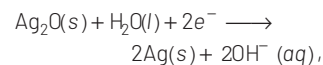
- (a) 1.10 V (b) 0.42 V
(c) 0.84 V (d) 1.34 V

Ans. (a)

Anode is always the site of oxidation thus, anode half-cell is



Cathode half-cell is



$$E^{\circ} = 0.34 \text{ V}$$

$$\begin{aligned} E_{\text{cell}}^{\circ} &= E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} \\ &= 0.34 - (-0.76) = +1.10 \text{ V} \end{aligned}$$

- 63** The efficiency of a fuel cell is given by **[CBSE AIPMT 2007]**

- (a) $\Delta G / \Delta S$ (b) $\Delta G / \Delta H$
(c) $\Delta S / \Delta G$ (d) $\Delta H / \Delta G$

Ans. (b)

$$\text{Efficiency of a fuel cell } (\phi) = \frac{\Delta G}{\Delta H} \times 100$$

Fuel cells are expected to have an efficiency of 100%.