10

Electrochemistry

Topic 1 Electrochemical Cells

Objective Questions I (Only one correct option)

1. Given,

$Co^{3} \quad e \quad Co^{2}\ ; E \quad 1.81\,V$

$Pb^{4} \quad 2e \quad Pb^{2}\ ; E \quad 1.67\,V$

$Ce^{4} \quad e \quad Ce^{3}\ ; E \quad 1.61\,V$

$Bi^{3} \quad 3e \quad Bi; E \quad 0.20\,V$

Oxidising power of the species will increase in the order **(2019 Main, 12 April I)**

(a) $Ce^{4} \quad Pb^{4} \quad Bi^{3+} \quad Co^{3}$
(b) $Bi^{3} \quad Ce^{4} \quad Pb^{4} \quad Co^{3}$
(c) $Co^{3} \quad Ce^{4} \quad Bi^{3} \quad Pb^{4}$
(d) $Co^{3} \quad Pb^{4} \quad Ce^{4} \quad Bi^{3}$

2. A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using 0.1 Faraday electricity. How many mole of Ni will be deposited at the cathode? **(2019 Main, 9 April II)**

(a) 0.20 (b) 0.10 (c) 0.15 (d) 0.05

3. Calculate the standard cell potential (in V) of the cell in which following reaction takes place

$Fe^{2+}(aq) + Ag^{+}(aq) \qquad Fe^{3+}(aq) + Ag(s)$

Given that,

$E \quad _{Ag^{+}/Ag} \quad x\,V$

$E \quad _{Fe^{2+}/Fe} \quad y\,V$

$E \quad _{Fe^{3+}/Fe} \quad z\,V$ **(2019 Main, 8 April II)**

(a) $x \quad 2y \quad 3z$ (b) $x \quad y$
(c) $x \quad y \quad z$ (d) $x \quad z$

4. Given, that $E^{\ominus}_{O_2/H_2O} = +1.23V$;

$E^{\ominus}_{S_2O_8^{2}\ /SO_4^{2}} = 2.05V$;

$E^{\ominus}_{Br_2/Br^{\ominus}} = +1.09V$,

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

The strongest oxidising agent is **(2019 Main, 8 April I)**

(a) Au^{3} (b) O_2 (c) $S_2O_8^{2}$ (d) Br_2

5. Consider the following reduction processes:

$Zn^{2} \quad 2e \quad Zn(s); E \quad 0.76\,V$

$Ca^{2} \quad 2e \quad Ca(s); E \quad 2.87\,V$

$Mg^{2} \quad 2e \quad Mg(s); E \quad 2.36\,V$

$Ni^{2} \quad 2e \quad Ni(s); E \quad 0.25\,V$

The reducing power of the metals increases in the order **(2019 Main, 10 Jan I)**

(a) Zn < Mg < Ni < Ca (b) Ni < Zn < Mg < Ca
(c) Ca < Zn < Mg < Ni (d) Ca < Mg < Zn < Ni

6. The anodic half-cell of lead-acid battery is recharged using electricity of 0.05 Faraday. The amount of $PbSO_4$ electrolysed in g during the process is (Molar mass of $PbSO_4 \quad 303\,g\,mol^{\ 1}$) **(2019 Main, 9 Jan I)**

(a) 11.4 (b) 7.6 (c) 15.2 (d) 22.8

7. How long (approximate) should water be electrolysed by passing through 100 amperes current so that the oxygen released can completely burn 27.66 g of diborane? (Atomic weight of $B \quad 10.8$) **(2018 Main)**

(a) 6.4 hours (b) 0.8 hours (c) 3.2 hours (d) 1.6 hours

8. Given, $E_{Cl_2/Cl} \quad 1.36\,V, E_{Cr^{3+}/Cr} \quad 0.74\,V$

$E_{Cr_2O_7^{2}\ /Cr^{3}} \quad 1.33\,V, E_{MnO_4/Mn^{2+}} \quad 1.51\,V$

Among the following, the strongest reducing agent is **(2017 Main)**

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

9. For the following electrochemical cell at 298 K,

$Pt(s) \mid H_2(g, 1bar) \mid H \ (aq, 1\,M)$

$\parallel M^{4} \ (aq), M^{2} \ (aq) \mid Pt(s)$

$E_{cell} \quad 0.092\,V \text{ when } \dfrac{[M^{2}\ (aq)]}{[M^{4}\ (aq)]} \quad 10^{x}$

Given : $E_{M^{4+}/M^{2+}} \quad 0.151\,V; 2.303\dfrac{RT}{F} \quad 0.059\,V$

The value of x is **(2016 Adv.)**

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

10. 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 u) **(2015 Main)**
(a) 0 g (b) 63.5 g (c) 2 g (d) 127 g

11. 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 **(2013 Main)**
(a) Cl (b) Cr^3 (c) Mn^2 (d) MnO_4

12. Electrolysis of dilute aqueous NaCl solution was carried out by passing 10 mA current. The time required to liberate 0.01 mole of H_2 gas at the cathode is (1 F 96500 C mol ^{1})
(a) 9.65 10^4 s (b) 19.3 10^4 s **(2008, 3M)**
(c) 28.95 10^4 s (d) 38.6 10^4 s

13. In the electrolytic cell, flow of electrons is from **(2003, 1M)**
(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

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 :

$$MnO_4(aq) + 8H^+(aq) + 5e \quad Mn^{2+}(aq) + 4H_2O(l), \quad E \; 1.51\,V$$
$$Cr_2O_7^2(aq) + 14H^+(aq) + 6e \quad 2Cr^{3+}(aq) + 7H_2O(l), \quad E \; 1.38\,V$$
$$Fe^{3+}(aq) + e \quad Fe^{2+}(aq) \quad E \; 0.77\,V$$
$$Cl_2(g) + 2e \quad 2Cl\;(aq) \quad E \; 1.40\,V$$

Identify the incorrect statement regarding the quantitative estimation of aqueous $Fe(NO_3)_2$ **(2002, 3M)**
(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. Saturated solution of KNO_3 is used to make 'salt-bridge' because **(2001, 1M)**
(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

16. The gas X at 1 atm is bubbled through a solution containing a mixture of 1 M Y and 1 M Z at 25 C. If the order of reduction potential is $Z \quad Y \quad X$, then **(1999, 2M)**
(a) Y will oxidise X and not Z
(b) Y will oxidise Z and not X
(c) Y will oxidise both X and Z
(d) Y will reduce both X and Z

17. The standard reduction potential values of three metallic cations, X, Y, Z are 0.52, 3.03 and 1.18 V respectively. The order of reducing power of the corresponding metals is
(a) $Y > Z > X$ (b) $X > Y > Z$ **(1998, 2M)**
(c) $Z > Y > X$ (d) $Z > X > Y$

18. The standard reduction potentials $E°$, for the half reactions are as

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

The emf for the cell reaction,

$$Fe^{2+} + Zn \quad Zn^{2+} \quad Fe \text{ is}$$ **(1989, 1M)**

(a) – 0.35 V (b) + 0.35 V (c) + 1.17 V (d) 1.17 V

19. When a lead storage battery is discharged **(1986, 1M)**
(a) SO_2 is evolved
(b) lead is formed
(c) lead sulphate is consumed
(d) sulphuric acid is consumed

20. The reaction,

$$\frac{1}{2}H_2(g) \quad AgCl(s) \rightleftharpoons H^+(aq) + Cl\;(aq) + Ag(s)$$

occurs in the galvanic cell **(1985, 1M)**
(a) Ag |AgCl (s)|KCl(soln) | $AgNO_3$ |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

21. The electric charge for electrode deposition of one gram equivalent of a substance is **(1984, 1M)**
(a) one ampere per second
(b) 96,500 coulombs per second
(c) one ampere for one hour
(d) charge on one mole of electrons

22. A solution containing one mole per litre of each $Cu(NO_3)_2$, $AgNO_3$, $Hg_2(NO_3)_2$ and $Mg(NO_3)_2$ is being electrolysed by using inert electrodes. The values of standard electrode potentials in volts (reduction potential) are

$$Ag^+/Ag \quad + 0.80, \; Hg_2^{2+}/2Hg \quad 0.79$$
$$Cu^{2+}/Cu \quad + 0.34, \; Mg^{2+}/Mg \quad 2.37$$

With increasing voltage, the sequence of deposition of metals on the cathode will be **(1984, 1M)**
(a) Ag, Hg, Cu, Mg (b) Mg, Cu, Hg, Ag
(c) Ag, Hg, Cu (d) Cu, Hg, Ag

23. Faraday's laws of electrolysis are related to the **(1983, 1M)**
(a) atomic number of the cation
(b) atomic number of the anion
(c) equivalent weight of the electrolyte
(d) speed of the cation

24. The standard reduction potentials at 298K for the following half cells are given :

$$Zn^2\;(aq) \quad 2e \rightleftharpoons Zn(s);\; E° = \; 0.762\,V$$
$$Cr^3\;(aq) \quad 3e \rightleftharpoons Cr(s);\; E° = \; 0.740\,V$$

$2\text{H}\ (aq)\quad 2e \rightleftharpoons \text{H}_2(g);\ E° = 0.000\ \text{V}$

$\text{Fe}^3\ (aq)\quad e \rightleftharpoons \text{Fe}^2\ (aq);\ E° =\ 0.770\ \text{V}$

Which is the strongest reducing agent? **(1981, 1M)**

(a) $\text{Zn}(s)$ (b) $\text{Cr}(s)$ (c) $\text{H}_2(g)$ (d) $\text{Fe}^2\ (aq)$

Objective Questions II

(One or more than one correct option)

25. In a galvanic cell, the salt-bridge **(2014 Adv.)**

(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

26. For the reduction of NO_3^- ion in an aqueous solution E is 0.96 V. Values of E for some metal ions are given below

$\text{V}^2\ (aq)\quad 2e^-\qquad \text{V};\qquad E\qquad 1.19\ \text{V}$

$\text{Fe}^{3+}(aq)\quad 3e^-\qquad \text{Fe};\qquad E\qquad 0.04\text{V}$

$\text{Au}^3\ (aq)\quad 3e^-\qquad \text{Au};\qquad E\qquad 1.40\ \text{V}$

$\text{Hg}^2\ (aq)\quad 2e^-\qquad \text{Hg};\qquad E\qquad 0.86\text{V}$

The pair(s) of metals that is/are oxidised 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

Numerical Value Based Question

27. For the electrochemical cell,

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

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

(Given, $\dfrac{F}{R}\quad 11500\ \text{K}\ \text{V}^{\ 1}$, where F is the Faraday constant and R is the gas contant, In (10) 2.30) **(2018 Adv.)**

28. Consider an electrochemical cell : $A(s)\,|\,A^n\ (aq,\ 2\text{M})||B^{2n}\ (aq, 1\text{M})\,|\,B(s)$. The value of $H^\ominus$ for the cell reaction is twice of $G^\ominus$ at 300 K. If the emf of the cell is zero, the $S^\ominus$ (in J K ^{1} mol ^{1}) of the cell reaction per mole of B formed at 300 K is …… .

(Given : ln(2) 0.7, R (universal gas constant) 8.3 J K ^{1} mol ^{1}. H, S and G are enthalpy, entropy and Gibbs energy, respectively.) **(2018 Adv.)**

Passage Based Questions

Passage

Chemical reactions involve interaction of atoms and molecules. A large number of atoms/molecules (approximately $6.023\quad 10^{23}$) 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 M 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 F 96500 C). **(2007, 3 4M = 12M)**

29. The total number of moles of chlorine gas evolved is

(a) 0.5 (b) 1.0

(c) 2.0 (d) 3.0

30. If the cathode is a Hg electrode, the maximum weight (in gram) of amalgam formed from this solution is

(a) 200 (b) 225

(c) 400 (d) 446

31. The total charge (coulombs) required for complete electrolysis is

(a) 24125 (b) 48250

(c) 96500 (d) 193000

Subjective Questions

32. The following electrochemical cell has been set-up :

$\text{Pt}(1)\,|\,\text{Fe}^{3+}, \text{Fe}^{2+}\ (a\quad 1)\,|\,\text{Ce}^{4+}, \text{Ce}^{3+}(a\quad 1)\,|\,\text{Pt}\,(2)$

$E\ \ (\text{Fe}^{3+}, \text{Fe}^{2+})\quad 0.77\ \text{V}$

and $E\ \ (\text{Ce}^{4+}, \text{Ce}^{3+})\quad 1.61\ \text{V}$

If an ammeter is connected between the two platinum electrodes, predict the direction of flow of current, will the current increases or decreases with time? **(2000, 2M)**

33. 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 min. 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, 3M)**

34. A cell, $\text{Ag}\,|\,\text{Ag}^+||\text{Cu}^{2+}\,|\,\text{Cu}$, initially 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, 6M)**

35. 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 h at a current of 8.46 A? 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, 3M)**

36. The Edison storage cell is represented as:

$\text{Fe}\ (s)/\ \text{FeO}(s)/\ \text{KOH}(aq)/\text{Ni}_2\text{O}_3(s)/\ \text{Ni}(s)$

The half-cell reactions are :

$\text{Ni}_2\text{O}_3(s) + \text{H}_2\text{O}\ (l) + 2e \rightleftharpoons 2\text{NiO}(s) + 2\text{OH}\ ,$

$E\quad + 0.40\ \text{V}$

$\text{FeO}\ (s)\quad \text{H}_2\text{O}(l)\quad 2e \rightleftharpoons \text{Fe}(s) + 2\text{OH}\ ,$

$E\qquad 0.87\ \text{V}$

(i) What is the cell reaction?
(ii) What is the cell emf ? 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, 4M)**

37. The standard reduction-potential for the half-cell

$NO_3\,(aq) + 2H^+ + e \qquad NO_2\,(g) + H_2O$ 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, 2M)**

38. Chromium metal can be plated out from an acidic solution containing CrO_3 according to the following equation.

$$CrO_3(aq) + 6H^+(aq) + 6e \qquad Cr\,(s) + 3H_2O$$

Calculate (i) How many grams of chromium will be plated out by 24,000 C and (ii) How long will it take to plate out 1.5 g of chromium by using 12.5 A current? **(1993, 2M)**

39. An aqueous solution of NaCl on electrolysis gives $H_2(g)$, $Cl_2(g)$ and NaOH according to the reaction.

$$2Cl^-\,(aq) + 2H_2O \rightleftharpoons 2OH\,\,(aq) + H_2(g) + Cl_2(g)$$

A direct current of 25 A with a current efficiency of 62% is passed through 20 L of NaCl solution (20% by weight). Write down the reactions taking place at the anode and cathode. How long will it take to produce 1kg of Cl_2? What will be the molarity of the solution with respect to hydroxide ion? (Assume no loss due to evaporation) **(1992, 3M)**

40. For the galvanic cell,

Ag | AgCl(s), KCl (0.2 M) || KBr (0.001 M), 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) $\quad 2.8 \quad 10^{\ 10}$, K_{sp} (AgBr) $\quad 3.3 \quad 10^{\ 13}]$ **(1992, 4M)**

41. A current of 1.70 A is passed through 300.0 mL of 0.160M solution of a $ZnSO_4$ for 230 s with a current efficiency of 90%. Find out the molarity of Zn^{2+} after the deposition Zn. Assume the volume of the solution to remain constant during the electrolysis. **(1991, 4M)**

42. 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%. If the potential drop across the cell is 3.0 V, how much energy will be consumed? **(1990, 3M)**

43. 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 A. Calculate the volume of gases evolved at NTP during the entire electrolysis. **(1989, 5M)**

44. In a fuel cell hydrogen and oxygen react to produces electricity. In the process hydrogen gas is oxidised at the anode and oxygen at the cathode. If 67.2 L of H_2 at STP react in 15 min, 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?

