CHAPTER 13 Electrochemistry

Section-A JEE Advanced/ IIT-JEE

A Fill in the Blanks

1. Of the halide ions, _____ is the most powerful reducing agent. *(1978)*
2. The more .... the standard reduction potential, the .... is its ability to displace hydrogen from acids. *(1986 - 1 Mark)*
3. 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

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

C MCQs with One Correct Answer

1. 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?
(a) Zn(s) (b) Cr(s)
(c) $H_2(g)$ (d) $Fe^{2+}(aq)$
2. Faraday's laws of electrolysis are related to the
(a) atomic number of the reactants. *(1983 - 1 Mark)*
(b) atomic number of the anion.
(c) equivalent weight of the electrolyte.
(d) speed of the cation.
3. 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 :
(a) Ag, Hg, Cu, Mg (b) Mg, Cu, Hg, Ag
(c) Ag, Hg, Cu (d) Cu, Hg, Ag
4. The electric charge for electrode deposition of one gram equivalent of a substance is : *(1984 - 1 Mark)*
(a) one ampere per second.
(b) 96,500 coloumbs per second.
(c) one ampere for one hour.
(d) charge on one mole of electrons.
5. 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
(a) $Ag\,|\,AgCl(s)\,|\,KCl\,(soln)\,|\,AgNO_3\,(soln)\,|\,Ag$
(b) $Pt\,|\,H_2(g)\,|\,HCl\,(soln)\,|\,AgNO_3\,(soln)\,|\,Ag$
(c) $Pt\,|\,H_2(g)\,|\,HCl\,(soln)\,|\,AgCl(s)\,|\,Ag$
(d) $Pt\,|\,H_2(g)\,|\,KCl\,(soln)\,|\,AgCl(s)\,|\,Ag$
6. 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
7. The standard oxidation potentials, E°, for the half reactions are as *(1988 - 1 Mark)*
$Zn = Zn^{2+} + 2e^{-}$; E° = +0.76 V
$Fe = Fe^{2+} + 2e^{-}$; E° = +0.41 V
The EMF for the cell reaction :
$Fe^{2+} + Zn \rightarrow Zn^{2+} + Fe$
(a) –0.35 V (b) +0.35 V
(c) +1.17 V (d) –1.17 V
8. 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) $S_2O_8^{2-}, H_2$
9. 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)*
(a) 0.184 V (b) 0.827 V
(c) 0.521 V (d) 0.490 V
10. A gas X at 1 atm is bubbled through a solution containing a mixture of 1 M Y^{-} and M Z^{-} at 25°C. If the reduction potential of Z > Y > X, then, *(1999 - 2 Marks)*
(a) Y will oxidize X and not Z
(b) Y will oxidize Z and not X
(c) Y will oxidize both X and Z
(d) Y will reduce both X and Z

11. For the electrochemical cell, $M|M^+||X^-|X, E°M^+/M = 0.44 V$ and $E°(X/X^-) = 0.33 V$.
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) $E_{cell} = 0.77 V$
(d) $E_{cell} = -0.77 V$

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)*

$MnO_4^-(aq.) + 8H^+(aq.) + 5e^- \rightarrow Mn^{2+}(aq.) + 4H_2O(\ell)$ $E° = 1.51 V$

$Cr_2O_7^{2-}(aq.) + 14H^+(aq.) + 6e^- \rightarrow 2Cr^{3+}(aq.) + 7H_2O(l)$ $E° = 1.38 V$

$Fe^{3+}(aq.) + e^- \rightarrow Fe^{2+}(aq.)$ $E° = 0.77 V$

$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq.)$ $E° = 1.40 V$

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

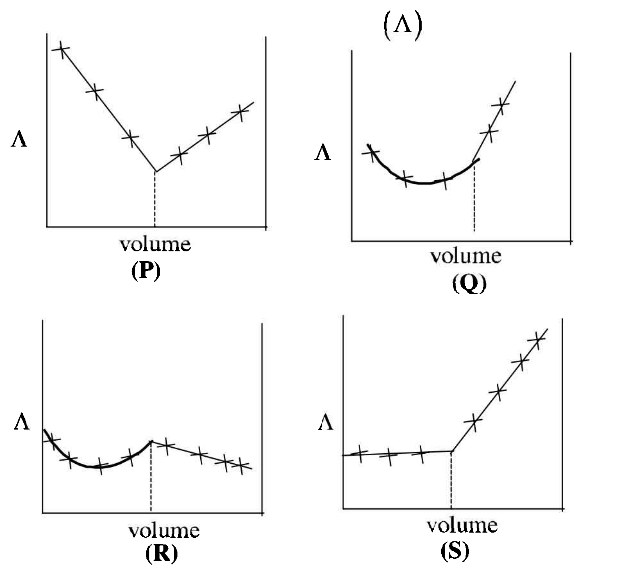
15. In the electrolytic cell, flow of electrons is from *(2003S)*
(a) Cathode to anode in solution
(b) Cathode to anode through external supply
(c) Cathode to anode through internal supply
(d) Anode to cathode through internal supply

16. The emf of the cell *(2004S)*
$Zn | Zn^{2+} (0.01 M) | | Fe^{2+} (0.001 M) | Fe$
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)*
$2H^+ + 2e^- + ½O_2 \longrightarrow H_2O(l); E° = +1.23 V$
$Fe^{2+} + 2e^- \longrightarrow Fe(s); E° = -0.44 V$
Calculate $\Delta G°$ for the net process
(a) $-322 kJ mol^{-1}$ (b) $-161 kJ mol^{-1}$
(c) $-152 kJ mol^{-1}$ (d) $-76 kJ mol^{-1}$

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 C mol^{-1}) *(2008S)*
(a) 9.65×10^4 sec (b) 19.3×10^4 sec
(c) 28.95×10^4 sec (d) 38.6×10^4 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 (Λ) versus the volume of $AgNO_3$ is *(2011)*



(a) (P) (b) (Q)
(c) (R) (d (S)

20. Consider the following cell reaction: *(2011)*

$2Fe_{(s)} + O_{2(g)} + 4H^+_{(aq)} \rightarrow 2Fe^{2+}_{(aq)} + 2H_2O_{(l)}; E° = 1.67V$

At $[Fe^{2+}] = 10^{-3}$ M, $P(O_2) = 0.1$ atm and pH = 3, the cell potential at 25ºC is
(a) 1.47V (b) 1.77V
(c) 1.87V (d) 1.57V

21. For the following electrochemical cell at 298 K,
$Pt(s)|H_2(g, 1 bar)| H^+(aq, 1 M) || M^{4+}(aq), M^{2+}(aq)|Pt(s)$

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

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

The value of x is
(a) –2 (b) –1
(c) 1 (d) 2

D MCQs with One or More Than One Correct

1. 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)*
   (a) Y > Z > X (b) X > Y > Z
   (c) Z > Y > X (d) Z > X > Y
2. For the reduction of NO_3^- ion in an aqueous solution, E° is + 0.96V. Values of E° for some metal ions are given below
   $V^{2+}(aq) + 2e^- \rightarrow V$ E° = – 1.19 V
   $Fe^{3+}(aq) + 3e^- \rightarrow Fe$ E° = – 0.04 V
   $Au^{3+}(aq) + 3e^- \rightarrow Au$ E° = + 1.40 V
   $Hg^{2+}(aq) + 2e^- \rightarrow Hg$ E° = + 0.86 V
   The pair(s) of metals that is(are) oxidized by NO_3^- in aqueous solution is(are) *(2009)*
   (a) V and Hg (b) Hg and Fe
   (c) Fe and Au (d) Fe and V
3. In a galvanic cell, the salt bridge *(JEE Adv. 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 occurrence of the cell reaction
   (d) Ensures mixing of the two electrolytic solutions

E Subjective Problems

1. The density of copper is 8.94 g/ml. Find out the number of coulombs needed to plate an area 10 cm × 10cm to a thickness 10^{-2} cm using $CuSO_4$ solution as electrolyte. *(1979)*
2. (a) 19 gm of molten $SnCl_2$ 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 $SnCl_2 : SnCl_4$ after electrolysis.
   (b) 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.
   (c) Find the charge in coulombs of 1 gram ion of N^{3-} *(1980)*
3. Complete and balance the following equations *(1980)*
   (i) $KNO_3 + FeSO_4 + H_2SO_{4(conc)} \longrightarrow$
   (ii) $H_2S + K_2CrO_4 + H_2SO_4 \longrightarrow$
   (iii) $KI + H_2SO_4(conc) \xrightarrow{\Delta}$
   (iv) $Mg_3N_2 + H_2O \longrightarrow$
   (v) $Al + KMnO_4 + H_2SO_4 \longrightarrow$
4. Consider the cell *(1982 - 2 Marks)*
   $Zn \mid Zn^{2+}(aq)\,(1.0\,M) \parallel Cu^{2+}(aq)\,(1.0\,M) \mid Cu$.
   The standard reduction potentials are :
   +0.350 volts for $2e^- + Cu^{2+}(aq) \rightarrow Cu$ and –0.763 volts for $2e^- + Zn^{2+}(aq) \rightarrow Zn$
   (i) Write down the cell reaction.
   (ii) Calculate the emf of the cell.
   (iii) Is the cell reaction spontaneous or not?
5. 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)*
6. How long a current of 3 ampere has to be passed through a solution of silver nitrate to coat a metal surface of 80 cm^2 with a 0.005 mm thick layer? Density of silver is 10.5 g/cm^3. *(1985 - 3 Marks)*
7. The EMF of a cell corresponding to the reaction :
   $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+} + (0.1\,M) + H_2(g)\,(1\,atm.)$
   is 0.28 volt at 25°C.
   Write the half-cell reactions and calculate the pH of the solution at the hydrogen electrode.
   $E^\circ_{Zn^{2+}/Zn} = -0.76$ volt; $E^\circ_{H^+/H_2} = 0$ *(1986 - 4 Marks)*
8. 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% H_2SO_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 :
   $Pb + SO_4^{2-} = PbSO_4 + 2e^-$ (discharging)
   Cathode :
   $PbO_2 + 4H^+ + SO_4^{2-} + 2e^- = PbSO_4 + 2H_2O$ (discharging)
   Note : Both the reactions take place at the anode and cathode respectively during discharge. Both reaction get reverse during charging.
9. 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)*
10. A cell contains two hydrogen electrodes. The negative electrode is in contact with a solution of 10^{-6} M hydrogen ions. The EMF of the cell is 0.118 V at 25°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 :

$Ni_2O_3(s) + H_2O(l) + 2e^- \rightleftharpoons 2NiO(s) + 2OH^-$; $E° = +0.40V$

$FeO(s) + H_2O(l) + 2e^- \rightleftharpoons Fe(s) + 2OH^-$; $E° = -0.87V$

(*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 1.0×10^{-3} M Fe^{3+}. It is found that 5% of Fe^{3+} remains at equilibrium at 25°C. Calculate $E^{\circ}_{Hg_2^{2+}|Hg}$, assuming that the only reaction that occurs is

$$2\,Hg + 2\,Fe^{3+} \longrightarrow Hg_2^{2+} + 2\,Fe^{2+}.$$

(Given $E^{\circ}_{Fe^{3+}|Fe^{2+}} = 0.77\,V$.) *(1995 - 4 Marks)*

26. The standard reduction potential for Cu^{2+}| Cu is +0.34 V. Calculate the reduction potential at pH = 14 for the above couple. K_{sp} of $Cu(OH)_2$ is 1.0×10^{-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 cm? Density of silver is 10.5 g/cm^3. *(1997 - 3 Marks)*

28. Calculate the equilibrium constant for the reaction

$$Fe^{2+} + Ce^{4+} \rightleftharpoons Fe^{3+} + Ce^{3+}$$ *(1997 - 2 Marks)*

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

29. Calculate the equilibrium constant for the reaction, $2Fe^{3+} + 3I^- \rightleftharpoons 2Fe^{2+} + I_3^-$. The standard reduction potentials in acidic conditions are 0.77 V and 0.54 V respectively for Fe^{3+} | Fe^{2+} and I_3^- | I^- couples. *(1998 - 3 Marks)*

30. Find the solubility product of a saturated solution of Ag_2CrO_4 in water at 298 K if the emf of the cell Ag | Ag^+ (satd. Ag_2CrO_4 soln.)||Ag+(0.1M)|Ag is 0.164 V at 298 K. *(1998 - 6 Marks)*

31. A cell, Ag | Ag^+||Cu^{2+}|Cu, initiallly contains 1 M Ag^+ and 1 M Cu^{2+} ions. Calculate the change in the cell potential after the passage of 9.65 A of current for 1 h. *(1999 - 6 Marks)*

32. Copper sulphate solution (250 mL) was electrolysed using a platinum anode and a copper cathode. A constant current of 2 mA was passed for 16 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.
Pt(1) |Fe^{3+}, Fe^{2+} (a = 1)| Ce^{4+}, Ce^{3+} (a = 1)| Pt (2)
E° (Fe^{3+}, Fe^{2+}) = 0.77 V : E° (Ce^{4+} / Ce^{3+}) = 1.61 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 V at 15°C and 0.21 V at 35°C. *(2001 - 10 Marks)*

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

(i) Write the cell reaction.
(ii) Calculate ΔH° and ΔS° for the cell reaction by assuming that these quantities remain unchanged in the range 15°C to 35°C.
(iii) Calculate the solubility of AgCl in water at 25°C.
Given : The standard reduction potential of the Ag^+(aq) / Ag(s) couple is 0.80 V at 25°C.

35. Two students use same stock solution of $ZnSO_4$ and a solution of $CuSO_4$. The emf of one cell is 0.03 V higher than the other. The conc. of $CuSO_4$ in the cell with higher emf value is 0.5 M. Find out the conc. of $CuSO_4$ in the other cell (2.203 RT/F = 0.06). *(2003 - 2 Marks)*

36. Find the equilibrium constant for the reaction,

$$In^{2+} + Cu^{2+} \longrightarrow In^{3+} + Cu^{+} \text{ at } 298\text{ K}$$

given :

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

(2004 - 4 Marks)

37. (a) For the reaction

$$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$$

Given :

Species	ΔG_f° (kJ/mol)
Ag^+(aq)	+77
Cl^-(aq)	– 129
AgCl (s)	– 109

Write the cell representation of above reaction and calculate E°_{cell} at 298 K. Also find the solubility product of AgCl.

(b) If 6.539×10^{-2} g of metallic zinc is added to 100 ml saturated solution of AgCl. Find the value of $\log_{10} \frac{[Zn^{2+}]}{[Ag^+]^2}$.

