

## CHAPTER

## 13

## Electrochemistry

## Section-A

## JEE Advanced/ IIT-JEE

## A Fill in the Blanks

- Of the halide ions, \_\_\_\_\_ is the most powerful reducing agent. (1978)
- The more \_\_\_\_\_ the standard reduction potential, the \_\_\_\_\_ is its ability to displace hydrogen from acids. (1986 - 1 Mark)
- The electrical conductivity of a solution of acetic acid will be \_\_\_\_\_ if a solution of sodium hydroxide is added. (1987 - 1 Mark)

## B True / False

- The dependence of electrode potential for the electrode  $M^{n+}/M$  with concentration under STP conditions is given by the expression :  $E = E^\circ + \frac{0.0591}{n} \log_{10}[M^{n+}]$  (1993 - 1 Mark)

## C MCQs with One Correct Answer

- The standard reduction potentials at 298 K for the following half reactions are given against each (1981 - 1 Mark)
 

$Zn^{2+}(aq) + 2e \rightleftharpoons Zn(s)$	-0.762
$Cr^{3+}(aq) + 2e \rightleftharpoons Cr(s)$	-0.740
$2H^+(aq) + 2e \rightleftharpoons H_2(g)$	0.000
$Fe^{3+}(aq) + 2e \rightleftharpoons Fe^{2+}(aq)$	0.770

 which is the strongest reducing agent?
  - Zn(s)
  - Cr(s)
  - $H_2(g)$
  - $Fe^{2+}(aq)$
- Faraday's laws of electrolysis are related to the (1983 - 1 Mark)
  - atomic number of the reactants.
  - atomic number of the anion.
  - equivalent weight of the electrolyte.
  - speed of the cation.
- A solution containing one mole per litre of each  $Cu(NO_3)_2$ ,  $AgNO_3$ ,  $Hg_2(NO_3)_2$ ; is being electrolysed by using inert electrodes. The values of standard electrode potentials in volts (reduction potentials) are : (1984 - 1 Mark)
 

$Ag/Ag^+ = +0.80$ ,	$2Hg/Hg_2^{++} = +0.79$
$Cu/Cu^{++} = +0.34$ ,	$Mg/Mg^{++} = -2.37$

 With increasing voltage, the sequence of deposition of metals on the cathode will be :
  - Ag, Hg, Cu, Mg
  - Mg, Cu, Hg, Ag
  - Ag, Hg, Cu
  - Cu, Hg, Ag
- The electric charge for electrode deposition of one gram equivalent of a substance is : (1984 - 1 Mark)
  - one ampere per second.
  - 96,500 coulombs per second.
  - one ampere for one hour.
  - charge on one mole of electrons.
- The reaction : (1985 - 1 Mark)
 
$$\frac{1}{2} Hg_2(g) + AgCl(s) \rightarrow H^+(aq) + Cl^-(aq) + Ag(s)$$
 occurs in the galvanic cell
  - $Ag | AgCl(s) | KCl(soln) | AgNO_3(soln) | Ag$
  - $Pt | H_2(g) | HCl(soln) | AgNO_3(soln) | Ag$
  - $Pt | H_2(g) | HCl(soln) | AgCl(s) | Ag$
  - $Pt | H_2(g) | KCl(soln) | AgCl(s) | Ag$
- A solution of sodium sulphate in water is electrolysed using inert electrodes. The products at the cathode and anode are respectively (1987 - 1 Mark)
 

(a) $H_2, O_2$	(b) $O_2, H_2$
(c) $O_2, Na$	(d) $O_2, SO_2$
- The standard oxidation potentials,  $E^\circ$ , for the half reactions are as (1988 - 1 Mark)
 

$Zn = Zn^{2+} + 2e^-; E^\circ = +0.76 V$
$Fe = Fe^{2+} + 2e^-; E^\circ = +0.41 V$

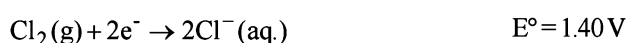
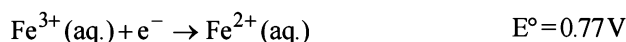
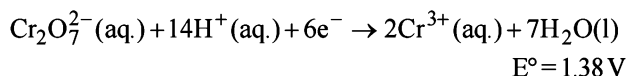
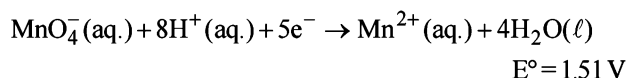
 The EMF for the cell reaction :
 
$$Fe^{2+} + Zn \rightarrow Zn^{2+} + Fe$$
  - 0.35 V
  - +0.35 V
  - +1.17 V
  - 1.17 V
- A dilute aqueous solution of  $Na_2SO_4$  is electrolyzed using platinum electrodes. The products at the anode and cathode are: (1996 - 1 Mark)
 

(a) $O_2, H_2$	(b) $S_2O_8^{2-}, Na$
(c) $O_2, Na$	(d) $S_2O_8^{2-}, H_2$
- The standard reduction potentials of  $Cu^{2+} | Cu$  and  $Cu^{2+} | Cu^+$  are 0.337 V and 0.153 respectively. The standard electrode potential of  $Cu^+ | Cu$  half cell is (1997 - 1 Mark)
  - 0.184 V
  - 0.827 V
  - 0.521 V
  - 0.490 V
- A gas X at 1 atm is bubbled through a solution containing a mixture of  $1 M Y^-$  and  $MZ^-$  at 25°C. If the reduction potential of  $Z > Y > X$ , then, (1999 - 2 Marks)
  - Y will oxidize X and not Z
  - Y will oxidize Z and not X
  - Y will oxidize both X and Z
  - Y will reduce both X and Z

11. For the electrochemical cell,  $M|M^+||X^-|X$ ,  $E^\circ M^+/M = 0.44V$  and  $E^\circ(X/X^-) = 0.33V$ .

From this data one can deduce that (2000S)

- (a)  $M + X \rightarrow M^+ + X^-$  is the spontaneous reaction  
 (b)  $M^+ + X^- \rightarrow M + X$  is the spontaneous reaction  
 (c)  $E_{\text{cell}} = 0.77V$   
 (d)  $E_{\text{cell}} = -0.77V$
12. Saturated solution of  $KNO_3$  is used to make 'salt-bridge' because (2001S)  
 (a) velocity of  $K^+$  is greater than that of  $NO_3^-$   
 (b) velocity of  $NO_3^-$  is greater than that of  $K^+$   
 (c) velocities of both  $K^+$  and  $NO_3^-$  are nearly the same  
 (d)  $KNO_3$  is highly soluble in water
13. The correct order of equivalent conductance at infinite dilution of  $LiCl$ ,  $NaCl$  and  $KCl$  is (2001S)  
 (a)  $LiCl > NaCl > KCl$  (b)  $KCl > NaCl > LiCl$   
 (c)  $NaCl > KCl > LiCl$  (d)  $LiCl > KCl > NaCl$
14. Standard electrode potential data are useful for understanding the suitability of an oxidant in a redox titration. Some half cell reactions and their standard potentials are given below: (2002S)

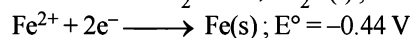
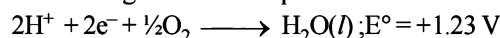


Identify the only incorrect statement regarding the quantitative estimation of aqueous  $Fe(NO_3)_2$

- (a)  $MnO_4^-$  can be used in aqueous  $HCl$   
 (b)  $Cr_2O_7^{2-}$  can be used in aqueous  $HCl$   
 (c)  $MnO_4^-$  can be used in aqueous  $H_2SO_4$   
 (d)  $Cr_2O_7^{2-}$  can be used in aqueous  $H_2SO_4$
15. In the electrolytic cell, flow of electrons is from (2003S)  
 (a) Cathode to anode in solution  
 (b) Cathode to anode through external supply  
 (c) Cathode to anode through internal supply  
 (d) Anode to cathode through internal supply
16. The emf of the cell (2004S)  
 $Zn|Zn^{2+}(0.01M)||Fe^{2+}(0.001M)|Fe$   
 at 298 K is 0.2905 then the value of equilibrium constant for the cell reaction is

