ELECTROCHEMISTRY

1. The electrode potential of M^{2+} / M of 3d-series elements shows positive value of :

(1) Zn (2) Fe (3) Co (4) Cu

2. The magnitude of the change in oxidising power of the MnO_4^- / Mn^{2+} couple is x × 10^{-4} V, if the H^+ concentration is decreased from 1 M to 10^{-4} M at 25°C. (Assume concentration of MnO_4^- and Mn^{2+} to be same on change in H^+ concentration). The value of x is _______. (Rounded off to the nearest integer)

$$\left[\text{Given}: \frac{2.303\ RT}{F} = 0.059\right]$$

3. Copper reduces NO_3^- into NO and NO_2 depending upon the concentration of HNO_3 in solution. (Assuming fixed $[Cu^{2+}]$ and $P_{NO} = P_{NO_2}$), the HNO_3 concentration at which the thermodynamic tendency for reduction of NO_3^- into NO and NO_2 by copper is same is 10^x M. The value of 2x is _______. (Rounded-off to the nearest integer)

[Given, $E^o_{Cu^{2+}/Cu}$ = 0.34 V, $E^o_{NO_3^-/NO}$ = 0.96 V, $E^o_{NO_3^-/NO_2}$ = 0.79 V and at 298 K, $\frac{RT}{F}(2.303) = 0.059$]

4. Consider the following reaction

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O, E^o = 1.51\ V.$$

The quantity of electricity required in Faraday to reduce five moles of MnO_4^- is____.

5 Emf of the following cell at 298 K in V is $x \times 10^{-2}$. Zn|Zn^{2+} (0.1 M)||Ag^+ (0.01 M)| Ag

The value of x is ______. (Rounded off to the nearest integer)

[Given : $E^0_{Zn^{2+}/Zn} = -0.76V$; $E^0_{Ag^+/Ag} = +0.80V$; $\frac{2.303RT}{F} = 0.059$]

6. A 5.0 m mol dm^{-3} aqueous solution of KCl has a conductance of 0.55 mS when measured in a cell constant 1.3 cm^{-1}. The molar conductivity of this solution is _______ $mSm^2\ mol^{-1}$. (Round off to the Nearest Integer)

7. A KCl solution of conductivity 0.14 S m^{-1} shows a resistance of 4.19 Ω in a conductivity cell. If the same cell is filled with an HCl solution, the resistance drops to 1.03 Ω. The conductivity of the HCl solution is ____× 10^{-2} S m^{-1}. (Round off to the Nearest Integer).

8. For the reaction

$$2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(s)$$

the magnitude of the standard molar free energy change, $\Delta_r G^\circ_m = -$ ______ kJ (Round off to the Nearest Integer).

$$\left[\begin{array}{l} E^o_{Fe^{2+}/Fe(s)} = -0.440\ V;\ E^o_{Fe^{3+}/Fe(s)} = -0.036\ V \\ E^o_{I_2/2I^-} = 0.539\ V; \qquad F = 96500\ C \end{array}\right]$$

9. The molar conductivities at infinite dilution of barium chloride, sulphuric acid and hydrochloric acid are 280, 860 and 426 $Scm^2\ mol^{-1}$ respectively. The molar conductivity at infinite dilution of barium sulphate is ________S $cm^2\ mol^{-1}$(Round off to the Nearest Integer).

10. Potassium chlorate is prepared by electrolysis of KCl in basic solution as shown by following equation.

$$6OH^- + Cl^- \rightarrow ClO_3^- + 3H_2O + 6e^-$$

A current of xA has to be passed for 10h to produce 10.0g of potassium chlorate. the value of x is _______. (Nearest integer)

(Molar mass of $KClO_3$ = 122.6 g mol^{-1}, F = 96500 C)

11. Assume a cell with the following reaction

$Cu_{(s)} + 2Ag^{+}(1 \times 10^{-3}\ M) \rightarrow Cu^{2+}(0.250\ M) + 2Ag_{(s)}$

$E^{\ominus}_{cell} = 2.97\,V$

E_{cell} for the above reaction is ___________V. (Nearest integer)

[Given : log 2.5 = 0.3979, T = 298 K]

12. Consider the cell at 25°C

$Zn \mid Zn^{2+}(aq), (1\ M) \parallel Fe^{3+}(aq), Fe^{2+}(aq) \mid Pt(s)$

The fraction of total iron present as Fe^{3+} ion at the cell potential of 1.500 V is $x \times 10^{-2}$. The value of x is _______ .

