PHYSICAL CHEMISTRY

ELECTROCHEMISTRY

1. Plotting $1/\Lambda_m$ against $c\Lambda_m$ for aqueous solutions of a monobasic weak acid (HX) resulted in a straight line with y-axis intercept of P and slope of S. The ratio $P\,/\,S$ is   **[JEE(Advanced) 2023]**

[Λ_m = molar conductivity

Λ_m° = limiting molar conductivity

c = molar concentration

K_a = dissociation constant of HX]

(A) $K_a\,\Lambda_m^{\circ}$ (B) $K_a\,\Lambda_m^{\circ}\,/\,2$ (C) $2\,K_a\Lambda_m^{\circ}$ (D) $1\,/\,(K_a\Lambda_m^{\circ})$

2. The reduction potential (E^0, in V) of MnO_4^- (aq)/Mn(s) is _____.   **[JEE(Advanced) 2022]**

[Given : $E^0_{\left(MnO_4^-(aq)/MnO_2(s)\right)} = 1.68\,V$; $E^0_{\left(MnO_2(s)/Mn^{2+}(aq)\right)} = 1.21\,V$; $E^0_{\left(Mn^{2+}(aq)/Mn(s)\right)} = -1.03\,V$]

3. Consider the strong electrolytes Z_mX_n, U_mY_p and V_mX_n. Limiting molar conductivity (Λ^0) of U_mY_p and V_mX_n are 250 and 440 S cm^2 mol^{-1}, respectively. The value of (m + n + p) is _____.
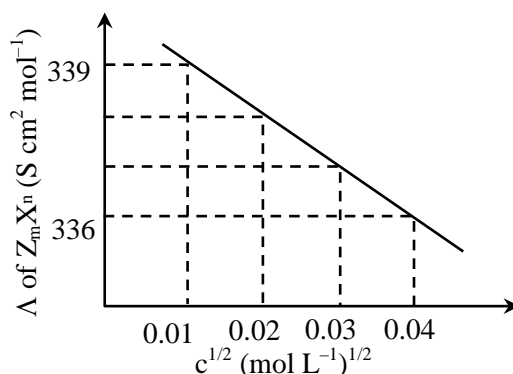
Given:

Ion	Z^{n+}	U^{p+}	V^{n+}	X^{m-}	Y^{m-}
λ^0(S cm^2 mol^{-1})	50.0	25.0	100.0	80.0	100.0

λ^0 is the limiting molar conductivity of ions

The plot of molar conductivity (Λ) of Z_mX_n *vs* $c^{1/2}$ is given below.   **[JEE(Advanced) 2022]**

4. The correct option(s) about entropy (S) is(are)   **[JEE(Advanced) 2022]**

[R = gas constant, F = Faraday constant, T = Temperature]

(A) For the reaction, $M(s) + 2H^+(aq) \rightarrow H_2(g) + M^{2+}(aq)$, if $\dfrac{dE_{cell}}{dT} = \dfrac{R}{F}$, then the entropy change of the reaction is R (assume that entropy and internal energy changes are temperature independent).

(B) The cell reaction, $Pt(s)\ |\ H_2(g,\ 1bar)\ |\ H^+(aq,\ 0.01M)\ \|\ H^+(aq,\ 0.1M)\ |\ H_2(g,\ 1bar)\ |\ Pt(s)$, is an entropy driven process.

(C) For racemization of an optically active compound, $\Delta S > 0$.

(D) $\Delta S > 0$, for $[Ni(H_2O)_6]^{2+} + 3\ en \rightarrow [Ni(en)_3]^{2+} + 6H_2O$ (where en = ethylenediamine).