Anode reaction : $\quad H_2 + 2OH \qquad 2H_2O + 2e$
Cathode reaction : $O_2 + 2H_2O + 2e \qquad 4OH$ **(1988, 4M)**

45. 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, 2M)**

46. A 100 watt, 110 V incandecent 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 h? **(1987, 5M)**

47. 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% H_2SO_4 by weight and that of density 1.139 g/mL is 20% H_2SO_4 by weight. The battery holds 3.5 L 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

$Pb + SO_4^{2} \qquad PbSO_4 + 2e$ (charging)
$PbO_2 + 4H^+ + SO_4^{2} \ + 2e$
$\qquad PbSO_4 + 2H_2O$ (discharging) **(1986, 5M)**

48. How long a current of 3 A 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, 3M)**

49. In an electrolysis experiment current was passed for 5 h 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 ampere.

(Atomic weight of Au 197 and atomic weight of Cu 63.5) **(1983, 3M)**

50. A current of 3.7 A is passed for 6 h between nickel electrodes in 0.5 L of a 2.0 M solution of $Ni(NO_3)_2$. What will be the molarity of solution at the end of electrolysis? **(1978, 2M)**

Topic 2 Conductivity of Electrolytic Solutions and their Measurement and Nernst Equation

Objective Questions I (Only one correct option)

1. The decreasing order of electrical conductivity of the following aqueous solution is

0.1 M formic acid (A),

0.1 M acetic acid (B),

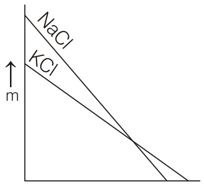
0.1 M benzoic acid (C). **(2019 Main, 12 April II)**

(a) $A > C > B$ (b) $C > B > A$

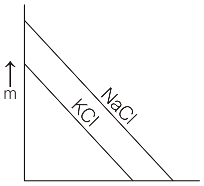
(c) $A > B > C$ (d) $C > A > B$

2. Which one of the following graphs between molar conductivity $_{\text{m}}$) *versus* $\sqrt{C}$ is correct? **(2019 Main, 10 April II)**

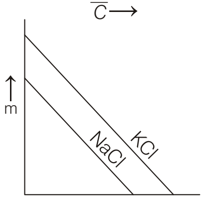
(a)



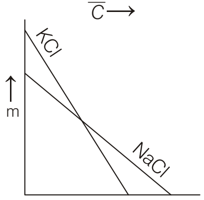
(b)



(c)



(d)



3. Consider the statements S_1 and S_2 :

S_1 : Conductivity always increases with decrease in the concentration of electrolyte.

S_2 : Molar conductivity always increases with decrease in the concentration of electrolyte.

The correct option among the following is **(2019 Main, 10 April I)**

(a) S_1 is correct and S_2 is wrong

(b) S_1 is wrong and S_2 is correct

(c) Both S_1 and S_2 are wrong

(d) Both S_1 and S_2 are correct

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

$\text{Zn}(s) \quad \text{Cu}^{2} \ (aq) \qquad \text{Zn}^{2} \ (aq) \quad \text{Cu}(s),$

$E \quad 2\text{V at } 298 \text{ K}$

(Faraday's constant, $F = 96000 \text{ C mol }^{1}$) **(2019 Main, 9 April I)**

(a) 384 (b) 192 (c) 384 (d) 192

5. $_{\text{m}}$ for NaCl, HCl and NaA are 126.4, 425.9 and 100.5 S cm^2 mol ^{1}, respectively. If the conductivity of 0.001 M HA is 5 10 ^{5} S cm ^{1}, degree of dissociation of HA is **(2019 Main, 12 Jan II)**

(a) 0.25 (b) 0.50 (c) 0.75 (d) 0.125

6. Given the equilibrium constant (K_C) of the reaction :

$$\text{Cu}(s) \quad 2\text{Ag}^+(aq) \qquad \text{Cu}^{2} \ (aq) \quad 2\text{Ag}(s)$$

is 10 10^{15}, calculate the E_{cell} of this reaction at 298 K.

$2.303 \dfrac{RT}{F}$ at 298 K $\quad 0.059$ V **(2019 Main, 11 Jan II)**

(a) 0.4736 V (b) 0.04736 mV

(c) 0.4736 mV (d) 0.04736 V

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

M^x **(aq)/M(s)**	Au^{3} (aq)/ Au(s)	Ag (aq)/ Ag(s)	Fe^{3} (aq)/ Fe^{2} (aq)	Fe^{2} (aq)/ Fe(s)
$E_{M^x \ /M}/V$	1.40	0.80	0.77	0.44

If $E_{\text{Zn}^{2} \ /\text{Zn}}$ 0.76 V, which cathode will give a maximum value of E_{cell} per electron transferred? **(2019 Main, 11 Jan I)**

(a) $\dfrac{\text{Ag}^+}{\text{Ag}}$ (b) $\dfrac{\text{Fe}^{2+}}{\text{Fe}}$ (c) $\dfrac{\text{Au}^{3}}{\text{Au}}$ (d) $\dfrac{\text{Fe}^{3+}}{\text{Fe}^{2+}}$

8. In the cell,

$\text{Pt}(s)\,|\text{H}_2\,(g, 1\text{ bar})|\text{HCl}(aq)|\text{AgCl}(s)|\text{Ag}(s)|\text{Pt}(s)$ the cell potential is 0.92 V when a 10 ^{6} molal HCl solution is used. The standard electrode potential of (AgCl/ Ag,Cl) electrode is Given, $\dfrac{2.303RT}{F}$ 0.06 V at 298 K

(a) 0.40 V (b) 0.20 V (c) 0.94 V (d) 0.76 V

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

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

at 300 K is approximately

(R 8 JK ^{1}mol ^{1}, F = 96000 C mol ^{1}) **(2019 Main, 9 Jan II)**

(a) $e^{\ 160}$ (b) e^{160} (c) $e^{\ 80}$ (d) e^{320}

10. For the following cell,

$\text{Zn}(s)|\ \text{ZnSO}_4(aq)||\ \text{CuSO}_4(aq)|\ \text{Cu}(s)$

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

[F is Faraday constant; R is gas constant; T is temperature; E (cell) 1.1 V] **(2017 Adv.)**

(a) 2.303 RT 1.1 F (b) 1.1 F

(c) 2.303 RT 2.2 F (d) 2.2 F

11. Galvanisation is applying a coating of **(2016 Main)**

(a) Cr (b) Cu

(c) Zn (d) Pb

12. Given below are the half-cell reactions **(2014 Main)**

$$Mn^{2} \quad 2e \qquad Mn\ ;\ E \qquad 1.18\ eV$$

$$2\,(Mn \qquad e \qquad Mn^{2}\ );\ E \qquad 1.51\,eV$$

The E for $3Mn^{2} \qquad Mn + 2Mn^{3+}$ 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

13. The equivalent conductance of NaCl at concentration C and at infinite dilution are $_C$ and , respectively. The correct relationship between $_C$ and is given as (where, the constant B is positive) **(2014 Main)**

(a) $_C \qquad (B)C$ (b) $_C \qquad (B)\ C$
(c) $_C \qquad (B)\sqrt{C}$ (d) $_C \qquad (B)\sqrt{C}$

14. Resistance of 0.2 M solution of an electrolyte is 50 The specific conductance of the solution of 0.5 M solution of same electrolyte is $1.4\ S\,m^{\ 1}$ and resistance of same solution of the same electrolyte is 280 . The molar conductivity of 0.5 M solution of the electrolyte in $Sm^{2}mol^{\ 1}$ is **(2014 Main)**

(a) $5 \quad 10^{\ 4}$ (b) $5 \quad 10^{\ 3}$
(c) $5 \quad 10^{3}$ (d) $5 \quad 10^{2}$

15. The standard reduction potential data at 25°C is given below.

$E\ (Fe^{3}\ \ /\ Fe^{2}\ \ )\quad 0.77\ V;\ E\ (Fe^{2}\ /\ Fe)\quad 0.44\ V;$

$E\ (Cu^{2}\ \ /\ Cu)\quad 0.34\ V;\ E\ (Cu\ \ /\ Cu)\quad 0.52\ V;$

$E\ (O_2(g)\quad 4H\quad 4e\ )\qquad 2H_2O)\quad 1.23\ V;$

$E\ (O_2(g)\quad 2H_2O\quad 4e\ )\qquad 4OH)\quad 0.40\ V$

$E\ (Cr^{3}\ \ /\ Cr)\quad 0.74\ V;\ E\ (Cr^{2}\ \ /\ Cr)\quad 0.91\ V$

Match E of the rebox pair in Column I with the values given in Column II and select the correct answer using the code given below the lists. **(2013 Adv.)**

	Column I		Column II
P.	$E\ (Fe^{3}\ \ /\ Fe)$	1.	0.18 V
Q.	$E\ (4H_2O \rightleftharpoons 4H \quad 4OH\ \ )$	2.	– 0.4 V
R.	$E\ (Cu^{2} \quad Cu \qquad 2\ Cu\ \ )$	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

16. An aqueous solution of X is added slowly to an aqueous solution of Y as shown in Column I. The variation in conductivity of these reactions is given in Column II. Match Column I with Column II and select the correct answer using the codes given below the Columns. **(2013 Adv.)**

	Column I		Column II
P.	$(C_2H_5)_3N \quad CH_3COOH$ $X \qquad Y$	1.	Conductivity decreases and then increases
Q.	$KI(0.1\ M) \quad AgNO_3(0.01\ M)$ $X \qquad Y$	2.	Conductivity decreases and then does not change much
R.	$CH_3COOH \quad KOH$ $X \qquad Y$	3.	Conductivity increases and then does not change much
S.	$NaOH \quad HI$ $X \qquad Y$	4.	Conductivity does not change much and then increases

Codes

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

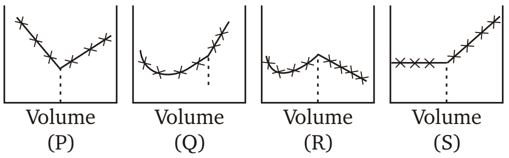
17. Consider the following cell reaction,

$$2Fe(s) + O_2(g) + 4H^{+}(aq) \qquad 2Fe^{2+}(aq) + 2H_2O(l),$$
$$E \qquad 1.67\ V$$

At $[Fe^{2+}]\quad 10^{\ 3}$ M, $P(O_2)\quad 0.1$ atm and pH 3, the cell potential at 25 C is **(2011)**

(a) 1.47 V (b) 1.77 V
(c) 1.87 V (d) 1.57 V

18. $AgNO_3$ (aqueous) was added to an aqueous KCl solution gradually and the conductivity of the solution was measured. The plot of conductance ( ) *versus* the volume of $AgNO_3$ is



(2011)

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

19. The half cell reactions for rusting of iron are :

$$2H^{+} \quad 2e \quad \frac{1}{2}O_2 \qquad H_2O(l); \qquad E \qquad 1.23\,V$$

$$Fe^{2} \quad 2e \qquad Fe(s); \qquad E \qquad 0.44\ V$$

G (in kJ) for the reaction is **(2005, 1M)**

(a) – 76 (b) – 322
(c) – 122 (d) – 176

20. $Zn\,|\,Zn^{2+}\ (a \quad 0.1M)\,||\,Fe^{2+}\ (a \quad 0.01M)\,|\,Fe.$

The emf of the above cell is 0.2905 V. Equilibrium constant for the cell reaction is **(2004, 1M)**

(a) $10^{0.32/0.059}$ (b) $10^{0.32/0.0295}$
(c) $10^{0.26/0.0295}$ (d) $10^{0.32/0.295}$

21. The correct order of equivalent conductance at infinite dilution of LiCl, NaCl and KCl is **(2001, 1M)**

(a) LiCl > NaCl > KCl (b) KCl > NaCl > LiCl
(c) NaCl > KCl > LiCl (d) LiCl > KCl > NaCl

22. For the electrochemical cell, $(M|M\quad)||(X\quad|X)$, $E\ (M\quad/M)\quad 0.44$ V and $E\ (X/X\quad)\quad 0.33$ V.

From this data one can deduce that **(2000, 1M)**

(a) $M + X \qquad M^{+} + X$ is the spontaneous reaction

(b) $M^{+} + X^{-} \qquad M + X$ is the spontaneous reaction

(c) $E_{\text{cell}}\quad 0.77$ V

(d) $E_{\text{cell}}\qquad 0.77$ V

23. The standard reduction potentials of Cu^{2+}/Cu and Cu^{2+}/Cu are 0.337 V and 0.153 V respectively. The standard electrode potential of Cu^{+}/Cu half-cell is **(1997, 1M)**

(a) 0.184 V (b) 0.827 V (c) 0. 521 V (d) 0.490 V

Numerical Value Based Question

24. The surface of copper gets tarnished by the formation of copper oxide. N_2 gas was passed to prevent the oxide formation during heating of copper at 1250 K. However, the N_2 gas contains 1 mole % of water vapour as impurity. The water vapour oxidises copper as per the reaction given below

$$2Cu(g) + H_2O(g) \qquad Cu_2O(s) + H_2(g)$$

p_{H_2} is the minimum partial pressure of H_2 (in bar) needed to prevent the oxidation at 1250 K. The value of $\ln(p_{H_2})$ is …… .