(Nearest integer)

(Given : $E^{0}_{Fe^{3+}/Fe^{2+}} = 0.77V, E^{0}_{Zn^{2+}/Zn} = -0.76V$)

13. The conductivity of a weak acid HA of concentration 0.001 mol L^{-1} is 2.0×10^{-5} S cm^{-1}. If $\Lambda^{o}_{m}(HA) = 190\ S\ cm^{2}\ mol^{-1}$, the ionization constant (K_a) of HA is equal to _________ × 10^{-6}.

(Round off to the Nearest Integer)

14. For the cell

$Cu(s) \mid Cu^{2+}(aq)\ (0.1M) \parallel Ag^{+}\ (aq)\ (0.01M) \mid Ag(s)$

the cell potential E_1 = 0.3095 V

For the cell

$Cu(s) \mid Cu^{2+}\ (aq)\ (0.01\ M) \parallel Ag^{+}(aq)\ (0.001\ M) \mid Ag(s)$

the cell potential = ______ × 10^{-2} V. (Round off the Nearest Integer).

[Use : $\frac{2.303\ RT}{F} = 0.059$]

15. Given below are two statements :

Statement I : The limiting molar conductivity of KCl (strong electrolyte) is higher compared to that of CH_3COOH (weak electrolyte).

Statement II : Molar conductivity decreases with decrease in concentration of electrolyte.

In the light of the above statements, choose the **most appropriate** answer from the options given below :

(1) **Statement I** is true but **Statement II** is false.

(2) **Statement I** is false but **Statement II** is true.

(3) Both **Statement I** and **Statement II** are true.

(4) Both **Statement I** and **Statement II** are false.

16. For the galvanic cell,

$Zn(s) + Cu^{2+}(0.02\ M) \rightarrow Zn^{2+}\ (0.04\ M) + Cu(s)$,

E_{cell} =_______ × 10^{-2} V. (Nearest integer)

[Use : $E^{0}_{Cu/Cu^{2+}} = -0.34$ V, $E^{0}_{Zn/Zn^{2+}} = +0.76$ V, $\frac{2.303\ RT}{F} = 0.059$ V]

17. The resistance of a conductivity cell with cell constant 1.14 cm^{-1}, containing 0.001 M KCl at 298 K is 1500 Ω. The molar conductivity of 0.001 M KCl solution at 298 K in S cm^{2} mol^{-1} is_______. (Integer answer)

18. Consider the following cell reaction :

$$Cd_{(s)} + Hg_2SO_{4(s)} + \frac{9}{5}H_2O_{(l)} \rightleftharpoons CdSO_4.\frac{9}{5}H_2O_{(s)} + 2Hg_{(l)}$$

The value of E^{0}_{cell} is 4.315 V at 25°C. If ΔH° = –825.2 kJ mol^{-1}, the standard entropy change ΔS° in J K^{-1} is ______. (Nearest integer)

[Given : Faraday constant = 96487 C mol^{-1}]

19. Match **List-I** with **List-II**

	List-I **(Parameter)**	**List-II** **(Unit)**
(a)	Cell constant	(i) S cm^2 mol^{-1}
(b)	Molar conductivity	(ii) Dimensionless
(c)	Conductivity	(iii) m^{-1}
(d)	Degree of dissociation of electrolyte	(iv) Ω^{-1} m^{-1}

Choose the **most appropriate** answer from the options given below :

(1) (a)-(iii), (b)-(i), (c)-(iv), (d)-(ii)
(2) (a)-(iii), (b)-(i), (c)-(ii), (d)-(iv)
(3) (a)-(i), (b)-(iv), (c)-(iii), (d)-(ii)
(4) (a)-(ii), (b)-(i), (c)-(iii), (d)-(iv)

20. If the conductivity of mercury at 0°C is 1.07×10^6 S m^{-1} and the resistance of a cell containing mercury is 0.243 Ω, then the cell constant of the cell is $x \times 10^4$ m^{-1}. The value of x is _______.(Nearest integer)

SOLUTION

1. Official Ans. by NTA (4)

Sol. Only copper shows positive value for electrode potential of M^{2+}/M of 3d-series elements.