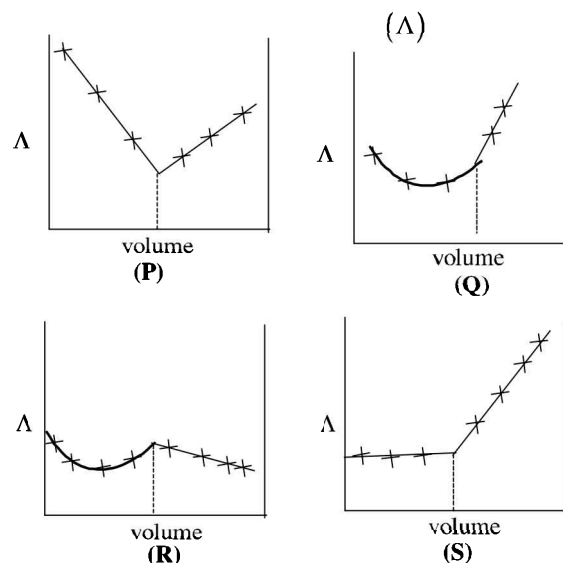
- (a)  $e^{\frac{0.32}{0.0295}}$  (b)  $10^{\frac{0.32}{0.0295}}$   
 (c)  $10^{\frac{0.26}{0.0295}}$  (d)  $10^{\frac{0.32}{0.0591}}$

17. The rusting of iron takes place as follows (2005S)

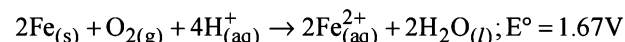


Calculate  $\Delta G^\circ$  for the net process

- (a)  $-322 \text{ kJ mol}^{-1}$  (b)  $-161 \text{ kJ mol}^{-1}$   
 (c)  $-152 \text{ kJ mol}^{-1}$  (d)  $-76 \text{ kJ mol}^{-1}$
18. Electrolysis of dilute aqueous  $NaCl$  solution was carried out by passing 10 milli ampere current. The time required to liberate 0.01 mol of  $H_2$  gas at the cathode is (1 Faraday =  $96500 \text{ C mol}^{-1}$ ) (2008S)  
 (a)  $9.65 \times 10^4 \text{ sec}$  (b)  $19.3 \times 10^4 \text{ sec}$   
 (c)  $28.95 \times 10^4 \text{ sec}$  (d)  $38.6 \times 10^4 \text{ sec}$
19.  $AgNO_3(aq.)$  was added to an aqueous  $KCl$  solution gradually and the conductivity of the solution was measured. The plot of conductance ( $\Lambda$ ) versus the volume of  $AgNO_3$  is (2011)



- (a) (P) (b) (Q)  
 (c) (R) (d) (S)
20. Consider the following cell reaction: (2011)



At  $[Fe^{2+}] = 10^{-3} M$ ,  $P(O_2) = 0.1 \text{ atm}$  and  $pH = 3$ , the cell potential at  $25^\circ C$  is

- (a) 1.47V (b) 1.77V  
 (c) 1.87V (d) 1.57V
21. For the following electrochemical cell at 298 K,  
 $Pt(s)|H_2(g, 1 \text{ bar})|H^+(aq, 1M)||M^{4+}(aq), M^{2+}(aq)|Pt(s)$

$$E_{\text{cell}} = 0.092V \text{ when } \frac{[M^{2+}(aq)]}{[M^{4+}(aq)]} = 10^x. \quad (JEE Adv. 2016)$$

$$\text{Given: } E^\circ_{M^{4+}/M^{2+}} = 0.151V; 2.303 \frac{RT}{F} = 0.059V$$

The value of x is

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

**D MCQs with One or More Than One Correct**

- The standard reduction potential values of three metallic cations, X, Y and Z are 0.52, -3.03 and -1.18 V respectively. The order of reducing power of the corresponding metals is (1998 - 2 Marks)
  - $Y > Z > X$
  - $X > Y > Z$
  - $Z > Y > X$
  - $Z > X > Y$
- For the reduction of  $\text{NO}_3^-$  ion in an aqueous solution,  $E^\circ$  is +0.96 V. Values of  $E^\circ$  for some metal ions are given below
 

$\text{V}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{V}$	$E^\circ = -1.19 \text{ V}$
$\text{Fe}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Fe}$	$E^\circ = -0.04 \text{ V}$
$\text{Au}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Au}$	$E^\circ = +1.40 \text{ V}$
$\text{Hg}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Hg}$	$E^\circ = +0.86 \text{ V}$

 The pair(s) of metals that is(are) oxidized by  $\text{NO}_3^-$  in aqueous solution is(are) (2009)
  - V and Hg
  - Hg and Fe
  - Fe and Au
  - Fe and V
- In a galvanic cell, the salt bridge (JEE Adv. 2014)
  - Does not participate chemically in the cell reaction
  - Stops the diffusion of ions from one electrode to another
  - Is necessary for the occurrence of the cell reaction
  - Ensures mixing of the two electrolytic solutions

**E Subjective Problems**

- The density of copper is 8.94 g/ml. Find out the number of coulombs needed to plate an area  $10 \text{ cm} \times 10 \text{ cm}$  to a thickness  $10^{-2} \text{ cm}$  using  $\text{CuSO}_4$  solution as electrolyte. (1979)
- 19 gm of molten  $\text{SnCl}_2$  is electrolysed for some time. Inert electrodes are used. 0.119 gm of Sn is deposited at the cathode. No substance is lost during the electrolysis. Find the ratio of the weights of  $\text{SnCl}_2$ :  $\text{SnCl}_4$  after electrolysis.
  - A hot solution of NaCl in water is electrolysed. Iron electrodes are used. Diaphragm cell is not used. Give equations for all the chemical reactions that take place during electrolysis.
  - Find the charge in coulombs of 1 gram ion of  $\text{N}^{3-}$  (1980)
- Complete and balance the following equations (1980)
  - $\text{KNO}_3 + \text{FeSO}_4 + \text{H}_2\text{SO}_{4(\text{conc})} \longrightarrow$
  - $\text{H}_2\text{S} + \text{K}_2\text{CrO}_4 + \text{H}_2\text{SO}_4 \longrightarrow$
  - $\text{KI} + \text{H}_2\text{SO}_{4(\text{conc})} \xrightarrow{\Delta}$
  - $\text{Mg}_3\text{N}_2 + \text{H}_2\text{O} \longrightarrow$
  - $\text{Al} + \text{KMnO}_4 + \text{H}_2\text{SO}_4 \longrightarrow$

- Consider the cell (1982 - 2 Marks)
 
$$\text{Zn} | \text{Zn}^{2+}(\text{aq}) (1.0 \text{ M}) || \text{Cu}^{2+}(\text{aq}) (1.0 \text{ M}) | \text{Cu}$$
 The standard reduction potentials are :  
 +0.350 volts for  $2\text{e}^- + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Cu}$  and -0.763 volts for  $2\text{e}^- + \text{Zn}^{2+}(\text{aq}) \rightarrow \text{Zn}$ 
  - Write down the cell reaction.
  - Calculate the emf of the cell.
  - Is the cell reaction spontaneous or not?
- In an electrolysis experiment current was passed for 5 hours through two cells connected in series. The first cell contains a solution of gold and the second contains copper sulphate solution. 9.85 g of gold was deposited in the first cell. If the oxidation number of gold is +3, find the amount of copper deposited on the cathode of the second cell. Also calculate the magnitude of the current in amperes. (1 faraday = 96,500 coulombs) (1983 - 3 Marks)
- How long a current of 3 ampere has to be passed through a solution of silver nitrate to coat a metal surface of  $80 \text{ cm}^2$  with a 0.005 mm thick layer? Density of silver is  $10.5 \text{ g/cm}^3$ . (1985 - 3 Marks)
- The EMF of a cell corresponding to the reaction :  

$$\text{Zn}(\text{s}) + 2\text{H}^+(\text{aq}) \rightarrow \text{Zn}^{2+} + (\text{O.1 M}) + \text{H}_2(\text{g}) (1 \text{ atm.})$$
 is 0.28 volt at  $25^\circ\text{C}$ .  
 Write the half-cell reactions and calculate the pH of the solution at the hydrogen electrode.  