5. Some standard electrode potentials at 298 K are given below: **[JEE(Advanced) 2021]**

    Pb^{2+}/Pb –0.13 V

    Ni^{2+}/Ni –0.24 V

    Cd^{2+}/Cd –0.40 V

    Fe^{2+}/Fe –0.44 V

    To a solution containing 0.001 M of X^{2+} and 0.1 M of Y^{2+}, the metal rods X and Y are inserted (at 298 K) and connected by a conducting wire. This resulted in dissolution of X. The correct combination(s) of X and Y, respectively, is (are)

    (Given: Gas constant, $R = 8.314$ J K^{-1} mol^{-1},

    Faraday constant, $F = 96500$ C mol^{-1})

    (A) Cd and Ni   (B) Cd and Fe   (C) Ni and Pb   (D) Ni and Fe

    Question Stem for Question Nos. 6 and 7

Question Stem
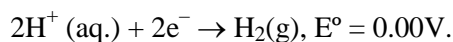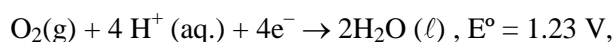
    At 298 K, the limiting molar conductivity of a weak monobasic acid is 4×10^2 S cm^2 mol^{-1}. At 298 K, for an aqueous solution of the acid the degree of dissociation of α and the molar conductivity is $y \times 10^2$ S cm^2 mol^{-1}. At 298 K, upon 20 times dilution with water, the molar conductivity of the solution becomes $3y \times 10^2$ S cm^2 mol^{-1}.

6. The value of α is _____.   **[JEE(Advanced) 2021]**
7. The value of y is _____.   **[JEE(Advanced) 2021]**
8. Consider a 70% efficient hydrogen-oxygen fuel cell working under standard conditions at 1 bar and 298 K. Its cell reaction is   **[JEE(Advanced) 2020]**

$$H_2 \text{ (g)} + \frac{1}{2} O_2(g) \rightarrow H_2O(\ell).$$
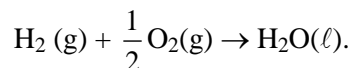
    The work derived from the cell on the consumption of 1.0×10^{-3} mol of $H_2(g)$ is used to compress 1.00 mol of a monoatomic ideal gas in a thermally insulted container. What is the change in the temperature (in K) of the ideal gas ?

    The standard reduction potentials for the two half-cells are given below.

    $O_2(g) + 4 H^+ \text{ (aq.)} + 4e^- \rightarrow 2H_2O \text{ } (\ell)$, $E^o = 1.23$ V,

    $2H^+ \text{ (aq.)} + 2e^- \rightarrow H_2(g)$, $E^o = 0.00$V.

    Use $F = 96500$ C mol^{-1}, $R = 8.314$ J $mol^{-1}K^{-1}$

9. For the electrochemical cell,   **[JEE(Advanced) 2018]**

    $Mg(s)|Mg^{2+}(aq, 1M)||Cu^{2+} \text{ (aq, 1M)} | Cu(s)$

    the standard emf of the cell is 2.70 V at 300 K. When the concentration of Mg^{2+} is changed to x M, the cell potential changes to 2.67 V at 300 K. The value of x is_____.

    (given, $\dfrac{F}{R} = 11500$ KV^{-1}, where F is the Faraday constant and R is the gas constant, $\ln(10) = 2.30$)

10. Consider an electrochemical cell: A(s) | A^{n+} (aq, 2M) || B^{2n+} (aq, 1M) | B(s). The value of ΔH^θ for the cell reaction is twice that of ΔG^θ at 300 K. If the emf of the cell is zero, the ΔS^θ (in JK^{-1} mol^{-1}) of the cell reaction per mole of B formed at 300 K is_____.