$E^{\ominus} / V_{(Cu^{2+}/Cu)} : +0.34$

2. Official Ans. by NTA (3776)

Sol. Eqn is-

$$MnO_4^- + H^{\oplus} + 5e^- \rightarrow Mn^{+2} + 4H_2O$$

Nernst equation:

$$E_{cell} = E^0_{Cell} - \frac{0.059}{5}\log\frac{[Mn^{+2}]}{[MnO_4^-]}\left[\frac{1}{H^+}\right]^8$$

(I) Given $[H^{\oplus}] = 1M$

$$E_1 = E^0 - \frac{0.059}{5}\log\frac{[Mn^{+2}]}{[MnO_4^-]}$$

(II) Now : $[H^{\oplus}] = 10^{-4}M$

$$E_2 = E^0 - \frac{0.059}{5}\log\frac{[Mn^{+2}]}{[MnO_4^-]} \times \frac{1}{(10^{-4})^8}$$

$$= E^0 - \frac{0.059}{5}\log\frac{Mn^{+2}}{[MnO_4^-]} + \frac{0.059}{5}\log 10^{-32}$$

therefore : $|E_1 - E_2| = \frac{0.059}{5} \times 32$

$= 0.3776\ V = 3776 \times 10^{-4}$

$x = 3776$

3. Official Ans. by NTA (4)

Sol. If the partial pressure of NO and NO_2 gas is taken as 1 bar, then Answer is 4, else the question is bonus.

$$NO_3^- + 4H^+ + 3e^- \longrightarrow NO + 2H_2O$$

$$E^o_{NO_3^-/NO} = 0.96V$$

$$NO_3^- + 2H^+ + e^- \longrightarrow NO_2 + H_2O$$

$$E^o_{NO_3^-/NO_2=0.79}$$

Let $[HNO_3] = y \Rightarrow [H^+] = y$ and $[NO_3^-] = y$

for same thermodynamic tendency

$$E_{NO_3^-/NO} = E_{NO_3^-/NO_2}$$

$$\text{or, } E^o_{NO_3^-/NO} - \frac{0.059}{3}\log\frac{P_{NO}}{y \times y^4}$$

$$= E^o_{NO_3^-/NO_2} - \frac{0.059}{1}\log\frac{P_{NO_2}}{y \times y^2}$$

$$\text{or, } 0.96 - \frac{0.059}{3}\log\frac{P_{NO}}{y^5} = 0.79 - \frac{0.059}{1}\log\frac{P_{NO_2}}{y^3}$$

$$\text{or, } 0.17 = -\frac{0.059}{1}\log\frac{P_{NO_2}}{y^3} + \frac{0.059}{3}\log\frac{P_{NO}}{y^5}$$

$$0.17 = -\frac{0.0591}{1}\log\frac{P_{NO_2}}{y^3} + \frac{0.0591}{3}\log\frac{P_{NO}}{y^5}$$

$$0.17 = -\frac{0.0591}{3}\log\frac{P^3_{NO_2}}{y^9} + \frac{0.0591}{3}\log\frac{P_{NO}}{y^5}$$

$$0.17 = \frac{0.0591}{3}\left[\log\frac{P_{NO}}{y^5} - \log\frac{P^3_{NO_2}}{y^9}\right]$$

$$0.17 = \frac{0.0591}{3}\left[\log\frac{P_{NO}}{y^5} \times \frac{y^9}{P^3_{NO_2}}\right]$$

Assume $P_{NO} \simeq P_{NO2} = 1$ bar

$$\frac{0.17 \times 3}{0.059} = \log y^4 = 8.644$$

$$\log y = \frac{8.644}{4}$$

$\log y = 2.161$

$y = 10^{2.16}$

$\therefore 2x = 2 \times 2.161 = 4.322$

Answer (4)