How many moles of Ag will be precipitated in the above reaction. Given that

$Ag^+ + e^- \longrightarrow Ag;\ E^{\circ} = 0.80\,V$;

$Zn^{2+} + 2e^- \longrightarrow Zn;\ E^{\circ} = -0.76\,V$ *(2005 - 6 Marks)*

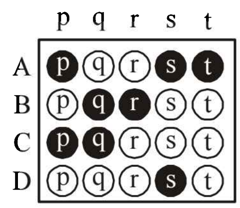
(It was given that Atomic mass of Zn = 65.39)

38. We have taken a saturated solution of AgBr. K_{sp} of AgBr is 12×10^{-14}. If 10^{-7} mole of $AgNO_3$ are added to 1 litre of this solution find conductivity (specific conductance) of this solution in terms of 10^{-7} S m^{-1} units. Given, Molar conductance of Ag^+, Br^- and NO_3^- are 6×10^{-3} Sm^{2}mol^{-1}, 8×10^{-3} Sm^{2}mol^{-1} and 7×10^{-3} Sm^{2}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.



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 × 4 matrix given in the ORS. ***(2007)***

Column I	**Column II**
(A) $O_2^- \rightarrow O_2 + O_2^{2-}$	(p) redox reaction
(B) $CrO_4^{2-} + H^+ \rightarrow$	(q) one of the products has trigonal planar structure
(C) $MnO_4^- + NO_2^- + H^+ \rightarrow$	(r) dimeric bridged tetrahedral metal ion
(D) $NO_3^- + H_2SO_4 + Fe^{2+} \rightarrow$	(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. $\underset{X}{(C_2H_5)_3N} + \underset{Y}{CH_3COOH}$	1. Conductivity decreases and then increases
Q. $\underset{X}{KI(0.1M)} + \underset{Y}{AgNO_3(0.01M)}$	2. Conductivity decreases and then does not change much
R. $\underset{X}{CH_3COOH} + \underset{Y}{KOH}$	3. Conductivity increases and then does not change much
S. $\underset{X}{NaOH} + \underset{Y}{HI}$	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°C is given below : ***(JEE Adv. 2013)***

$E°(Fe^{3+}, Fe^{2+}) = +0.77\ V$; $E°(Fe^{2+}, Fe) = -0.44\ V$; $E°(Cu^{2+}, Cu) = +0.34\ V$; $E°(Cu^+, Cu) = +0.52\ V$

$E°[O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O] = +1.23\ V$; $E°[O_2(g) + 2H_2O + 4e^- \rightarrow 4OH^-] = +0.40\ V$

$E°(Cr^{3+}, Cr) = -0.74\ V$; $E°(Cr^{2+}, Cr) = -0.91\ V$

Match E° 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. $E°(Fe^{3+}, Fe)$	1. −0.18 V
Q. $E°(4H_2O \rightleftharpoons 4H^+ + 4OH^-)$	2. −0.4 V
R. $E°(Cu^{2+} + Cu \rightarrow 2Cu^+)$	3. −0.04 V
S. $E°(Cr^{3+}, Cr^{2+})$	4. −0.83 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.

$Ag^+ + e^- \longrightarrow Ag;\ E^\circ_{red} = +0.800\,V$

$C_6H_{12}O_6 + H_2O \longrightarrow \underset{\text{Gluconic acid}}{C_6H_{12}O_7} + 2H^+ + 2e^-;\ E^\circ_{ox} = -0.05V$

$[Ag(NH_3)_2]^+ + e^- \longrightarrow Ag + 2NH_3;\ E^\circ_{red} = 0.373V$

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

1. Calculate (ln K) for
   $C_6H_{12}O_6 + 2Ag^+ + H_2O \longrightarrow C_6H_{12}O_7 + 2H^+ + 2Ag$
   (a) 55.6 (b) 29.6 *(2006 - 5M, –2)*
   (c) 66 (d) 58.38
2. On adding NH_3, pH of the solution increases to 11 then, identify the effect on potential of half-cell *(2006 - 5M, –2)*
   (a) E_{ox} increased from E°_{ox} by 0.65 V
   (b) E_{ox} decreased from E°_{ox} by 0.65 V
   (c) E_{red} increased from E°_{red} by 0.65 V
   (d) E_{red} decreased from E°_{red} by 0.65 V
3. NH_3 is used in this reaction rather than any other base. Select the correct statement out of the following *(2006 - 5M, –2)*
   (a) $[Ag(NH_3)_2]^+$ is a weaker oxidizing agent than Ag^+
   (b) to dissolve the insoluble silver oxide formed under the reaction conditions
   (c) Ag precipitates gluconic acid as its silver salt
   (d) NH_3 changes the standard reduction potential of $[Ag(NH_3)_2]^+$

PASSAGE : II

Chemical reactions involve interaction of atoms and molecules. A large number of atoms/molecules (approximately 6.023×10^{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°) 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° (V with respect to normal hydrogen electrode) values. Using this data obtain the correct explanations to questions given.

$I_2 + 2e^- \rightarrow 2I^-$ E° = 0.54
$Cl_2 + 2e^- \rightarrow 2Cl^-$ E° = 1.36
$Mn^{3+} + e^- \rightarrow Mn^{2+}$ E° = 1.50
$Fe^{3+} + e^- \rightarrow Fe^{2+}$ E° = 0.77
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ E° = 1.23

7. Among the following, identify the correct statement.
   (a) Chloride ion is oxidised by O_2 *(2007)*
   (b) Fe^{2+} is oxidised by iodine
   (c) Iodide ion is oxidised by chlorine
   (d) Mn^{2+} is oxidised by chlorine
8. While Fe^{3+} is stable, Mn^{3+} is not stable in acid solution because *(2007)*
   (a) O_2 oxideses Mn^{2+} to Mn^{3+}
   (b) O_2 oxideses both Mn^{2+} to Mn^{3+} and Fe^{2+} to Fe^{3+}
   (c) Fe^{3+} oxideses H_2O to O_2
   (d) Mn^{3+} oxideses H_2O to O_2
9. Sodium fusion extract, obtained from aniline, on treatment with iron (II) sulphate and H_2SO_4 in presence of air gives a Prussian blue precipitate. The blue colour is due to the formation of *(2007)*
   (a) $Fe_4[Fe(CN)_6]_3$ (b) $Fe_3[Fe(CN)_6]_2$
   (c) $Fe_4[Fe(CN)_6]_2$ (d) $Fe_3[Fe(CN)_6]_3$

PASSAGE : IV

The concentration of potassium ions inside a biological cell is atleast 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
M(s) | M^+(aq; 0.05 molar) || M^+(aq; 1 molar) | M(s)
For the above electrolytic cell the magnitude of the cell potential $|E_{cell}| = 70$ mV. *(2010)*

10. For the above cell
    (a) $E_{cell} < 0; \Delta G > 0$ (b) $E_{cell} > 0; \Delta G < 0$
    (c) $E_{cell} < 0; \Delta G^\circ > 0$ (d) $E_{cell} > 0; \Delta G^\circ < 0$
11. If the 0.05 molar solution of M^+ is replaced by a 0.0025 molar 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^{-3}) | 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 DG (kJ mol^{-1}) for the given cell is (take 1F = 96500 C mol^{-1})
(a) –5.7 (b) 5.7 (c) 11.4 (d) –11.4

13. The solubility product (K_{sp}; $mol^3\ dm^{-9}$) 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) 1×10^{-15} (b) 4×10^{-15}
(c) 1×10^{-12} (d) 4×10^{-12}

I Integer Value Correct Type

1. All the energy released from the reaction $X \rightarrow Y$, $\Delta_r G° = -193$ kJ mol^{-1} is used for oxidizing M^+ as $M^+ \rightarrow M^{3+} + 2e^-$, $E° = -0.25$ 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 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 $\lambda^0_{x^-} \approx \lambda^0_{y^-}$ 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 Adv. 2015)*

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) S m mol^{-1} (b) $Sm^2\ mol^{-1}$ **[2002]**
(c) $S^{-2}m^2$ mol (d) $S^2m^2\ mol^{-2}$.

2. EMF of a cell in terms of reduction potential of its left and right electrodes is **[2002]**
(a) $E = E_{left} - E_{right}$ (b) $E = E_{left} + E_{right}$
(c) $E = E_{right} - E_{left}$ (d) $E = -(E_{right} + E_{left})$.

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) $\frac{RT}{F}\log_e\frac{P_2}{P_1}$ (c) 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

	Cathode	Anode	**[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) $CaC_2O_4 + 2HCl \rightarrow CaCl_2 + H_2C_2O_4$
(c) $Mg(OH)_2 + 2NH_4Cl \rightarrow MgCl_2 + 2NH_4OH$
(d) $Zn + 2AgCN \rightarrow 2Ag + Zn(CN)_2$.

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) 29.5×10^{-2} (b) 10 **[2003]**
(c) 1×10^{10} (d) 1×10^{-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, $E^°_{cell}$ is 1.10 volt. E_{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 **[2003]**
(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 elctrode surfaces

13. Consider the following E° values

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

Under standard conditions the potential for the reaction

$Sn_{(s)} + 2Fe^{3+}(aq) \rightarrow 2Fe^{2+}(aq) + Sn^{2+}(aq)$ is **[2004]**

(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 ($F = 96,500\ C\ mol^{-1}$; $R = 8.314\ JK^{-1}\ mol^{-1}$)
(a) 1.0×10^{10} (b) 1.0×10^{5} **[2004]**
(c) 1.0×10^{1} (d) 1.0×10^{30}

15. The limiting molar conductivities Λ° for NaCl, KBr and KCl are 126, 152 and 150 S $cm^2\ mol^{-1}$ respectively. The Λ° for NaBr is **[2004]**
(a) 278 S $cm^2\ mol^{-1}$ (b) 176 S $cm^2\ mol^{-1}$
(c) 128 S $cm^2\ mol^{-1}$ (d) 302 S $cm^2\ mol^{-1}$

16. In a cell that utilises the reaction

$Zn_{(s)} + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_{2(g)}$ addition of H_2SO_4 to cathode compartment, will **[2004]**
(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 equlibrium to the left
(d) increase the E and shift equilibrium to the left

17. The $E^\circ_{M^{3+}/M^{2+}}$ values for Cr, Mn, Fe and Co are – 0.41, + 1.57, + 0.77 and + 1.97V 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 ΔG, equilibrium constant (K) and E^o_{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°C to furnish aluminium metal (At. Mass = 27 amu; 1 Faraday = 96,500 Coulombs). The cathode reaction is– $Al^{3+} + 3e^- \rightarrow Al^\circ$
To prepare 5.12 kg of aluminium metal by this method we require **[2005]**
(a) 5.49×10^1 C of electricity
(b) 5.49×10^4 C of electricity
(c) 1.83×10^7 C of electricity
(d) 5.49×10^7 C of electricity

21.

Electrolyte:	KCl	KNO_3	HCl	NaOAc	NaCl
$\Lambda^\infty (S\ cm^2\ mol^{-1})$:	149.9	145	426.2	91	126.5

Calculate Λ^∞_{HOAc} using appropriate molar conductances of the electrolytes listed above at infinite dilution in H_2O at 25°C **[2005]**
(a) 217.5 (b) 390.7
(c) 552.7 (d) 517.2

22. Which of the following chemical reactions depict the oxidizing beahviour of H_2SO_4? **[2006]**
(a) $NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$
(b) $2PCl_5 + H_2SO_4 \longrightarrow 2POCl_3 + 2HCl + SO_2Cl_2$
(c) $2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$
(d) $Ca(OH)_2 + H_2SO_4 \longrightarrow CaSO_4 + 2H_2O$

23. The molar conductivities Λ^o_{NaOAc} and Λ^o_{HCl} at infinite dilution in water at 25°C are 91.0 and 426.2 S cm^2/mol respectively. To calculate Λ^o_{HOAc}, the additional value required is **[2006]**
(a) Λ^o_{NaOH} (b) Λ^o_{NaCl}
(c) $\Lambda^o_{H_2O}$ (d) Λ^o_{KCl}

24. Resistance of a conductivity cell filled with a solution of an electrolyte of concentration 0.1 M is 100 Ω. The conductivity of this solution is 1.29 S m^{-1}. Resistance of the same cell when filled with 0.2 M of the same solution is 520 Ω. The molar conductivity of 0.2 M solution of electrolyte will be **[2006]**
(a) 1.24×10^{-4} S $m^2\ mol^{-1}$ (b) 12.4×10^{-4} S $m^2\ mol^{-1}$
(c) 124×10^{-4} S $m^2\ mol^{-1}$ (d) 1240×10^{-4} S $m^2\ mol^{-1}$

25. The equivalent conductances of two strong electrolytes at infinite dilution in H_2O (where ions move freely through a solution) at 25°C are given below: **[2007]**

$\Lambda^\circ_{CH_3COONa} = 91.0\ S\ cm^2/equiv.$

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

What additional information/ quantity one needs to calculate Λ° of an aqueous solution of acetic acid?
(a) Λ° of chloroacetic acid ($ClCH_2COOH$)
(b) Λ° of NaCl
(c) Λ° of CH_3COOK
(d) the limiting equivalent coductance of $H^+ (\lambda^\circ_{H^+})$.

26. The cell, $Zn | Zn^{2+}(1\ M) || Cu^{2+}(1\ M) | Cu\ (E°_{cell} = 1.10\ v)$ was allowed to be completely discharged at 298 K. The relative concentration of Zn^{2+} to Cu^{2+} $\left(\frac{[Zn^{2+}]}{[Cu^{2+}]}\right)$ is **[2007]**

(a) 9.65×10^4 (b) antilog(24.08)
(c) 37.3 (d) $10^{37.3}$.

27. Given $E°_{Cr^{3+}/Cr} = -0.72$ V, $E°_{Fe^{2+}/Fe} = -0.42$ V. The potential for the cell
$Cr|Cr^{3+}(0.1M)||Fe^{2+}(0.01\ M)|Fe$ is **[2008]**

(a) 0.26V (b) 0.336V
(c) −0.339 (d) 0.26V

28. In a fuel cell methanol is used as fuel and oxygen gas is used as an oxidizer. The reaction is

$$CH_3OH(l) + 3/2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

At 298 K standard Gibb's energies of formation for $CH_3OH(l)$, $H_2O(l)$ and and $CO_2(g)$ are −166.2 −237.2 and −394.4 *kJ* mol^{-1} respectively. If standard enthalpy of combustion of methonal is – 726 kJ mol^{-1}, efficiency of the fuel cell will be:

(a) 87% (b) 90% **[2009]**
(c) 97% (d) 80%

29. Given:

$$E°_{Fe^{3+}/Fe} = -0.036V,\ E°_{Fe^{2+}/Fe} = -0.439V$$

The value of standard electrode potential for the change,

$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$ will be: **[2009]**

(a) 0.385V (b) 0.770V
(c) −0.270V (d) −0.072V

30. The Gibbs energy for the decomposition of Al_2O_3 at 500°C is as follows :

$$\frac{2}{3}Al_2O_3 \rightarrow \frac{4}{3}Al + O_2, \Delta_r G = +966\,kJ\,mol^{-1}$$

The potential difference needed for electrolytic reduction of Al_2O_3 at 500°C is at least **[2010]**

(a) 4.5V (b) 3.0V
(c) 2.5V (d) 5.0V

31. The correct order of $E°_{M^{2+}/M}$ values with negative sign for the four successive elements Cr, Mn, Fe and Co is **[2010]**

(a) Mn > Cr > Fe > Co (b) Cr < Fe > Mn > Co
(c) Fe > Mn > Cr > Co (d) Cr > Mn > Fe > Co

32. The reduction potential of hydrogen half-cell will be negative if:

(a) $p(H_2) = 1$ atm and $[H^+] = 2.0$ M **[2011]**
(b) $p(H_2) = 1$ atm and $[H^+] = 1.0$ M
(c) $p(H_2) = 2$ atm and $[H^+] = 1.0$ M
(d) $p(H_2) = 2$ atm and $[H^+] = 2.0$ M

33. The standard reduction potentials for Zn^{2+}/Zn, Ni^{2+}/Ni and Fe^{2+}/Fe are −0.76,−0.23 and −0.44 V respectively.