$$E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ volt}; E^\circ_{\text{H}^+/\text{H}_2} = 0 \quad (1986 - 4 \text{ Marks})$$
- During the discharge of a lead storage battery, the density of sulphuric acid fell from 1.294 to 1.139 g/ml. Sulphuric acid of density 1.294 g/ml is 39% by weight and that of 1.139 g/ml is 20%  $\text{H}_2\text{SO}_4$  by weight. The battery holds 3.5 litres of the acid and the volume remained practically constant during the discharge.  
 Calculate the number of ampere-hours for which the battery must have been used. The charging and discharging reactions are : (1986 - 5 Marks)
 

**Anode :**

$$\text{Pb} + \text{SO}_4^{2-} = \text{PbSO}_4 + 2\text{e}^- \text{ (discharging)}$$

**Cathode :**

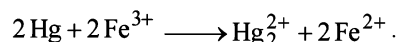
$$\text{PbO}_2 + 4\text{H}^+ + \text{SO}_4^{2-} + 2\text{e}^- = \text{PbSO}_4 + 2\text{H}_2\text{O} \text{ (discharging)}$$

**Note :** Both the reactions take place at the anode and cathode respectively during discharge. Both reaction get reverse during charging.
- A 100 watt, 110 volt incandescent lamp is connected in series with an electrolyte cell containing cadmium sulphate solution. What weight of cadmium will be deposited by the current flowing for 10 hours? (1987 - 5 Marks)
- A cell contains two hydrogen electrodes. The negative electrode is in contact with a solution of  $10^{-6} \text{ M}$  hydrogen ions. The EMF of the cell is 0.118 V at  $25^\circ\text{C}$ . Calculate the concentration of hydrogen ions at the positive electrode. (1988 - 2 Marks)

11. In a fuel cell hydrogen and oxygen react to produce electricity. In the process hydrogen gas is oxidised at the anode and oxygen at the cathode. If 67.2 litre of  $H_2$  at STP react in 15 minutes, what is the average current produced? If the entire current is used for electro deposition of copper from copper (II) solution, how many grams of copper will be deposited? (1988 - 4 Marks)
- Anode reaction :  $H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$
- Cathode reaction :  $\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^-$
12. An acidic solution of  $Cu^{2+}$  salt containing 0.4 g of  $Cu^{2+}$  is electrolysed until all the copper is deposited. The electrolysis is continued for seven more minutes with the volume of solution kept at 100 ml. and the current at 1.2 amp. Calculate the volume of gases evolved at NTP during the entire electrolysis. (1989 - 5 Marks)
13. The standard reduction potential at 25°C of the reaction,  $2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$  is  $-0.8277V$ . Calculate the equilibrium constant for the reaction  $2H_2O \rightleftharpoons H_3O^+ + OH^-$  at 25°C. (1989 - 3 Marks)
14. The standard reduction potential of  $Cu^{++}/Cu$  and  $Ag^+/Ag$  electrodes are 0.337 and 0.799 volt respectively. Construct a galvanic cell using these electrodes so that its standard e.m.f. is positive. For what concentration of  $Ag^+$  will the e.m.f. of the cell, at 25°C, be zero if the concentration of  $Cu^{++}$  is 0.01 M? (1990 - 3 Marks)
15. Calculate the quantity of electricity that would be required to reduce 12.3 g of nitrobenzene to aniline, if the current efficiency for the process is 50 per cent. If the potential drop across the cell is 3.0 volts, how much energy will be consumed? (1990 - 3 Marks)
16. Zinc granules are added in excess to a 500 ml. of 1.0 M nickel nitrate solution at 25°C until the equilibrium is reached. If the standard reduction potential of  $Zn^{2+} | Zn$  and  $Ni^{2+} | Ni$  are  $-0.75 V$  and  $-0.24 V$  respectively, find out the concentration of  $Ni^{2+}$  in solution at equilibrium. (1991 - 2 Marks)
17. A current of 1.70 A is passed through 300.0 ml of 0.160 M solution of a  $ZnSO_4$  for 230 sec. with a current efficiency of 90%. Find out the molarity of  $Zn^{2+}$  after the deposition of Zn. Assume the volume of the solution to remain constant during the electrolysis. (1991 - 4 Marks)
18. For the galvanic cell. (1992 - 4 Marks)
- $Ag|AgCl(s), KCl(0.2 M) || KBr(0.001M), AgBr(s)|Ag$
- Calculate the EMF generated and assign correct polarity to each electrode for a spontaneous process after taking into account the cell reaction at 25°C.
- $[K_{sp}(AgCl) = 2.8 \times 10^{-10}, K_{sp}(AgBr) = 3.3 \times 10^{-13}]$
19. An aqueous solution of NaCl on electrolysis gives  $H_2(g)$ ,  $Cl_2(g)$  and NaOH according to the reaction :
- $2Cl^-(aq) + 2H_2O = 2OH^-(aq) + H_2(g) + Cl_2(g)$
- A direct current of 25 amperes with a current efficiency of 62% is passed through 20 litres of NaCl solution (20% by weight). Write down the reactions taking place at the anode and the cathode. How long will it take to produce 1 kg of  $Cl_2$ ? What will be the molarity of the solution with respect to hydroxide ion? (Assume no loss due to evaporation.) (1992 - 3 Marks)
20. The standard reduction potential for the half-cell
- $NO_3^-(aq) + 2H^+(aq) + e^- \rightarrow NO_2(g) + H_2O$  is 0.78 V.
- (i) Calculate the reduction potential in 8 M  $H^+$
- (ii) What will be the reduction potential of the half-cell in a neutral solution? Assume all the other species to be at unit concentration. (1993 - 2 Marks)
21. Chromium metal can be plated out from an acidic solution containing  $CrO_3$  according to the following equation.
- $CrO_3(aq) + 6H^+(aq) + 6e^- \rightarrow Cr(s) + 3H_2O$
- Calculate (i) how many grams of chromium will be plated out by 24,000 coulombs and (ii) how long will it take to plate out 1.5 g of chromium by using 12.5 amp current. (1993 - 2 Marks)
22. The standard reduction potential of the  $Ag^+ / Ag$  electrode at 298 K is 0.799 V. Given that for  $AgI$ ,  $K_{sp} = 8.7 \times 10^{-17}$ , evaluate the potential of the  $Ag^+ / Ag$  electrode in a saturated solution of  $AgI$ . Also calculate the standard reduction potential of the  $I^- / AgI / Ag$  electrode. (1994 - 3 Marks)
23. The Edison storage cells is represented as
- $Fe(s) | FeO(s) | KOH(aq) | Ni_2O_3(s) | Ni(s)$
- The half-cell reactions are :
- $Ni_2O_3(s) + H_2O(l) + 2e^- \rightleftharpoons 2NiO(s) + 2OH^- ;$   
 $E^\circ = +0.40V$
- $FeO(s) + H_2O(l) + 2e^- \rightleftharpoons Fe(s) + 2OH^- ;$   
 $E^\circ = -0.87V$
- (i) What is the cell reaction ?
- (ii) What is the cell e.m.f ? How does it depend on the concentration of KOH?
- (iii) What is the maximum amount of electrical energy that can be obtained from one mole of  $Ni_2O_3$ ? (1994 - 4 Marks)
24. Although aluminium is above hydrogen in the electrochemical series, it is stable in air and water. Explain. (1994 - 1 Mark)



