ELECTROCHEMISTRY

1. The standard electrode potential $E^{\ominus}$ and its temeprature coefficient $\left(\frac{dE^{\ominus}}{dT}\right)$ for a cell are 2V and -5×10^{-4} VK^{-1} at 300 K respectively. The cell reaction is

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

The standard reaction enthalpy $\left(\Delta_r H^{\ominus}\right)$ at 300 K in kJ mol^{-1} is,

[Use R = $8JK^{-1}$ mol^{-1} and F = 96,000 $Cmol^{-1}$]

(1) –412.8 (2) –384.0

(3) 206.4 (4) 192.0

2. $\wedge_m^{\circ}$ for NaCl, HCl and NaA are 126.4, 425.9 and 100.5 S cm^2mol^{-1}, respectively. If the conductivity of 0.001 M HA is 5×10^{-5} S cm^{-1}, degree of dissociation of HA is :

(1) 0.75 (2) 0.125

(3) 0.25 (4) 0.50

3. Consider the following reduction processes :

$Zn^{2+} + 2e^- \rightarrow Zn(s)$; $E^{\circ} = -0.76$ V

$Ca^{2+} + 2e^- \rightarrow Ca(s)$; $E^{\circ} = -2.87$ V

$Mg^{2+} + 2e^- \rightarrow Mg(s)$; $E^{\circ} = -2.36$ V

$Ni^{2+} + 2e^- \rightarrow Ni(s)$; $E^{\circ} = -0.25$ V

The reducing power of the metals increases in the order :

(1) Ca < Zn < Mg < Ni

(2) Ni < Zn < Mg < Ca

(3) Zn < Mg < Ni < Ca

(4) Ca < Mg < Zn < Ni

4. In the cell :

$Pt(s)|H_2(g, 1bar|HCl(aq)|AgCl(s)|Ag(s)|Pt(s)$

the cell potential is 0.92V when a 10^{-6} molal HCl solution is used. The standard electrode potential of (AgCl/Ag,Cl^-) electrode is :

$\left\{given, \frac{2.303RT}{F} = 0.06V at 298K\right\}$

(1) 0.20 V (2) 0.76 V

(3) 0.40 V (4) 0.94 V

5. The anodic half-cell of lead-acid battery is recharged unsing electricity of 0.05 Faraday. The amount of $PbSO_4$ electrolyzed in g during the process in :

(Molar mass of $PbSO_4$ = 303 g mol^{-1})

(1) 22.8 (2) 15.2

(3) 7.6 (4) 11.4

6. For the cell $Zn(s)\,|\,Zn^{2+}(aq)\,||\,M^{x+}(aq)\,|\,M(s)$, different half cells and their standard electrode potentials are given below :

$M^{x+}(aq/M(s)$	$Au^{3+}(aq)/Au(s)$	$Ag^{+}(aq)/Ag(s)$	$Fe^{3+}(aq)/Fe^{2+}(aq)$	$Fe^{2+}(aq)/Fe(s)$
$E^{o}_{M^{x+}/M^{(v)}}$	1.40	0.80	0.77	–0.44

If $E^{o}_{Zn^{2+}/Zn} = -0.76V$, which cathode will give a mximum value of E^{o}_{cell} per electron transferred ?

(1) Fe^{3+} / Fe^{2+} (2) Ag^{+} / Ag

(3) Au^{3+} / Au (4) Fe^{2+} / Fe

7. If the standard electrode potential for a cell is 2 V at 300 K, the equilibrium constant (K) for the reaction

$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$

at 300 K is approximately.

(R = 8 JK^{-1} mol^{-1} , F = 96000 C mol^{-1})

(1) e^{160} (2) e^{320}

(3) e^{-160} (4) e^{-80}

8. Given the equilibrium constant :

K_C of the reaction :

$Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$ is 10×10^{15}, calculate the E^0_{cell} of this reaction at 298 K

$$\left[2.303\frac{RT}{F}\text{at}\,298\,K = 0.059V\right]$$

(1) 0.04736 V

(2) 0.4736 V

(3) 0.4736 mV

(4) 0.04736 mV

9. Given that : $E^0_{O_2/H_2O} = +1.23V$,

$E^0_{S_2O_8^{2-}/SO_4^{2-}} = +2.05V$

$E^0_{Br_2/Br^-} = +1.09V$

$E^0_{Au^{3+}/Au} = +1.4V$

The strongest oxidizing agent is -

(1) O_2 (2) Br_2

(3) $S_2O_8^{2-}$ (4) Au^{3+}

10. Calculate the standard cell potential in(V) of the cell in which following reaction takes place :
$Fe^{2+}(aq) + Ag^+(aq) \rightarrow Fe^{3+}(aq) + Ag(s)$
Given that

$E^o_{Ag^+/Ag} = xV$

$E^o_{Fe^{2+}/Fe} = yV$

$E^o_{Fe^{3+}/Fe} = zV$

(1) x + 2y – 3z (2) x – z

(3) x – y (4) x + y – z

11. The standard Gibbs energy for the given cell reaction in kJ mol^{-1} at 298 K is :

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

$E^\circ = 2$ V at 298 K

(Faraday's constant, F = 96000 C mol^{-1})

(1) –384 (2) –192

(3) 192 (4) 384

12. A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using 0.1 Faraday electricity. How many mole of Ni will be deposited at the cathode?