The reaction $X + Y^{2+} \longrightarrow X^{2+} + Y$ will be spontaneous when : **[2012]**

(a) X = Ni, Y = Fe (b) X = Ni, Y = Zn
(c) X= Fe, Y = Zn (d) X= Zn, Y = Ni

34. Given : $E°_{Cr^{3+}/Cr} = -0.74$ V; $E°_{MnO_4^-/Mn^{2+}} = 1.51$ V

$E°_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33$ V; $E°_{Cl/Cl^-} = 1.36$ V

Based on the data given above, strongest oxidising agent will be : **[JEE M 2013]**

(a) Cl (b) Cr^{3+}
(c) Mn^{2+} (d) MnO_4^-

35. Resistance of 0.2 M solution of an electrolyte is 50 Ω. The specific conductance of the solution is 1.4 S m^{-1}. The resistance of 0.5 M solution of the same electrolyte is 280 Ω. The molar conductivity of 0.5 M solution of the electrolyte in S m^2 mol^{-1} is: **[JEE M 2014]**

(a) 5×10^{-4} (b) 5×10^{-3}
(c) 5×10^3 (d) 5×10^2

36. Given below are the half-cell reactions: **[JEE M 2014]**

$$Mn^{2+} + 2e^- \rightarrow Mn;\ E° = -1.18V$$
$$2\left(Mn^{3+} + e^- \rightarrow Mn^{2+}\right);\ E° = +1.51V$$

The E° for $3Mn^{2+} \rightarrow Mn + 2Mn^{3+}$ will be:

(a) −2.69 V; the reaction will not occur
(b) −2.69 V; the reaction will occur
(c) −0.33 V; the reaction will not occur
(d) −0.33 V; the reaction will occur

37. The equivalent conductance of NaCl at concentration C and at infinite dilution are λ_C and λ_∞, respectively. The correct relationship between λ_C and λ_∞ 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 $CuSO_4$. The mass of copper deposited at the cathode is (at. mass of Cu = 63.5 amu) **[JEE M 2015]**

(a) 2g (b) 127 g
(c) 0 g (d) 63.5 g

39. Galvanization is applying a coating of: **[JEE M 2016]**

(a) Cu (b) Zn
(c) Pb (d) Cr

13 Electrochemistry

Section-A : JEE Advanced/ IIT-JEE

A **1.** I^- **2.** negative, greater **3.** increased

B **1.** F

C **1.** (a) **2.** (c) **3.** (c) **4.** (d) **5.** (c) **6.** (a) **7.** (a) **8.** (a) **9.** (c)
10. (a) **11.** (b) **12.** (c) **13.** (b) **14.** (a) **15.** (c) **16.** (b) **17.** (a) **18.** (b)
19. (d) **20.** (d) **21.** (d)

D **1.** (a) **2.** (a,b,c) **3.** (a)

E **1.** 27171.96 coulombs **2.** (a) 71.34 : 1, (c) 2.06×10^4 coulombs
4. (ii) 1.113 volts, (iii) spontaneous **5.** 4.7625 g, 0.8042 A
6. 125.09 sec **7.** 8.62 **8.** 265.02 Ah **9.** 19.06 g
10. 10^{-4} M **11.** 643.3 A, 190.50 g **12.** 99.79 ml, 58.48 ml **13.** 9.88×10^{-15}
14. 1.48×10^{-9} M **15.** 115800 C, 347.4 kJ **16.** $5.128 \times 10^{-18}\, mol\, l^{-1}$ **17.** 0.154 M
18. –0.037 V **19.** 48.69 hrs., 1.408 M **20.** (i) 0.887 V, (ii) 0.046 V **21.** (i) 2.1554 g of Cr, (ii) 1336.15 sec
22. 0.325 V, –0.149 V **23.** (ii) 1.27 V, (iii) 2.45×10^5 J **25.** 0.792 V **26.** –0.22 V
27. 34.02 g, 1275.6 cm^2 **28.** 7.6×10^{12} **29.** 6.26×10^7 **30.** 2.44×10^{-12}
31. 0.010 V **32.** 7.95×10^{-5} mol L^{-1} **33.** Ce electrode to iron electrode, decrease
34. (ii) – 22195 J mole, –49987 J/mole; (iii) 1.24×10^{-5} mol/L **35.** 0.05 M
36. 10^{10} **37.** **(a)** 0.59 V, 10^{-10} **(b)** 52.9, 10^{-6} **38.** 55

F **1.** (A - p, s); (B - r); (C - p, q); (D - p).
2. (a)
3. (d)

G **1.** (d) **2.** (a) **3.** (b) **4.** (b) **5.** (d) **6.** (d) **7.** (c) **8.** (d) **9.** (a)
10. (b) **11.** (c) **12.** (d) **13.** (b)

I **1.** 4 **2.** 3

Section-B : JEE Main/ AIEEE

1. (b)	**2.** (c)	**3.** (b)	**4.** (a)	**5.** (d)	**6.** (d)	**7.** (c)
8. (d)	**9.** (a)	**10.** (b)	**11.** (b)	**12.** (b)	**13.** (a)	**14.** (a)
15. (c)	**16.** (a)	**17.** (c)	**18.** (d)	**19.** (a)	**20.** (d)	**21.** (b)
22. (c)	**23.** (b)	**24.** (b)	**25.** (b)	**26.** (d)	**27.** (d)	**28.** (c)
29. (b)	**30.** (c)	**31.** (a)	**32.** (c)	**33.** (d)	**34.** (d)	**35.** (a)
36. (a)	**37.** (c)	**38.** (d)	**39.** (b)			

Section-A JEE Advanced/ IIT-JEE

A. Fill in the Blanks

1. I^- ($\because I_2$ is weakest oxidising agent)

2. **negative, greater;** Among the various metals, since sodium has the minimum reduction potential, it must be strongest reducing agent. In general, more the reduction potential lesser is its reducing action.

3. **increased;**

B. True/False

1. **False :** When the temperature is 273, the value of the factor will come out as 0.0541 instead of 0.0591. The value 0.0591 comes out at 298 K and not at 273 K.

C. MCQs with One Correct Answer

1. **(a)** More negative is the value of reduction potential, higher will be the reducing property, i.e., the power to give up electrons.

2. **(c)** $\frac{W_1}{W_2} = \frac{E_1}{E_2} = \frac{Z_1 it}{Z_2 it} \quad \therefore \quad \frac{Z_1}{Z_2} = \frac{E_1}{E_2}$

Here E_1 & E_2 are equivalent weights of the ions.

3. **(c)** The reduction potentials (as given) of the ions are in the order :

$Ag^+ > Hg_2^{2+} > Cu^{2+} > Mg^{2+}$

Mg^{2+} (aq.) will not be reduced as its reduction potential is much lower than that of water (–0.83 V).

Hence the sequence of deposition of the metals will be Ag, Hg, Cu.

4. **(d)** Charge of one mole of electrons = 96500 C ∴ 1 mole gram equivalent of substance will be deposited by one mole of electrons.
5. **(c)** **NOTE :** Oxidation is loss of electron and in a galvanic cell it occurs at anode. Reduction is gain of electron and in a galvanic cell it occurs at cathode.
Cell representation :
Anode / Anodic electrolyte || Cathodic electrolyte / Cathode
Reaction at Anode : $H_2 \rightarrow 2H^+ + 2e^-$
Reaction at Cathode : $AgCl + e^- \rightarrow Ag + Cl^-$
6. **(a)** Water is reduced at the cathode and oxidized at the anode instead of Na^+ and SO_4^{2-}.
Cathode : $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
Anode : $H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-$.
7. **(b)** **TIPS/FORMULAE:**
(i) In a galvanic cell oxidation occurs at anode and reduction occurs at cathode.
(ii) Oxidation occurs at electrode having higher oxidation potential and it behaves as anode and other electrode acts as cathode.
(iii) $E_{Cell} = E_C - E_A$
(substitute reduction potential at both places).

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

$\because Zn \longrightarrow Zn^{++} + 2e^-$ and $Fe^{2+} + 2e^- \longrightarrow Fe$
∴ Zn is anode and Fe is cathode.
$E_{cell} = E_C - E_A = -0.41 - (-0.76) = 0.35V.$
8. **(a)** H_2O is more readily reduced at cathode than Na^+. It is also more readily oxidized at anode than SO_4^{2-}. Hence, the electrode reactions are

$$2H_2O + 2e^- \longrightarrow H_2\uparrow + 2OH^- \text{ [at cathode]}$$

$$H_2O \longrightarrow \frac{1}{2}O_2\uparrow + 2H^+ + 2e^- \text{ [at anode]}$$

9. **(c)** We have

Half-cell	Half-cell reaction	$\Delta G° = -nFE°$
$Cu^{2+} \mid Cu$	$Cu^{2+} + 2e^- = Cu$	$\Delta G_1^\circ = -2FE^\circ_{Cu^{2+}\mid Cu}$
$Cu^{2+} \mid Cu^+$	$Cu^{2+} + e^- = Cu^+$	$\Delta G_2^\circ = -FE^\circ_{Cu^{2+}\mid Cu^+}$
$Cu^+ \mid Cu$	$Cu^+ + e^- = Cu$	$\Delta G_3^\circ = -FE^\circ_{Cu^+\mid Cu}$

From the half-cell reactions, it follows that

$$\Delta G_3^\circ = \Delta G_1^\circ - \Delta G_2^\circ$$

i.e.,

$$-FE^\circ_{Cu^+\mid Cu} = -2FE^\circ_{Cu^{2+}\mid Cu} - \left(-FE^\circ_{Cu^{2+}\mid Cu^+}\right)$$

or $E^\circ_{Cu^+\mid Cu} = 2E^\circ_{Cu^{2+}\mid Cu} - E^\circ_{Cu^{2+}\mid Cu^+}$
$= 2(0.337\text{ V}) - 0.153\text{ V} = 0.521\text{ V}$

10. **(a)** The given order of reduction potentials is Z > Y > X. A spontaneous reaction will have the following characteristics
Z reduced and Y oxidised
Z reduced and X oxidised
Y reduced and X oxidised
Hence, Y will oxidise X and not Z.
11. **(b)** For $M^+ + X^- \longrightarrow M + X$, $E^\circ_{cell} = 0.44 - 0.33 = 0.11V$ is positive, hence reaction is spontaneous.
12. **(c)** The salt used to make 'salt–bridge' must be such that the ionic mobility of cation and anion are of comparable order so that they can keep the anode and cathode half cells neutral at all times. KNO_3 is used becasue velocities of K^+ and NO_3^- ions are nearly same
13. **(b)** As we go down the group 1 (i.e. from Li^+ to K^+), the ionic radius increases, degree of solvation decreases and hence effective size decreases resulting in increase in ionic mobility.Hence equivalent conductance at infinite dilution increases in the same order.
14. **(a)** MnO_4^- will oxidise Cl^- ion according to the following equation

$$2MnO_4^- + 16H^+ + 10Cl^- \longrightarrow 2Mn^{2+} + 8H_2O + 5Cl_2\uparrow$$

The cell corresponding to this reaction is as follows :
Pt, Cl_2 (1 atm) | Cl^- || MnO_4^-, Mn^{2+}, H^+ | Pt

$$E^\circ_{cell} = 1.51 - 1.40 = 0.11\text{ V}$$

E°_{cell} being +ve, $\Delta G°$ will be -ve and hence the above reaction is feasible. MnO_4^- will not only oxidise Fe^{2+} ion but also Cl^- ion simultaneously. So the quantitative estimation of aq $Fe(NO_3)_2$ cannot be done by this.
15. **(c)** **NOTE :** In an electrolytic cell, electrons do not flow themselves. It is the migration of ions towards oppositely charged electrodes that indirectly constitutes the flow of electrons from cathode to anode through internal supply.
16. **(b)** **TIPS/FORMULAE:**
Use Nernst's equation;
Cell reaction : $Zn + Fe^{2+} \longrightarrow Zn^{2+} + Fe$
Using Nernst equation

$$E_{cell} = E°_{cell} - \frac{0.0591}{n}\log\left[\frac{Zn^{2+}}{Fe^{2+}}\right]$$

$$E = E° - \frac{0.0591}{2}\log\frac{10^{-2}}{10^{-3}}$$

$$E° = 0.2905 + \frac{0.0591}{2} = 0.32$$

or $0.32 = \frac{0.0591}{2}\log K_{eq.}$ or $K_{eq} = 10^{\frac{0.32}{0.0295}}$.

17. (a) $Fe(s) \longrightarrow Fe^{2+} + 2e^-$; $E° = 0.44$ V

$2H^+ + 2e^- + ½O_2 \longrightarrow H_2O(l)$; $E° = +1.23$V

$Fe(s) + 2H^+ + ½O_2 \longrightarrow Fe^{2+} + H_2O$;

$$E^{\circ}_{cell} = 0.44 + 1.23 = 1.67V$$

$$\therefore \Delta G° = -nFE^{\circ}_{cell} = -2 \times 96500 \times 1.67 = -322\,kJ$$

18. (b) Give: $I = 10$ milliamperes; $IF = 96500\,C\,mol^{-1}$
$t = ?$; Moles of H_2 produces $= 0.01$ mol
From the law of electrolysis, we have

$$\text{Equivalents of } H_2 \text{ produces} = \frac{I \times t(sec)}{96500}$$

Substituting given values, we get

$$0.01 \times 2 = \frac{10 \times 10^{-3}(\text{amperes}) \times t(\text{sec})}{96500}$$

or $$t = \frac{0.01 \times 2 \times 96500}{10 \times 10^{-3}} \text{sec} = 19.3 \times 10^4 \text{ sec.}$$

i.e. (b) is the correct answer.

19. (d) $AgNO_3(aq) + KCl(aq) \longrightarrow AgCl(s) + KNO_3(aq)$
Conductivity of the solution is almost compensated due to formation of $KNO_3(aq)$. However, after at end point, conductivity increases more rapidly due to addition of excess $AgNO_3$ solution.