4. Official Ans. by NTA (25)

5 Official Ans by NTA (147)

Sol. $Zn_{(s)} \rightarrow Zn^{2+}_{(aq.)} + 2e^-$

$2Ag^+_{(aq.)} + 2e^- \rightarrow 2Ag_{(s)}$

$$Zn_{(s)} + 2Ag^+_{(aq.)} \rightarrow Zn^{2+}_{(aq.)} + 2Ag_{(s)}$$

$E^0_{cell} = E^0_{Ag^+/Ag} - E^0_{Zn^{2+}/Zn}$

$= 0.80 - (-0.76)$

$= 1.56$ V

$$E_{cell} = 1.56 \frac{-0.059}{2}\log\frac{[Zn^{2+}]}{[Ag^+]^2}$$

$$= 1.56 - \frac{0.059}{2}\log\frac{0.1}{(0.01)^2}$$

$$= 1.56 - \frac{0.059}{2}\times 3$$

$= 1.56 - 0.0885$

$= 1.4715$

$= 147.15 \times 10^{-2}$

6. Official Ans. by NTA (14)

Sol. Given $conc^n$ of KCl $= \frac{m.mol}{L}$

: Conductance (G) = 0.55 mS

: Cell constant $\left(\frac{\ell}{A}\right) = 1.3\ cm^{-1}$

To Calculate : Molar conductivity (λ_m) of sol.

→ Since $\boxed{\lambda_m = \frac{1}{1000}\times\frac{k}{m}}$ ......(1)

→ Molarity $= 5 \times 10^{-3}\ \frac{mol}{L}$

→ Conductivity $= G\times\left(\frac{\ell}{A}\right) = 0.55\ mS\times\frac{1.3}{\frac{1}{100}}m^{-1}$

$= 55 \times 1.3\ mSm^{-1}$

eq^n (1) $\lambda_m = \frac{1}{1000}\times\frac{55\times1.3}{\left(\frac{5}{1000}\right)}\ \frac{mSm^2}{mol}$

$\Rightarrow \lambda_m = 14.3\frac{mSm^2}{mol}$

7. Official Ans. by NTA (57)

Sol. $\kappa = \frac{1}{R}\cdot G*$

For same conductivity cell, G* is constant and hence κ.R. = constant.

$\therefore\ 0.14 \times 4.19 = \kappa \times 1.03$

or, κ of HCl solution $= \frac{0.14\times4.19}{1.03}$

$= 0.5695\ Sm^{-1}$

$= 56.95 \times 10^{-2}\ Sm^{-1} \approx 57 \times 10^{-2}\ Sm^{-1}$

8. Official Ans. by NTA (46)

Official Ans. by ALLEN (45)

Sol.

$$\begin{tikzcd} Fe^{3+} \arrow[r, "E_1^0"] \arrow[rr, bend right, dash, "E_3^0"'] & Fe^{2+} \arrow[r, "E_2^0"] & Fe \end{tikzcd}$$

$E^0_1 + 2E^0_2 = 3E^0_3$

$E^0_1 = 3E^0_3 - 2E^0_2$

$= 3\ (-0.036) - 2(-0.44)$

$= +\ 0.772$ V

$E^0_{cell} = E^0_{Fe^{3+}/Fe^{2+}} + E^0_{I^-/I_2} = 0.233$

$\Delta_r G^0 = -\ 2 \times 96.5 \times 0.233 = -45$ kJ

9. Official Ans. by NTA (288)

Sol. From Kohlrausch's law

$\Lambda^\infty_m(BaSO_4) = \lambda^\infty_m(Ba^{2+}) + \lambda^\infty_m(SO_4^{2-})$

$\Lambda^\infty_m(BaSO_4) = \Lambda^\infty_m(BaCl_2) + \Lambda^\infty_m(H_2SO_4)$

$-2\ \Lambda^\infty_m(HCl)$

$= 280 + 860 - 2\ (426)$

$= 288\ Scm^2mol^{-1}$

10. Official Ans. by NTA (1)

Sol. Given balanced equation is

$$6\overset{\ominus}{O}H + \overset{\ominus}{Cl} \longrightarrow ClO_3^- + 3H_2O + 6e^-$$

→ 10g $KClO_3 \Rightarrow \frac{10}{122.6}$ mol KCO_3 in obtained

→ from the above reaction, it is concluded that by 6F charge 1 mol $KClO_3$ is obtained.