(Given : total pressure 1 bar, R (universal gas constant) 8 J K ^{1} mol ^{1}, ln(10) 2.30 $Cu(s)$ and $Cu_2O(s)$ are mutually immiscible.)

At 1250 K : $2Cu(s) + 1/2\,O_2(g) \qquad Cu_2O(s)$;

$$G^{\ominus}\qquad 78{,}000\text{ J mol }^{1}$$

$$H_2(g) + \frac{1}{2}O_2(g) \qquad H_2O(g);$$

$G^{\ominus}\qquad 1{,}78{,}000$ J mol ^{1}; G is the Gibbs energy **(2018 Adv.)**

Passage Based Questions

Passage I

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 concetration of M^{2} ions at the two electrodes. The emf of the cell at 298K is 0.059 V. **(2012)**

25. The solubility product (K_{sp} : mol^{3}dm ^{9}) of MX_2 at 298 based on the information available the given concentration cell is (take 2.303 R 298/ F 0.059 V)

(a) 1 10 ^{15} (b) 4 10 ^{15}

(c) 1 10 ^{12} (d) 4 10 ^{12}

26. The value of G (kJ mol ^{1}) for the given cell is (take 1 F 96500 C mol ^{1})

(a) 5.7 (b) 5.7 (c) 11.4 (d) –11.4

Passage II

The concentration of potassium ions inside a biological cell is at least twenty times higher than the outside. The resulting potential difference across the cell is important in several processes such as transmission of nerve impulses and maintaining the ion balance. A simple model for such a concentration cell involving a metal M is :

$$M(s)\,|\,M\quad(aq;\,0.05\text{ molar})\,||\,M\quad(aq;\,1\text{ molar})\,|\,M(s)$$

For the above electrolytic cell the magnitude of the cell potential $|E_{\text{cell}}|\quad 70$ mV. **(2010)**

27. For the above cell

(a) $E_{\text{cell}}\quad 0;\ G\quad 0$ (b) $E_{\text{cell}}\quad 0;\ G\quad 0$

(c) $E_{\text{cell}}\quad 0;\ G\quad 0$ (d) $E_{\text{cell}}\quad 0;\ G\quad 0$

28. 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) 35 mV (b) 70 mV

(c) 140 mV (d) 700 mV

Passage III

Redox reaction 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 Daniell 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 17–19. **(2007, 4 3M = 12M)**

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

29. Among the following, identify the correct statement.

(a) Chloride ion is oxidised by O_2

(b) Fe^{2} is oxidised by iodine

(c) Iodide ion is oxidised by chlorine

(d) Mn^{2} is oxidised by chlorine

30. While Fe^{3} is stable, Mn^{3} is not stable in acid solution because

(a) O_2 oxidises Mn^{2} to Mn^{3}

(b) O_2 oxidises both Mn^{2} to Mn^{3} and Fe^{2} to Fe^{3}

(c) Fe^{3} oxidises H_2O to O_2

(d) Mn^{3} oxidises H_2O to O_2

31. Sodium fusion extract, obtained from aniline, on treatment with iron (II) sulphate and H_2SO_4 in the presence of air gives a Prussian blue precipitate. The blue colour is due to the formation of

(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

Tollen's reagent is used for the detection of aldehydes. When a solution of $AgNO_3$ is added to glucose with NH_4OH, then gluconic acid is formed.

$$Ag \quad e \qquad Ag; \quad E_{red} \quad 0.80\ V$$

$$C_6H_{12}O_6 \quad H_2O \qquad \underset{\text{Gluconic acid}}{C_6H_{12}O_7} \quad 2H \quad 2e\ ; \qquad E_{oxi} \quad 0.05\ V$$

$$Ag(NH_3)_2 \quad e \qquad Ag\,(s) \quad 2NH_3; \qquad E_{red} = 0.337\,V$$

$$[\text{Use } 2.303\ \frac{RT}{F}\ \ 0.0592 \text{ and } \frac{F}{RT}\ \ 38.92 \text{ at } 298\ K]$$

(2006, 3 4M 12M)

32. $2Ag \quad C_6H_{12}O_6 \quad H_2O \qquad 2Ag\,(s) \quad C_6H_{12}O_7 \quad 2H$

Find ln K of this reaction.

(a) 66.13 (b) 58.38 (c) 28.30 (d) 46.29

33. When ammonia is added to the solution, pH is raised to 11. Which half-cell reaction is affected by pH and by how much?

(a) E_{oxi} will increase by a factor of 0.65 from E_{oxi}

(b) E_{oxi} will decrease by a factor of 0.65 from E_{oxi}

(c) E_{red} will increase by a factor of 0.65 from E_{red}

(d) E_{red} will decrease by a factor of 0.65 from E_{red}

34. Ammonia is always added in this reaction. Which of the following must be incorrect?

(a) NH_3 combines with Ag to form a complex

(b) $Ag(NH_3)_2$ is a stronger oxidising reagent than Ag

(c) In the absence of NH_3 silver salt of gluconic acid is formed

(d) NH_3 has affected the standard reduction potential of glucose/gluconic acid electrode

Subjective Questions

35. We have taken a saturated solution of AgBr, K_{sp} is $12 \quad 10^{14}$. If 10^{7} M of $AgNO_3$ are added to 1 L of this solution, find conductivity (specific conductance) of this solution in terms of $10^{7}\ Sm^{1}$ units. **(2006, 6M)**

Given, $\quad_{(Ag\ )} \quad 6 \quad 10^{3}\ Sm^2\ mol^{1}$,

$\quad_{(Br\ )} \quad 8 \quad 10^{3}\ Sm^2\ mol^{1}$,

$\quad_{(NO_3^-)} \quad 7 \quad 10^{3}\ Sm^2\ mol^{1}$.

36. Calculate G_r of the following reaction:

(a) $Ag\ (aq) \quad Cl\ (aq) \qquad AgCl(s)$

Given

G_f (AgCl)	109 kJ/mol
G_f (Cl)	129 kJ/mol
G_f (Ag^+)	77 kJ/mol

Represent the above reaction in form of a cell. Calculate $E°$ of the cell. Find $\log_{10} K_{sp}$ of AgCl. **(2005, 6M)**

(b) $6.539 \quad 10^{2}$ g of metallic Zn(u 65.39) was added to 100 mL of saturated solution of AgCl. Calculate $\log_{10} \frac{[Zn^2\ ]}{[Ag\ ]^2}$. Given that

$$Ag \quad e \qquad Ag; \qquad E \quad 0.80V$$

$$Zn^2 \quad 2e \qquad Zn; \qquad E \quad 76V$$

Also find how many moles of Ag will be formed?

37. Find the equilibrium constant for the reaction

$$Cu^{2+} \quad In^2 \rightleftharpoons Cu \quad In^{3+}$$

Given that $E_{Cu^{2+}/Cu^+} \quad 0.15V,$

$E_{In^{2+}/In^+} \quad 0.4V,$

$E_{In^{3+}/In^+} \quad 0.42\,V$ **(2004, 4M)**

38. (a) Will pH value of water be same at temperature 25°C and 4°C? Justify in not more than 2 or 3 sentences.

(b) 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 concentration of $CuSO_4$ in the cell with higher emf value is 0.5 M. Find out the concentration of $CuSO_4$ in the other cell. Given : $2.303\,RT/F \quad 0.06V$. **(2003, 2M)**

39. The standard potential of the following cell is 0.23 V at 15 C and 0.21 V at 35 C.

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

(i) Write the cell reaction.

(ii) Calculate H and S 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 $(Ag^+ (aq)/Ag\ (s)$ is 0.80 V at 25 C. **(2001, 10M)**

40. Find the solubility product of a saturated solution of Ag_2CrO_4 in water at 298 K, if the emf of the cell $Ag \mid Ag^+$ (Saturated Ag_2CrO_4 solution.) $\|Ag \quad (0.1\,M) \mid Ag$ is 0.164 V at 298 K. **(1998, 6M)**

41. Calculate the equilibrium constant for the reaction, $2Fe^{3+} \quad 3I \rightleftharpoons 2Fe^{2+} + I_3$. 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, 3M)**

42. Calculate the equilibrium constant for the reaction

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

Given, $E\ \ (Ce^{4+}/Ce^{3}\ )\ \ 1.44\ V, E\ \ (Fe^{3+}/Fe^{2}\ ) = 0.68\ V$ **(1997, 2M)**

43. 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 $1.0 \quad 10^{19}$. **(1996, 3M)**

44. An excess of liquid mercury is added to an acidified solution of $1.0 \quad 10^{3}$ M Fe^{3+}. It is found that 5 % of Fe^{3+} remains at equilibrium at 25 C. Calculate $E\ \ (Hg^{2+}/Hg\ )$ assuming that the only reaction that occurs is

$$2Hg + 2Fe^{3+} \qquad Hg_2^{2+} + 2Fe^{2+}$$

Given, $\quad E\ \ (Fe^{3+}/Fe^{2+}) \quad 0.77\ V$ **(1995, 4M)**

45. The standard reduction potential of the Ag^+/Ag electrode at 298 K is 0.799 V. Given that for AgI, K_{sp} 8.7 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, 3M)**

46. 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 Vrespectively. Find out the concentration of Ni^{2+} in solution at equilibrium. **(1991, 2M)**

47. The standard reduction potential of Cu^{2+}/ Cu and Ag^+/ Ag electrodes are 0.337 and 0.799 V respectively. Construct a galvanic cell using these electrodes so that its standard emf is positive. For what concentration of Ag^+ will the emf of the cell, at 25 C, be zero if the concentration of Cu^{2+} is 0.01 M? **(1990, 3M)**

48. The standard reduction potential at 25 C of the reaction, $2H_2O + 2e \rightleftharpoons H_2 + 2OH$, is 0.8277 V. Calculate the equilibrium constant for the reaction,

$$2H_2O \rightleftharpoons H_3O^+ + OH \quad \text{at } 25\ \text{C}.$$ **(1989, 3M)**

49. The emf of a cell corresponding to the reaction.

$Zn(s) + 2H^+(aq) \qquad Zn^{2+}\ (0.1M) + H_2, (g, 1\,atm)$

is 0.28 V at 25 C.

Write the half-cell reactions and calculate the pH of the solution at the hydrogen electrode.

$E\ (Zn^{2+}/Zn) \quad 0.76\ V\ E_{H^+/H_2} \quad 0$ **(1986, 4M)**

50. Give reasons in one or two sentences.

"Anhydrous HCl is a bad conductor of electricity but aqueous HCl is a good conductor." **(1985, 1M)**

51. Consider the cell,

$$Zn\ |\ Zn^2\ (aq)\ (1.0\ M)\ ||\ Cu^2\ (aq)\ (1.0\ M)\ |\ Cu$$

The standard reduction potentials are 0.350 V for

$$Cu^2\ (aq) \quad 2e \qquad Cu$$

and 0.763 V for $Zn^2\ (aq) \quad 2e \qquad Zn$

(i) Write down the cell reaction.
(ii) Calculate the emf of the cell.
(iii) Is the cell reaction spontaneous or not? **(1982, 2M)**

Integer Type Questions

52. The conductance of a 0.0015 M aqueous solution of a weak monobasic acid was determined by using a conductivity cell consisting of platinised Pt electrodes. The distance between the electrodes is 120 cm with an area of cross section of 1 cm ^{2}. The conductance of this solution was found to be 5 10 ^{7} S. The pH of the solution is 4. The value of limiting molar conductivity ($_m$) of this weak monobasic acid in aqueous solution is Z 10^2 S cm ^{1} mol ^{1}. The value of Z is **(2017 Adv.)**

53. All the energy released from the reaction $X \quad Y$, $_rG$ = 193 kJ mol ^{1} is used for oxidising M as $M \quad M^3 \quad 2e$, E 0.25 V.

Under standard conditions, the number of moles of M oxidised when one mole of X is converted to Y is [F 96500 C mol] **(2015 Adv.)**

Answers

Topic 1

1. (b)	**2.** (d)	**3.** (a)	**4.** (c)
5. (b)	**6.** (b)	**7.** (c)	**8.** (a)
9. (d)	**10.** (b)	**11.** (d)	**12.** (b)
13. (c)	**14.** (a)	**15.** (c)	**16.** (a)
17. (a)	**18.** (b)	**19.** (d)	**20.** (c)
21. (d)	**22.** (c)	**23.** (c)	**24.** (a)
25. (a, b)	**26.** (a,b,d)	**27.** (10)	
28. (−11.62 JK mol ^{1})		**29.** (b)	**30.** (d)
31. (d)	**33.** (8 10 ^{5} M)	**34.** (0001 V)	**35.** (300 cm^2)
36. (245.11 kJ)	**39.** (1.4085 M)	**40.** (0.037 V)	**41.** (0.154 M)
42. (347.40 kJ)	**44.** (190.50 g)	**45.** (10 ^{4} M)	**46.** (19.1 g)
47. (265 Ah)	**48.** (125 s)	**49.** (0.80 A)	**50.** (1.172 M)

Topic 2

1. (a)	**2.** (c)	**3.** (b)	**4.** (c)
5. (d)	**6.** (a)	**7.** (a)	**8.** (b)
9. (b)	**10.** (c)	**11.** (c)	**12.** (a)
13. (c)	**14.** (a)	**15.** (d)	**16.** (a)
17. (d)	**18.** (d)	**19.** (b)	**20.** (b)
21. (b)	**22.** (b)	**23.** (c)	**24.** (−14.16)
25. (b)	**26.** (d)	**27.** (b)	**28.** (c)
29. (c)	**30.** (d)	**31.** (a)	**32.** (b)
33. (c)	**34.** (d)	**35.** (55)	**37.** (10^{10})
38. (0.05 M)	**40.** (2.45 10 ^{12})		**41.** (5.89 10^7)
42. (6.88 10^{12})	**43.** (0.222 V)	**44.** (0.7926 V)	**46.** (1.7 10^{17})
47. (1.57 10 ^{9})	**48.** (1.04 10 ^{14})		**49.** (8.6)
52. (6 10^2 S cm ^{1} mol ^{1})		**53.** (4 mol)	

Hints & Solutions

Topic 1 Electrochemical Cells

1. **Key Idea** Negative E means that redox couple is weaker oxidising agent than H /H_2 couple. Positive $E°$ means that redox couple is a stronger oxidising agent than H / H_2 couple

$$\text{Given, } Co^{3} \quad e \qquad Co^{2} \ ; E \quad 1.81\text{ V}$$
$$Pb^{4} \quad 2e \qquad Pb^{2} \ ; E \quad 1.67\text{ V}$$
$$Ce^{4} \quad e \qquad Ce^{3} \ ; E \quad 1.61\text{ V}$$
$$Bi^{3} \quad 3e \qquad Bi; E \quad 0.20\text{ V}$$

Oxidising power of the species increases in the order of $Bi^{3+} \quad Ce^{4} \quad Pb^{4} \quad Co^{3}$.