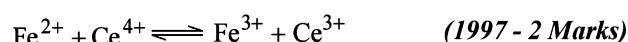
25. An excess of liquid mercury is added to an acidified solution of  $1.0 \times 10^{-3} \text{ M Fe}^{3+}$ . It is found that 5% of  $\text{Fe}^{3+}$  remains at equilibrium at  $25^\circ\text{C}$ . Calculate  $E^\circ_{\text{Hg}_2^{2+}/\text{Hg}}$ , assuming that the only reaction that occurs is



(Given  $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.77 \text{ V}$ .) (1995 - 4 Marks)

26. The standard reduction potential for  $\text{Cu}^{2+}|\text{Cu}$  is  $+0.34 \text{ V}$ . Calculate the reduction potential at  $\text{pH} = 14$  for the above couple.  $K_{\text{sp}}$  of  $\text{Cu}(\text{OH})_2$  is  $1.0 \times 10^{-19}$  (1996 - 3 Marks)
27. How many grams of silver could be plated out on a serving tray by electrolysis of a solution containing silver in  $+1$  oxidation state for a period of 8.0 hours at a current of 8.46 amperes? What is the area of the tray if the thickness of the silver plating is  $0.00254 \text{ cm}$ ? Density of silver is  $10.5 \text{ g/cm}^3$ . (1997 - 3 Marks)

28. Calculate the equilibrium constant for the reaction



(given  $E^\circ_{\text{Ce}^{4+}/\text{Ce}^{3+}} = 1.44 \text{ V}$ ;  $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.68 \text{ V}$ ;) )

29. Calculate the equilibrium constant for the reaction,  $2\text{Fe}^{3+} + 3\text{I}^- \rightleftharpoons 2\text{Fe}^{2+} + \text{I}_3^-$ . The standard reduction potentials in acidic conditions are  $0.77 \text{ V}$  and  $0.54 \text{ V}$  respectively for  $\text{Fe}^{3+}|\text{Fe}^{2+}$  and  $\text{I}_3^-|\text{I}^-$  couples.

(1998 - 3 Marks)

30. Find the solubility product of a saturated solution of  $\text{Ag}_2\text{CrO}_4$  in water at  $298 \text{ K}$  if the emf of the cell  $\text{Ag}|\text{Ag}^+(\text{satd. } \text{Ag}_2\text{CrO}_4 \text{ soln.})||\text{Ag}^+(0.1\text{M})|\text{Ag}$  is  $0.164 \text{ V}$  at  $298 \text{ K}$ . (1998 - 6 Marks)
31. A cell,  $\text{Ag}|\text{Ag}^+||\text{Cu}^{2+}|\text{Cu}$ , initially contains  $1 \text{ M Ag}^+$  and  $1 \text{ M Cu}^{2+}$  ions. Calculate the change in the cell potential after the passage of  $9.65 \text{ A}$  of current for  $1 \text{ h}$ . (1999 - 6 Marks)
32. Copper sulphate solution ( $250 \text{ mL}$ ) was electrolysed using a platinum anode and a copper cathode. A constant current of  $2 \text{ mA}$  was passed for  $16 \text{ minutes}$ . It was found that after electrolysis the absorbance of the solution was reduced to  $50\%$  of its original value. Calculate the concentration of copper sulphate in the solution to begin with.

(2000 - 3 Marks)

33. The following electrochemical cell has been set up.  
 $\text{Pt}(1)|\text{Fe}^{3+}, \text{Fe}^{2+} (a=1)||\text{Ce}^{4+}, \text{Ce}^{3+} (a=1)|\text{Pt}(2)$   
 $E^\circ(\text{Fe}^{3+}, \text{Fe}^{2+}) = 0.77 \text{ V}$ ;  $E^\circ(\text{Ce}^{4+}/\text{Ce}^{3+}) = 1.61 \text{ V}$   
 If an ammeter is connected between the two platinum electrodes, predict the direction of flow of current. Will the current increase or decrease with time? (2000 - 2 Marks)
34. The standard potential of the following cell is  $0.23 \text{ V}$  at  $15^\circ\text{C}$  and  $0.21 \text{ V}$  at  $35^\circ\text{C}$ . (2001 - 10 Marks)
- $$\text{Pt}|\text{H}_2(\text{g})|\text{HCl}(\text{aq})|\text{AgCl}(\text{s})|\text{Ag}(\text{s})$$

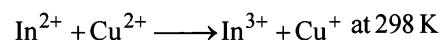
- (i) Write the cell reaction.  
 (ii) Calculate  $\Delta H^\circ$  and  $\Delta S^\circ$  for the cell reaction by assuming that these quantities remain unchanged in the range  $15^\circ\text{C}$  to  $35^\circ\text{C}$ .

- (iii) Calculate the solubility of  $\text{AgCl}$  in water at  $25^\circ\text{C}$ .

**Given :** The standard reduction potential of the  $\text{Ag}^+(\text{aq})/\text{Ag}(\text{s})$  couple is  $0.80 \text{ V}$  at  $25^\circ\text{C}$ .

35. Two students use same stock solution of  $\text{ZnSO}_4$  and a solution of  $\text{CuSO}_4$ . The emf of one cell is  $0.03 \text{ V}$  higher than the other. The conc. of  $\text{CuSO}_4$  in the cell with higher emf value is  $0.5 \text{ M}$ . Find out the conc. of  $\text{CuSO}_4$  in the other cell ( $2.203 \text{ RT/F} = 0.06$ ). (2003 - 2 Marks)

36. Find the equilibrium constant for the reaction,

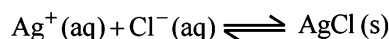


given :

$$E_{\text{Cu}^{2+}/\text{Cu}^+} = 0.15 \text{ V}; \quad E_{\text{In}^{2+}/\text{In}^+}^0 = -0.40 \text{ V}, \quad E_{\text{In}^{3+}/\text{In}^+}^0 = -0.42 \text{ V}$$

(2004 - 4 Marks)

37. (a) For the reaction



Given :

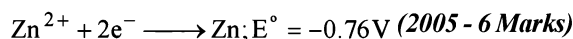
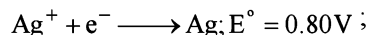
Species	$\Delta G_f^\circ \text{ (kJ/mol)}$
$\text{Ag}^+(\text{aq})$	$+77$
$\text{Cl}^-(\text{aq})$	$-129$
$\text{AgCl}(\text{s})$	$-109$

Write the cell representation of above reaction and calculate  $E^\circ_{\text{cell}}$  at  $298 \text{ K}$ . Also find the solubility product of  $\text{AgCl}$ .

- (b) If  $6.539 \times 10^{-2} \text{ g}$  of metallic zinc is added to  $100 \text{ ml}$  saturated

solution of  $\text{AgCl}$ . Find the value of  $\log_{10} \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2}$ .