20. (d) Here $n = 4$, and $[H^+] = 10^{-pH} = 10^{-3}$
Applying Nernst equation

$$E = E° - \frac{0.059}{n}\log\frac{[Fe^{2+}]^2}{[H^+]^4 p_{O_2}}$$

$$= 1.67 - \frac{0.059}{4}\log\frac{(10^{-3})^2}{(10^{-3})^4 \times 0.1}$$

$$= 1.67 - \frac{0.03}{2}\log 10^7 = 1.67 - 0.105 = 1.565\text{ V}$$

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

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

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

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

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

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

D. MCQs with One or More Than One Correct

1. **(a) NOTE :** More negative or lower is the reduction potential , more is the reducing property. Thus the reducing power of the corresponding metal will follow the reverse order, i.e. $Y > Z > X$.
2. **(a,b,d)** The species having less reduction potential with respect to NO_3^- ($E° = +0.96$ V) will be oxidised by NO_3^-. These species are V, Fe and Hg.
3. **(a)** Salt bridge is introduced to keep the solutions of two electrodes separate, so that the ions in electrodes do not mix freely with each other. Salt bridge maintains the diffusion of ions from one electrode to another.

E. Subjective Problems

1. Wt. of Cu deposited = Zit

$$\text{Electrochemical equivalent of Cu} = \frac{63.5}{2} = 31.75$$

Volume of surface = area × thickness
$= 10 \times 10 \times 10^{-2} = 1$ cc
Weight of Cu = density × volume = $8.94 \times 1 = 8.94$ g
According to Faraday's laws of electrolysis
31.75 g of Cu is deposited by = 96500 coulombs of electricity

$$\therefore 8.94 \text{ g of Cu is deposited by} = \frac{96500}{31.75} \times 8.94$$

$$= \mathbf{27171.96\ coulombs}$$

2. (a) $2SnCl_2 \longrightarrow Sn + SnCl_4$

$2[119 + (2 \times 35.5)] = 380$; 119; $119 + (4 \times 35.5) = 261$

$\because$ 119g Sn deposits from = 380g $SnCl_2$

$$\therefore 0.119\text{g Sn deposits from} = \frac{380}{119} \times 0.119 = 0.380\text{g } SnCl_2$$

$\because$ 380g $SnCl_2$ gives = 261g $SnCl_4$

$$\therefore 0.380\ SnCl_2 \text{ gives} = \frac{261}{380} \times 0.380 = 0.261\text{g } SnCl_4$$

$\therefore$ Wt of $SnCl_2$ left after decomposition $= 19.00 - 0.380 = 18.620$ g.

Ratio $SnCl_2 : SnCl_4$
$\Rightarrow 18.620 : 0.261 \Rightarrow$ **71.34 : 1**

(b) $NaCl \xrightarrow{\text{Electricity}} Na^+ + Cl^-$

At Cathode; $Na^+ + e^- \longrightarrow Na$

$2Na + H_2O \longrightarrow 2NaOH + H_2$

At anode; $Cl^- \longrightarrow Cl + e^-$

$Cl + Cl \longrightarrow Cl_2$

$2OH^- + Cl_2 \longrightarrow Cl^- + OCl^- + H_2O$

$OCl^- + 2HOCl \longrightarrow ClO_3^- + 2Cl^- + 2H^+$

$Na^+ + ClO_3^- \longrightarrow \underset{\text{Sod.Chlorate}}{NaClO_3}$

On prolonged electrolysis

$ClO_3^- + ClO^- \longrightarrow Cl^- + ClO_4^-$

$Na^+ + ClO_4^- \longrightarrow \underset{\text{Sod. perchlorate}}{NaClO_4}$

(c) Charge on $N^{3-} = 3$

No. of ions in 14 g of $N^{3-} = 6.02 \times 10^{23}$

No. of ions in 1g of $N^{3-} = \dfrac{6.02 \times 10^{23}}{14}$

No. of electronic charges on 1 g $N^{3-} = \dfrac{6.02 \times 10^{23}}{14} \times 3$

Charge on 1 gm of N^{3-}

$= \dfrac{6.023 \times 10^{23} \times 3 \times 1.6 \times 10^{-19}}{14}$ Coulombs

($\because$ Charge on one electron is 1.6×10^{-19} Coulombs)

= 2.06×10^4 Coulombs

3. (i) $2KNO_3 + 8FeSO_4 + 4H_2SO_{4\,(conc)}$

$\longrightarrow 2(FeSO_4.NO) + K_2SO_4 + 3Fe_2(SO_4)_3 + 4H_2O$

(ii) $3H_2S + 2K_2CrO_4 + 5H_2SO_4$

$\longrightarrow 2K_2SO_4 + Cr_2(SO_4)_3 + 3S + 8H_2O$

(iii) $2KI + 2H_2SO_4(conc) \xrightarrow{\Delta} I_2 + SO_2 + K_2SO_4 + 2H_2O$

(iv) $Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$

(v) Al is covered by layer of Al_2O_3

4. (i) The two half cell reactions can be written as below :

Oxidation half reaction : $Zn \rightarrow Zn^{2+} + 2e^-$

Reduction half reaction : $Cu^{2+} + 2e^- \rightarrow Cu$

Thus the cell reaction will be : $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

(ii) EMF of cell, $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$E^\circ_{cell} = 0.350 - (-0.763)$

$= 0.350 + 0.763$ volts **= 1.113 volts**

(iii) Since emf of the cell is **positive**, the reaction as written is **spontaneous**.

5. Gold deposited in the first cell = 9.85 g

At. wt. of Gold = 197, Oxidation number of gold = +3

Eq. Wt. of Gold = $\dfrac{197}{3}$

$W = Zit$

(where W stands for the weight of ions deposited, i for current and t for time and Z for electro-chemical equivalent of the electrolyte.)

$\because$ Charge required to deposit 1 g eq. of gold = 1F = 96,500 C

$\therefore$ Charge required to deposit 9.85 g of gold or

$\dfrac{9.85}{197/3}$ g eq. of gold $= \dfrac{96{,}500 \times 9.85 \times 3}{197}$ C

$= 965 \times 5 \times 3\,C = 14475\,C$

According to Faraday's second law,

$\dfrac{\text{Wt. of Cu}}{\text{Eq. wt. of Cu}} = \dfrac{\text{Wt. of Gold}}{\text{Eq. wt. of Gold}}$

$\Rightarrow$ Wt. of Cu deposited $= \dfrac{9.85 \times 3}{197} \times \dfrac{63.5}{2}$ **= 4.7625 g**

Current $= \dfrac{Q}{t} = \dfrac{14475}{5 \times 3600}\,A = \dfrac{193}{240}\,A$ **= 0.8042 A**

6. Volume of the surface = area × thickness

$= 80\,cm^2 \times \dfrac{0.005}{10}\,cm = \dfrac{1}{25}\,cm^3$

Mass of Ag deposited = Volume × Density

$= \dfrac{1}{25} \times 10.5\,g/cm^3 = \dfrac{21}{50}\,g$

Cell reaction : $Ag^+ + e^- \rightarrow Ag$

We know that, $\dfrac{W}{E} = \dfrac{Q}{F} = \dfrac{it}{F}$

E = Eq. wt. of Ag = 108

$\therefore \dfrac{21/50}{108} = \dfrac{i \times t}{96500}$

$\dfrac{21}{50 \times 108} = \dfrac{3 \times t}{96500}$ $\therefore$ **t = 125.09 sec**

7. Half cell reactions will be

$Zn^{2+} + 2e^- \rightleftharpoons Zn$ ......(*i*)

$H^+ + e^- \rightleftharpoons \frac{1}{2} H_2$ or $2H^+ + 2e^- \rightleftharpoons H_2$ ......(*ii*)

We know that $E_{Zn/Zn^{2+}} = E^\circ_{Zn/Zn^{2+}} - \dfrac{RT}{nF} \ln \dfrac{[Zn^{2+}]}{[Zn]}$

Here R = 8.314 $Jmol^{-1} deg^{-1}$, T = 298 K, F = 96,500 coul/equi, n = 2, $E^\circ_{Zn/Zn^{2+}} = 0.76$ V.

Substituting the values in the above equation

$E_{Zn/Zn^{2+}} = 0.76 - \dfrac{8.314 \times 298}{2 \times 96500} \ln \dfrac{0.1}{1} = 0.79\,V$

Similarly, $E_{H^+/H_2} = E^{\circ}_{H^+/H_2} - \frac{RT}{nF} \ln \frac{[H_2]}{[H^+]^2}$

$$= 0 - \frac{8.314 \times 298}{2 \times 96500} \ln \frac{[1]}{[H^+]^2}$$

$$= 0.05915 \log_{10} [H^+] = -0.05915 pH$$

$(\because -\log_{10} [H^+] = pH)$

Now since $E = E_{Zn/Zn^{2+}} + E_{H^+/H_2}$

$0.28 = 0.79 - 0.05915\ pH \Rightarrow pH = \frac{0.51}{0.05915} = \mathbf{8.62}$

8. In lead storage battery the anodic and cathodic reactions during discharge (or operation or working) are as :

(i) **Anodic reaction :**

$$Pb(s) + SO_4^{2-}{}_{(aq)} \rightarrow PbSO_{4(s)} + 2e^-$$

(ii) **Cathodic reaction :**

$$PbO_{2(s)} + SO^{2-}_{4(aq)} + 4H^+{}_{(aq)} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O_{(\ell)}$$

In both the half cell reactions H_2SO_4 is consumed and hence conc. of H_2SO_4 decreases during the working (discharging of the battery. For the withdrawl of 2F = 2 × 96500 C of electric charge, 2 mol of H_2SO_4 are consumed. Density of H_2SO_4 solution (used as electrolyte) falls during working of the cell.

Both reactions get reversed on charging the battery leading to regeneration of H_2SO_4 as :

Formerly anode but now cathode (recharging)

$$PbSO_4 + 2e^- \rightarrow Pb_{(s)} + SO^{2-}_{4(aq)}$$

Formerly cathode but now anode :

$$PbSO_{4(s)} + 2H_2O_{(\ell)} \rightarrow PbO_{2(s)} + SO^{2-}_{4(aq)} + 4H^+_{(aq)} + 2e^-$$

[**NOTE :** In 1986 IIT-JEE paper there was a mistake in the question paper itself. Reaction (ii) was shown to take place during recharging of the battery which is infact the reaction occuring at cathodic half cell during operation (discharging) of the battery.]

9. **TIPS/FORMULAE:**

Watt = Volt × Current ⇒ 100 = 110 × Current

or Current $= \frac{100}{110} = \frac{10}{11}$ amp.

Now we know that,

$$Q = i \times t = \frac{10}{11} \times 10 \times 3600 \times \frac{1}{96500} = 0.339\,F$$

Wt. of cadmium deposited $= \frac{0.339 \times 112.4}{2} = \mathbf{19.06\ g}$

10. **TIPS/FORMULAE:**

For a concentration cell

$$E_{cell} = \frac{0.059}{n} \log \frac{C_1}{C_2}$$

NOTE : It is a concentration cell as both the electrodes are made of same element. Negative electrode acts as anode in a galvanic cell.

At anode; $H_2 \longrightarrow 2H^+ + 2e^-$ $[H^+] = 10^{-6} M$

At cothode; $2H^+ + 2e^- \longrightarrow H_2$ $[H^+] = ?$

$$E_{cell} = \frac{0.059}{1} \log \left[\frac{C_{H^+}}{10^{-6}}\right] \text{ or } 0.118 = \frac{0.059}{1} \log \left(\frac{C_{H^+}}{10^{-6}}\right)$$

$$\log \frac{C_{H^+}}{10^{-6}} = \frac{0.118}{0.059} = 2 \Rightarrow C_{H^+} = \mathbf{10^{-4}\,M}$$

11. For the given reactions, it is obvious that 22.4 litres of H_2 gas require 2 Faraday electricity.

∴ 67.2 litres of H_2 will produce = 6 Faraday electricity

Q = C × t; 6 × 96500 = C × 15 × 60

$$C = \frac{6 \times 96500}{15 \times 60} = \mathbf{643.3\ ampere}$$

Calculation of amount of Cu deposited by 6 F

Since 1 F deposits $= \frac{63.5}{2} = 31.75$ g of Cu

6 F will deposit = 31.75 × 6 g = **190.50 g**

12. The chemical reactions taking place at the two electrodes are

At cathode : $Cu^{2+} + 2e^- \rightarrow Cu$

$H_2O \rightleftharpoons H^+ + OH^-$

NOTE : Only Cu^{2+} ions will be discharged so as these are present in solution and H^+ ions will be discharged only when all the Cu^{2+} ions have been deposited.

At anode : $2OH^- \rightarrow H_2O + O + 2e^-$

$O + O \rightarrow O_2$

Thus in first case, Cu^{2+} ion will be discharged at the cathode and O_2 gas at the anode. Let us calculate the volume of gas (O_2) discharged during electrolysis.

According to Faraday's second law

31.75 g Cu ≡ 8 g of oxygen ≡ 5.6 litres of O_2 at NTP

0.4 g Cu $= \frac{5.6}{31.75} \times 0.4$ litres of O_2 at NTP

= 0.07055 litres = 70.55 ml

As explained earlier, when all the Cu^{2+} ion will be deposited at cathode, H^+ ions will start going to cathode liberating hydrogen (H_2) gas, *i.e.*

$H^+ + e^- \rightleftharpoons H \rightleftharpoons H + H \rightarrow H_2$

NOTE THIS STEP : However, the anode reaction remains same as previous. Thus in the second (latter) case, amount of H_2 collected at cathode should be calculated.

8 g of O_2 ≡ 1 g of H_2

5.6 litres of O_2 at NTP = 11.2 litres of hydrogen

Quantity of electricity passed after 1st electrolysis,

i.e. Q = i × t = 1.2 × 7 × 60 = 504 coulombs

504 coulombs will liberate $= \frac{5.6 \times 504}{96500} = 29.24$ ml of O_2.