Higher the emf value, stronger the oxidising power. The maximum value of emf is possessed by Co^{3} . Hence, it has maximum oxidising power. Whereas Bi^{3} possess the lowest emf value. Hence, it has minimum oxidising power.

2. A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using 0.1 Faraday electricity. It means that 0.1 equivalent of Ni^{2} will be discharged.

Electrolysis of $Ni(NO_3)_2$ gives

$$Ni^{2+} + 2e \qquad Ni \quad (\text{Atomic mass of Ni} \quad 58.7)$$

Number of equivalents Number of moles number of electrons.

0.1 Number of moles 2

$$\text{Number of moles of Ni} \quad \frac{0.1}{2} \quad 0.05$$

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

$$E^{\circ}_{\text{cell}} \quad E^{\circ}_{Ag^{+}/Ag} \quad E^{\circ}_{Fe^{3+}/Fe^{2}} \quad x\text{V} \quad E^{\circ}_{Fe^{3+}/Fe^{2}} \qquad \ldots \text{(i)}$$

Now, for two half-cells

(i) $Fe^{2+} + 2e \qquad Fe; \ E^{\circ}_{Fe^{2+}/Fe} \quad E^{\circ}_1 \quad y\text{V} \quad G^{\circ}_2 \qquad 2FE^{\circ}_1$

(ii) $Fe^{3+} + 3e \qquad Fe; \ E^{\circ}_{Fe^{3+}/Fe} \quad E^{\circ}_2 \quad z\text{V} \quad G^{\circ}_2 \qquad 3FE^{\circ}_2$

So, $Fe^{3+} + e^{-} \qquad Fe^{2+} ; E^{\circ}_{Fe^{3+}/Fe^{2}} \qquad E^{\circ}_3 \quad ?$

$$; \quad G^{\circ}_3 \qquad 1 \quad FE^{\circ}_3$$

Again, $G^{\circ}_3 \qquad G^{\circ}_2 \qquad G^{\circ}_1$

$$FE^{\circ}_3 \qquad 3FE^{\circ}_2 \quad (\quad 2FE^{\circ}_1)$$
$$E^{\circ}_3 \quad 2E^{\circ}_1 \quad 3E^{\circ}_2 \quad E^{\circ}_3 \quad 3E^{\circ}_2 \quad 2E^{\circ}_1$$
$$E^{\circ}_{Fe^{3+}/Fe^{2}} \qquad (3z \quad 2y)\text{V}$$

So, from equation (i)

$$E^{\circ}_{\text{cell}} \quad xV \quad (3z \quad 2y)\text{ V} \quad (x \quad 3z \quad 2y)\text{ V}$$

4. Higher the standard reduction potential ($E^{\circ}_{M^{n} \ /M}$), better is oxidising agent. Among the given, $E_{S_2O_8^{2} \ /SO_4^{2}}$ is highest, hence $S_2O_8^{2}$ is the strongest oxidising agent.

The decreasing order of oxidising agent among the given option is as follows:

$$S_2O_8^{2} \qquad Au^{3} \qquad O_2 \qquad Br_2$$

5. Reducing power of an element

$$\frac{1}{\text{Standard reduction potential}}$$

Here, $E_{M^{2} \ /M}$ values of the given metals are as,

Metals	Ni	Zn	Mg	Ca
E **(V)**	0.25	0.76	2.36	2.87

Thus, the correct $\overset{\text{Reducing power}}{\text{order of increasing}}$ reducing power of the given metal is,

$$Ni < Zn < Mg < Ca.$$

6. **Key Idea** This question is based upon Faraday's first law which states that "Mass of any substance deposited or liberated at any electrode is directly proportional to the quantity of electricity passed."

During charging:

$$Pb \quad SO_4^{2} \qquad PbSO_4 \quad 2e$$
$$1\text{ F} \quad 1\text{ g-equiv. of } PbSO_4$$
$$\frac{1}{2}\text{mol of } PbSO_4 \qquad \frac{303}{2}\text{g } PbSO_4$$
$$0.05\text{ F} \quad \frac{303}{2} \quad 0.05\text{ g of } PbSO_4$$
$$7.575\text{ g of } PbSO_4$$

7. Given that, i 100 amp. also, 27.66 g of diborane (B_2H_6)

Molecular mass of B_2H_6 10.8 2 6 27.6

$$\text{Number of moles of } B_2H_6 \text{ in } 27.66\text{ g} \quad \frac{\text{Given mass}}{\text{Molar mass}} \quad \frac{27.66}{27.6} \quad 1$$

Now consider the equation

$$B_2H_6 \quad 3O_2 \qquad B_2O_3 + 3H_2O$$

From the equation we can interpret that 3 moles of oxygen is required to burn 1 mole (i.e. 27.6 g) B_2H_6 completely.

Also consider the electrolysis reaction of water i.e.

$$H_2O \rightleftharpoons 2H \qquad O$$
$$2H \quad \underset{\text{Cathode}}{\overset{2e}{\qquad}} \quad 2H \qquad H_2$$
$$O \quad \underset{2e}{\overset{\text{Anode}}{\qquad}} \quad O \quad \underset{\text{atoms}}{\overset{\text{2 such}}{\qquad}} \quad O_2$$

From the above equation it can be easily interpreted that in electrolysis of water for the production of 1 mole of oxygen from 1 mole of H_2O at anode 4 moles electrons are required.

Likewise for the production of 3 moles of O_2 12(3 4) moles of electrons will be needed.

So, the total amount of charge required to produce 3 moles of oxygen will be 12 F or 12 96500

We know $\qquad Q \quad it$

So, $\qquad 12 \quad 96500 \quad 100 \quad t$ in seconds

or $\dfrac{12 \quad 96500}{100 \quad 3600}$ t in hours 3.2 hours

8. The substances which have lower reduction potentials are stronger reducing agents. Therefore, Cr ($E_{\text{Cr}^{3+}/\text{Cr}}$ 0.74 V) is the strongest reducing agent among all the other given options.

9. Oxidation at anode

$H_2(g) \quad 2H^+(aq) + 2e\,;\ E_{\text{SHE}}\ \ 0.00\ \text{V}$

Reduction at cathode

$M^{4+}(aq)\ \ 2e \quad M^{2+}(aq);\ E_{M^{4+}/M^{2+}}\ \ 0.151\ \text{V}$

Net: $M^4\ \ (aq)\ \ H_2(g) \quad M^2\ \ (aq)\ \ 2H^+(aq);$

$$K\ \ \frac{[M^{2+}]\,[H^+]^2}{[M^{4+}]\,p_{H_2}}(E_{\text{cell}}\ \ 0.151\ \text{V})\ \ \frac{[M^{2+}]}{[M^{4+}]}$$

$$E_{\text{cell}}\ \ E_{\text{cell}}\ \ \frac{0.059}{2}\log K$$

$$0.092\ \ 0.151\ \ \frac{0.059}{2}\log\frac{[M^2\ \ ]}{[M^4\ \ ]}$$

$$0.059\ \ \frac{0.059}{2}\log 10^x$$

$$\log 10^x\ \ 2$$

$$x\ \ 2$$

10. Given, $Q\ \ 2F$

Atomic mass of Cu 63.5u

Valency of the metal Z 2

We have, $CuSO_4 \quad Cu^2 \quad SO_4^2$

$$\underset{\text{1mol}}{Cu^2}\quad \underset{\substack{\text{2mol}\\ 2F}}{2\,e}\quad \underset{\text{1mol}=63.5\text{g}}{Cu}$$

Alternatively.

$$W\ \ ZQ\ \ \frac{E}{F}\ \ 2F\ \ 2E\ \ \frac{2\ \ 63.5}{2}\ \ 63.5$$

11. Higher the standard reduction potential, better is oxidising agent. Among the given $E_{MnO_4/Mn^{2+}}$ is highest, hence MnO_4 is the strongest oxidising agent.

12. 0.01 mol of H_2 0.02 g equivalent

Coulombs required 0.02 96500 1930 C

$$Q\ \ It\ \ 1930\ \text{C}$$

$$t\ \ \frac{1930}{10\ \ 10^{\ \ 3}}\ \ 19.3\ \ 10^4\ \text{s}$$

13. In electrolytic cell electrolysis occur at the cost of electricity :

At cathode : $M^{n+} \quad ne \quad M$

(electron gone in solution)

At anode : $X^n \quad X \quad ne$

(electron supplied to anode)

Therefore, electron is moving from cathode to anode *via* internal circuit.

14. MnO_4 cannot be used for oxidation of Fe^{2+} in HCl medium because the following reaction is spontaneous :

$MnO_4\ \ Cl \quad Mn^{2+}\ \ Cl_2;\quad E\ \ 1.51\ \ 1.40 = 0.11\ \text{V}$

In all other cases, the redox process between oxidising agent and medium (HCl or H_2SO_4) are non-spontaneous, would not interfere oxidation of Fe^{2+}.

15. One of the requirement for electrolyte used in salt-bridge is, both cation and anion must have comparable size so that they migrate towards electrodes of opposite polarity at comparable speeds.

16. Higher the value of reduction potential, stronger the oxidising agent.

∵ $E\ :Z\ \ Y\ \ X$

Y will oxidise X but not Z.

17. Lower the value of E , stronger the reducing agent.

Reducing power:

$Y\ (E\ \ 3.03\ \text{V})\ \ Z(E\ \ 1.18\ \text{V})\ \ X\ (E\ \ 0.52\ \text{V}).$

18. $Fe^{2+}\ \ 2e \quad Fe\,;\quad E\ \ 0.41\text{V}$

$Zn \quad Zn^{2+} + 2e\ ;E\ \ 0.76\text{V}$

$Fe^{2+}\ \ Zn \quad Zn^{2+} + Fe;\quad E\ \ 0.35\text{V}$

19. In a lead storage battery, sulphuric acid is consumed as :

$$Pb + PbO_2 + 2H_2SO_4 \quad 2PbSO_4 + 2H_2O$$

20. In a galvanic cell, oxidation occur in the left hand electrode chamber and reduction in right hand electrode chamber. In the following cell.

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

The cell reactions are :

$\frac{1}{2}H_2(g) \quad H^+ \quad e$ At anode

$AgCl(s) + e \quad Ag \quad Cl$ At cathode

Net : $\frac{1}{2}H_2(g)\quad AgCl(s)\quad H\quad Ag(s)\quad Cl$

21. One gram equivalent of an electrolyte required 1.0 mole of electronic charge for discharging.

22. In aqueous solution, only those ions who are less electropositive than hydrogen ($E\ \ > 0$) would be deposited.

Therefore, in the present case, only Ag, Hg and Cu would be deposited on passing electricity through aqueous solution of these ions, Mg will not be deposited.

Also, higher the value of E , easier will be their reduction, therefore, the sequence in which ions will be deposited on increasing voltage across the electrodes is :

Ag, Hg, Cu.

23. Faraday's law of electrolysis is related to equivalent weight of electrolytes as "the number of Faraday's passed is equal to the number of gram equivalent of electrolytes discharged."

24. Lower the value of E , stronger the reducing agent.

25. **PLAN** This problem is based on characteristics of salt-bridge.

Functions of salt-bridge are

(i) It connects the two half-cells and completes the cell circuit.

(ii) It keeps the solutions of two half-cells and complete the cell circuit but does not participate chemically in the cell reaction.

(iii) It maintains the diffusion of ions from one electrode to another electrode.

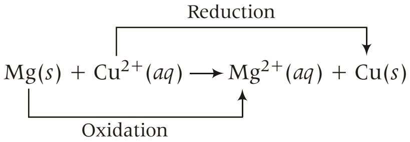
(iv) A cell reaction may also occur in the absence of salt-bridge. Sometimes, both the electrodes dip in the same electrolyte solution and in such cases we do not require a salt-bridge." So, option (c) is incorrect.

(v) This prevent mixing of two electrolytic solutions hence, option (d) is incorrect choice.

Hence, correct choices are (a), (b).

26. Metals with $E°$ value less than 0.96 V will be able to reduce NO_3 in aqueous solution.Therefore, metals V (E 1.19 V), Fe ($E°$ = – 0.04 V), Hg ($E°$ = 0.86 V) will all reduce NO_3 but Au ($E°$ = 1.40 V) cannot reduce NO_3 in aqueous solution.