How many moles of  $\text{Ag}$  will be precipitated in the above reaction. Given that



(It was given that Atomic mass of  $\text{Zn} = 65.39$ )

38. We have taken a saturated solution of  $\text{AgBr}$ .  $K_{\text{sp}}$  of  $\text{AgBr}$  is  $12 \times 10^{-14}$ . If  $10^{-7} \text{ mole}$  of  $\text{AgNO}_3$  are added to  $1 \text{ litre}$  of this solution find conductivity (specific conductance) of this solution in terms of  $10^{-7} \text{ S m}^{-1}$  units. Given, Molar conductance of  $\text{Ag}^+$ ,  $\text{Br}^-$  and  $\text{NO}_3^-$  are  $6 \times 10^{-3} \text{ Sm}^2\text{mol}^{-1}$ ,  $8 \times 10^{-3} \text{ Sm}^2\text{mol}^{-1}$  and  $7 \times 10^{-3} \text{ Sm}^2\text{mol}^{-1}$ . (2006 - 6M)

## F Match the Following

**DIRECTION (for Q. 1) :** Each question contains statements given in two columns, which have to be matched. The statements in Column-I are labelled A, B, C and D, while the statements in Column-II are labelled p, q, r, s and t. Any given statement in Column-I can have correct matching with ONE OR MORE statement(s) in Column-II. The appropriate bubbles corresponding to the answers to these questions have to be darkened as illustrated in the following example :

If the correct matches are A-p, s and t; B-q and r; C-p and q; and D-s then the correct darkening of bubbles will look like the given.

	p	q	r	s	t
A	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input checked="" type="radio"/>	<input checked="" type="radio"/>
B	<input type="radio"/>	<input checked="" type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>
C	<input checked="" type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>
D	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>

1. Match the reactions in Columns I with nature of the reactions/type of the products in Column II. Indicate your answer by darkening the appropriate bubbles of the  $4 \times 4$  matrix given in the ORS. (2007)

Column I	Column II
(A) $\text{O}_2^- \rightarrow \text{O}_2 + \text{O}_2^{2-}$	(p) redox reaction
(B) $\text{CrO}_4^{2-} + \text{H}^+ \rightarrow$	(q) one of the products has trigonal planar structure
(C) $\text{MnO}_4^- + \text{NO}_2^- + \text{H}^+ \rightarrow$	(r) dimeric bridged tetrahedral metal ion
(D) $\text{NO}_3^- + \text{H}_2\text{SO}_4 + \text{Fe}^{2+} \rightarrow$	(s) disproportionation

**DIRECTION (for Q. 2 & 3) :** Following questions have matching lists. The codes for the lists have choices (a), (b), (c) and (d) out of which ONLY ONE is correct.

2. An aqueous solution of X is added slowly to an aqueous solution of Y as shown in List I. The variation in conductivity of these reactions is given in List II. Match list I with List II and select the correct answer using the code given below the lists : (JEE Adv. 2013)

List I	List II
P. $\text{(C}_2\text{H}_5)_3\text{N} + \text{CH}_3\text{COOH}$ X Y	1. Conductivity decreases and then increases
Q. $\text{KI} (0.1\text{M}) + \text{AgNO}_3 (0.01\text{M})$ X Y	2. Conductivity decreases and then does not change much
R. $\text{CH}_3\text{COOH} + \text{KOH}$ X Y	3. Conductivity increases and then does not change much
S. $\text{NaOH} + \text{HI}$ X Y	4. Conductivity does not change much and then increases

**Codes :**

	P	Q	R	S
(a)	3	4	2	1
(b)	4	3	2	1
(c)	2	3	4	1
(d)	1	4	3	2

3. The standard reduction potential data at  $25^\circ\text{C}$  is given below : (JEE Adv. 2013)

$E^\circ(\text{Fe}^{3+}, \text{Fe}^{2+}) = +0.77\text{ V}$ ;  $E^\circ(\text{Fe}^{2+}, \text{Fe}) = -0.44\text{ V}$ ;  $E^\circ(\text{Cu}^{2+}, \text{Cu}) = +0.34\text{ V}$ ;  $E^\circ(\text{Cu}^+, \text{Cu}) = +0.52\text{ V}$   
 $E^\circ[\text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}] = +1.23\text{ V}$ ;  $E^\circ[\text{O}_2(\text{g}) + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-] = +0.40\text{ V}$   
 $E^\circ(\text{Cr}^{3+}, \text{Cr}) = -0.74\text{ V}$ ;  $E^\circ(\text{Cr}^{2+}, \text{Cr}) = -0.91\text{ V}$

Match  $E^\circ$  of the redox pair in List I with the values given in List II and select the correct answer using the code given below the lists :

List I	List II
P. $E^\circ(\text{Fe}^{3+}, \text{Fe})$	1. $-0.18\text{ V}$
Q. $E^\circ(4\text{H}_2\text{O} \rightleftharpoons 4\text{H}^+ + 4\text{OH}^-)$	2. $-0.4\text{ V}$
R. $E^\circ(\text{Cu}^{2+} + \text{Cu} \rightarrow 2\text{Cu}^+)$	3. $-0.04\text{ V}$
S. $E^\circ(\text{Cr}^{3+}, \text{Cr}^{2+})$	4. $-0.83\text{ V}$

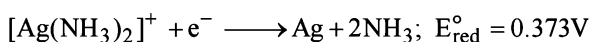
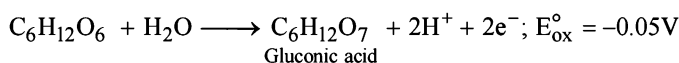
**Codes :**

	P	Q	R	S
(a)	4	1	2	3
(b)	2	3	4	1
(c)	1	2	3	4
(d)	3	4	1	2

## G Comprehension Based Questions

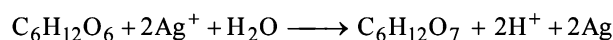
### PASSAGE : I

Tollen's test is given by aldehydes.



Given  $\frac{2.303RT}{F} = 0.0591$  &  $\left(\frac{F}{RT}\right) = 38.92 \text{ V}^{-1}$

1. Calculate (ln K) for



- (a) 55.6 (b) 29.6 (2006 - 5M, -2)  
(c) 66 (d) 58.38
2. On adding  $\text{NH}_3$ , pH of the solution increases to 11 then, identify the effect on potential of half-cell (2006 - 5M, -2)
- (a)  $E_{\text{ox}}$  increased from  $E_{\text{ox}}^\circ$  by 0.65 V  
(b)  $E_{\text{ox}}$  decreased from  $E_{\text{ox}}^\circ$  by 0.65 V  
(c)  $E_{\text{red}}$  increased from  $E_{\text{red}}^\circ$  by 0.65 V  
(d)  $E_{\text{red}}$  decreased from  $E_{\text{red}}^\circ$  by 0.65 V
3.  $\text{NH}_3$  is used in this reaction rather than any other base. Select the correct statement out of the following (2006 - 5M, -2)
- (a)  $[\text{Ag}(\text{NH}_3)_2]^+$  is a weaker oxidizing agent than  $\text{Ag}^+$   
(b) to dissolve the insoluble silver oxide formed under the reaction conditions  
(c) Ag precipitates gluconic acid as its silver salt  
(d)  $\text{NH}_3$  changes the standard reduction potential of  $[\text{Ag}(\text{NH}_3)_2]^+$

### PASSAGE : II

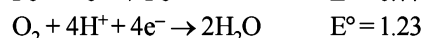
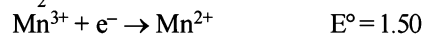
Chemical reactions involve interaction of atoms and molecules. A large number of atoms/molecules (approximately  $6.023 \times 10^{23}$ ) are present in a few grams of any chemical compound varying with their atomic/molecular masses. To handle such large numbers conveniently, the mole concept was introduced. This concept has implications in diverse areas such as analytical chemistry, biochemistry, electrochemistry and radiochemistry. The following example illustrates a typical case, involving chemical/electrochemical reaction, which requires a clear understanding of the mole concept. A 4.0 molar aqueous solution of NaCl is prepared and 500 mL of this solution is electrolysed. This leads to the evolution of chlorine gas at one of the electrodes (atomic mass : Na = 23, Hg = 200; 1 Faraday = 96500 coulombs).

4. The total number of moles of chlorine gas evolved is (2007)
- (a) 0.5 (b) 1.0  
(c) 2.0 (d) 3.0

5. If the cathode is a Hg electrode, the maximum weight (g) of amalgam formed from this solution is (2007)
- (a) 200 (b) 225  
(c) 400 (d) 446
6. The total charge (coulombs) required for complete electrolysis is (2007)
- (a) 24125 (b) 48250  
(c) 96500 (d) 193000

### PASSAGE : III

Redox reactions play a pivotal role in chemistry and biology. The values of standard redox potential ( $E^\circ$ ) of two half-cell reactions decide which way the reaction is expected to proceed. A simple example is a Daniel cell in which zinc goes into solution and copper gets deposited. Given below are a set of half-cell reactions (acidic medium) along with their  $E^\circ$  (V with respect to normal hydrogen electrode) values. Using this data obtain the correct explanations to questions given.