Similarly, H_2 liberated by 504 coulombs

$$= 11.2 \times \frac{504}{96500} = 58.48 \text{ ml}$$

(Twice the volume of O_2 liberated in latter phase
$= 2 \times 29.24 = 58.48$ ml)

Total volume of O_2 liberated $= 70.55 + 29.24 =$ **99.79 ml**

Vol. of H_2 liberated = **58.48 ml**

13. **TIPS/FORMULAE:**

$$E^o_{cell} = \frac{0.0591}{n}\log K_c \text{ or } \frac{RT}{nF}\log K_c$$

Let us split the desired reaction into two half cell reactions:

Oxidation half reaction :

$$H_2O + \frac{1}{2}H_2(g) \rightleftharpoons H_3O^+ + e^- \quad E^o = 0.00 \text{ V}$$

Reduction half reaction :

$$H_2O + e^- \longrightarrow \frac{1}{2}H_2 + OH^- \qquad E^o = -08.277 \text{ V}$$

Net reaction :

$$2H_2O \rightleftharpoons H_3O^+ + OH^- \qquad E^o_{cell} = -0.8277 \text{ V}$$

So, the number of electrons involved in redox reaction, (n) = 1

We know that $E^o_{cell} = \frac{0.0591}{n}\log K_c$

$$\log K_c = \frac{E^o_{cell} \times n}{0.0591} = \frac{(-0.8277)\times 1}{0.0591} = -14.005$$

K_c = Antilog [15.995] = $\mathbf{9.88 \times 10^{-15}}$

14. $E^o_{Cu^{2+}/Cu} = 0.337$ and $E^o_{Ag^+/Ag} = 0.799$ V

$$E^o_{Ag^+/Ag} + E^o_{Cu/Cu^{2+}} = 0.799 - 0.337 = 0.462 \text{ V}$$

$\therefore Cu + 2Ag^+ \to Cu^{2+} + 2Ag;\ E^o_{cell} = 0.462$ V

Hence the galvanic cell in question will consist of **anode of copper and cathode of silver.**

Calculation of concentration :

$$E_{cell} = E^o - \frac{0.059}{n}\log\frac{[\text{Products}]}{[\text{Reactants}]}$$

$$E^o_{cell} = \frac{0.059}{n}\log\frac{[\text{Products}]}{[\text{Reactants}]} \qquad [\because E_{cell} = 0]$$

$$0.462 = \frac{0.059}{2}\log\frac{0.01}{[Ag^+]^2} \qquad [n = 2]$$

$$\frac{462 \times 2}{59} = \log(10^{-2}) - \log[Ag^+]^2$$

$$\frac{924}{59} = -2 - 2\log[Ag^+] \Rightarrow [Ag^+] = \mathbf{1.48 \times 10^{-9}\ M}$$

15. $C_6H_5NO_2 + 6H^+ + 6e^- \longrightarrow C_6H_5NH_2 + 2H_2O$

$$\text{Eq. wt of } C_6H_5NO_2 = \frac{\text{M.wt.}}{6} = \frac{123}{6}$$

$$w = \frac{Eit}{96500} \qquad \because \text{current efficiency} = 50\%$$

$$\therefore\ i = \frac{50 i_0}{100}$$

$$\therefore\ 12.3 = \frac{123 \times i \times t \times 50}{6 \times 100 \times 96500}$$

$i \times t = Q =$ **115800 Coulomb**

Energy used = 115800 × 3 = **347.4 kJ.**

16. The following chemical cell sets up :

$Zn \mid Zn^{2+} \parallel Ni^{2+} \mid Ni$

The net cell reaction is : $Zn + Ni^{2+} \rightleftharpoons Zn^{2+} + Ni$

The e.m.f. is given by

$$E_{cell} = E^o_{Ni^{2+}/Ni} - E^o_{Zn^{2+}/Zn} - \frac{0.059}{2}\log\frac{[Zn^{2+}]}{[Ni^{2+}]}$$

$$= -0.24 - (-0.75) - 0.0295\log\frac{[Zn^{2+}]}{[Ni^{2+}]}$$

$$= 0.51 - 0.0295\log\frac{[Zn^{2+}]}{[Ni^{2+}]}$$

At equilibrium $E_{cell} = 0$

Let x mol l^{-1} be the concentration of Ni^{2+} at equilibrium.

Then $[Zn^{2+}] = 1 - x$ [$\because$ 1 mole of Ni^{2+} gives 1 mole of Zn^{2+}]

$$\therefore 0.0295\log\frac{1-x}{x} = 0.51$$

$$\text{or } \log\frac{1-x}{x} = \frac{0.51}{0.0295} = 17.29 \text{ or } \frac{1-x}{x} = 1.95 \times 10^{17}$$

$$\text{or } x = \frac{1}{1.95 \times 10^{17}} = \mathbf{5.128 \times 10^{-18}\ mol\ l^{-1}}$$

17. $i = \frac{1.70 \times 90}{100}$ ampere

No. of equivalents of Zn^{2+} which are lost

$$= \frac{i \times t}{96500} = \frac{1.70 \times 90 \times 230}{100 \times 96500} = 3.646 \times 10^{-3}$$

$\therefore$ Milli equivalents of Zn^{2+} which are lost 3.646

$\therefore$ Initial value of $Zn^{2+} = 300 \times 0.160 \times 2 = 96$

$\therefore$ Mili equivalents of Zn^{2+} left in solution
$= 96 - 3.646 = 92.354$

$$[ZnSO_4] = \frac{92.354}{2 \times 300} = 0.154 \text{ M}$$

$\therefore$ Molarity of Zn^{2+} = **0.154 M**

18. $Ag \mid AgCl(s), KCl(0.2M) \parallel KBr(0.001M), AgBr(s) \mid Ag$

Anode Cathode

$K_{sp}(AgCl) = 2.8 \times 10^{-10}$ $K_{sp}(AgBr) = 3.3 \times 10^{-13}$

At anode, ${}_1Ag \to {}_1Ag^+ + e^-$

At cathode, ${}_2Ag^+ + e^- \to {}_2Ag$

$\therefore$ Cell reaction ${}_1Ag + {}_2Ag^+ \to {}_2Ag + {}_1Ag^+$

NOTE : The subscripts 1 and 2 on Ag denote the species concerned with anode and cathode respectively.

Applying Nernst equation

$$E = E^o - \frac{0.059}{n}\log\left[\frac{\text{Products}}{\text{Reactants}}\right]$$

$$= 0 - \frac{0.059}{1}\log\left[\frac{{}_2Ag \times {}_1Ag^+}{{}_1Ag \times {}_2Ag^+}\right]$$

$[{}_1Ag] = [{}_2Ag] = 1$ ($\because$ these are in solid state)

$K_{sp}(AgCl) = 2.8 \times 10^{-10}$ *or* $[{}_1Ag^+][Cl^-] = 2.8 \times 10^{-10}$

$$[{}_1Ag^+] = \frac{2.8 \times 10^{-10}}{0.2} = 14 \times 10^{-10} \quad (\because [Cl^-] = 0.2)$$

$K_{sp}(AgBr) = 3.3 \times 10^{-13}$ *or* $[{}_2Ag^+][Br^-] = 3.3 \times 10^{-13}$

$$[{}_2Ag^+] = \frac{3.3 \times 10^{-13}}{0.001} = 3.3 \times 10^{-10} \quad (\because [Br^-] = 0.001)$$

$$\therefore E = -\frac{0.059}{1}\log\left[\frac{14 \times 10^{-10}}{3.3 \times 10^{-10}}\right]$$

$$= -0.059\log\left[\frac{14}{3.3}\right] = -0.059 \times 0.6276 = \mathbf{-0.037\ V}$$

Since emf is negative this shows that the reaction is non-spontaneous.

NOTE : For the reaction to be spontaneous, its emf should be positive i.e. **E = 0.037 V** and its polarities should be reversed i.e. anode should be made cathode and *vice-versa*. So the galvanic cell is : Ag | AgBr(s), KBr || AgCl(s), KCl | Ag

In other words, Ag | AgBr acts as anode and AgCl | Ag acts as cathode.

19. $2Cl^-(aq) + 2H_2O = 2OH^-(aq) + H_2(g) + Cl_2(g)$

Reaction at anode : $2Cl^- \rightarrow Cl_2 + 2e^-$

Reaction at cathode : $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

$$i = \frac{62}{100} \times 25 = 15.4 \text{ amperes}$$

Weight of Cl_2 deposited = 1 kg or 1000 gm

We know that $\frac{W}{E} = \frac{Q}{F} = \frac{it}{F}$; $\frac{1000}{35.5} = \frac{15.4 \times t}{96500}$

t = 175300 sec. or **48.69 hours**

No. of moles of Cl_2 thus produced $= \frac{1000}{71} = 14.08$

Amount of OH^- released in the electrolysis
= 2 × 14.08 moles = 28.16 moles

$$\therefore \text{Molarity with respect to } OH^- = \frac{28.16 \text{ moles}}{20l} = \mathbf{1.408\ M}$$

20. For the half-cell reaction

$NO_3^-(aq) + 2H^+(aq) + e^- \longrightarrow NO_2(g) + H_2O(l)$

The Nernst equation is $E = E^\circ - \frac{0.059}{n}\log\frac{[\text{Products}]}{[\text{Reactants}]}$

Substituting the values in case of (a)

$$E = 0.78 - \frac{0.059}{1}\log\frac{1}{(8)^2} = 0.78 + 0.059\log 64 = \mathbf{0.887\ V}$$

Substituting the value in the Nernst equation in case (b)

$$E = 0.78 - \frac{0.059}{1}\log\frac{1}{(10^{-7})^2} = 0.78 - 0.059\log 10^{-14}$$

$$= 0.78 - (0.059) \times (14) = \mathbf{-0.046\ V}$$

21. $CrO_3 + 6H^+ + 6e^- \longrightarrow Cr + 3H_2O$

Eq. wt. of Cr

$$= \frac{\text{At. wt.}}{\text{No. of Electrons lost or gained by one molecule of Cr}}$$

$$= \frac{52}{6}$$

(i) $\because$ 96500 coulomb deposit $= \left(\frac{52}{6}\right)$ g Cr

$\therefore$ 24000 coulomb deposit $= \frac{52}{6} \times \frac{24000}{96500}$

= 2.1554 g of Cr

(ii) Also given, $w_{Cr} = 1.5$ g, i = 12.5 ampere, t = ?, $E_{Cr} = \frac{52}{6}$

$$\therefore w = \frac{E.i.t}{96500} \text{ or } 1.5 = \frac{52 \times 12.5 \times t}{6 \times 96500}$$

$\therefore$ **t = 1336.15 second**

22. E° = Standard reduction potential of the Ag^+/Ag electrode = 0.799 V

$AgI(s) \rightleftharpoons Ag^+ + I^-$

$K_{sp} = [Ag^+][I^-] = 8.7 \times 10^{-17}$ (given)

If 'S' is the solubility of AgI, then $K_{sp} = S^2$

$$\therefore S = \sqrt{K_{sp}} = \sqrt{8.7 \times 10^{-17}} = 9.327 \times 10^{-9} \text{ mol L}^{-1}$$

$\therefore [Ag^+] = [I^-] = 9.327 \times 10^{-9}$ M

Reaction : $Ag^+ + e^- \longrightarrow Ag$

$$\therefore E = E^\circ - \frac{0.059}{n}\log\frac{a_{Ag}}{a_{Ag^+}}$$

$$= 0.799\text{ V} - \frac{0.059}{1}\log\frac{1}{9.327 \times 10^{-9}}$$

[$\because$ Activity of the electrode material in pure solid state is taken as one]

$= 0.799 - 0.059\log 0.1072 \times 10^9$

$= 0.799 - 0.474 = \mathbf{0.325\ V}$

Again,

L.H.S. Electrode reaction :

$Ag \rightarrow Ag^+ + e^-$

R.H.S. Electrode reaction : $AgI(s) \rightarrow Ag + I^-$

Cell reaction : $AgI(s) \rightarrow Ag^+ + I^-$

K = Equilibrium constant = $[Ag^+][I^-] = 8.7 \times 10^{-17}$

The standard cell emf E° and the equilibrium constant *k* are related by the expression.

$$E^o_{cell} = \frac{0.059}{n}\log K \text{ at } 298\text{ K}, \quad \text{Here, } n = 1, K = 8.7 \times 10^{-17}$$

$E^o_{cell} = 0.059\log 8.7 \times 10^{-17} = 0.059[0.9395 - 17] = -0.948$ V

But $E^o_{cell} = E^o_{R.H.S.} - E^o_{L.H.S.}$

$\therefore E^o_{R.H.S.} = E^o_{cell} + E^o_{L.H.S.} = -0.948 + 0.799 = \mathbf{-0.149\ V}$

23. (*i*) Given $E^\circ_{Ni_2O_3/NiO} = +0.40\,V$; $E^\circ_{FeO/Fe} = -0.87\,V$

$E^\circ_{NiO/Ni_2O_3} = -0.40\,V$; $E^\circ_{Fe/FeO} = +0.87\,V$

Since $E^o_{ox.\,pot.}$ for Fe/FeO > $E^o_{ox.\,pot.}$ for NiO/Ni_2O_3.

Redox changes can be written as

At anode : $Fe(s) + 2OH^- \rightarrow FeO(s) + H_2O(l) + 2e^-$

At cathode : $Ni_2O_3(s) + H_2O(l) + 2e^- \rightarrow 2NiO(s) + 2OH^-$

Cell reaction : $Fe(s) + Ni_2O_3(s) \rightarrow FeO(s) + 2NiO(s)$

(*ii*) $E_{cell} = E^o_{OP\,Fe/FeO} + E^o_{RP\,Ni_2O_3/NiO}$

$= 0.87 + 0.40 = \mathbf{1.27\,V}$

It is independent of conc. of KOH

(*iii*) Electrical energy $= nFE_{cell} = 2 \times 96500\,J\,V^{-1} \times 1.27\,V$

$= \mathbf{2.45 \times 10^5\,J}$

24. The thin protective layer of oxides of aluminium is formed which protects the metal from further attack of water and air and make it stable.

25.