27. (10) Equation of cell reaction according to the cell notation given, is



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

Given, $E_{cell} \quad 2.70\,V, T \quad 300\,K$

with $[Mg^{2+}(aq)] \quad 1\,M$ and $[Cu^{2+}(aq)] \quad 1\,M$

and $n \quad 2$

Further, $E_{cell} \quad 2.67\,V$

with $[Cu^{2+}(aq)] \quad 1M$

and $[Mg^{2+}(aq)] \quad xM$

and $\frac{F}{R} \quad 11500\,KV^{\quad 1}$

where F Faraday constant, R gas constant

From the formula,

$$E_{cell} \quad E_{cell} \quad \frac{RT}{nF}\ln\frac{[Mg^{2}\ (aq)]}{[Cu^{2+}(aq)]}$$

After putting the given values

$$2.67 \quad 2.70 \quad \frac{RT}{2F}\ln\frac{x}{1}$$

or $$2.67 \quad 2.70 \quad \frac{R \quad 300}{2F} \quad \ln x$$

$$0.03 \quad \frac{R \quad 300}{2F} \quad \ln x$$

or $$\ln x \quad \frac{0.03 \quad 2}{300} \quad \frac{F}{R}$$

$$\frac{0.03 \quad 2 \quad 11500}{300} \quad 2.30$$

So, $\ln x \quad 2.30$

or $x \quad 10$ (as given $\ln(10) \quad 2.30$)

28. Given,

$$A(s)|A^{n} \quad (aq, 2\,M) \,||\, B^{2n} \quad (aq, 1\,M) \,|\, B(s)$$

So, reactions at respective electrode will be

Anode $A(s) \qquad A^{n} \qquad ne \quad 2$

Cathode $B^{2n} \qquad 2ne \qquad B(s)$

Overall reaction

$$2A(s) \quad B^{2n} \ (aq) \qquad 2A^{n} \ (aq) \quad B(s)$$

Further,

$H \quad 2 \ G$ and $E_{cell} \quad 0$ is also given

Now by using the Nernst equation

$$E_{cell} \quad E_{cell} \quad \frac{RT}{nF}\ln\frac{[Product]}{[Reactant]}$$

After putting the values

$$0 \quad E_{cell} \quad \frac{RT}{2nF}\ln\frac{[A^{n}\ ]^2}{[B^{2n}\ ]}$$

or $$E \quad \frac{RT}{2nF}\ln\frac{[2]^2}{[1]} \quad \frac{RT}{2nF}\ln 4 \qquad \ldots(i)$$

Further from the formula,

$$G \quad nFE \qquad G \quad 2nFE$$

Now putting the value of E from eq. (i)

$$G \quad 2nF \quad \frac{RT}{2nF}\ln 4 \qquad \ldots(ii)$$

$$G \quad RT\ln 4$$

Finally, using the formula

$$G \quad H \quad T \ S$$

$$G \quad 2 \ G \quad T \ S \qquad (as \ H \quad 2 \ G, given)$$

$$G \quad T \ S$$

or $$S \quad \frac{G}{T} \quad \frac{RT\ln 4}{T}$$

(from eq. (ii), $G \quad RT\ln 4$)

$$R\ln 4 \quad 8.3 \quad 2 \quad 0.7$$

(as all values given)

$$11.62\,J/K\text{-}mol$$

29. Moles of NaCl electrolysed $4 \quad \frac{500}{1000} \quad 2.0$

moles of Cl_2 produced = 1.0

$$2Cl \qquad Cl_2 \quad 2e$$

30. **At cathode** $Na^{+} + e \quad \overset{Hg}{} \quad \underset{Amalgam}{Na(Hg)}$

Two moles of Na formed during electrolysis would produce two moles of Na(Hg) amalgam.

mass of amalgam 2 (23 200) 446 g

31. Two Faraday of electric charge would be required for electrolysis of 2.0 moles of NaCl.

total coulombs 2 96500 = 193000 C

32. Since, activities of all the ions are unity, $E_{cell} \quad E_{cell}$. Also, left hand electrode is at lower reduction potential, it act as anode and

$$E \quad E\ (Ce^{4+}, Ce^{3+}) \quad E\ (Fe^{3+}, Fe^{2+}) = 0.84$$

i.e. electrons will flow from left to right hand electrode and current from right hand electrode [Pt (2)] to left hand electrode [Pt(1)].

Also, $$E \quad E \quad 0.0592 \log\frac{[Fe^{3+}][Ce^{3+}]}{[Fe^{2+}][Ce^{4+}]}$$

As electrolysis proceeds, E will decrease and therefore, current.

33. The number of Faraday's passed $\frac{2 \quad 10^{\ 3} \quad 16 \quad 60}{96500}$

$$1.99 \quad 10^{\ 5}$$

number of gram equivalent of Cu^{2+} deposited

$$1.99 \quad 10^{\ 5}$$

number of moles of Cu^{2+} deposited $\frac{1.99}{2}\quad 10^{\ 5}\quad 10^{\ 5}$

Absorbance is directly proportional to $[Cu^{2+}]$. Therefore, if '*C*' be the initial molarity, 0.5 C will be the final molarity.

$0.5\ C\quad 0.25\quad 10^{\ 5}\qquad C\quad 8\quad 10^{\ 5}$ M

34. The number of Faraday's passed $\frac{9.65\quad 60\quad 60}{96500} = 0.36$ F

After electrolysis : $[Ag^{+}] = 1.36$ M

$[Cu^{2+}] = 1 - \frac{0.36}{2}\quad 0.82$ M

E_1 (before electrolysis) $\quad E$

E_2 (after electrolysis) $\quad E\quad \frac{0.0592}{2}\log\frac{[Ag^{+}]^2}{[Cu^{2+}]}$

$E_1\quad E_2\quad \frac{0.0592}{2}\log\frac{(1.36)^2}{0.82} = 0.01$ V (decreased)

35. Coulombs passed = 8.46 8 60 60 = 243648 C

Number of Faraday's passed $\frac{243648}{96500}\quad 2.52$

Weight of Cu plated $\quad 2.52\quad \frac{63.5}{2}$ g $\quad 80.01$ g

Volume of Cu plated $\quad \frac{80.01}{10.5}\quad 7.62\ cm^3$

Area plated out $\quad \frac{7.62}{0.00254}\quad 3000\ cm^2$

36. Given, $FeO\ (s)/Fe\ (s)\qquad E° = -0.87$ V

and $Ni_2O_3/NiO\ (s)\qquad E° = +0.40$ V

Electrode at lower reduction potential act as anode and that at higher reduction potential act as cathode.

(i) Electrodes reaction :

$Fe(s) + 2OH\qquad FeO\ (s) + H_2O\ (l)$

$E° = +0.87$ V

$Ni_2O_3\ (s) + H_2O\ (l) + 2e\qquad 2NiO\ (s) + 2OH\quad E° = 0.40$ V

Net : $Fe\ (s) + Ni_2O_3\ (s)\qquad 2NiO\ (s) + FeO\ (s)$

$E° = 1.27$ V

(ii) Emf is independent of concentration of KOH.

(iii) Maximum amount of energy that can be obtained $\quad G$

$G\qquad nE\ F = -2\quad 1.27\quad 96500$ J = – 245.11 kJ

i.e. 245.11 kJ is the maximum amount of obtainable energy.

37. (i) $E\quad 0.78 - 0.0592\log\frac{1}{8^2} = 0.887$ V

(ii) $E\quad 0.78 - 0.0592\log\frac{1}{(10^{\ 7})^2} = -0.0488$ V

38. Molar mass of Cr = 52 g

Equivalent mass of Cr $\quad \frac{52}{6}$ g

(i) Mass of Cr deposited on passing 24000 Coulombs

$\frac{24000}{96500}\quad \frac{52}{6}$ g $\quad 2.15$ g

(ii) Number of gram equivalent of Cr $\quad \frac{1.5}{52}\quad 6\quad \frac{9}{52}$

Coulombs required for 1.5 g Cr $\quad \frac{9}{52}\quad 96500\quad It$

$t\quad \frac{9\quad 96500}{52\quad 12.5}$ s $\quad 22.27$ min

39. At anode $\qquad 2Cl\qquad Cl_2\quad 2e$

At cathode $\quad 2H_2O + 2e\qquad H_2 + 2OH$

1 kg $Cl_2\quad \frac{1000}{35.5}$ equivalent of $Cl_2\quad$ 28.17 equivalent

Theoretical electricity requirement = 28.17 F

∵ Efficiency is only 62%

Electricity requirement (experimental)

$\frac{28.17\quad 100}{62}$ F = 45.44 F

45.44 96500 = 25 *t* (in second)

t = 48.72 h

Also, gram equivalent of HO produced = 28.17

Molarity of HO $\quad \frac{28.17}{20}\quad 1.4085$ M

40. $[Ag^{+}]$ in left hand electrode chamber $\quad \frac{2.8\quad 10^{\ 10}}{0.2}$

$1.4\quad 10^{\ 9}$ M

$[Ag^{+}]$ in right hand electrode chamber $\quad \frac{3.3\quad 10^{\ 13}}{0.001}$

$3.3\quad 10^{\ 10}$ M

$\text{emf} = 0 - 0.0592\log\frac{[Ag^{+}]_{\text{anode}}}{[Ag^{+}]_{\text{cathode}}}$

$= -0.0592\log\frac{1.4\quad 10^{\ 9}}{3.3\quad 10^{\ 10}} = -0.037$ V

Therefore, the cell as written is non-spontaneous and its reverse will be spontaneous with emf = 0.037 V.

41. Faraday's passed $\quad \frac{1.7\quad 230}{96500}\quad 4.052\quad 10^{\ 3}$ F

Faradays used for reduction of $Zn^{2+}\quad 4.052\quad 10^{\ 3}\quad 0.9$

$= 3.65\quad 10^{\ 3}$

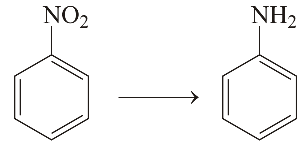
Meq. of Zn^{2+} reduced = 3.65

Initial meq. of $Zn^{2+}\quad 300\quad 0.16\quad 2\quad 96$

Meq. of Zn^{2+} remaining $\quad 96\quad 3.65\quad 92.35$

Molarity of $Zn^{2+}\quad \frac{92.35}{2}\quad \frac{1}{300}\quad 0.154$ M

42.



Change in oxidation number at nitrogen $\quad 4\quad (\ 2)\quad 6$

Equivalent weight of nitrobenzene $\quad \frac{123}{6}$ g gram equivalent of nitrobenzene $\frac{12.3 \quad 6}{123} = 0.60$

Theoretical requirement 0.60 96500 C = 57900 C

Actual requirement of electricity 2 57900 115800 C

∵ $V \quad C \quad J$

Energy consumed 115800 3 J 347.40 kJ

43. If the salt is $CuSO_4$

During deposition of Cu at cathode, $O_2(g)$ will evolve at anode

gram-equivalent of Cu deposited $\frac{0.4 \quad 2}{63.5} \quad 0.0126$

Volume of O_2 liberated at NTP at anode

= 0.0126 5600 mL = 70.56 mL

In the next 7 min, H_2 at cathode and O_2 at anode would be produced.

Faraday's passed $\frac{1.2 \quad 7 \quad 60}{96500} \quad 5.22 \quad 10^{\ 3}$

Volume of H_2 (at NTP) $5.22 \quad 10^{\ 3} \quad 11200$ mL

= 58.46 mL

Volume of O_2 (at NTP) $5.22 \quad 10^{\ 3} \quad 5600$ mL = 29.23 mL

Therefore, $O_2(g)$ at NTP 70.56 + 29.23 99.79 mL

$H_2(g)$ at NTP 58.46 mL

44. Total number of gram equivalent of H_2 used $\frac{67.2}{11.2} \quad 6$

$6 \quad 96500 \quad 15 \quad 60 \quad I \qquad I \quad 643.33$ A

Mass of Cu deposited $6 \quad \frac{63.5}{2}$ g 190.50 g

45. ∵ Emf = 0.118 V > 0, it is galvanic cell and anode is negative electrode :

At anode : $H_2(g) \qquad 2H^+(10^{\ 6}\,M) \quad 2e$

At cathode : $2H^+\ (x) + 2e \qquad H_2$

Cell reaction : $H^+(x) \qquad H^+\ (10^{\ 6}\,M)$

$\text{Emf} = 0.118\ V = 0 - 0.0592 \log \frac{10^{\ 6}}{x} \qquad x \quad 10^{\ 4}\ M$

46. 100 W lamp will produce 100 Js $^{\ 1}$.

$100\ J \quad 110 \quad C \qquad C \quad \frac{10}{11}$ Coulombs

Therefore, total Coulomb passed in 10 h

$\frac{10}{11} \quad 10 \quad 60 \quad 60 = 32727.27$ C

Number of gram equivalent of Cd^{2+} deposited

$\frac{32727.27}{96500} = 0.34$

Weight of Cd deposited = $0.34 \quad \frac{112.4}{2}$ g 19.1 g

47. For 1.0 L H_2SO_4 :

Initial mass of $H_2SO_4 = 1294 \quad \frac{39}{100} \quad 504.66$ g

Final mass of $H_2SO_4 = 1139 \quad \frac{20}{100} \quad 227.80$ g

H_2SO_4 consumed/litre 504.66 – 227.80 = 276.86 g

Total H_2SO_4 used up 276.86 3.5 = 969.01 g

$\frac{969.01}{98}$ mol = 9.888 mol

∵ 1 mole of H_2SO_4 is associated with transfer of 1.0 mole of electrons, total of 9.888 moles of electron transfer has occurred.

Coulomb produced = 9.888 96500

Ampere-hour $\frac{9.888 \quad 96500}{3600} \quad 265$ Ah

48. Volume of Ag coating $80\ cm^2 \quad \frac{0.005}{10}$ cm $0.04\ cm^3$

mass of Ag coating 0.04 10.5 g = 0.42 g

gram equivalent of Ag $\frac{0.42}{108}$ number of Faraday's

$\frac{0.42}{108} \quad 96500\ C = 3 \quad t \qquad t \quad 125\ s$

49. Moles of Au deposited $\frac{9.85}{197} \quad 0.05$

gram equivalent of Au deposited 0.05 3 = 0.15

Now, according to Faraday's law of electrolysis, if same quantity of electricity is passed through different cells connected in series, same number of gram equivalents of electrolytes are discharged at respective electrodes.

gram equivalent of Cu deposited = 0.15

amount of Cu deposited $0.15 \quad \frac{63.5}{2} \quad 4.7625$ g

Also, Coulombs passed $0.15 \quad 96500 \quad I \quad 5 \quad 60 \quad 60$

$I \quad \frac{0.15 \quad 96500}{5 \quad 3600} \quad 0.80$ A

50. During electrolysis, Ni^{2+} will be reduced at cathode and H_2O will be oxidised at anode.

Number of Faraday's passed $\frac{3.7 \quad 6 \quad 60 \quad 60}{96500} = 0.828$

0.828 g equivalent of Ni^{2+} will be deposited at cathode.