7. Among the following, identify the correct statement. (2007)
- (a) Chloride ion is oxidised by  $\text{O}_2$   
(b)  $\text{Fe}^{2+}$  is oxidised by iodine  
(c) Iodide ion is oxidised by chlorine  
(d)  $\text{Mn}^{2+}$  is oxidised by chlorine
8. While  $\text{Fe}^{3+}$  is stable,  $\text{Mn}^{3+}$  is not stable in acid solution because (2007)
- (a)  $\text{O}_2$  oxidises  $\text{Mn}^{2+}$  to  $\text{Mn}^{3+}$   
(b)  $\text{O}_2$  oxidises both  $\text{Mn}^{2+}$  to  $\text{Mn}^{3+}$  and  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$   
(c)  $\text{Fe}^{3+}$  oxidises  $\text{H}_2\text{O}$  to  $\text{O}_2$   
(d)  $\text{Mn}^{3+}$  oxidises  $\text{H}_2\text{O}$  to  $\text{O}_2$
9. Sodium fusion extract, obtained from aniline, on treatment with iron (II) sulphate and  $\text{H}_2\text{SO}_4$  in presence of air gives a Prussian blue precipitate. The blue colour is due to the formation of (2007)
- (a)  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$  (b)  $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$   
(c)  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_2$  (d)  $\text{Fe}_3[\text{Fe}(\text{CN})_6]_3$

### PASSAGE : IV

The concentration of potassium ions inside a biological cell is at least twenty times higher than the outside. The resulting potential difference across the cell is important in several processes such as transmission of nerve impulses and maintaining the ion balance. A simple model for such a concentration cell involving a metal M is  $\text{M(s)} | \text{M}^+(\text{aq}; 0.05 \text{ molar}) || \text{M}^+(\text{aq}; 1 \text{ molar}) | \text{M(s)}$ . For the above electrolytic cell the magnitude of the cell potential  $|E_{\text{cell}}| = 70 \text{ mV}$ . (2010)

10. For the above cell
- (a)  $E_{\text{cell}} < 0; \Delta G > 0$  (b)  $E_{\text{cell}} > 0; \Delta G < 0$   
(c)  $E_{\text{cell}} < 0; \Delta G^\circ > 0$  (d)  $E_{\text{cell}} > 0; \Delta G^\circ < 0$
11. If the 0.05 molar solution of  $\text{M}^+$  is replaced by a 0.0025 molar  $\text{M}^+$  solution, then the magnitude of the cell potential would be
- (a) 35mV (b) 70mV (c) 140mV (d) 700mV

## PASSAGE : V

The electrochemical cell shown below is a concentration cell.

$M | M^{2+}$  (saturated solution of a sparingly soluble salt,  $MX_2$ )  $|| M^{2+}$  (0.001 mol dm<sup>-3</sup>)  $| M$ .

The emf of the cell depends on the difference in concentrations of  $M^{2+}$  ions at the two electrodes. The emf of the cell at 298 K is 0.059 V. (2012)

12. The value of  $\Delta G$  (kJ mol<sup>-1</sup>) for the given cell is (take  $1F = 96500$  C mol<sup>-1</sup>)  
 (a) -5.7 (b) 5.7 (c) 11.4 (d) -11.4
13. The solubility product ( $K_{sp}$ ; mol<sup>3</sup> dm<sup>-9</sup>) of  $MX_2$  at 298 K based on the information available for the given concentration cell is (take  $2.303 \times R \times 298/F = 0.059$  V)  
 (a)  $1 \times 10^{-15}$  (b)  $4 \times 10^{-15}$   
 (c)  $1 \times 10^{-12}$  (d)  $4 \times 10^{-12}$

## Section-B

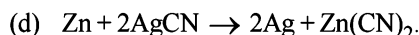
## JEE Main / AIEEE

1. Conductivity (unit Siemen's S) is directly proportional to area of the vessel and the concentration of the solution in it and is inversely proportional to the length of the vessel then the unit of the constant of proportionality is  
 (a) Sm mol<sup>-1</sup> (b) Sm<sup>2</sup> mol<sup>-1</sup> [2002]  
 (c) S<sup>-2</sup>m<sup>2</sup> mol (d) S<sup>2</sup>m<sup>2</sup> mol<sup>-2</sup>.
2. EMF of a cell in terms of reduction potential of its left and right electrodes is [2002]  
 (a)  $E = E_{\text{left}} - E_{\text{right}}$  (b)  $E = E_{\text{left}} + E_{\text{right}}$   
 (c)  $E = E_{\text{right}} - E_{\text{left}}$  (d)  $E = -(E_{\text{right}} + E_{\text{left}})$ .
3. What will be the emf for the given cell [2002]  
 $Pt | H_2(P_1) | H^+(aq) || H_2(P_2) | Pt$   
 (a)  $\frac{RT}{F} \log_e \frac{P_1}{P_2}$  (b)  $\frac{RT}{2F} \log_e \frac{P_1}{P_2}$   
 (c)  $\frac{RT}{F} \log_e \frac{P_2}{P_1}$  (d) None of these.
4. Which of the following reaction is possible at anode?  
 (a)  $2Cr^{3+} + 7H_2O \rightarrow Cr_2O_7^{2-} + 14H^+$  [2002]  
 (b)  $F_2 \rightarrow 2F^-$   
 (c)  $(1/2)O_2 + 2H^+ \rightarrow H_2O$   
 (d) None of these.
5. When the sample of copper with zinc impurity is to be purified by electrolysis, the appropriate electrodes are  

<b>Cathode</b>	<b>Anode</b>	[2002]
(a) pure zinc	pure copper	
(b) impure sample	pure copper	
(c) impure zinc	impure sample	
(d) pure copper	impure sample.	
6. Which of the following is a redox reaction? [2002]  
 (a)  $NaCl + KNO_3 \rightarrow NaNO_3 + KCl$   
 (b)  $CaC_2O_4 + 2HCl \rightarrow CaCl_2 + H_2C_2O_4$

## I Integer Value Correct Type

1. All the energy released from the reaction  $X \rightarrow Y$ ,  $\Delta_r G^\circ = -193$  kJ mol<sup>-1</sup> is used for oxidizing  $M^+$  as  $M^+ \rightarrow M^{3+} + 2e^-$ ,  $E^\circ = -0.25$  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<sup>-1</sup>] (JEE Adv. 2015)
2. 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 (0.10 M). If  $\lambda_{X^-}^0 \approx \lambda_{Y^-}^0$  the difference in their  $pK_a$  values,  $pK_a(HX) - pK_a(HY)$ , is (consider degree of ionization of both acids to be  $\ll 1$ ) (JEE Adv. 2015)



7. For a cell reaction involving a two-electron change, the standard e.m.f. of the cell is found to be 0.295 V at 25°C. The equilibrium constant of the reaction at 25°C will be  
 (a)  $29.5 \times 10^{-2}$  (b) 10 [2003]  
 (c)  $1 \times 10^{10}$  (d)  $1 \times 10^{-10}$
8. Standard reduction electrode potentials of three metals A, B & C are respectively +0.5 V, -3.0 V & -1.2 V. The reducing powers of these metals are [2003]  
 (a)  $A > B > C$  (b)  $C > B > A$   
 (c)  $A > C > B$  (d)  $B > C > A$
9. When during electrolysis of a solution of  $AgNO_3$  9650 coulombs of charge pass through the electroplating bath, the mass of silver deposited on the cathode will be  
 (a) 10.8 g (b) 21.6 g [2003]  
 (c) 108 g (d) 1.08 g
10. For the redox reaction : [2003]  
 $Zn(s) + Cu^{2+}(0.1M) \rightarrow Zn^{2+}(1M) + Cu(s)$   
 taking place in a cell,  $E_{\text{cell}}^\circ$  is 1.10 volt.  $E_{\text{cell}}$  for the cell will be  $\left(2.303 \frac{RT}{F} = 0.0591\right)$   
 (a) 1.80 volt (b) 1.07 volt [2003]  
 (c) 0.82 volt (d) 2.14 volt
11. Several blocks of magnesium are fixed to the bottom of a ship to  
 (a) make the ship lighter  
 (b) prevent action of water and salt  
 (c) prevent puncturing by under-sea rocks  
 (d) keep away the sharks