    (Given : $\ln (2) = 0.7$, R (universal gas constant) $= 8.3$ J K^{-1} mol^{-1}. H, S and G are enthalpy, entropy and Gibbs energy, respectively.)   **[JEE(Advanced) 2018]**

11. The conductance of a 0.0015 M aqueous solution of a weak monobasic acid was determined by using a conductivity cell consisting of platinized Pt electrodes. The distance between the electrodes is 120 cm with an area of cross section of 1 cm^2. The conductance of this solution was found to be 5×10^{-7}S. The pH of the solution is 4. The value of limiting molar conductivity $\left(\Lambda_m^0 \right)$ of this weak monobasic acid in aqueous solution is $Z \times 10^2$S cm^{-1}mol^{-1}. The value of Z is.   **[JEE(Advanced) 2017]**

12. For the following cell :   **[JEE(Advanced) 2017]**

Zn(s) | ZnSO$_4$ (aq.) || CuSO$_4$ (aq.) | Cu(s)

when the concentration of Zn^{2+} is 10 times the concentration of Cu^{2+}, the expression for ΔG (in J mol^{-1}) is

[F is Faraday constant , R is gas constant, T is temperature , E°(cell) = 1.1V]

(A) 2.303 RT + 1.1F   (B) 2.303 RT – 2.2F

(C) 1.1 F   (D) –2.2 F

13. For the following electrochemical cell at 298K,   **[JEE(Advanced) 2016]**

Pt(s) | H$_2$(g, 1bar) | H$^+$ (aq, 1M) || M^{4+}(aq.), M^{2+}(aq.) | Pt(s)

$E_{cell} = 0.092$ V when $\dfrac{[M^{2+}(aq.)]}{[M^{4+}(aq.)]} = 10^x$

Given : $E^0_{M^{4+}/M^{2+}} = 0.151$V ; $2.303 \dfrac{RT}{F} = 0.059$

The value of x is -

(A) –2   (B) –1   (C) 1   (D) 2

14. All the energy released from the reaction X $\to$ Y, $\Delta_r G° = -193$ kJ mol^{-1} is used for the oxidizing M$^+$ and M$^+ \to$ M$^{3+} + 2e^-$, E° = –0.25 V.

Under standard conditions, the number of moles of M$^+$ oxidized when one mole of X is converted to Y is

[F = 96500 C mol^{-1}]   **[JEE(Advanced) 2015]**

15. The molar conductivity of a solution of a weak acid HX (0.01 M) is 10 times smaller than the molar conductivity of a solution of a weak acid HY (0.1 M). If $\lambda^0_{X-} \approx \lambda^0_{Y-}$, the difference in their pK$_a$ values, pK$_a$(HX) – pK$_a$(HY), is (consider degree of ionization of both acids to be <<1).

                                             [JEE(Advanced) 2015]

16. In a galvanic cell , the salt bridge -   **[JEE(Advanced) 2014]**

(A) Does not participate chemically in the cell reaction

(B) Stops the diffusion of ions from one electrode to another

(C) Is necessary for the occurence of the cell reaction

(D) Ensures mixing of the two electrolytic solutions

SOLUTIONS

1.   **Ans. (A)**

Sol.   For weak acid, $\alpha = \dfrac{\Lambda_m}{\Lambda_0}$

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

$$\Rightarrow \; K_a\left(1 - \frac{\Lambda_m}{\Lambda_0}\right) = C\left(\frac{\Lambda_m}{\Lambda_0}\right)^2$$

$$\Rightarrow K_a - \frac{\Lambda_m K_a}{\Lambda_0} = \frac{C\Lambda_m^2}{(\Lambda_0)^2}$$

Divide by $'\Lambda_m'$

$$\Rightarrow \frac{K_a}{\Lambda_m} = \frac{C\Lambda_m}{(\Lambda_0)^2} + \frac{K_a}{\Lambda_0}$$

$$\Rightarrow \; \frac{1}{\Lambda_m} = \frac{C\Lambda_m}{K_a(\Lambda_0)^2} + \frac{1}{\Lambda_0}$$
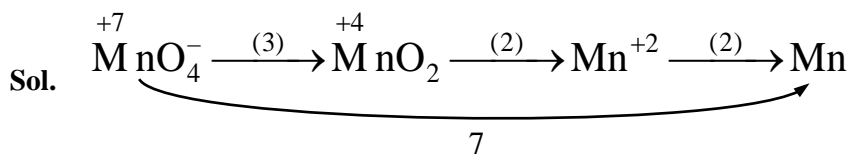
Plot $\dfrac{1}{\Lambda_m}$ vs $C\Lambda_m$ has