Initial moles of Ni^{2+} ion 2 0.5 = 1.0

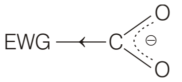
Moles of Ni^{2+} ion remaining after electrolysis = $1.0 - \frac{0.828}{2}$

= 0.586

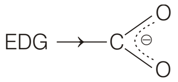
Molarity of Ni^{2+} in final solution $\frac{0.586}{0.50} \quad 1.172$ M

Topic 2 Conductivity of Electrolytic Solutions and their Measurement and Nernst Equation

1. Electrical conductivity of the given aqueous solutions depends on the degree of ionisation. Degree of ionisation is directly proportional to the acidic strength. Electron withdrawing groups (EWGs) increases the stability of the carboxylate ion by dispersing the negative charge through resonance effect on the conjugate while electron donating groups (EDGs) decreases the stability of the carboxylate ion by intensifying the negative charge.



Acidity of carboxylic acids increases due to the presence of electron withdrawing groups (EWGs)



Acidity of carboxylic acids decreases due to the presence of electron donating groups

The correct order of acidic strength and electrical conductivity is as follows:

$$\underset{A}{\text{HCOOH}} \quad \underset{C}{\text{PhCOOH}} \quad \underset{B}{\text{CH}_3\text{COOH}}$$

2. NaCl and KCl are strong electrolytes. So, the study of their molar conductances ($_{\text{m}}$) can be experimentally verified by Debye-Huckel Onsagar equation,

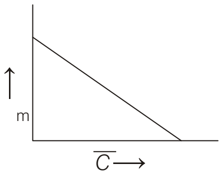
$$^{c}_{\text{m}} \quad ^{0}_{\text{m}} \quad B\sqrt{C}$$

$^{c}_{\text{m}}$ molar conductance at concentration.

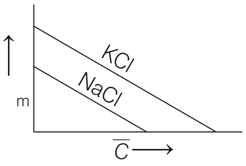
$^{0}_{\text{m}}$ molar conductance at infinite dilution. i.e. C 0

B Debye-Huckel Onsagar constant.

For (both NaCl and KCl) a strong binary electrolyte like AB, the nature of the plot of $_{\text{m}}$ vs $\sqrt{C}$ will be



Size of Na is being smaller than K and Na will remain in more hydrated state, i.e. larger sized in aqueous solution. As a result, ionic mobility as well as ionic conductance of Na (or NaCl as Cl$^{\ominus}$ is common to NaCl and KCl) will be lower than K (or KCl). Thus, the plot of $_{\text{m}}$ vs $\sqrt{C}$ for NaCl and KCl is as follows :



3. The explanation of statements (S_1 and S_2) are as follows :

In conductivity cell, conductivity ( ) is equal to the sum of ionic conductances (c), of an electrolytic solution present is unit volume of the solution enclosed by two electrodes of unit area (a 1) separated by a unit length (l 1).

$$c \ \frac{l}{a} \qquad c \text{when } l \ \ 1, a \ \ 1$$

So, with decrease in the concentration of electrolyte, number of ions in the given unit volume also decreases, i.e. [conductivity] also decreases.

Thus, statement S_1 is wrong. S_2 : Molar conductivity ($_m$) is defined as the conducting power of all the ions present in a solution containing 1 mole of an electrolyte.

$$_m \qquad V_{\text{mL}} \qquad \frac{1000}{M}$$

where, V_{mL} volume in mL containing 1 mole of electrolyte

m molar concentration (mol/L)

So, in a conductivity cell

$$_m \quad \frac{1}{M}$$

i.e. molar conductivity increases with decrease in the concentration (M) of electrolyte.

Thus, statement S_2 is correct.

4. **Key Idea** Gibbs energy of the reaction is related to E $_{\text{cell}}$ by the following formula

$G^o \quad nFE$ $_{\text{cell}}$

G^{o} Gibbs energy of cell

nF amount of charge passed

E EMF of a cell

Given reaction is,

$$\text{Zn} \quad \text{Cu}^2 \qquad \text{Zn}^2 \quad \text{Cu}$$

$E^{\text{o}}_{\text{cell}}$ 2.0 V

F 96000 C

n 2

To find the value of G^{o} (kJ mol), we use the formula

$$G^{\text{o}} \quad nFE^{\text{o}}_{\text{cell}}$$

$$G^{\text{o}} \quad 2 \quad 96000 \quad 2 \qquad 384000 \text{ J/mol}$$

In terms of kJ/mol, G^{o} $\dfrac{384000}{1000}$ 384 kJ/mol

5. According to Kohlrausch's law, the molar conductivity of HA at infinite dilution is given as,

$$_{\text{m}}(\text{H}A) \quad [\ _{\text{m}}(\text{H}\ ) \quad _{\text{m}}(\text{Cl}\ )] \quad [\ _m(\text{Na}\ ) \quad _m(A\ )] \quad [\ _{\text{m}}(\text{Na}\ ) \quad _{\text{m}}(\text{Cl}\ )]$$

$$425.9 \quad 100.5 \quad 126.4 \quad 400 \text{ S cm}^2 \text{ mol}^{\ 1}$$

Also, molar conductivity at given concentration is given as,

$$_{\text{m}} \quad \frac{1000}{M}$$

Given, conductivity 5 10 ^{5} S cm ^{1}

M Molarity 0.001 M

$$_{\text{m}} \quad \frac{1000 \quad 5 \quad 10^{\ 5}\text{S cm}^{\ 1}}{10^{\ 3}\text{ M}} \quad 50 \text{ S cm}^2 \text{ mol}^{\ 1}$$

Therefore, degree of dissociation (, of HA is,

$$\frac{_{\text{m}}}{_{\text{m}}} \quad \frac{50 \text{S cm}^2 \text{mol}^{\ 1}}{400 \text{ S cm}^2 \text{mol}^{\ 1}} \quad 0.125$$

6. According to Nernst equation,

$$E_{\text{cell}} \quad E_{\text{ cell}} \quad \frac{2.303\ RT}{nF} \log Q$$

Given, $\dfrac{2.303\ RT}{F}$ 0.059 V

$$E_{\text{cell}} \quad E_{\text{ cell}} \quad \frac{0.059}{n} \log Q$$

At equilibrium, E_{cell} 0

$$E_{\text{ cell}} \quad \frac{0.059}{n} \log K_C$$

For the given reaction, n 2

Also, K_C 10 10^{15} [given]

$$E_{\text{ cell}} \quad \frac{0.059}{2} \log (10 \quad 10^{15}) \quad 0.472\text{V} \quad 0.473\text{V}$$

7.

Cell Anode (A) Cathode (C)	E_{cell} (SRP) E_C E_A	E_{cell} free $\bar{e}$ transfer
Zn Ag 1. $[\text{Zn} + 2\text{Ag}^{+} \quad \text{Zn}^{2+} \quad 2\text{Ag}]$	0.80 (0.76) 1.56 V for 2*e*	$\frac{1.56}{2}$ 0.78 V
Zn Fe 2. $[\text{Zn} \quad \text{Fe}^{2} \quad \text{Zn}^{2+} \quad \text{Fe}]$	0.44 (0.76) 0.32 V for 2*e*	$\frac{0.32}{2}$ 0.16 V
Zn Au 3. $[3\text{Zn} \quad 2\text{Au}^{3} \quad 3\text{Zn}^{2} \quad 2\text{Au}]$	1.40 (0.76) 2.4 V for 6*e*	$\frac{2.16}{6}$ 0.36 V
Zn Fe 4. $[3\text{Zn} \quad 2\text{Fe}^{3} \quad \text{Zn}^{2} \quad 2\text{Fe}^{2+}]$	0.77 (0.76) 1.53 V for 2*e*	$\frac{1.53}{2}$ 0.765 V

8. It is an electrochemical cell. The overall cell reaction can be written, as

$$\underset{(1\ \text{bar})}{\text{H}_2(g)} \quad 2\text{AgCl}(s) \qquad \underset{(10\ ^{6}\ \text{M})}{2\text{HCl}(aq)} \quad 2\text{Ag(s)}$$

(i) According to Nernst equation,

$$E_{\text{cell}} \quad (E_{\text{cathode}} \quad E_{\text{anode}}) \quad \frac{2.303 \quad RT}{n \quad F} \log \frac{[\text{HCl}]^2[\text{Ag}]^2}{p_{\text{H}_2}[\text{AgCl}]^2}$$

Here, (i) $E_{\text{c}} \quad E_{\text{AgCl/Ag, Cl}} \qquad E_{\text{cathode}}$

(ii) $E_{\text{anode}} \quad E_{\text{2H} \ /\text{H}_2} \quad 0.00\ \text{V}$

(Standard hydrogen electrode)

$$0.92 \quad (E_{\text{c}} \quad 0) \quad 0.06 \quad \log \frac{(10\ ^{6})^2 \quad 1^2}{1 \quad 1^2}$$

$$E_{\text{c}} \quad 0.06 \quad 6 \quad 2$$

$$E_{\text{c}} \quad 0.92 \quad 0.72 \quad 0.20\ \text{V}$$

Note 10 ^{6} molal HCl is a very dilute solution.
So, 10 ^{6} m ~ 10 ^{6} M

9. The relationship between standard electrode potential (E) and equilibrium constant (K) of the cell reaction,

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

can be expressed as,

$$E \quad \frac{RT}{nF} \ln K \qquad K \quad e^{nFE\ /RT}$$

Given, $n \quad 2, F \quad 96000\,\text{C mol}^{\ 1}$

$E \quad 2\,\text{V}, R \quad 8\,\text{JK}^{\ 1}\text{mol}^{\ 1}$

$T \quad 300\,\text{K}$

$$K \quad e^{\frac{2 \quad 96000 \quad 2}{8 \quad 300}} \qquad e^{160}$$

10. The redox reaction is : Zn(s) + Cu^{2+} Zn^{2+} + Cu

The Nernst equation is $E \quad E \quad \frac{2.303RT}{2F} \log 10$

$$1.1 \quad \frac{2.303RT}{2F}$$

Also, $G \quad nEF \quad 2F \ 1.1 \quad \frac{2.303RT}{2F}$

$$2.2F \quad 2.303RT$$

$$2.303RT \quad 2.2F$$

11. Zinc metal is the most stable metal to cover iron surfaces. The process of coating the iron surface by zinc is called galvanisation.

12. Standard electrode potential of reaction $[E \quad]$ can be calculated as

$$E^{\circ}_{\text{cell}} \quad E_R \quad E_P$$

where, E_R SRP of reactant , E_P = SRP of product

If E°_{cell} +ve, then reaction is spontaneous otherwise non-spontaneous.

$$\text{Mn}^{3} \quad \xrightarrow{E_1 = 1.51\ \text{V}} \quad \text{Mn}^{2}$$

$$\text{Mn}^{2} \quad \xrightarrow{E_2 = \quad 1.18\ \text{V}} \quad \text{Mn}$$

For Mn^{2} disproportionation,

$$E \qquad 1.51\ \text{V} \quad 1.18\ \text{V} \qquad 2.69\ \text{V} \quad 0$$

Thus, all reaction will not occur.

13. According to Debye Huckel Onsager equation,

$$_C \qquad B\sqrt{C}$$

where, $_C$ limiting equivalent conductivity at concentration C
limiting equivalent conductivity at infinite dilution
C concentration

14. In order to solve the problem, calculate the value of cell constant of the first solution and then use this value of cell constant to calculate the value of k of second solution. Afterwards, finally calculate molar conductivity using value of k and m.

For first solution,

$$k \quad 1.4\ \text{Sm}^{\ 1}, \ R \quad 50 \quad , \ M \quad 0.2$$

Specific conductance ( ) $\frac{1}{R} \quad \frac{l}{A}$

$$1.4\ \text{Sm}^{\ 1} \quad \frac{1}{50} \quad \frac{l}{A}$$

$$\frac{l}{A} \quad 50 \quad 1.4\ \text{m}^{\ 1}$$

For second solution, $R \quad 280, \frac{l}{A} \quad 50 \quad 1.4\text{ m}^{1}$

$$\frac{1}{280} \quad 1.4 \quad 50 \quad \frac{1}{4}$$

Now, molar conductivity

$$_{\text{m}} \quad \frac{}{1000 \quad m} \quad \frac{1/4}{1000 \quad 0.5} \quad \frac{1}{2000}$$

$$5 \quad 10^{4}\text{ S m}^{2}\text{ mol}^{1}$$

15. **PLAN** When different number of electrons are involved in a redox reaction

$$G_{\text{net}} \quad G_{1} \quad G_{2}$$

$$n_3FE_{3} \quad n_1FE_{1} \quad n_2FE_{2}$$

$$E_{3} \quad \frac{n_1E_{1} \quad n_2E_{2}}{n_3}$$

(P) $E_3\ \text{Fe}^{3}\ /\text{Fe}$

Net reaction $\text{Fe}^{3} \qquad \text{Fe}$

is obtained from

$$\begin{array}{lll} & \underline{n} & \underline{E} \\ \text{Fe}^{3} \quad e \quad \text{Fe}^{2} & n_1 \quad 1 & E_1^{d} \quad 0.77\text{ V} \\ \text{Fe}^{2} \quad 2e \quad \text{Fe} & n_2 \quad 2 & E_2 \quad 0.44\text{ V} \\ \hline \because\ \text{Fe}^{3} \quad 3e \quad \text{Fe} & n_3 \quad 3 & E_3 \quad ? \end{array}$$

$$E_{3} \quad \frac{n_1E_{1} \quad n_2E_{2}}{n_3} \quad \frac{0.77 \quad 2(\ 0.44)}{3} \quad \frac{0.11}{3} \quad 0.04\text{ V}$$

Thus, P — (3)

Net reaction

$$4\text{H}_2\text{O} \rightleftharpoons 4\text{H} \quad 4\text{OH}$$

is obtained from

$$\begin{array}{lll} & \underline{n} & \underline{E} \\ 2\text{H}_2\text{O} \quad \text{O}_2 \quad 4\text{H} \quad 4e & n_1 \quad 4 & 1.23\text{ V} \\ 2\text{H}_2\text{O} \quad \text{O}_2 \quad 4e \quad 4\text{OH} & n_2 \quad 4 & 0.40\text{ V} \\ \hline 4\text{H}_2\text{O} \quad 4\text{H} \quad 4e & n_3 \quad 4 & ? \end{array}$$

$$E_{3} \quad \frac{n_1E_{1} \quad n_2E_{2}}{n_3} \quad E_{1} \quad E_{2}$$

$$1.23 \quad 0.40 \quad 0.83\text{ V}$$

Thus, Q — (4)