	$2Hg\ +$	$2Fe^{3+}$	$\longrightarrow$	Hg_2^{2+}	$+\ 2Fe^{2+}$
Initial conc.		1.0×10^{-3}		0	0
Eqilb. conc.		0.05×10^{-3}		$\frac{0.95\times10^{-3}}{2}$	0.95×10^{-3}

$$E = E^o_{Fe^{3+}/Fe^{2+}} - E^o_{Hg_2^{2+}/Hg} - \frac{0.059}{n}\log\frac{[Fe^{2+}]^2[Hg_2^{2+}]}{[Fe^{3+}]^2}$$

NOTE : At equilibrium, E = 0

$$\Rightarrow 0 = 0.77 - E^o_{Hg_2^{2+}/Hg} - \frac{0.059}{2}\log\frac{(0.95\times10^{-3})^2(0.475\times10^{-3})}{(0.05\times10^{-3})^2}$$

On usual calculations, $E^o_{Hg_2^{2+}/Hg} = \mathbf{0.792V}$

26. At pH = 14; $[H^+] = 1 \times 10^{-14}$ M; $[OH^-] = 10^0 = 1M$

$(\because [H^+][OH^-]] = 1 \times 10^{-14})$

$\therefore$ Cu $(OH)_2$ ionises as follows:

$Cu(OH)_2 \rightleftharpoons Cu^{2+} + 2OH^-$

$\therefore K_{sp}$ of $Cu(OH)_2 = [Cu^{2+}][OH^-]^2$

$1.0 \times 10^{-19} = [Cu^{2+}][1]^2$; $[Cu^{2+}] = 1.0 \times 10^{-19}$ M

The standard reduction potential of Cu^{2+}/Cu is represented in the form of following equation:

$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

On applying Nernst equation

$$E = E^o - \frac{0.0591}{n}\log\frac{1}{[Cu^{2+}]}$$

$$= +0.34 - \frac{0.0591}{2}\log\frac{1}{1\times10^{-19}}$$

$$= +0.34 - \frac{0.0591}{2}[-\log_{10}10^{-19}]$$

$$= \left[0.34 - \frac{0.0591}{2}\times19\right] = 0.34 - 0.56 = \mathbf{-0.22V}$$

27. $$W_{Ag} = \frac{E.i.t}{96500} = \frac{107.8\times8.46\times8\times60\times60}{96500} = \mathbf{34.02g}$$

$$\text{Volume of Ag} = \frac{34.02}{10.5} = 3.24\,ml$$

$$\therefore \text{Surface area} = \frac{3.24}{0.00254} = \mathbf{1275.6\,cm^2}$$

28. $Fe^{2+}_{(aq)} \longrightarrow Fe^{3+}_{(aq)} + e^-$; $E^\circ = 0.68V$

$Ce^{4+}_{(aq)} + e^- \longrightarrow Ce^{3+}_{(aq)}$; $E^\circ = 1.44V$

$E^\circ_{cell} = 1.44 - 0.68 = +0.76\,V$

at equilibriums, $E_{cell} = 0$

$$E^\circ_{cell} = \frac{0.0591}{n}\log_{10}K_c;\ 0.76 = \frac{0.0591}{1}\log_{10}K_c$$

or $\log_{10}K_c = \frac{0.76}{0.0591} = 12.859 \quad \therefore \mathbf{K_c = 7.6\times10^{12}}$

29. For the change $2Fe^{3+} + 3I^- \rightleftharpoons 2Fe^{2+} + I_3^-$,

$$E = E^\circ - \frac{0.059}{2}\log K_c \text{ or } E^\circ = \frac{0.059}{2}\log K_c$$

$(\because$ at equilibrium, E = 0)

Also $E^o_{cell} = E^o_{RP_{Fe^{3+}/Fe^{2+}}} + E^o_{OP_{I^-/I_3^-}}$

$= 0.77 - 0.54 = 0.23\,V$

$$E_{cell} = E^o_{cell} - \frac{0.059}{2}\log K_c$$

At equilibrium, $E_{cell} = 0$ (Using Nernst equation)

Thus, $0.23 = \frac{0.059}{2}\log K_c \quad \therefore K_C = \mathbf{6.26 \times 10^7}$

30. The cell reaction can be written as

$Ag\,|\,Ag^+(Ag_2CrO_4 Sat.)\,||\,Ag^+(0.1M)\,|\,Ag$; E = 0.164 V

At cathode : $Ag^+_{cathode} + e^- \longrightarrow Ag$

At anode : $Ag \longrightarrow Ag^+_{anode} + e^-$

Net reaction : $Ag^+_{cathode} \longrightarrow Ag^+_{anode}$; E = 0.164 V

Thus here, n = 1, E = 0.164 V, $[Ag^+]_{cathode} = 0.1$ M

Let the solubility of Ag_2CrO_4 be S M

Since Ag_2CrO_4 gives 2 Ag^+

$\therefore$ Here concentration of $[Ag^+]_{anode} = 2$ S M

$$\therefore 0.164 = -\frac{0.059}{1}\log\frac{[Ag^+]_{anode}}{[Ag^+]_{cathode}}$$

$$0.164 = -\frac{0.059}{1}\log\frac{2S}{0.1}$$

or $0.164 = \frac{0.059}{1}\log\frac{0.1}{2S} \quad \therefore 2S = 1.697 \times 10^{-4}$

Hence $S = 0.8485 \times 10^{-4}$ M

For Ag_2CrO_4; $Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$

$K_{sp} = (2S)^2(S) = 4S^3$

$\therefore K_{sp} = 4 \times (0.8485 \times 10^{-4})^3 = \mathbf{2.44 \times 10^{-12}}$

31. Note that the given cell will not work as electrochemical cell since $E^\circ_{OP_{Cu}} > E^\circ_{OP_{Ag+}}$

The equation for electro-chemical cells will be:

$Cu \to Cu^{2+} + 2e^-$

$2Ag^+ + 2e^- \to 2Ag$

Thus, e.m.f. of cell $Cu \mid Cu^{2+} \parallel Ag^+ \mid Ag$ will be

$$E_{cell} = E^\circ_{OP_{Cu}} + E^\circ_{RP_{Ag}} + \frac{0.059}{2}\log\frac{[Ag^+]^2}{[Cu^{2+}]}$$

$\because [Ag^+] = 1M$ and $[Cu^{2+}] = 1M$

$\therefore E_{cell} = E^\circ_{OP_{Cu}} + E^\circ_{RP_{Ag}}$

$\left(E^\circ_{cell} = E^\circ_{OP_{Cu}} + E^\circ_{RP_{Ag}}\right) \Rightarrow E_{cell} = E^\circ_{cell}$

After the passage of 9.65 ampere for 1 hr i.e. $9.65 \times 60 \times 60$ Coulomb charge, during which the cell reactions are reversed, the Ag metal passes in solution state and Cu^{2+} ions are discharged. The reactions during the passage of current are:

$2Ag \to 2Ag^+ + 2e^-$ $\qquad Cu^{2+} + 2e^- \to Cu$

Thus, Ag^+ formed $= \dfrac{9.65 \times 60 \times 60}{96500} = 0.36$ eq. $= 0.36$ mole

Cu^{2+} discharged $= \dfrac{9.65 \times 60 \times 60}{96500} = 0.36$ eq. $= 0.18$ mole

Thus $[Ag^+]$ left $= 1 + 0.36 = 1.36$ mole

$[Cu^{2+}]$ left $= 1 - 0.18 = 0.82$ mole.

Now e.m.f. can be given as:

$$E_{cell} = E^\circ_{cell} + \frac{0.059}{2}\log\frac{(1.36)^2}{0.82} = E^\circ_{cell} + 0.010\,V$$

Thus E_{cell} increases by **0.010 V.**

32. $m = Zit$

Z for Cu $= \dfrac{63.5/2}{96500}$; $t = 16 \times 60$ sec

$$\therefore\ m = \frac{63.5}{2 \times 96500} \times 2 \times 10^{-3} \times 16 \times 60$$

$$= \frac{63.5 \times 16 \times 60 \times 10^{-3}}{96500}\,g$$

Wt. of Cu at 50% electrolysis of $CuSO_4$

$$= \frac{63.5 \times 16 \times 60 \times 10^{-3}}{96500}\,g$$

Wt. of Cu at 100% electrolysis of $CuSO_4$

$$= \frac{63.5 \times 2 \times 16 \times 60 \times 10^{-3}}{96500}\,g = 0.198 \times 63.5 \times 10^{-4}\,g$$

$CuSO_4 \equiv Cu$ $\qquad = 0.198 \times 10^{-4}$ mol.

$\therefore$ Conc. of $CuSO_4 = 0.198 \times 10^{-4} \times \dfrac{1000}{250}$

$= \mathbf{7.95 \times 10^{-5}}$ **mol/L**

33. Given, $E^o_{Ce^{4+}/Ce^{3+}} = 1.61V$; $E^o_{Fe^{3+}/Fe^{2+}} = 0.77V$

Thus for E^o_{cell} to be positive, following reaction should occur

$$Ce^{4+} + Fe^{2+} \longrightarrow Fe^{3+} + Ce^{3+}$$

Hence Ce^{4+} / Ce^{3+} electrode will act as cathode and Fe^{3+} / Fe^{2+} electrode will act as anode.

Therefore **current will flow from Ce electrode to iron electrode.**

Current will **decrease** with time.

34. (*i*) The half cell reactions are

At anode $\qquad \frac{1}{2}H_2(g) \longrightarrow H^+(aq) + e^-$

At cathode $\qquad AgCl_{(s)} + e^- \longrightarrow Ag_{(s)} + Cl^-_{(aq)}$

The cell reaction $\frac{1}{2}H_{2(g)} + AgCl_{(s)} \rightleftharpoons H^+_{(aq)} + Ag_{(s)} + Cl^-_{(aq)}$

(*ii*) **TIPS/FORMULAE:**

We know that $\Delta S = nF\dfrac{dE}{dT}$

$n \to$ No. of transferred electrons = 1

$F \to$ faraday number = 96500 coulombs

$dE \to$ Difference of electrode potential at two different temperatures $= (0.21 - 0.23) = -0.02V$

$dT \to$ Difference of two temperatures $= (35°C - 15°C) = 20°C$

$\therefore \Delta S^\circ = 1 \times 96500 \times \dfrac{-0.02}{20} = -96.5\,J/K$ mole ;

$\therefore E^o_{15} = 0.23V$; $\Delta G^\circ = -nE^\circ F$

so $\Delta G^\circ_{15} = -1 \times 0.23 \times 96500J = \mathbf{-22195}$ **Jmole**

$\Delta H^\circ = \Delta G^\circ - T\Delta S^\circ = -22195 - 288 \times (-96.5)$

$= \mathbf{-49987}$ **J/mole.**

(*iii*) $E^o_{25°C}$ of cell

$$= E^o_{15} - \frac{dE}{dT} \times \Delta T = \left(0.23 - \frac{0.02}{20} \times 10\right)V = 0.22V$$

The corresponding cell is represented as :

$Ag_{(s)} \mid Ag^+_{(aq)} \parallel Cl^-_{(aq)}(AgCl_{(s)}) \mid Ag_{(s)}$

In form of oxidised electrode potential

$E^\circ_{cell} = E^\circ_{anode} - E^\circ_{Cathode} = E^\circ_{Ag/Ag^+} - E^\circ_{Ag/AgCl/Cl^-}$

$= -0.80 - (0.22) = 0.58V$

$$E^\circ_{cell} = \frac{0.0591}{n}\log_{10} K_{eq}$$

$$AgCl_{(s)} \rightleftharpoons Ag^+ + Cl^-$$

$$E^\circ_{cell} = \frac{0.0591}{n}\log_{10}[Ag^+][Cl^-] = \frac{0.0591}{n}\log_{10} K_{sp}$$

Therefore $-0.58 = \dfrac{0.0591}{1}\log_{10} K_{sp}$

or $\log_{10}K_{sp} = -9.8139 = \overline{10}.1861$; $K_{sp} = 1.54 \times 10^{-10}$

K_{sp} of AgCl $= 1.54 \times 10^{-10}$ (mole Litre^{-1})^2

Solubility of AgCl

$= \sqrt{K_{sp}} = \sqrt{1.54 \times 10^{-10}} = \mathbf{1.24 \times 10^{-5}}$ **mole/L**

35. Daniel cell is : $Zn \mid Zn^{2+} \mid\mid Cu^{2+} \mid Cu$

Let there be two Daniel cells with their E_{cell} as given below:

$Zn \mid Zn^{2+}(C_1) \mid\mid Cu^{2+}(C = ?) \mid Cu$,

$E_{cell} = E_1$

$Zn \mid Zn^{2+}(C_2) \mid\mid Cu^{2+}(C = 0.5\,M) \mid Cu$

$E_{cell} = E_2$ where $E_2 > E_1$

According to question, $E_2 - E_1 = 0.03$ and $C_2 = C_1$

The cell reaction is

$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu, Q = \frac{[Zn^{2+}]}{[Cu^{2+}]}.$$

So, $E_{cell} = E^o_{cell} - \frac{0.06}{2}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$

Thus, $E_1 = E^o_{cell} - \frac{0.06}{2}\log\frac{C_1}{C}$;

and $E_2 = E^o_{cell} - \frac{0.06}{2}\log\frac{C_2}{0.5}$;

Since same $ZnSO_4$ is used in both cells $C_1 = C_2$

So, $E_2 - E_1 = \frac{0.06}{2}\left[\log\frac{C_1}{C} \times \frac{0.5}{C_1}\right]$

$\Rightarrow 0.03 = \frac{0.06}{2}\log\frac{0.5}{C} \Rightarrow \log\frac{0.5}{C} = 1$ or $C = \mathbf{0.05\,M}$

36. The required reaction can be obtained in the following way.

$Cu^{2+} + e^- \longrightarrow Cu^+$ $\quad \Delta G° = -0.15F$

$(\Delta G° = -nFE°)$

$In^{2+} + e^- \longrightarrow In^+,$ $\quad \Delta G° = +0.40F$

$In^+ \longrightarrow In^{3+} + 2e^-,$ $\quad \Delta G° = -0.84F$

On adding, $Cu^{2+} + In^{2+} \longrightarrow In^{3+} + Cu^+,\ E° = -0.59F$

Now we know that $-nFE° = -0.59\,F$

or $-E^o_{cell} = -0.59V$ or $E^o_{cell} = 0.59V$

$E_{cell} = E^o_{cell} - \frac{0.0591}{n}\log K_c$;

$E^o_{cell} = 0$, then $E^o_{cell} = \frac{0.0591}{n}\log K_c$

$0.59 = \frac{0.0591}{1}\log K_c$

$\log K_c = \frac{0.59}{0.0591} = 10$; $\quad \mathbf{K_c = 10^{10}}$

37. **(a)** From the given details, the reactions can be written as:

At anode: $Ag(s) + Cl^-(aq) \longrightarrow AgCl(s) + e^-$

At anode: $Ag^+(aq) + e^- \longrightarrow Ag(s)$

Complete reaction $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$

Hence cell representation is

$Ag(s) \mid AgCl(s) \mid Cl^-(aq) \mid\mid Ag^+(aq) \mid Ag(s)$

$$\Delta G° = \Delta G^\circ_f(AgCl) - [\Delta G^\circ_f(Ag^+) + \Delta G^\circ_f(Cl^-)]$$

$$= -109 - (-129 + 77) = -57\,kJ/mol = -57000\,J/mol$$

We know that, $\Delta G° = -nFE^\circ_{cell}$

$-57000 = -1 \times 96500 \times E^\circ_{cell}$

($\because$ n = electron transferred = 1)

$E^\circ_{cell} = \frac{57000}{96500} = \mathbf{0.59\ volts}$

Again $E^\circ_{cell} = \frac{0.0591}{n}\log K_c$

or $E^\circ_{cell} = \frac{0.0591}{n}\log\frac{AgCl}{[Ag^+][Cl^-]}$

$E^\circ_{cell} = \frac{0.0591}{1}\log\left(\frac{1}{K_{sp}}\right)$

($\because$ [AgCl (s) = 1 and $K_{sp} = [Ag^+][Cl^-]$)

or $0.59 = -0.059\log K_{sp}$

or $\log K_{sp} = -10 \Rightarrow K_{sp} = \mathbf{10^{-10}}$

(b) When Zn is added to 100 ml of saturated AgCl solution.

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

$Ag^+ + e^- \rightleftharpoons Ag;\ E° = 0.80\,V$

$Zn^{2+} + 2e^- \rightleftharpoons Zn;\ E° = -0.76\,V$

$E^\circ_{cell} = E^\circ_{Ag^+|Ag(s)} - E^\circ_{Zn^{2+}|Zn(s)}$

$= 0.80 - (-0.76) = 1.56\,V$

$E^\circ_{cell} = \frac{0.059}{n}\log_{10}\frac{[Zn^{2+}]}{[Ag^+]^2}$

$\Rightarrow 1.56 = \frac{0.059}{2}\log_{10}\frac{[Zn^{2+}]}{[Ag^+]^2}$

$\Rightarrow \log_{10}\frac{[Zn^{2+}]}{[Ag^+]^2} = \mathbf{52.9}$

NOTE : As the value of equilbrium constant is very high so the reaction moves in forward direction completely.