(1) 0.20 (2) 0.05

(3) 0.10 (4) 0.15

13. Consider the statements S1 and S2 :

S1 : Conductivity always increases with decrease in the concentration of electrolyte.

S2 : Molar conductivity always incrteases with decrease in the concentration of electrolyte.

The correct option among the following is :

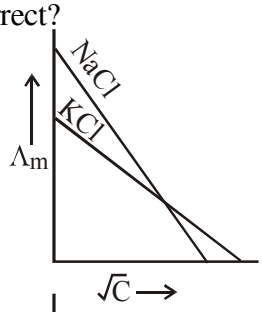
(1) Both S1 and S2 are correct

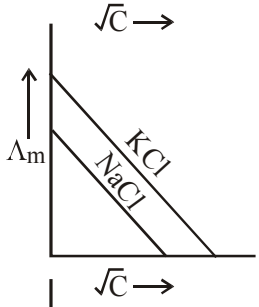
(2) S1 is wrong and S2 is correct

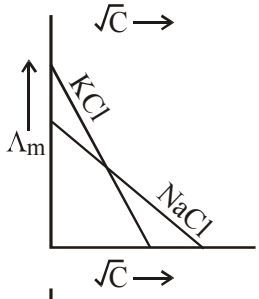
(3) S1 is correct and S2 is wrong

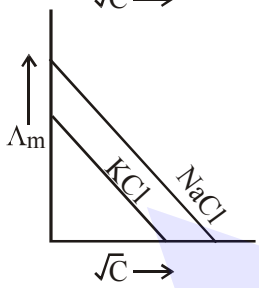
(4) Both S1 and S2 are wrong

14. Which one of the following graphs between molar conductivity (Λ_m) versus $\sqrt{C}$ is correct?

(1)


(2)


(3)


(4)


15. Given :

$Co^{3+} + e^- \rightarrow Co^{2+}$; $E^o = + 1.81$ V

$Pb^{4+} + 2e^- \rightarrow Pb^{2+}$; $E^o = + 1.67$ V

$Ce^{4+} + e^- \rightarrow Ce^{3+}$; $E^o = + 1.61$ V

$Bi^{3+} + 3e^- \rightarrow Bi$; $E^o = + 0.20$ V

Oxidizing power of the species will increase in the order :

(1) $Ce^{4+} < Pb^{4+} < Bi^{3+} < Co^{3+}$

(2) $Co^{3+} < Pb^{4+} < Ce^{4+} < Bi^{3+}$

(3) $Co^{3+} < Ce^{4+} < Bi^{3+} < Pb^{4+}$

(4) $Bi^{3+} < Ce^{4+} < Pb^{4+} < Co^{3+}$

16. The decreasing order of electrical conductivity of the following aqueous solutions is :

0.1 M Formic acid (A),

0.1 M Acetic acid (B)

0.1 M Benzoic acid (C)

(1) C > B > A (2) A > B > C

(3) A > C > B (4) C > A > B

SOLUTION

1. Ans. (1)

$\Delta G = \Delta H - \Delta S$

$$-nFE_{cell} = \Delta H - nFT\frac{dE_{cell}}{dT}$$

$(n = 2)$

2. Ans. (2)

$$\Lambda_m^0(HA) = \Lambda_m^0(HCl) + \Lambda_m^0(NaA) - \Lambda_m^0(NaCl)$$

$= 425.9 + 100.5 - 126.4$

$= 400\ S\ cm^2\ mol^{-1}$

$$\Lambda_m = \frac{1000K}{M} = \frac{1000\times 5\times 10^{-5}}{10^{-3}} = 50\ S\ cm^2\ mol^{-1}$$

$$\alpha = \frac{\Lambda_m}{\Lambda_m^0} = \frac{50}{400} = 0.125$$

3. Ans. (2)

Higher the oxidation potential better will be reducing power.

4. Ans. (1)

$$Pt(s)\left|H_2(g, 1bar)\right|HCl(aq)\left|AgCl(s)\right|Ag(s)\left|Pt(s)\right.$$

10^{-6} m

Anode: $H_2 \longrightarrow 2H^+ + 2e \times 1$

Cathode : $e^- + AgCl(s) \longrightarrow Ag(s) + Cl^-(aq) \times 2$

$$H_2(g) + 2AgCl(s) \longrightarrow 2H^+ + 2Ag(s) + 2Cl^-(aq)$$

$$E_{cell} = E_{cell}^0 - \frac{0.06}{2}\log_{10}\left((H^+)^2\cdot(Cl^-)^2\right)$$

$$0.92 = \left(E^0_{H_2/H^+} + E^0_{AgCl/Ag,Cl^-}\right) - \frac{0.06}{2}\log_{10}\left((10^{-6})^2\,(10^{-6})^2\right)$$