(R) $\text{Cu}^{2} \quad \text{Cu} \quad 2\text{Cu}$

For thus E of $\text{Cu}^{2} \qquad \text{Cu}$

is also required.

$$\begin{array}{lll} & \underline{n} & \underline{E} \\ \text{Cu}^{2} \quad 2e \quad \text{Cu} & 2 & 0.34\text{ V} \\ \text{Cu} \quad \text{Cu} \quad e & 1 & 0.52\text{ V} \\ \hline \text{Cu}^{2} \quad e \quad \text{Cu} & E_{3} & ? \end{array}$$

$$E_3 \quad \frac{n_1E_1 \quad n_2E_2}{n_3} \quad \frac{2 \quad 0.34 \quad 1 \quad (\ 0.52)}{1} \quad 0.16\text{ V}$$

Also,

$$\begin{array}{lll} & \underline{n} & \underline{E} \\ \text{Cu} \quad \text{Cu} \quad e & n_1 \quad 1, & 0.52\text{ V} \\ \text{Cu}^{2} \quad e \quad \text{Cu} & n_2 \quad 1 & 0.10\text{ V} \\ \hline \text{Cu}^{2} \quad \text{Cu} \quad 2\text{Cu} & & \end{array}$$

$$E \quad 0.52 \quad 0.16 \quad 0.36\text{ V}$$

Thus, (R) — (1)

(S) $\text{Cr}^{3} \qquad \text{Cr}^{2}$

is obtained from

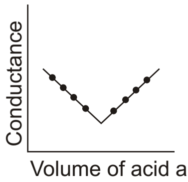
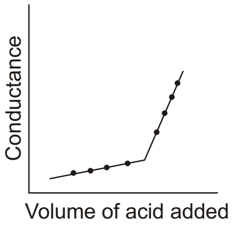
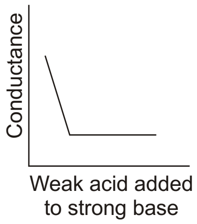
$$\begin{array}{lll} & \underline{n} & \underline{E} \\ \text{Cr}^{3} \quad 3e \quad \text{Cr} & 3 & 0.74\text{ V} \\ \text{Cr} \quad \text{Cr}^{2} \quad 2e & 2 & 0.91\text{ V} \\ \hline \text{Cr}^{3} \quad e \quad \text{Cr}^{2} & 1 & ? \end{array}$$

$$E_3 \quad \frac{0.74 \quad 3 \quad 2 \quad 0.91}{1} \quad 0.4\text{ V}$$

Thus, $S \quad (2)$

P — (3), Q — (4), R — (1), S — (2)

16. The variation is conductivities in general can be seen as :

	In burette acid	**In flask base**	**Curve**
I.	Strong (HI)	Strong (NaOH)	Conductance first decreases due to formation of H_2O and then increases due to addition of strong electrolyte. 
II.	Strong (CH_3COOH)	Weak (KOH)	Conductance increases slightly as NH_4 (salt) is hydrolysed forming HCl. After neutral point, it acid increases rapidly due to addition of strong 
III.	Weak (CH_3COOH)	Strong (KOH)	Conductivity decreases due to neutralisation of conducting strong base and then remains constant due to addition of weak acid. 

	In burette acid	In flask base	Curve
IV.	Weak $[(C_2H_5)_3N]$	Weak (CH_3COOH)	Conductivity increases due to formation of ions and then remains constant due to addition of weak base.
V.	K*X*	$AgNO_3$	Insoluble salt Ag*X* is formed, hence conductance remains constant. It increases due to addition of K*X*.

17. The half reactions are $Fe(s) \quad Fe^{2+}(aq) + 2e^{-} \quad 2$

$$O_2(g) + 4H^+ + 4e^- \quad 2H_2O$$

$$2Fe(s) + O_2(g) + 4H^+ \quad 2Fe^{2+}(aq) + 2H_2O(l);$$

$$E = E^o - \frac{0.059}{4}\log\frac{(10^{-3})^2}{(10^{-3})^4(0.1)} \quad 1.57V$$

18. As $AgNO_3$ is added to solution, KCl will be displaced according to following reaction.

$$AgNO_3(aq) + KCl(aq) \quad AgCl(s) + KNO_3(aq)$$

For every mole of KCl displaced from solution, one mole of KNO_3 comes in solution resulting in almost constant conductivity. As the end point is reached, added $AgNO_3$ remain in solution increasing ionic concentration, hence conductivity increases.

19. The net reaction is

$$2H^+ + \frac{1}{2}O_2 + Fe \quad H_2O + Fe^{2+};\ E \quad 1.67\ V$$

$$G \quad nE\ F \quad \frac{2 \quad 1.67 \quad 96500}{1000}\ kJ \quad -322.31\ kJ$$

20. The cell reaction is :

$$Zn + Fe^{2+} \rightleftharpoons Zn^{2+} \quad Fe;\ E_{cell} \quad 0.2905\ V$$

$$E \quad E \quad \frac{0.059}{2}\log\frac{[Zn^{2+}]}{[Fe^{2+}]}$$

$$E \quad 0.2905 + \frac{0.059}{2}\log\frac{0.1}{0.01} \quad 0.32\ V$$

Also $E \quad \dfrac{0.059}{n}\log K$

$$\log K \quad \frac{2E}{0.059} \quad \frac{0.32}{0.0295}$$

$$K \quad (10)^{0.32/0.0295}$$

21. In LiCl, NaCl and KCl, anions are same.

Cations have same charge but different size. Smaller cations are more heavily hydrated in aqueous solution giving larger hydrated radius and thus smaller ionic speeds and equivalent conductance.

Equivalent conductance : KCl > NaCl > LiCl

22. The spontaneous cell reaction is

$$X \quad M \quad M \quad X;\ E \quad 0.11V$$

23. E is an intensive property :

$$E \quad G \quad nE\ F$$

(i) $Cu^{2+} \quad 2e \quad Cu \quad 0.337\ V \quad -0.674\ F$

(ii) $Cu^{2+} \quad e \quad Cu^+ \quad 0.153\ V \quad -0.153\ F$

Subtracting (ii) from (i) gives :

$$Cu^+ \quad e \quad Cu \quad G \quad 0.521\,F = \quad nE \quad F$$

$$E \quad 0.521\ V$$

$\because \quad n \quad 1$

24. Given

(i) $2Cu(s) + \frac{1}{2}O_2(g) \quad Cu_2O(s);\quad G^o = \quad 78000\ J\,mol^{\ 1}$

$$= 78\ kJ\ mol^{\ 1}$$

(ii) $H_2(g) \quad \frac{1}{2}O_2(g) \quad H_2O(g);\quad G^o = \quad 178000\ J\ mol^{\ 1}$

$$= 178\ kJ\ mol^{\ 1}$$

So, net reaction is (By (i)-(ii))

$$2Cu(s) + H_2O(g) \quad Cu_2O(s) + H_2(g);$$

$$G = 100000\ J/mol\ or\ 10^5 J/mol = 100\ kJ\ mol^{\ 1}$$

Now , for the above reaction

$$G \quad G^o + RT\ \ln\frac{p_{H_2}}{p_{H_2O}}$$

and to prevent above reaction,

$$G \quad 0$$

So,

$$G^o \quad RT\ln\frac{p_{H_2}}{p_{H_2O}} \quad 0$$

After putting the values,

$$10^5 \quad 8 \quad 1250\ \ln\frac{p_{H_2}}{p_{H_2O}} \quad 0$$

or $$10^5 \quad 10^4\ \ln\frac{p_{H_2}}{p_{H_2O}} \quad 0$$

or $$10^4(\ln p_{H_2} \quad \ln p_{H_2O}) \quad 10^5$$

or $$\ln p_{H_2} \quad 10 \quad \ln p_{H_2O}$$

or $\ln p_{H_2} \quad 10 \quad 2.3\log(0.01)\ (as\ p_{H_2O} \quad 1\%)$

$$10 \quad 4.6$$

so $$\ln p_{H_2} \quad 14.6$$

25. For the given concentration cell, the cell reaction are $M \quad M^2$ at left hand electrode.

$$M^2 \quad M \text{ at right hand electrode}$$

$$M^2\ \text{(RHS electrode)} \quad M^2\ \text{(LHS electrode)}$$

$$E \quad 0$$

Applying Nernst equation

$$E_{cell} \quad 0.059 \quad 0 \quad \frac{0.059}{2}\log\frac{[M^2\ ]\text{ at LHS electrode}}{0.001}$$

$$\log\frac{[M^2\ ]\text{ at LHS electrode}}{0.001} \quad 2$$

$$[M^2\ ]\text{ at LHS electrode} \quad 10^{\ 2} \quad 0.001 \quad 10^{\ 5}\ M$$

The solubility equilibrium for MX_2 is

$$MX_2(s) \rightleftharpoons M^{2}\ (aq) \quad 2X\ (aq)$$

Solubility product, $K_{sp} \quad][M^{2}\ ][X\ ]^2$

$$10^{\ 5} \quad (2 \quad 10^{\ 5})^2 \quad 4 \quad 10^{\ 15}$$

[∵ In saturated solution of $MX_2, [X\ ] \quad 2[M^{2}\ ]]$

26. $G \qquad nEF \qquad \dfrac{2 \quad 0.059 \quad 96500}{1000}\ \text{kJ} \qquad 11.4\ \text{kJ}$

27. $M(s) \quad M\ (aq, 1\,\text{M}) \qquad M\ (aq, 0.05\,\text{M}) \quad M(s)$

$$E_{\text{cell}} \quad 0 \quad \frac{2.303\ RT}{F} \log \frac{0.05}{1} \quad 0$$

Hence, $|E_{\text{cell}}| \quad E_{\text{cell}} \quad 0.70$ V and $G \quad 0$ for spontaneity of reaction.

28. $E_{\text{cell}} \quad E \quad \dfrac{0.0538}{1} \log 0.0025 \quad 0.139\ \text{V} \quad 140\ \text{mV}$

29. For spontaneous redox reaction : $E_{\text{cell}} \quad 0$

For $\qquad 2\text{I} \ + \text{Cl}_2 \qquad 2\text{Cl} \ + \text{I}_2$

$$E \quad 1.36 - 0.54 = 0.82\ \text{V} > 0$$

i.e. Cl_2 will spontaneously oxidise I .

In other cases $E_{\text{cell}} \quad 0$, they are non-spontaneous.

30. For the reaction :

(i) $4\text{Fe}^{3+} + 2\text{H}_2\text{O} \qquad 4\text{Fe}^{2+} + 4\text{H}^+ + \text{O}_2; E \qquad 0.46\ \text{V}$

(ii) $4\text{Mn}^{3+} + 2\text{H}_2\text{O} \qquad 4\text{Mn}^{2+} + 4\text{H}^+ + \text{O}_2; E \qquad 0.27\ \text{V}$

As evidenced above, reaction (i) is non-spontaneous, therefore, Fe^{3+} is stable in acid solution. However, reaction (ii) is spontaneous Mn^{3+} oxidises H_2O to O_2 and itself reduced to Mn^{2+} in acidic medium.

31. Sodium fusion extract from aniline produces NaCN which reacts with Fe^{2+} to form $[\text{Fe(CN)}_6]^4$. The complex ion then reacts with Fe^{3+} to give blue precipitate of prussian blue.

$$\text{Fe}^{3+} + [\text{Fe(CN)}_6]^4 \quad \rightleftharpoons \quad \underset{\text{Prussian blue}}{\text{Fe}_4[\text{Fe(CN)}_6]_3}$$

32. $E°$ for $2\text{Ag}^+ + \text{C}_6\text{H}_{12}\text{O}_6 + \text{H}_2\text{O} \rightleftharpoons 2\text{Ag}(s) + \text{C}_6\text{H}_{12}\text{O}_7 + 2\text{H}^+$ is 0.75 V

Also $E \quad \dfrac{0.0592}{2} \log K \qquad \log K \quad \dfrac{2E}{0.0592} \quad 25.33$

$$\ln K \quad 2.303 \log K \quad 58.35$$

33. On increasing concentration of NH_3, the concentration of H^+ ion decreases, therefore,

$$E_{\text{red}} \quad E_{\text{red}} \quad \frac{0.0592}{2} \log [\text{H}\ ]^2 \quad 0 \quad \frac{0.0592}{2} \quad 2 \log 10^{\ 11}$$

$$0.65\ \text{V}$$

i.e. E_{red} increases by 0.65 V.