→ By the passage of 6F charge = 1 mol $KClO_3$

$\therefore$ By the passage of $\frac{x \times 10 \times 60 \times 60}{96500}$ F charge

$$= \frac{1}{6} \times \frac{x \times 10 \times 60 \times 60}{96500}$$

Now $\frac{x \times 10 \times 60 \times 60}{6 \times 96500} = \frac{10}{122.6}$

$$\Rightarrow x = \frac{10 \times 965}{60 \times 122.6} = \frac{965}{735.6} = 1.311 \simeq 1$$

OR

$$W = \frac{E}{F} \times I \times t$$

$$10 = \frac{122.6}{96500 \times 6} \times x \times 10 \times 3600$$

X = 1.311

Ans.(1)

11. Official Ans. by NTA (3)

Sol. $E = E° - \frac{0.059}{2} \log \frac{[Cu^{+2}]}{[Ag^+]^2}$

$$= 2.97 - \frac{0.059}{2} \log \frac{0.25}{(10^{-3})^2} = 2.81V$$

12. Official Ans. by NTA (24)

Sol. $Zn \longrightarrow Zn^{2+} + 2e^-$

$2Fe^{3+} \longrightarrow 2e^- + 2e^{2+}$

$Zn + 2Fe^{3+} \longrightarrow Zn^{2+} + 2Fe^{2+}$

$E^0_{cell} = 0.77 - (0.76)$

$= 1.53$ V

$$1.50 = 1.53 - \frac{0.06}{2} \log\left(\frac{Fe^{2+}}{Fe^{3+}}\right)^2$$

$$\log\left(\frac{Fe^{2+}}{Fe^{3+}}\right) = \frac{0.03}{0.06} = \frac{1}{2}$$

$$\frac{[Fe^{2+}]}{[Fe^{3+}]} = 10^{1/2} = \sqrt{10}$$

$$\frac{[Fe^{3+}]}{[Fe^{2+}]} = \frac{1}{\sqrt{10}}$$

$$\frac{[Fe^{3+}]}{[Fe^{2+}] + [Fe^{3+}]} = \frac{1}{1 + \sqrt{10}} = \frac{1}{4.16}$$

= 0.2402

= 24×10^{-2}

13. Official Ans. by NTA (12)

Sol. $\Lambda_m = 1000 \times \frac{\kappa}{M}$

$$= 1000 \times \frac{2 \times 10^{-5}}{0.001} = 20 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Rightarrow \alpha = \frac{\Lambda_m}{\Lambda_m^\infty} = \frac{20}{190} = \left(\frac{2}{19}\right)$$

$$HA \rightleftharpoons H^+ + A^-$$

0.001 (1– α) 0.001α 0.001 α

$$\Rightarrow k_a = 0.001\left(\frac{\alpha^2}{1-\alpha}\right) = \frac{0.001 \times \left(\frac{2}{19}\right)^2}{1 - \left(\frac{2}{19}\right)}$$

$= 12.3 \times 10^{-6}$

14. Official Ans. by NTA (28)

Sol. Cell reaction is :

$Cu(s) + 2\,Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$

Now, $E_{cell} = E^o_{Cell} - \frac{0.059}{2} \log \frac{\left[Cu^{2+}\right]}{\left[Ag^+\right]^2}$ ... (1)

$\therefore$ $E_1 = 0.3095 = E^o_{Cell} - \frac{0.059}{2} . \log \frac{0.01}{(0.001)^2}$ ... (2)

From (1) and (2) , $E_2 = 0.28$ V $= 28 \times 10^{-2}$ V

15. Official Ans. by NTA (4)

Sol.