Slope $= \dfrac{1}{K_a(\Lambda_0)^2} = S$

y-intercept $= \dfrac{1}{\Lambda_0} = P$

Then, $\dfrac{P}{S} = \dfrac{\dfrac{1}{\Lambda_0}}{\dfrac{1}{K_a(\Lambda_0)^2}} = K_a\Lambda_0$

2.   **Ans. (0.74 - 0.80)**

Sol.
$$\underbrace{\overset{+7}{M}nO_4^- \xrightarrow{(3)} \overset{+4}{M}nO_2 \xrightarrow{(2)} Mn^{+2} \xrightarrow{(2)} Mn}_{7}$$

For the required reaction $\Delta G° = \Delta G°_1 + \Delta G°_2 + \Delta G°_3$

$$\Rightarrow 7 \times E = 1.68 \times 3 + 1.21 \times 2 + (-1.03) \times 2$$

$$E = \frac{5.4}{7} = 0.7714$$

Ans. $= 0.77$

3.   **Ans. (7)**

Sol. $\Lambda^\circ \left(U_m Y_p \right) = m \times \lambda^\circ_{U^{p+}} + p \times \lambda^\circ_{Y^{m-}} = 250$

      $25m + 100p = 250$

      $m + 4p = 10$ ....(1)

      $\Lambda^\circ \left(V_m X_n \right) = m \times \lambda_{V^{n+}} + n \times \lambda^\circ_{X^{m-}} = 440$

      $100m + 80n = 440$

      $5m + 4n = 22$ ....(2)
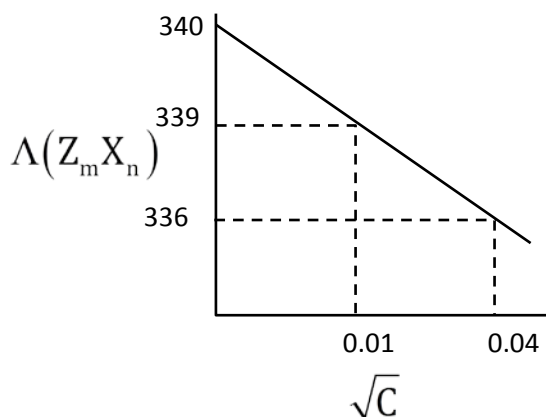
      From the extrapolation of curve

      $\Lambda^\circ \left(Z_m X_n \right) = 340$

      $m \times \lambda^\circ_{Z^{n+}} + n\lambda^\circ_{X^{m-}} = 340$

      $50m + 80n = 340$

      $5m + 8n = 34$ ....(3)

      (3) — (2) $\Rightarrow$ $4n = 12 \Rightarrow n = 3$

      Putting in (2) we get m = 2

      Putting in (1) we get p = 2

      $m + n + p = 2 + 3 + 2 = 7$

4.   **Ans. (B, C, D)**

Sol. $\Delta G = \Delta H - T\Delta S$

      $\Delta G = \Delta H + T \left(\dfrac{d\Delta G}{dT} \right)_p$

      $-nF \left(\dfrac{dE_{cell}}{dT} \right) = -\Delta S$

      $\dfrac{dE_{cell}}{dT} = \dfrac{\Delta S}{nF} = \dfrac{R}{F} \left(\text{given} \right)$

           $\Rightarrow \Delta S = nR$

      For the reaction, $M(g) + 2H^{\oplus}(aq) \longrightarrow H_2(g) + M^{2\oplus}(aq)$

                $n = 2$

      $\Rightarrow$ $\Delta S = 2R$

      Hence, option (A) is incorrect

For the reaction, $Pt_{(s)} |H_{2(g)}, 1 \text{ bar}| H^{\oplus}_{aq}(0.01M)|| H^{\oplus}(aq, 0.1M) | H_2(g, 1 \text{ bar})| Pt_{(s)}$

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{1} \log \frac{0.01}{0.1} = 0.0591V$$

E_{cell} is positive $\Rightarrow \Delta G < 0$ and $\Delta S > 0$ ($\Delta H = 0$ for concentration cells)

Hence, option (B) is correct

Racemization of an optically active compound is a spontaneous process.