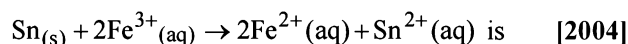
12. In a hydrogen-oxygen fuel cell, combustion of hydrogen occurs to [2004]

(a) produce high purity water  
(b) create potential difference between two electrodes  
(c) generate heat  
(d) remove adsorbed oxygen from electrode surfaces

13. Consider the following  $E^\circ$  values

$$E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = +0.77\text{V}; \quad E^\circ_{\text{Sn}^{2+}/\text{Sn}} = -0.14\text{V}$$

Under standard conditions the potential for the reaction



(a) 0.91 V (b) 1.40 V  
(c) 1.68 V (d) 0.63 V

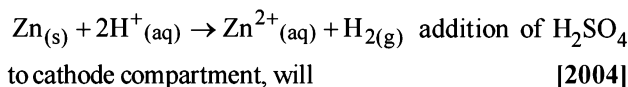
14. The standard e.m.f. of a cell involving one electron change is found to be 0.591 V at 25°C. The equilibrium constant of the reaction is ( $F = 96,500 \text{ C mol}^{-1}$ ;  $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ )

(a)  $1.0 \times 10^{10}$  (b)  $1.0 \times 10^5$  [2004]  
(c)  $1.0 \times 10^1$  (d)  $1.0 \times 10^{30}$

15. The limiting molar conductivities  $\Lambda^\circ$  for NaCl, KBr and KCl are 126, 152 and  $150 \text{ S cm}^2 \text{ mol}^{-1}$  respectively. The  $\Lambda^\circ$  for NaBr is [2004]

(a)  $278 \text{ S cm}^2 \text{ mol}^{-1}$  (b)  $176 \text{ S cm}^2 \text{ mol}^{-1}$   
(c)  $128 \text{ S cm}^2 \text{ mol}^{-1}$  (d)  $302 \text{ S cm}^2 \text{ mol}^{-1}$

16. In a cell that utilises the reaction



(a) increase the E and shift equilibrium to the right  
(b) lower the E and shift equilibrium to the right  
(c) lower the E and shift equilibrium to the left  
(d) increase the E and shift equilibrium to the left

17. The  $E^\circ_{\text{M}^{3+}/\text{M}^{2+}}$  values for Cr, Mn, Fe and Co are  $-0.41$ ,  $+1.57$ ,  $+0.77$  and  $+1.97\text{V}$  respectively. For which one of these metals the change in oxidation state from +2 to +3 is easiest?

(a) Fe (b) Mn [2004]  
(c) Cr (d) Co

18. For a spontaneous reaction the  $\Delta G$ , equilibrium constant (K) and  $E^\circ_{\text{Cell}}$  will be respectively [2005]

(a)  $-ve, >1, -ve$  (b)  $-ve, <1, -ve$   
(c)  $+ve, >1, -ve$  (d)  $-ve, >1, +ve$

19. The highest electrical conductivity of the following aqueous solutions is of [2005]

(a) 0.1 M difluoroacetic acid  
(b) 0.1 M fluoroacetic acid  
(c) 0.1 M chloroacetic acid  
(d) 0.1 M acetic acid

20. Aluminium oxide may be electrolysed at  $1000^\circ\text{C}$  to furnish aluminium metal (At. Mass = 27 amu; 1 Faraday = 96,500

Coulombs). The cathode reaction is—  $\text{Al}^{3+} + 3e^- \rightarrow \text{Al}^\circ$

To prepare 5.12 kg of aluminium metal by this method we require [2005]

- (a)  $5.49 \times 10^1 \text{ C}$  of electricity  
(b)  $5.49 \times 10^4 \text{ C}$  of electricity  
(c)  $1.83 \times 10^7 \text{ C}$  of electricity  
(d)  $5.49 \times 10^7 \text{ C}$  of electricity

21.

Electrolyte:	KCl	KNO <sub>3</sub>	HCl	NaOAc	NaCl
$\Lambda^\infty (\text{S cm}^2 \text{ mol}^{-1})$ :	149.9	145	426.2	91	126.5

Calculate  $\Lambda^\infty_{\text{HOAc}}$  using appropriate molar conductances of the electrolytes listed above at infinite dilution in  $\text{H}_2\text{O}$  at  $25^\circ\text{C}$  [2005]

(a) 217.5 (b) 390.7  
(c) 552.7 (d) 517.2

22. Which of the following chemical reactions depict the oxidizing behaviour of  $\text{H}_2\text{SO}_4$ ? [2006]

(a)  $\text{NaCl} + \text{H}_2\text{SO}_4 \longrightarrow \text{NaHSO}_4 + \text{HCl}$   
(b)  $2\text{PCl}_5 + \text{H}_2\text{SO}_4 \longrightarrow 2\text{POCl}_3 + 2\text{HCl} + \text{SO}_2\text{Cl}_2$   
(c)  $2\text{HI} + \text{H}_2\text{SO}_4 \longrightarrow \text{I}_2 + \text{SO}_2 + 2\text{H}_2\text{O}$   
(d)  $\text{Ca}(\text{OH})_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{CaSO}_4 + 2\text{H}_2\text{O}$

23. The molar conductivities  $\Lambda^\circ_{\text{NaOAc}}$  and  $\Lambda^\circ_{\text{HCl}}$  at infinite dilution in water at  $25^\circ\text{C}$  are 91.0 and  $426.2 \text{ S cm}^2/\text{mol}$  respectively. To calculate  $\Lambda^\circ_{\text{HOAc}}$ , the additional value required is [2006]

(a)  $\Lambda^\circ_{\text{NaOH}}$  (b)  $\Lambda^\circ_{\text{NaCl}}$   
(c)  $\Lambda^\circ_{\text{H}_2\text{O}}$  (d)  $\Lambda^\circ_{\text{KCl}}$

24. Resistance of a conductivity cell filled with a solution of an electrolyte of concentration 0.1 M is  $100 \Omega$ . The conductivity of this solution is  $1.29 \text{ S m}^{-1}$ . Resistance of the same cell when filled with 0.2 M of the same solution is  $520 \Omega$ . The molar conductivity of 0.2 M solution of electrolyte will be [2006]

(a)  $1.24 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$  (b)  $12.4 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$   
(c)  $124 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$  (d)  $1240 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$

25. The equivalent conductances of two strong electrolytes at infinite dilution in  $\text{H}_2\text{O}$  (where ions move freely through a solution) at  $25^\circ\text{C}$  are given below: [2007]

$$\Lambda^\circ_{\text{CH}_3\text{COONa}} = 91.0 \text{ S cm}^2/\text{equiv.}$$

$$\Lambda^\circ_{\text{HCl}} = 426.2 \text{ S cm}^2/\text{equiv.}$$

What additional information/ quantity one needs to calculate  $\Lambda^\circ$  of an aqueous solution of acetic acid?

- (a)  $\Lambda^\circ$  of chloroacetic acid ( $\text{ClCH}_2\text{COOH}$ )  
(b)  $\Lambda^\circ$  of NaCl  
(c)  $\Lambda^\circ$  of  $\text{CH}_3\text{COOK}$   
(d) the limiting equivalent conductance of  $\text{H}^+$  ( $\lambda^\circ_{\text{H}^+}$ ).