$[Ag^+]$ from (a) $= \sqrt{10^{-10}} = 10^{-5}$

$[(\because K_{sp} = 10^{-10} = [Ag^+][Cl^-]]$

$\therefore$ Ag^+ in 100 ml of solution $= \frac{10^{-5} \times 100}{1000} = \mathbf{10^{-6}\ mol.}$

38. Given: $\wedge^\infty_m(Ag^+) = 6 \times 10^{-3}$; $\wedge^\infty_m(Br^-) = 8 \times 10^{-3}$;

$\wedge^\infty_m(NO_3^-) = 7 \times 10^{-3}$ and $K_{sp}(AgBr) = 12 \times 10^{-14}$

NOTE THIS STEP: To find the specific conductivity (κ) of the final solution of AgBr in which $AgNO_3$ (10^{-7} M) is mixed we must find the individual κ of the ions.

or $\kappa_{soln} = \kappa_{Ag^+} + \kappa_{Br^-} + \kappa_{NO_3^-}$

Again, $\kappa = \wedge^\infty_m \times$ molar concentration

Calculation of molar concentration of ions :

Concentration,

$[NO_3^-] = 10^{-7}$ moles/l $\equiv 10^{-4}$ moles/m^3

Let x be the molar concentration of Ag^+ from AgBr

$\Rightarrow (x + 10^{-7})x = 12 \times 10^{-14}$

or $x^2 + 10^{-7}x - 12 \times 10^{-14} = 0$

or, $(x + 4 \times 10^{-7})(x - 3 \times 10^{-7}) = 0 \Rightarrow x = 3 \times 10^{-7} M$

$\Rightarrow [Br^-] = 3 \times 10^{-7}$ M $\equiv 3 \times 10^{-4}$ moles/m^3 and

$[Ag^+] = 3 \times 10^{-7} + 10^{-7} = 4 \times 10^{-7}$ M $= 4 \times 10^{-4}$ moles/m^3

$\kappa_{Ag^+} = \mathbf{6 \times 10^{-3} \times 4 \times 10^{-4}}$

$= 24 \times 10^{-7}$ $(Sm^2 mol^{-1} \times mol/m^3) = 24 \times 10^{-7} S/m$

Similarly, $\kappa_{Br^-} = 8 \times 10^{-3} \times 3 \times 10^{-4} = \mathbf{24 \times 10^{-7}}$ **S/m** and

$\kappa_{NO_3^-} = 7 \times 10^{-3} \times 10^{-4} = 7 \times 10^{-7}$ S/m

$\Rightarrow \kappa = (24 + 24 + 7) \times 10^{-7}$ S/m $= 55 \times 10^{-7}$ S/m

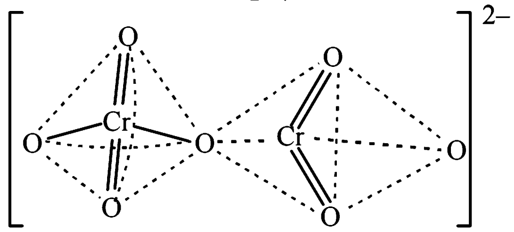
So the correct answer is **55**.

F. Match the Following

1. **(A - p, s); (B - r); (C - p, q); (D - p).**

A→ p, s; The reaction is redox reaction because the O.N. of O in O_2^- is – 0.5 and that in O_2 is zero. In O_2^{2-} is –1.0. It involves reduction oxidation reaction. Since here a part of molecule is oxidised and a part is reduced so it is disproportionation.

B → r; The structure of $Cr_2O_7^{2-}$ is given below



[**NOTE :** In any solution dichromate ions and chromate ions exist in equilibrium. In alkali solution, dichromate ions are converted into chromate ions and on acidification chromate ions are converted back into dichromate ion.]

C → p, q; The reaction is

$2MnO_4^- + 6H^+ + 5NO_2^- \rightarrow 2Mn^{2+} + 3H_2O + 5NO_3^-$

In involves change in O.N of Mn (from + 7 in MnO_4^-) to + 2(in Mn^{2+}), So Mn is reduced and NO_2^- is oxidised to NO_3^- it is a redox reaction.

The structure of NO_3^- (one of the products is **trigonal planar**)

D → p, It is a **redox reaction.**

2. **(a)** (P) $\underset{X}{(C_2H_5)_3N} + \underset{Y}{CH_3COOH} \longrightarrow$

$(C_2H_5)_3NH^+CH_3COO^-$

Initially conductivity increases because on neutralisation ions are created. After that it becomes practically constant because X alone can not form ions.

(Q) $\underset{x}{KI(0.1M)} + \underset{y}{AgNO_3(0.01M)} \longrightarrow AgI\downarrow + KNO_3$

Number of ions in the solution remains constant as only $AgNO_3$ precipitated as AgI. Thereafter conductance increases due to increase in number of ions.

(R) Initially conductance decreases due to the decrease in the number of $\overline{O}H$ ions as OH^- is getting replaced by CH_3COO^- which has poorer conductivity thereafter it slowly increases due to the increase in number of H^+ ions.

(S) Initially it decreases due to decrease in H^+ ions and then increases due to the increase in OH^- ions.

3. **(d)** (P) $Fe^{3+} \xrightarrow[n=1]{+0.77V} Fe^{2+} \xrightarrow[n=2]{-0.44V} Fe$; $Fe^{3+} \rightarrow Fe$: x V, n = 3

$\Delta G^o_{Fe^{3+}/Fe} = \Delta G^o_{Fe^{3+}/Fe^{2+}} + \Delta G^o_{Fe^{2+}/Fe}$

$\Rightarrow -3 \times FE^o_{(Fe^{+3}/Fe)} = -1 \times FE^o_{(Fe^{+3}/Fe^{+2})} + \left(-2 \times FE^o_{(Fe^{+2}/Fe)}\right)$

$\Rightarrow 3 \times x = 1 \times 0.77 + 2 \times (-0.44)$

$\Rightarrow x = -\frac{0.11}{3} V \simeq -0.04 V.$

(Q)

$$\begin{array}{ll} 2H_2O \longrightarrow O_2 + 4H^+ + 4e^- & E° = -1.23 V \\ 4e + O_2 + 2H_2O \longrightarrow 4OH^- & E° = +0.40 V \\ \hline 4H_2O \longrightarrow 4H^+ + 4OH^- & E° = -0.83 V \end{array}$$

(R)

$$\begin{array}{ll} Cu^{2+} + 2e \longrightarrow Cu & E° = +0.34 V \\ 2Cu \longrightarrow 2Cu^+ + 2e & E° = -0.52 V \\ \hline Cu^{2+} + Cu \longrightarrow 2Cu^+ & E° = -0.18 V \end{array}$$

(S) $Cr^{3+} \xrightarrow[n=1]{x} Cr^{2+} \xrightarrow[n=2]{-0.91V} Cr$; $Cr^{3+} \rightarrow Cr$: – 0.74V, n = 3

$x \times 1 + 2 \times (-0.91) = 3 \times (-0.74)$

$x - 1.82 = -2.22 \Rightarrow x = -0.4V$

G. Comprehension Based Questions

1. **(d)** In the given reaction,

Ag ions are reduce to Ag and Glucose is oxidised to gluconic acid as per the given reactions,

$Ag^+ + e^- \longrightarrow Ag;\ E^o_{red} = +0.800 V$ and

$C_6H_{12}O_6 + H_2O \longrightarrow \underset{\text{Gluconic acid}}{C_6H_{12}O_7} + 2H^+ + 2e^-;$

$E^{o}_{ox} = -0.05V$

Hence, $E^{o}_{cell} = 0.8 - 0.05 = 0.75\,V$

$\Delta G^{o}_{cell} = -nFE = -2F \times 0.75 = -RT\ln K$

$\Rightarrow \ln K = \dfrac{2F}{RT}(0.75) = 2 \times 38.92 \times 0.75 = 58.38$

2. **(a)** For the reaction,

$C_6H_{12}O_6 + H_2O \longrightarrow \underset{\text{Gluconic acid}}{C_6H_{12}O_7} + 2H^+ + 2e^-$

$E = E° - \dfrac{0.0591}{n}\ln\dfrac{[P]}{[R]} = E° - \dfrac{0.0591}{2}\ln[H^+]^2$

$E - E° = -\dfrac{0.0591}{2} \times 2\ln(-pH) = 0.0591 \times 11 = 0.65$

So, $E_{oxidation}$ increases over $E^{o}_{oxidation}$ by 0.65 V.

3. **(b)** During Tollen's test, oxidation of silver ion requires an alkaline medium. Under these conditions it forms insoluble silver oxide, hence to dissolve this oxide a complexing agent, ammonia is added, which brings silver ion as diamminosilver (I) ion, $[Ag(NH_3)_2]^+$. It is a soluble complex.

4. **(b)** Reaction at anode: $2Cl^- \longrightarrow Cl_2 + 2e^-$
moles of $Cl^- = 4 \times 500 \times 10^{-3} = 2$

moles $Cl_2 = \dfrac{1}{2} \times 2 = 1$

5. **(d)** 500 ml of 4.0 molar NaCl has 2 mole of NaCl.
By electrolysis we can get a maximum of 2 moles of sodium which can combine with exactly 2 moles of mercury to give amalgam.
∴ The maximum weight of amalgam which can be formed from this solution
= weight of 2 mole of sodium + weight of 2 mole of mercury
$= 2 \times 23 + 2 \times 200 = 446g$

6. **(d)** $Na^+ + e^- \longrightarrow Na$
Total number of moles of Na^+ discharged at cathode
= 2 mole
∴ The number of electron required for this purpose
= 2 mole
∴ Total charge required
= 2 faraday = 2×96500 = 193000 coulombs.

7. **(c)** $2I^- + Cl_2 \longrightarrow I_2 + 2Cl^-$

$E° = E^{o}_{I^-/I_2} + E^{o}_{Cl_2/Cl^-} = -0.54 + 1.36\,;\ E° = 0.82V$

E° is positive hence, iodide ion is oxidized by chlorine.

8. **(d)** $4Mn^{3+} + 2H_2O \longrightarrow 4Mn^{2+} + O_2 + 4H^+$

$E^{o}_{Mn^{3+}/Mn^{2+}} + E^{o}_{H_2O/O_2} = 1.50 + (-1.23) = 0.27V$

Reaction is feasible. [∴ E^{o} is positive]

9. **(a)** The precipitate formed in this reaction is of $Fe_4[Fe(CN)_6]_3$

10. **(b)** $M_{(s)} + M^+_{(aq)1M} \longrightarrow M^+_{(aq).05M} + M_{(s)}$
According to Nernst equation,

$E_{cell} = 0 - \dfrac{2.303RT}{F}\log\dfrac{M^+_{.05M}}{M^+_{1M}}$

$= 0 - \dfrac{2.303RT}{F}\log(5 \times 10^{-2}) = +\text{ ve}$

Hence, $|E_{cell}| = E_{cell} = 0.70$ V and $\Delta G < 0$ for the feasibility of the reaction.

11. **(c)** From above equation $\dfrac{2.303RT}{F} = 0.0538$

So, $E_{cell} = E^{\circ}_{cell} - \dfrac{0.0538}{1}\log 0.0025$

$= 0 - \dfrac{0.0538}{1}\log 0.0025 \approx 0.13988V \approx 140\,mV$

12. **(d)** **At anode :** $M(s) + 2X^-(aq) \longrightarrow MX_2(aq) + 2e^-$
At cathode : $M^{+2}(aq) + 2e^- \longrightarrow M(s)$
Thus, here $n = 2$
$\Delta G = -nFE_{cell}$
$= -2 \times 96500 \times 0.059 \times 10^{-3}$ kJ/mole $= -11.4$ kJ/mole

13. **(b)** $M|M^{2+}(aq)\,||\,\underset{0.001\,M}{M^{2+}(aq)}|M$

Anode : $M \longrightarrow M^{2+}(aq) + 2e^-$

Cathode : $M^{2+}(aq) + 2e^- \longrightarrow M$

$M^{2+}(aq)_c \rightleftharpoons M^{2+}(aq)_a$

$E_{cell} = 0 - \dfrac{0.059}{2}\log\left\{\dfrac{M^{2+}(aq)_a}{10^{-3}}\right\}$

$\Rightarrow 0.059 = -\dfrac{0.059}{2}\log\left\{\dfrac{M^{2+}(aq)_a}{10^{-3}}\right\}$

$-2 = \log\left\{\dfrac{M^{2+}(aq)_a}{10^{-3}}\right\}$

$\Rightarrow 10^{-2} \times 10^{-3} = M^{2+}(aq)_a$ = solubility = s

$\Rightarrow K_{sp} = 4s^3 = 4 \times (10^{-5})^3 = 4 \times 10^{-15}$

I. Integer Value Correct Type

1. **(4)** $X \longrightarrow Y;$ $\Delta G° = -193\ kJ\ mol^{-1}$

$M^+ \longrightarrow M^{3+} + 2e^-$ $E° = -0.25V$

Hence ΔG° for oxidation will be

$\Delta G° = -nFE°$
$= -2 \times 96500 \times (-0.25) = 48250\,J = 48.25\,kJ$

48.25 kJ energy oxidises one mole M^+

∴ 193 kJ energy oxidises $\dfrac{193}{48.25}$ mole $M^+ = 4$ mole M^+

2. **(3)** $1 \rightarrow HX$ $2 \rightarrow HY$

$\alpha_1 = \dfrac{(\lambda_m)_{HX}}{\lambda^{\circ}_m}$ $\alpha_2 = \dfrac{(\lambda_m)_{HY}}{\lambda^{\circ}_m}$

$K_{a_1} = C_1\alpha_1^2$ $K_{a_2} = C_2\alpha_2^2$

$= 0.01\dfrac{(\lambda_m)^2_{HX}}{(\lambda^{\circ}_m)^2}$ $= 0.1\dfrac{(\lambda_m)^2_{HY}}{(\lambda^{\circ}_m)^2}$

∴ $\dfrac{K_{a_1}}{K_{a_2}} = \dfrac{0.01(\lambda_m)^2_{HX}}{0.1(\lambda_m)^2_{HY}} = 0.1\left(\dfrac{(\lambda_m)_{HX}}{(\lambda_m)_{HY}}\right)^2$

$= 0.1\left(\dfrac{1}{10}\right)^2 = 10^{-3}$

$pK_a(HX) - pK_a(HY) = -\log\dfrac{K_{a_1}}{K_{a_2}} = -\log 10^{-3} = 3$

Section-B JEE Main/ AIEEE

1. (b) given $S \propto \frac{\text{area} \times \text{conc}}{\ell} = \frac{\kappa m^2 mol}{m \times m^3}$ $\therefore \kappa = Sm^2mol^{-1}$

2. (c) E_{cell} = Reduction potential of cathode (right) – Reduction potential of anode (left) $= E_{right} - E_{left}$.