Here, $\Delta H = 0$ (similar type of bonds are present in enantiomers)

$\Rightarrow \Delta S > 0$

Hence, option (C) is correct.

$$\left[Ni(H_2O)_6\right]^{2+} + 3\,en \rightarrow \left[Ni(en)_3\right]^{2+} + 6H_2O \text{ is a spontaneous process}$$

more stable complex is formed

$\Rightarrow \Delta S > 0$

Hence, option (D) is correct.

5.   Ans. (A, B, C)

Sol. $x(s) \longrightarrow x^{+2} (0.001 \text{ M}) + 2e^-$ (anode)

$y^{+2} (0.1 \text{ M}) + 2e^- \longrightarrow y (s)$ (cathode)

_____

$$E_{cell} = E^{\circ}{}_{cell} - \frac{0.06}{2} \log \frac{x^{+2}}{y^{+2}}$$

$E_{cell} = E^{\circ}{}_{cell} + 0.06$

(A) Cd and Ni $E^{\circ}{}_{cell} = +0.4 - 0.24$; $E_{cell} = 0.22$

(B) Cd and Fe $E^{\circ}{}_{cell} = -0.04$; $E_{cell} = 0.02$

(C) Ni and Pb $E^{\circ}{}_{cell} = 0.11$; $E_{cell} = 0.17$

(D) Ni and Fe $E^{\circ}{}_{cell} = -0.2$; $E_{cell} = -0.14$

since in (A) (B) (C) E_{cell} is positive hence answer is (A) (B) (C).

6.   Ans. (0.21 or 0.22)

Sol. $$K_a = \frac{\Lambda_m^2 C}{\Lambda_m^{\circ}\left(\Lambda_m^{\circ} - \Lambda_m\right)}$$

$$K_a = \frac{(y \times 10^2)^2 \times C}{4 \times 10^2 (4 \times 10^2 - y \times 10^2)} = \frac{(3y \times 10^2)^2 \times \dfrac{C}{20}}{4 \times 10^2 (4 \times 10^2 - 3y \times 10^2)}$$

$$\Rightarrow \frac{1}{(4-y)} = \frac{9}{20(4-3y)} \Rightarrow y = \frac{44}{51}$$

$$\alpha = \frac{\dfrac{44}{51} \times 10}{4 \times 10^2}$$

$\alpha = 0.2156$ ($\alpha = 0.22$ or 0.21)

$y = 0.86$

7. **Ans. (0.86)**

8. **Ans. (13.00 - 13.60)**

Sol. $E^0_{cell} = 1.23 - 0.00 = 1.23$ V

$\Delta G^0_{cell} = -nF\, E^0_{cell} = -2 \times 96500 \times 1.23$ J

∴ Work derived from this fuel cell

$$= \frac{70}{100} \times \left(-\Delta G^0_{cell}\right) \times 10^{-3} = xJ$$

Since insulated vessel, hence q = 0

From equation, for monoatomic gas,

$$w = \Delta U \qquad \Rightarrow \qquad x = nC_{V,m}\Delta T \left\{C_{V,m} = \frac{3R}{2}\right\}$$

or, $\quad \dfrac{70}{100} \times \left(2 \times 96500 \times 1.23\right) \times 10^{-3} = 1 \times \dfrac{3}{2} \times 8.314 \times \Delta T$