26. The cell,  $\text{Zn} | \text{Zn}^{2+} (1 \text{ M}) || \text{Cu}^{2+} (1 \text{ M}) | \text{Cu}$  ( $E^\circ_{\text{cell}} = 1.10 \text{ V}$ ) was allowed to be completely discharged at 298 K. The relative concentration of  $\text{Zn}^{2+}$  to  $\text{Cu}^{2+}$   $\left( \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \right)$  is [2007]
- (a)  $9.65 \times 10^4$  (b)  $\text{antilog}(24.08)$   
(c) 37.3 (d)  $10^{37.3}$
27. Given  $E^\circ_{\text{Cr}^{3+}/\text{Cr}} = -0.72 \text{ V}$ ,  $E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.42 \text{ V}$ . The potential for the cell  $\text{Cr} | \text{Cr}^{3+} (0.1 \text{ M}) || \text{Fe}^{2+} (0.01 \text{ M}) | \text{Fe}$  is [2008]
- (a) 0.26 V (b) 0.336 V  
(c) -0.339 (d) 0.26 V
28. In a fuel cell methanol is used as fuel and oxygen gas is used as an oxidizer. The reaction is
- $$\text{CH}_3\text{OH}(l) + 3/2 \text{O}_2(g) \longrightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l)$$
- At 298 K standard Gibbs energies of formation for  $\text{CH}_3\text{OH}(l)$ ,  $\text{H}_2\text{O}(l)$  and  $\text{CO}_2(g)$  are  $-166.2$ ,  $-237.2$  and  $-394.4 \text{ kJ mol}^{-1}$  respectively. If standard enthalpy of combustion of methanol is  $-726 \text{ kJ mol}^{-1}$ , efficiency of the fuel cell will be: [2009]
- (a) 87% (b) 90%  
(c) 97% (d) 80%
29. Given:  $E^\circ_{\text{Fe}^{3+}/\text{Fe}} = -0.036 \text{ V}$ ,  $E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.439 \text{ V}$
- The value of standard electrode potential for the change,  $\text{Fe}^{3+}(\text{aq}) + \text{e}^- \longrightarrow \text{Fe}^{2+}(\text{aq})$  will be: [2009]
- (a) 0.385 V (b) 0.770 V  
(c) -0.270 V (d) -0.072 V
30. The Gibbs energy for the decomposition of  $\text{Al}_2\text{O}_3$  at  $500^\circ\text{C}$  is as follows:
- $$\frac{2}{3} \text{Al}_2\text{O}_3 \rightarrow \frac{4}{3} \text{Al} + \text{O}_2, \Delta_r G = +966 \text{ kJ mol}^{-1}$$
- The potential difference needed for electrolytic reduction of  $\text{Al}_2\text{O}_3$  at  $500^\circ\text{C}$  is at least [2010]
- (a) 4.5 V (b) 3.0 V  
(c) 2.5 V (d) 5.0 V
31. The correct order of  $E^\circ_{\text{M}^{2+}/\text{M}}$  values with negative sign for the four successive elements Cr, Mn, Fe and Co is [2010]
- (a)  $\text{Mn} > \text{Cr} > \text{Fe} > \text{Co}$  (b)  $\text{Cr} < \text{Fe} > \text{Mn} > \text{Co}$   
(c)  $\text{Fe} > \text{Mn} > \text{Cr} > \text{Co}$  (d)  $\text{Cr} > \text{Mn} > \text{Fe} > \text{Co}$
32. The reduction potential of hydrogen half-cell will be negative if: [2011]
- (a)  $p(\text{H}_2) = 1 \text{ atm}$  and  $[\text{H}^+] = 2.0 \text{ M}$   
(b)  $p(\text{H}_2) = 1 \text{ atm}$  and  $[\text{H}^+] = 1.0 \text{ M}$   
(c)  $p(\text{H}_2) = 2 \text{ atm}$  and  $[\text{H}^+] = 1.0 \text{ M}$   
(d)  $p(\text{H}_2) = 2 \text{ atm}$  and  $[\text{H}^+] = 2.0 \text{ M}$
33. The standard reduction potentials for  $\text{Zn}^{2+}/\text{Zn}$ ,  $\text{Ni}^{2+}/\text{Ni}$  and  $\text{Fe}^{2+}/\text{Fe}$  are  $-0.76$ ,  $-0.23$  and  $-0.44 \text{ V}$  respectively.
- The reaction  $\text{X} + \text{Y}^{2+} \longrightarrow \text{X}^{2+} + \text{Y}$  will be spontaneous when: [2012]
- (a)  $\text{X} = \text{Ni}$ ,  $\text{Y} = \text{Fe}$  (b)  $\text{X} = \text{Ni}$ ,  $\text{Y} = \text{Zn}$   
(c)  $\text{X} = \text{Fe}$ ,  $\text{Y} = \text{Zn}$  (d)  $\text{X} = \text{Zn}$ ,  $\text{Y} = \text{Ni}$
34. Given:  $E^\circ_{\text{Cr}^{3+}/\text{Cr}} = -0.74 \text{ V}$ ;  $E^\circ_{\text{MnO}_4^-/\text{Mn}^{2+}} = 1.51 \text{ V}$
- $$E^\circ_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}} = 1.33 \text{ V}; E^\circ_{\text{Cl}^-/\text{Cl}_2} = 1.36 \text{ V}$$
- Based on the data given above, strongest oxidising agent will be: [JEE M 2013]
- (a)  $\text{Cl}_2$  (b)  $\text{Cr}^{3+}$   
(c)  $\text{Mn}^{2+}$  (d)  $\text{MnO}_4^-$
35. Resistance of 0.2 M solution of an electrolyte is  $50 \Omega$ . The specific conductance of the solution is  $1.4 \text{ S m}^{-1}$ . The resistance of 0.5 M solution of the same electrolyte is  $280 \Omega$ . The molar conductivity of 0.5 M solution of the electrolyte in  $\text{S m}^2 \text{ mol}^{-1}$  is: [JEE M 2014]
- (a)  $5 \times 10^{-4}$  (b)  $5 \times 10^{-3}$   
(c)  $5 \times 10^3$  (d)  $5 \times 10^2$
36. Given below are the half-cell reactions: [JEE M 2014]
- $$\text{Mn}^{2+} + 2\text{e}^- \rightarrow \text{Mn}; E^\circ = -1.18 \text{ V}$$
- $$2(\text{Mn}^{3+} + \text{e}^- \rightarrow \text{Mn}^{2+}); E^\circ = +1.51 \text{ V}$$
- The  $E^\circ$  for  $3\text{Mn}^{2+} \rightarrow \text{Mn} + 2\text{Mn}^{3+}$  will be:
- (a)  $-2.69 \text{ V}$ ; the reaction will not occur  
(b)  $-2.69 \text{ V}$ ; the reaction will occur  
(c)  $-0.33 \text{ V}$ ; the reaction will not occur  
(d)  $-0.33 \text{ V}$ ; the reaction will occur
37. The equivalent conductance of  $\text{NaCl}$  at concentration  $C$  and at infinite dilution are  $\lambda_C$  and  $\lambda_\infty$ , respectively. The correct relationship between  $\lambda_C$  and  $\lambda_\infty$  is given as: (Where the constant  $B$  is positive) [JEE M 2014]
- (a)  $\lambda_C = \lambda_\infty + (B)C$  (b)  $\lambda_C = \lambda_\infty - (B)C$   
(c)  $\lambda_C = \lambda_\infty - (B)\sqrt{C}$  (d)  $\lambda_C = \lambda_\infty + (B)\sqrt{C}$
38. Two Faraday of electricity is passed through a solution of  $\text{CuSO}_4$ . The mass of copper deposited at the cathode is (at. mass of  $\text{Cu} = 63.5 \text{ amu}$ ) [JEE M 2015]
- (a) 2g (b) 127g  
(c) 0g (d) 63.5g
39. Galvanization is applying a coating of: [JEE M 2016]
- (a)  $\text{Cu}$  (b)  $\text{Zn}$   
(c)  $\text{Pb}$  (d)  $\text{Cr}$