3. (b) Oxidation half call:-
$H_2(g) \longrightarrow \underset{P_1}{2H^+(1M)} + 2e^-$
Reduction half cell
$2H^+(1M) + 2e^- \longrightarrow \underset{P_2}{H_2(g)}$
The net cell reaction
$\underset{P_1}{H_2(g)} \longrightarrow \underset{P_2}{H_2(g)}$
$E^\circ_{cell} = 0.00\,V$ $n = 2$
$\therefore E_{cell} = E^\circ_{cell} - \frac{RT}{nF}\log_e K = 0 - \frac{RT}{nF}\log_e \frac{P_2}{P_1}$
or $E_{cell} = \frac{RT}{2F}\log_e \frac{P_2}{P_1}$

4. (a) $2Cr^{3+} + 7H_2O \to Cr_2O_7^{2-} + 14H^+$
O.S. of Cr changes from +3 to +6 by loss of electrons. At anode oxidation takes place.

5. (d) Pure metal always deposits at cathode.

6. (d) $\overset{0}{Zn} + 2\overset{+1}{Ag}CN \xrightarrow{-2e^-} \overset{0}{Ag} + \overset{+2}{Zn}(CN)_2$ (+2e⁻)
The oxidation state shows a change only in (d)

7. (c) The equilibrium constant is related to the standard emf of cell by the expression
$\log K = E^\circ_{cell} \times \frac{n}{0.059} = 0.295 \times \frac{2}{0.059}$
$\log K = \frac{590}{59} = 10$ or $K = 1 \times 10^{10}$

8. (d) A B C
+0.5C –3.0V –1.2V
NOTE : The higher the negative value of reduction potential, the more is the reducing power.
Hence B > C > A.

9. (a) When 96500 coulomb of electricity is passed through the electroplating bath the amount of Ag deposited = 108g
$\therefore$ when 9650 coulomb of electricity is passed deposited Ag.
$= \frac{108}{96500} \times 9650 = 10.8\,g$

10. (b) $E_{cell} = E^\circ_{cell} + \frac{0.059}{n}\log\frac{[Cu^{+2}]}{[Zn^{+2}]}$
$= 1.10 + \frac{0.059}{2}\log[0.1] = 1.10 - 0.0295 = 1.07\,V$

11. (b) Magnesium provides cathodic protection and prevent rusting or corrosion.

12. (b) In $H_2 - O_2$ fuel cell, the combustion of H_2 occurs to create potential difference between the two electrodes

13. (a) $Fe^{3+} + e^- \to Fe^{2+}\ \Delta G^\circ = -1 \times F \times 0.77$
$Sn^{2+} + 2e^- \to Sn(s)\ \Delta G^\circ = -2 \times F(-0.14)$
for $Sn(s) + 2Fe^{3+}(aq) \to 2Fe^{2+}(aq) + Sn^{2+}(aq)$
$\therefore$ Standard potential for the given reaction
or $E^o_{cell} = E^o_{Sn/Sn^{2+}} + E^o_{Fe^{3+}/Fe^{2+}} = 0.14 + 0.77 = 0.91\,V$

14. (a) $E^o_{cell} = E^o_{cell} - \frac{0.059}{n}\log K_c$
or $0 = 0.591 - \frac{0.0591}{1}\log K_c$
or $\log K_c = \frac{0.591}{0.0591} = 10$ or $K_c = 1 \times 10^{10}$

15. (c) $\Lambda^\circ NaCl = \lambda^\circ Na^+ + \lambda Cl^-$ ....(i)
$\Lambda^\circ KBr = \lambda^\circ K^+ + \lambda^\circ Br^-$ ....(ii)
$\Lambda^\circ KCl = \lambda^\circ K^+ + \lambda Cl^-$ ....(iii)
operating (i) + (ii) - (iii)
$\Lambda^\circ NaBr = \lambda^\circ Na^+ + \lambda^\circ Br^-$
$= 126 + 152 - 150 = 128\ S\ cm^2\ mol^{-1}$

16. (a) $Zn(s) + 2H^+ + (aq) \rightleftharpoons Zn^{2+}(aq) + H_2(g)$
$E_{cell} = E^\circ_{cell} - \frac{0.059}{2}\log\frac{[Zn^{2+}][H_2]}{[H^+]^2}$
Addition of H_2SO_4 will increase $[H^+]$ and E_{cell} will also increase and the equilibrium will shift towards RHS

17. (c) The given values show that Cr has maximum oxidation potential, therefore its oxidation will be easiest. (Change the sign to get the oxidation values)

18. (d) **NOTE :** For spontaneous reaction ΔG should be negative. Equilibrium constant should be more than one
($\Delta G = -2.303\,RT\log K_c$, If $K_c = 1$ then $\Delta G = 0$; If $K_c < 1$ then $\Delta G = +ve$). Again $\Delta G = -nFE^o_{cell}$.
E^o_{cell} must be +ve to have ΔG –ve.

GP_3021

19. (a) Thus difluoro acetic acid being strongest acid will furnish maximum number of ions showing highest electrical conductivity. The decreasing acidic strength of the carboxylic acids given is difluoro acetic acid > fluoro acetic acid > chloro acitic acid > acetic acid.

20. (d) 1 mole of $e^- = 1F = 96500$ C
27g of Al is deposited by 3 × 96500 C
5120 g of Al will be deposited by

$$= \frac{3 \times 96500 \times 5120}{27} = 5.49 \times 10^7 C$$

21. (b)
$\Lambda^{\infty}_{HCl} = 426.2$ (i)

$\Lambda^{\infty}_{AcONa} = 91.0$ (ii)

$\Lambda^{\infty}_{NaCl} = 126.5$ (iii)

$$\Lambda^{\infty}_{AcOH} = (i) + (ii) - (iii) = [426.2 + 91.0 - 126.5] = 390.7$$

22. (c) $2H\overset{-1}{I} + H_2\overset{+6}{S}O_4 \longrightarrow \overset{0}{I_2} + \overset{+4}{S}O_2 + 2H_2O$ in this reaction oxidation number of S is decreasing from + 6 to +4 hence undergoing reduction and for HI oxidation Number of I is increasing from –1 to 0 hence underegoing oxidation therefore H_2SO_4 is acting as oxidising agent.

23. (b) $\Lambda^{o}_{CH_3COOH}$ is given by the following equation

$$\Lambda^{o}_{CH_3COOH} = \left(\Lambda^{o}_{CH_3COONa} + \Lambda^{o}_{HCl}\right) - \left(\Lambda^{o}_{NaCl}\right)$$

Hence Λ^{o}_{NaCl} is required.

24. (b) $R = 100\,\Omega$, $\kappa = \frac{1}{R}\left(\frac{l}{a}\right)$, $\frac{l}{a}$ (cell constant) $= 1.29 \times 100 m^{-1}$
Given, $R = 520\Omega$, $C = 0.2$ M, μ (molar conductivity) = ?

$\mu = \kappa \times V$ (κ can be calculated as $\kappa = \frac{1}{R}\left(\frac{1}{a}\right)$ now cell constant is known.)

Hence,

$$\mu = \frac{1}{520} \times 129 \times \frac{1000}{0.2} \times 10^{-6} m^3 = 12.4 \times 10^{-4} Sm^2 mol^{-1}$$

25. (b) **NOTE :** According to Kohlrausch's law, molar conductivity of weak electrolyte acetic acid (CH_3COOH) can be calculated as follows:

$$\Lambda^{\circ}_{CH_3COOH} = \left(\Lambda^{\circ}_{CH_3COONa} + \Lambda^{\circ}_{HCl}\right) - \Lambda^{\circ}_{NaCl}$$

∴ Value of Λ°_{NaCl} should also be known for calculating value of $\Lambda^{\circ}_{CH_3COOH}$.

26. (d) $E_{cell} = 0$; when cell is completely discharged.

$$E_{cell} = E^{\circ}_{cell} - \frac{0.059}{2}\log\left(\frac{[Zn^{2+}]}{[Cu^{2+}]}\right)$$

or $0 = 1.1 - \frac{0.059}{2}\log\left(\frac{[Zn^{2+}]}{[Cu^{2+}]}\right)$

$$\log\left(\frac{[Zn^{2+}]}{[Cu^{2+}]}\right) = \frac{2 \times 1.1}{0.059} = 37.3 \quad \therefore \left(\frac{[Zn^{2+}]}{[Cu^{2+}]}\right) = 10^{37.3}$$

27. (d) From the given representation of the cell, E_{cell} can be found as follows.

$$E_{cell} = E^{o}_{Fe^{2+}/Fe} - E^{o}_{Cr^{3+}/Cr} - \frac{0.059}{6}\log\frac{[Cr^{3+}]^2}{[Fe^{2+}]^3}$$

[Nernst -Equ.]

$$= -0.42 - (-0.72) - \frac{0.059}{6}\log\frac{(0.1)^2}{(0.01)^3}$$

$$= -0.42 + 0.72 - \frac{0.059}{6}\log\frac{0.1 \times 0.1}{0.01 \times 0.01 \times 0.01}$$

$$= 0.3 - \frac{0.059}{6}\log\frac{10^{-2}}{10^{-6}} = 0.3 - \frac{0.059}{6} \times 4$$

$= 0.30 - 0.0393 = 0.26$ V
Hence option (d) is correct answer.

28. (c) $CH_3OH(l) + \frac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

$$\Delta G_r = \Delta G_f(CO_2, g) + 2\Delta G_f(H_2O, \ell) - \Delta G_f(CH_3OH, \ell) - \frac{3}{2}\Delta G_f(O_2, g)$$

$= -394.4 + 2(-237.2) - (-166.2) - 0$
$= -394.4 - 474.4 + 166.2 = -702.6$ kJ

$$\% \text{ efficiency} = \frac{702.6}{726} \times 100 = 97\%$$

29. (b) Given

$Fe^{3+} + 3e^- \rightarrow Fe$, $E^{\circ}_{Fe^{3+}/Fe} = -0.036$ V ... (i)

$Fe^{2+} + 2e^- \rightarrow Fe$, $E^{\circ}_{Fe^{2+}/Fe} = -0.439$ V ... (ii)

we have to calculate

$Fe^{3+} + e^- \rightarrow Fe^{2+}$, $\Delta G = ?$

To obtain this equation subtract equ (ii) from (i) we get

$Fe^{3+} + e^- \rightarrow Fe^{2+}$ ... (iii)

As we know that $\Delta G = -nFE$
Thus for reaction (iii)

$\Delta G = \Delta G_1 - \Delta G$; $-nFE^{\circ} = -nFE_1 - (-nFE_2)$
$-nFE^{\circ} = nFE_2 - nFE_1$
$-1FE^{\circ} = 2 \times 0.439F - 3 \times 0.036$ F
-1 $FE^{\circ} = 0.770$ F ∴ $E^{\circ} = -0.770$V

$O^{--} > F^- > Na^+ > Mg^{++} > Al^{3+}$

30. **(c)** $\Delta G = -nFE$

or $E = \frac{\Delta G}{-nF} = \frac{966\times10^3}{4\times96500} = -2.5$ V

$\therefore$ The potential difference needed for the reduction $= 2.5$ V.

31. **(a)** The value of $E^\circ_{M^{2+}/M}$ for given metal ions are

$E^\circ_{Mn^{2+}/Mn} = -1.18$ V, $E^\circ_{Cr^{2+}/Cr} = -0.9$ V,

$E^\circ_{Fe^{2+}/Fe} = -0.44$ V and $E^\circ_{Co^{2+}/Co} = -0.28$ V.

The correct order of $E^\circ_{M^{2+}/M}$ values without considering negative sign would be

$Mn^{2+} > Cr^{2+} > Fe^{2+} > Co^{2+}$.

32. **(c)** $H^+ + e^- \longrightarrow \frac{1}{2}H_2$; $E = E^\circ - \frac{0.059}{1}\log\frac{P_{H_2}^{1/2}}{[H^+]}$

Now if $P_{H_2} = 2$ atm and $[H^+] = 1M$

then $E = 0 - \frac{0.059}{1}\log\frac{2^{1/2}}{1} = -2$

33. **(d)** For a spontaneous reaction ΔG must be –ve

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

Hence for ΔG to be -ve ΔE° has to be positive. Which is possible when X = Zn, Y = Ni

$Zn + Ni^{++} \longrightarrow Zn^{++} + Ni$

$E^\circ_{Zn/Zn^{+2}} + E^\circ_{Ni^{2+}/Ni} = 0.76 + (-0.23) = +0.53$ (positive)

34. (d) higher the value of standard reduction potential stronger will be the oxidising agent, hence MnO_4^- is the strongest oxidising agent.

35. **(a)** Given for 0.2 M solution

$R = 50\,\Omega$

$\kappa = 1.4$ S $m^{-1} = 1.4 \times 10^{-2}$ S cm^{-1}

Now, $R = \rho\frac{\ell}{a} = \frac{1}{\kappa}\times\frac{\ell}{a}$

$\Rightarrow \frac{\ell}{a} = R\times\kappa = 50\times1.4\times10^{-2}$

For 0.5 M solution

$R = 280\,\Omega$; $\kappa = ?$

$\frac{\ell}{a} = 50\times1.4\times10^{-2} \Rightarrow R = \rho\frac{\ell}{a} = \frac{1}{\kappa}\times\frac{\ell}{a}$

$\Rightarrow \kappa = \frac{1}{280}\times50\times1.4\times10^{-2}$

$= \frac{1}{280}\times70\times10^{-2} = 2.5\times10^{-3}$ S cm^{-1}

Now, $\Lambda_m = \frac{\kappa\times1000}{M} = \frac{2.5\times10^{-3}\times1000}{0.5}$

$= 5$ S cm^2 mol^{-1} $= 5\times10^{-4}$ S m^2 mol^{-1}

36. **(a)** (a) $Mn^{2+} + 2e^- \rightarrow Mn; E^\circ = -1.18V$; ... (i)

(b) $Mn^{3+} + e \rightarrow Mn^{2+}; E^\circ = -1.51V$; ... (ii)

Now multiplying equation (ii) by two and subtracting from equation (i)

$3Mn^{2+} \rightarrow Mn^+ + 2Mn^{3+}$;

$E^\circ = E_{Ox.} + E_{Red.} = -1.18 + (-1.51) = -2.69$ V

[–ve value of EMF (i.e., ΔG = +ve) shows that the reaction is non-spontaneous]

37. **(c)** According to Debye Huckle onsager equation,

$$\lambda_C = \lambda_\infty - B\sqrt{C}$$

38. **(d)** $Cu^{2+} + 2e^- \longrightarrow Cu$

2F i.e. 2 × 96500 C deposit Cu = 1 mol = 63.5 g

39. **(b)** **Galvanization** is the process by which zinc is coated over corrosive (easily rusted) metals to prevent them from corrosion.