∴ $\quad \Delta T = 13.32$

9. **Ans. (10)**

Sol. $Mg(s) + Cu^{2+}(aq) \longrightarrow Mg^{2+}(aq) + Cu(s)$

$E^\circ_{Cell} = 2.70 \qquad E_{Cell} = 2.67 \qquad Mg^{2+} = x$ M

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad Cu^{2+} = 1$ M

$E_{Cell} = E^\circ_{Cell} - \dfrac{RT}{nF}\ln x$

$2.67 = 2.70 - \dfrac{RT}{2F}\ln x$

$-0.03 = -\dfrac{R \times 300}{2F} \times \ln x$

$\ln x = \dfrac{0.03 \times 2}{300} \times \dfrac{F}{R} = \dfrac{0.03 \times 2 \times 11500}{300 \times 1}$
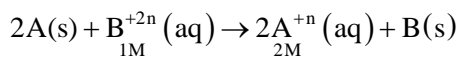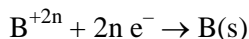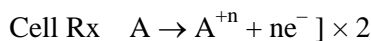
$\ln x = 2.30 = \ln(10)$

$x = 10$

10. **Ans. (–11.62)**

Sol. $A(s) \mid A^{+n}(aq, 2M) \parallel B^{+2n}(aq, 1M) \mid B(s)$

$\qquad \Delta H^\circ = 2\Delta G^\circ_0 \qquad\qquad E_{cell} = 0$

Cell Rx $\quad A \rightarrow A^{+n} + ne^-]\times 2$

$\qquad\qquad B^{+2n} + 2n\, e^- \rightarrow B(s)$

$2A(s) + \underset{1M}{B^{+2n}}(aq) \rightarrow \underset{2M}{2A^{+n}}(aq) + B(s)$

$\Delta G = \Delta G^\circ + RT \ln \dfrac{\left[A^{+n}\right]^2}{\left[B^{+2n}\right]}$

$\Delta G^\circ = -RT \ln \dfrac{\left[A^{+n}\right]^2}{\left[B^{+2n}\right]} = -RT. \ln \dfrac{2^2}{1} = -RT.\ln 4$

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$\Delta G^\circ = 2\Delta G^\circ - T\Delta S^\circ$

$\Delta S^\circ = \dfrac{\Delta G^\circ}{T} = -\dfrac{RT \ln 4}{T} = -8.3 \times 2 \times 0.7 = -11.62$ J/K.mol

11.   **Ans. (6)**

Sol.   For weak acid $[H^+] = c\alpha = c\dfrac{\Lambda_m^C}{\Lambda_m^\infty} = c \times \dfrac{\kappa \times \dfrac{1000}{c}}{\Lambda_m^\infty} = \dfrac{\kappa \times 1000}{\Lambda_m^\infty} = \dfrac{G \times \left(\dfrac{l}{a}\right) \times 1000}{\Lambda_m^\infty}$

$$10^{-4} = \dfrac{5 \times 10^{-7} \times \left(\dfrac{120}{1}\right) \times 1000}{Z \times 10^2} \Rightarrow Z = 6$$

12.   **Ans. (B)**
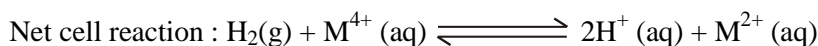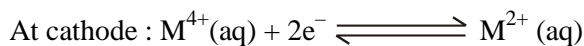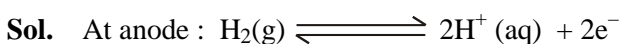
Sol. $\Delta G = \Delta G^0 + 2.303 RT \log Q$

$\Delta G = -nFE^0 + 2.303 RT \log Q$

Given : $E^\circ = 1.1$ V and $n = 2$

$\Delta G = (-2 \times 1.1 \times F) + 2.303 RT \log[\dfrac{[Zn^{+2}]}{Cu^{+2}}]$