$$0.92 = 0 + E^0_{AgCl/Ag,Cl^-} - 0.03\log_{10}(10^{-6})^4$$

$$E^0_{AgCl}/Ag, Cl^- = .92 + .03 \times (-24) = 0.2\ V$$

5. Ans. (3)

(A) $PbSO_4(s) + 2OH^- \rightarrow PbO_2 + H_2SO_4 + 2e^-$

0.05/2 mole 0.05F

(C) $PbSO_4 + 2e^- + 2H^+ \longrightarrow Pb(s) + H_2SO_4$

0.05/2 mole 0.05 F

$n_T(PbSO_4) = 0.05$ mole

$m_{PbSO_4} = 0.05\times 303 = 15.2$ gm

6. Ans. (2)

(1) $3Zn_{(s)} + 2Au^{+3}_{(aq)} \xrightarrow{n=6} 3Zn^{+2}_{(aq)} + 2Au_{(s)}$

$$\frac{E^0_{cell}}{n} = 0.36$$

(2) $Zn_{(s)} + 2Ag^+_{(aq)} \xrightarrow{n=2} Zn^{+2}_{(aq)} + 2Ag_{(s)}$

$$\frac{E^0_{cell}}{n} = 0.78$$

(3) $Zn_{(s)} + 2Fe^{+3}_{(aq)} \xrightarrow{n=2} Zn^{+2}_{(aq)} + 2Fe^{+2}_{(aq)}$

$$\frac{E^0_{cell}}{n} = 0.765$$

(4) $Zn_{(s)} + Fe^{+2}_{(aq)} \xrightarrow{n=2} Zn^{+2}_{(aq)} + Fe_{(s)}$

$$\frac{E^0_{cell}}{n} = 0.16$$

We have maximum value of $\left(\frac{E^0_{cell}}{n}\right)$ for reaction (2)

7. Ans. (1)

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

$$\ln k = \frac{n\times F\times E^\circ}{R\times T} = \frac{2\times 96000\times 2}{8\times 300}$$

$\ln k = 160$

$k = e^{160}$

8. Ans. (2)

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

At equilibrium

$$E^{\circ}_{Cell} = \frac{0.059}{2}\log 10^{16}$$

$= 0.059 \times 8$

$= 0.472$ V

$\simeq 0.4736$ V

9. Ans. (3)

For strongest oxidising agent, standard reduction potential should be highest.

Correct option : (3)

10. Ans. (1)

Sol. $Fe^{+2}(aq) + Ag^{+}(aq) \rightarrow Fe^{+3}(aq) + Ag(s)$

Cell reaction

anode : $Fe^{+2}(aq) \rightarrow Fe^{+3}(aq) + e^{\Theta}$;

$$E^{o}_{Fe^{+2}/Fe^{+3}} = mV$$

cathode : $Ag^{+}(aq) + e^{\Theta} \rightarrow Ag(s)$;

$$E^{o}_{Ag^{+}/Ag} = xV$$

$\Rightarrow$ cell standard potential = (m + x)V

$\therefore$ to find 'm';

$Fe^{+2} + 2e^{\Theta} \rightarrow Fe$;

$$E^{o}_{1} = yV \Rightarrow \Delta^{o}_{1}G = -(2Fy)$$

$Fe^{+3} + 3e^{\Theta} \rightarrow Fe$;

$$E^{o}_{2} = zV \Rightarrow \Delta^{o}_{2}G = -(3Fz)$$

$Fe^{+2}(aq) \rightarrow Fe^{+3}(aq) + e^{\Theta}$;

$$E^{o}_{3} = mV \Rightarrow \Delta^{o}_{3}G = -(1Fm)$$

$\Delta^{o}_{3}G = \Delta G^{o}_{1} - \Delta G^{o}_{2} = (-2Fy + 3Fz) = -Fm$

$\Rightarrow m = (2y - 3z)$

$\Rightarrow E^{o}_{cell} = (x + 2y - 3z)V$

11. Ans. (1)

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

$= -2 \times 96000 \times 2$

$= -384000$ J

$= -384$ kJ

$\therefore$ Ans. is (1)

12. Ans. (2)

0.1 eq. of Ni^{+2} will be discharged.

No. of eq = (No of moles) × (n-factor)

0.1 = (No. of moles) × 2

No. of moles of Ni = $\frac{0.1}{2} = 0.05$

13. Ans. (2)

On dilution, no. of ions per ml decreases so conductivity decreases hence S1 is wrong.

$$\wedge_{M} = \frac{1000 \times \kappa}{C}$$

On dilution C and κ both decreases but effect of C is more dominating so $\wedge_{M}$ increases hence S2 is right.

14. Ans. (2)

Both NaCl and KCl are strong electrolytes and as $Na^{+}(aq.)$ has less conductance than $K^{+}(aq.)$ due to more hydration therefore the graph of option (2) is correct.

15. Ans. (4)

$E^{\circ}_{Red} \uparrow \Rightarrow$ oxidizing power $\uparrow$

16. Ans. (3)

Order of acidic strength

A > C > B

Acidic strength $\uparrow \Rightarrow$ degree of ionization $\uparrow$