Ion	H^+	K^+	Cl^-	CH_3COO^-
$\Lambda^\infty_{m\ Scm^2/mole}$	349.8	73.5	76.3	40.9

So $\Lambda^\infty_{m\ CH_3COOH} = \Lambda^\infty_{m\ (H^+)} + \Lambda^\infty_{m\ CH_3COO^-}$

= 349.8 + 40.9

= 390.7 Scm^2/mole

$\Lambda^\infty_{m\ KCl} = \Lambda^\infty_{m\ (K^+)} + \Lambda^\infty_{m\ (Cl^-)}$

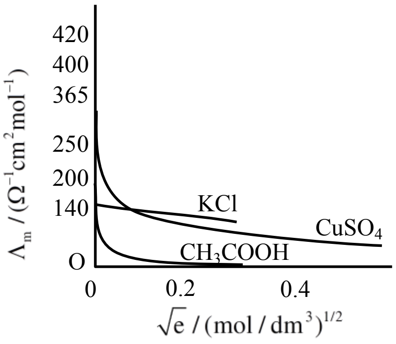
= 73.5 + 76.3

= 149.3 Scm^2/mole

So statement-I is wrong or False.

As the concentration decreases, the dilution increases which increases the degree of dissociation, thus increasing the no. of ions, which increases the molar conductance.

So statement-II is false.



16. Official Ans. by NTA (109)

Sol. Galvanic cell:

$$\underset{}{Zn_{(s)}} + \underset{0.02M}{Cu^{+2}_{(aq.)}} \rightarrow \underset{0.04M}{Zn^{+2}} + Cu(s)$$

$$\text{Nernst equation} = F_{cell} = E^o_{cell} - \frac{0.059}{2}\log\frac{[2n^{+2}]}{[Cu^{+2}]}$$

$$\Rightarrow E_{cell}\left[E^o_{cell} - E^o_{Zn^{+2}/Zn}\right] - \frac{0.059}{2}\log\frac{0.04}{0.02}$$

$$\Rightarrow E_{cell}[0.34-(-0.76)] - \frac{0.059}{2}\log^2$$

$$\Rightarrow E_{cell}1-1-\frac{0.059}{2}\times 0.3010$$

$= 1.0911 = 109.11 \times 10^{-2}$

$= 109$

17. Official Ans. by NTA (760)

Sol. $K = \frac{1}{R}\times \ell/_A = \left(\left(\frac{1}{1500}\right)\times 1.14\right) S\ cm^{-1}$

$$\Rightarrow \wedge_m = 1000\times\frac{\left(\frac{1.14}{1500}\right)}{0.001} S\ cm^2mol^{-1}$$

$= 760\ S\ cm^2\ mol^{-1}$

$\Rightarrow$ 760

18. Official Ans. by NTA (25)

Sol. $\Delta G^o = -nFE^o = \Delta H^o - T\Delta S^o$

$$= \frac{\Delta H^o + nFE^o}{T}$$

$$= \frac{(-825.2\times 10^3) + (2\times 96487\times 4.315)}{298}$$

$$= \frac{-825.2\times 10^3 + 832.682\times 10^3}{298}$$

$$= \frac{7.483\times 10^3}{298} = 25.11\ JK^{-1}mol^{-1}$$

$\therefore$ Nearest integer answer is 25

19. Official Ans. by NTA (1)

Sol. Cell constant = $\left(\frac{\ell}{A}\right) \Rightarrow$ Units = m^{-1}

Molar conductivity (Λ_m) $\Rightarrow$ Units = $Sm^2\ mole^{-1}$

Conductivity (K) $\Rightarrow$ Units = $S\ m^{-1}$

Degree of dissociation (α) $\rightarrow$ Dimensionless

$\therefore$ (a) – (iii)

(b) – (i)

(c) – (iv)

(d) – (ii)

20. Official Ans. by NTA (26)

Sol. $k = 1.07 \times 10^6\ Sm^{-1}$, $R = 0.243\ \Omega$

$$G = \frac{1}{R} = \frac{1}{0.243}\Omega^{-1}$$

$k = G \times G^*$

$$G^* = \frac{k}{G} = \frac{1.07\times 10^6}{\frac{1}{0.243}} \simeq 26 \times 10^4\ m^{-1}$$