$\Delta G = -2.2\,F + 2.303 RT$

13.   **Ans. (D)**

Sol.   At anode : $H_2(g) \rightleftharpoons 2H^+ (aq) + 2e^-$

At cathode : $M^{4+}(aq) + 2e^- \rightleftharpoons M^{2+} (aq)$

Net cell reaction : $H_2(g) + M^{4+} (aq) \rightleftharpoons 2H^+ (aq) + M^{2+} (aq)$

Now, $E_{cell} = \left(E^\circ_{M^{4+}/M^{2+}} - E^\circ_{H^+/H_2}\right) - \dfrac{0.059}{n}.\log \dfrac{\left[H^+\right]^2\left[M^{2+}\right]}{P_{H_2}.\left[M^{4+}\right]}$

or, $0.092 = (0.151 - 0) - \dfrac{0.059}{2}.\log \dfrac{1^2 \times \left[M^{2+}\right]}{1 \times \left[M^{4+}\right]}$

$\therefore \dfrac{\left[M^{2+}\right]}{\left[M^{4+}\right]} = 10^2 \Rightarrow x = 2$

14.   **Ans. (4)**

Sol. $|\Delta G| = -nFE$

$193 \times 10^3 = x \times 2 \times 96500 \times 0.25$
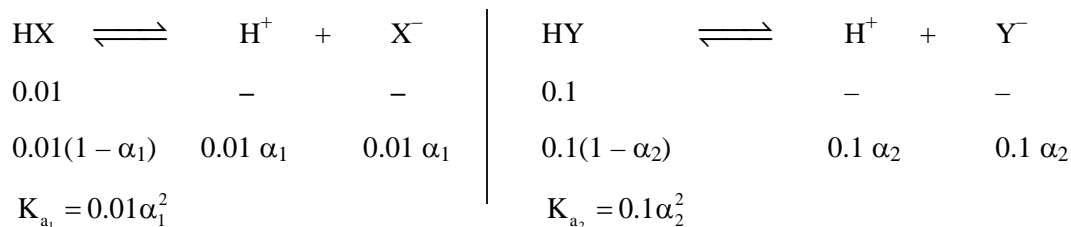
(where x is the number of moles of M^+ oxidised)

$x = 4$

15.   **Ans. (3)**

Sol. $\Lambda_m(HX) = \dfrac{x}{10}$ $\Lambda_m(HY) = x$

$$\frac{\Lambda_m(HX) / \Lambda_m^0(HX)}{\Lambda_m(HY) / \Lambda_m^0(HY)} = \frac{(x/10) / \Lambda_m^0(HX)}{x / \Lambda_m^0(HY)} = \frac{\alpha_1}{\alpha_2} = \frac{1}{10}$$

HX	$\rightleftharpoons$	H^+	$+$	X^-		HY	$\rightleftharpoons$	H^+	$+$	Y^-
0.01		–		–		0.1		–		–
$0.01(1-\alpha_1)$		$0.01\,\alpha_1$		$0.01\,\alpha_1$		$0.1(1-\alpha_2)$		$0.1\,\alpha_2$		$0.1\,\alpha_2$

$K_{a_1} = 0.01\alpha_1^2$ $K_{a_2} = 0.1\alpha_2^2$

$$\frac{K_{a_1}}{K_{a_2}} = \frac{1}{10}\cdot\frac{\alpha_1^2}{\alpha_2^2} = \frac{1}{1000}$$

$\log K_{a1} - \log K_{a2} = -3$

$pK_{a1} - pK_{a2} = 3$

16.   **Ans. (A, B)**

Sol.   **Note :** We feel option (C) is incorrect because in some type of concentration cells, salt bridge is not required. Which can be confirmed from NCERT (XII-Chemistry, Part-1) in Sub section 3.2 Galvanic Cell.

"*The electrolytes of the two half-cells are connected internally through a salt bridge as shown in Fig. 3.1. Sometimes, both the electrodes dip in the same electrolyte solution and in such cases we do not require a salt bridge.*"