34. NH_3 has no effect on the $E°$ of glucose/gluconic acid electrode.

35. The solubility of AgBr in $10^{\ 7}$ M AgNO_3 solution is determined as

$$\text{AgBr} \rightleftharpoons \underset{S + 10^{\ 7}}{\text{Ag}^+} + \underset{S}{\text{Br}}$$

$$\text{AgNO}_3 \qquad \underset{S + 10^{\ 7}}{\text{Ag}^+} + \underset{10^{\ 7}}{\text{NO}_3}$$

$$K_{sp} \quad 14 \quad 10^{\ 14} \quad S\,(S \quad 10^{\ 7})$$

Solving for S gives : $S \quad 3 \quad 10^{\ 7}$ M

$[\text{Br}\ ] \quad 3 \quad 10^{\ 7}\,\text{M},$

$[\text{Ag}^+] = 4 \quad 10^{\ 7}\,\text{M},$

$[\text{NO}_3] \quad 10^{\ 7}\ \text{M}$

(sp. conductance)

$$[8 \quad 10^{\ 3} \quad 3 \quad \overset{\text{Br}}{10}^{\ 7} \quad \overset{\text{Ag}}{6} \quad 10^{\ 3} \quad \overset{\text{NO}_3}{4} \quad 10^{\ 7}$$

$$7 \quad 10^{\ 3} \quad 10^{\ 7}]1000$$

$$24 \quad 10^{\ 7} \quad 24 \quad 10^{\ 7} \quad 7 \quad 10^{\ 7}$$

$$55 \quad 10^{\ 7}\,\text{S m}^{\ 1}$$

$$55\ (\text{in terms of } 10^{\ 7}\ \text{S m}^{\ 1})$$

36. (a) $G \qquad G_f$ (products) $\qquad G_f$ (reactants)

$$= -109 - (-129 + 77)\ \text{kJ} = -57\ \text{kJ}$$

Cell : $\qquad \text{Ag} \mid \text{AgCl, Cl} \ \parallel \text{Ag}^+ \mid \text{Ag}$

For K_{sp}; reaction is AgCl $(s) \rightleftharpoons \text{Ag}^+ + \text{Cl}$

$$G \quad 57\,\text{kJ}$$

$$G \quad RT \ln K_{sp}$$

$$\log K_{sp} \quad \frac{G}{2.3\,RT} \quad \frac{57 \quad 1000}{2.3 \quad 8.314 \quad 298} \qquad 10$$

Now, $\qquad E°$ of $\text{Ag}^+ + \text{Cl} \ \rightleftharpoons \text{AgCl}$

$$E \quad \frac{G}{nF} \quad \frac{57000}{96500} \quad 0.59\ \text{V}$$

(b) The cell reaction is :

$$\text{Zn} + 2\text{Ag}^+ \rightleftharpoons \text{Zn}^{2+} + 2\text{Ag}; E° = 1.56\ \text{V}$$

$$0 \quad E \quad \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2}$$

$$\log \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2} \quad \frac{2E}{0.059} \quad \frac{2 \quad 1.56}{0.059} \quad 52.88$$

Moles of Zn added $\quad \dfrac{6.539 \quad 10^{\ 2}}{65.39} \quad 10^{\ 3}$

Moles of Ag formed $\quad 2 \quad 10^{\ 3}$.

37. Given,

$\text{In}^{2+} + e \qquad \text{In}^+ \quad E° = -0.40 \qquad$ …(i)

$G \quad 0.40\ \text{F}$

$\text{In}^{3+} + 2e \qquad \text{In}^+ \quad E° = -0.42 \qquad$ …(ii)

$G \quad 0.84\ \text{F}$

Subtracting (i) from (ii)

$\text{In}^{3+} + e \qquad \text{In}^{2+}; \qquad G \quad 0.44\ \text{F} = -E\ F$

$$E \quad 0.44\ \text{V}$$

Now, for : $\quad \text{Cu}^{2+} + \text{In}^{2+} \qquad \text{Cu}^+ + \text{In}^{3+}$

$$E \quad E\ (\text{Cu}^{2+}/\text{Cu}^+) \quad E\ (\text{In}^{3+}/\text{In}^{2+})$$

$$0.15 - (-0.44) = 0.59\ \text{V}$$

Also $\qquad E° \quad 0.0590 \log K$

$$\log K \quad \frac{E}{0.059} \quad 10 \qquad K \quad 10^{10}$$

38. (a) pH = – log $[H^+]$

In pure water, $[H^+]$ depends on value of K_w which is

$$K_w \quad [H^+][OH \ ]$$

∵ K_w is a function of temperature, $[H^+]$ will change with temperature.

(b) Let the emf of first cell be X volt.

emf of 2nd cell $(X \quad 0.03)$ volt

$[Cu^{2+}]$ in 2nd cell = 0.50 M

$[Cu^{2+}]$ in 1st cell = ?

$$E_1 \quad E_1 \quad \frac{2.303RT}{2F}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$E_2 \quad E_1 \quad \frac{2.303RT}{2F}\log\frac{[Zn^{2+}]}{[Cu^{2+}]_2}$$

$$E_2 \quad E_1 \quad \frac{2.303RT}{2F} \quad \log\frac{[Cu^{2+}]_2}{[Cu^{2+}]_1}$$

$$0.03 = 0.03\log\frac{0.50}{[Cu^{2+}]_1}$$

$$\frac{0.50}{[Cu^{2+}]_1} \quad 10 \qquad [Cu^{2+}]_1 \quad 0.05\text{ M}$$

39. **At anode** $\frac{1}{2}H_2 \qquad H^+ \quad e \ ; E° = 0$

At cathode AgCl (s) + e Ag + Cl ; $E°$ = ?

(i) Cell reaction : $\frac{1}{2}H_2 \quad AgCl\ (s) \qquad Ag + H^+ + Cl$

(ii) $G \quad nE\ F \quad H \quad T\ S$

At 15°C : $-0.23 \quad 96500 \quad H \quad 288 \quad S$ …(i)

At 35°C : $-0.21 \quad 96500 \quad H \quad 308 \quad S$ …(ii)

$$96500\ (0.23 \quad 0.21) \quad 20 \quad S$$

$$S \quad \frac{96500 \quad 0.02}{20} \quad 96.5\text{ J}$$

Substituting value of S in (i)

$$H \quad 288 \quad (\ 96.5) \quad 0.23 \quad 96500 \quad -49.987\text{ kJ}$$

(iii) At 25°C

$$E \quad 96500 \quad 49987 \quad 298\ (\ 96.5)$$

$$E \quad 0.22\text{ V}$$

AgCl (s) + e Ag + Cl ; $E°$ = 0.22 V

Ag $Ag^+ + e$; $E°$ = – 0.80 V

Adding : AgCl (s) Ag^+ + Cl ; $E°$ = – 0.58 V

$$E \quad 0.0592\log K_{sp}$$

$$\log K_{sp} \quad \frac{0.58}{0.0592} \quad 9.79$$

$$K_{sp} \quad 1.6 \quad 10^{\ 10}$$

40. $$E \quad 0 \quad \frac{0.0592}{1}\log\frac{[Ag^+]_{anode}}{[Ag^+]_{cathode}}$$

$$0.164 \quad 0.0592\log\frac{[Ag^+]_{anode}}{0.10}$$

$$[Ag^+]_{anode} \quad 1.7 \quad 10^{\ 4}\text{ M}$$

In saturated Ag_2CrO_4 solution present in anode chamber :

$$Ag_2CrO_4\ (s) \rightleftharpoons 2Ag \quad + \quad CrO_4^2$$

$$1.7 \quad 10^{\ 4}\text{ M} \qquad \frac{1.7}{2} \quad 10^{\ 4}\text{M}$$

$$K_{sp} \quad [Ag^+]^2\,[CrO_4^2\ ]$$

$$(1.7 \quad 10^{\ 4})^2 \ \frac{1.7}{2} \quad 10^{\ 4}$$

$$2.45 \quad 10^{\ 12}$$

41. For $2\,Fe^{3+} \quad 3I \rightleftharpoons 2Fe^{2+} \quad I_3$

$$E \quad E\ (Fe^{3+}/Fe^{2+}) \quad E\ (I_3/I\ )$$

$$0.77 - 0.54 = 0.23\text{ V}$$

∵ $$E \quad \frac{0.0592}{2}\log K \qquad (n \quad 2)$$

$$\log K \quad \frac{2E}{0.0592} \quad \frac{2 \quad 0.23}{0.0592} = 7.77$$

$$K \quad 5.89 \quad 10^7$$

42. $$Fe^{2+} + Ce^{4+} \rightleftharpoons Fe^{3+} + Ce^{3+}$$

$$E° \quad E°\,(Ce^{4+}/Ce^{3+}) - E\ (Fe^{3+}/Fe^{2+})$$

$$1.44 - 0.68 = 0.76\text{ V}$$

∵ $$E° \quad 0.0592\log K$$

$$\log K \quad \frac{E}{0.0592} \quad \frac{0.76}{0.0592} \quad 12.83$$

$$K \quad 6.88 \quad 10^{12}$$

43. pH = 14

pOH = 0

$[OH \ ] = 1.0$ M

$$K_{sp} \quad 10^{\ 19} \quad [Cu^{2+}][OH \ ]^2$$

$$[Cu^{2+}] \quad \frac{10^{\ 19}}{[OH \ ]^2} \quad 10^{\ 19}$$

For reaction : $Cu^{2+} + 2e \qquad Cu$; $E°$ = 0.34 V

$$E \quad E \quad \frac{0.0592}{2}\log\frac{1}{[Cu^{2+}]}$$

$$0.34 - \frac{0.0592}{2}\log 10^{19} \quad -0.222\text{ V}$$

44. For reaction,

$$2Hg + 2Fe^{3+} \rightleftharpoons Hg_2^{2+} + 2Fe^{2+}$$

Initial :	$10^{\ 3}$ M	0	0
Equilibrium :	$5 \quad 10^{\ 5}$	$4.75 \quad 10^{\ 4}$	$9.5 \quad 10^{\ 4}$

$$K \quad \frac{[Fe^{2+}]^2\,[Hg_2^{2+}]}{[Fe^{3+}]^2}$$

$$\frac{(9.5 \quad 10^{\ 4})^2\ (4.75 \quad 10^{\ 4})}{(5 \quad 10^{\ 5})^2} = 0.17$$

∵ $$E \quad \frac{0.0592}{2}\log K \quad 0.0226\text{ V}$$

$$E\ (Fe^3 \ /Fe^2\ ) \quad E\ (Hg_2^2 \ /Hg)$$

$$E\ (Hg_2^{2+}/Hg) = 0.77 + 0.0226 \quad 0.7926\text{ V}$$

45. In a saturated AgI solution;

$$[Ag^+] \quad \sqrt{8.7 \quad 10^{\ 17}}\ M$$
$$9.32 \quad 10^{\ 9}\ M$$
$$E_{Ag^+/Ag} \quad E \quad 0.0592 \log \frac{1}{[Ag^+]}$$
$$0.799 - 0.0592 \log \frac{1}{9.32 \quad 10^{\ 9}}$$
$$0.324\ V$$

Also, for $AgI \rightleftharpoons Ag^+ + I$; $E° = 0.0592 \log K_{sp}$

$= -0.95$ V

$Ag \qquad Ag^+ \quad e$; $E° = -0.799$ V

$AgI + e \qquad Ag + I \qquad E° = x$

Adding : $AgI \qquad Ag^+ + I$; $E° = -0.95$ V

$= x - 0.799$

$x \qquad 0.151$ V

46. The redox reaction is

$Zn + Ni^{2+} \rightleftharpoons Zn^{2+} + Ni \quad E° = +0.51$ V

$$E \quad \frac{0.0592}{2} \log K$$
$$\log K \quad \frac{0.51 \quad 2}{0.0592} \quad 17.23$$
$$K \quad 1.7 \quad 10^{17}$$

Such a high value of equilibrium constant indicates that the reaction is almost complete. Therefore, concentration of Zn^{2+} in solution will be equal to initial concentration of Ni^{2+} ion, i.e. 1.0 M.

47. The galvanic cell is : $Cu \mid Cu^{2+} \parallel Ag^+ \mid Ag$

Cell reaction : $Cu + 2Ag^+ \rightleftharpoons Cu^{2+} + 2Ag$; $E° = 0.462$ V

$$E \quad 0 \quad 0.462 \quad \frac{0.0592}{2} \log \frac{(0.01)}{[Ag^+]^2}$$
$$[Ag^+] = 1.57 \quad 10^{\ 9}\ M$$

48. $H_2O + e \rightleftharpoons \frac{1}{2} H_2 + HO$; $E° = -0.8277$ V

$\frac{1}{2} H_2 + H_2O \rightleftharpoons H_3O^+ + e$; $E° = 0$ V

$2H_2O \rightleftharpoons H_3O^+ + HO \qquad E° = -0.8277$ V

$$E° \quad 0.0592 \log K$$
$$\log K \quad \frac{0.8277}{0.0592} \quad 13.98$$
$$K \quad 1.04 \quad 10^{\ 14}.$$

49. **At anode** $Zn \qquad Zn^{2+} \quad 2e \quad E \quad 0.76$ V

At cathode $2H^+ \quad 2e \qquad H_2(g) \qquad E° \quad 0.00$ V

For $Zn + 2H^+ \qquad Zn^{2+} + H_2(g)\ E° \quad 0.76$ V

$$E \quad E \quad \frac{0.0592}{2} \log \frac{[Zn^{2+}]}{[H^+]^2}$$
$$\frac{2\,(E \quad E\ )}{0.0592} \quad \log [Zn^{2+}] \quad 2 \log \frac{1}{[H^+]}$$
$$16.2 = -\log (0.1) - 2\ pH$$
$$pH \quad \frac{1 \quad 16.2}{2} \quad 8.6$$

50. For conductivity, the charge carriers are required. In anhydrous state, HCl is not ionised and no charge carrier ions are available, hence bad conductor. However, in aqueous solution, HCl is fully ionised producing H and Cl and conducts electricity.

51. (i) The cell reaction is

$Zn \quad Cu^{2+} \qquad Zn^{2+} + Cu$

(ii) $E_{cell} \quad E_{cathode} \quad E_{anode} = 0.350 - (-0.763) = 1.113$ V

∵ Both Zn^{2+} and Cu^{2+} are at unit concentrations,

$E \quad E \quad 1.113$ V

(iii) ∵ $E_{cell} \quad 1.113\ V > 0$

$G \qquad nEF \quad 0$

Therefore, the cell reaction is spontaneous.

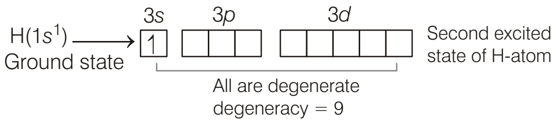
52. pH $\quad C \qquad 10^{\ 4}$

$$\frac{10^{\ 4}}{0.0015}$$

Also, conductance (G) $\quad \frac{A}{l}$

$$G \ \frac{l}{A} \quad 5 \quad 10^{\ 7} \quad \frac{120}{1} \quad 6 \quad 10^{\ 5}$$
$$_{c} \quad \frac{1000}{C}$$
$$\frac{6 \quad 10^{\ 5} \quad 1000}{0.0015}$$
$$\frac{_{c}}{} \quad \frac{6 \quad 10^{\ 5} \quad 1000}{0.0015} \quad \frac{0.0015}{10^{\ 4}}$$
$$600 \quad 6 \quad 10^2\ S\ cm^{\ 1} mol^{\ 1}$$

53. Energy obtained as one mole X is converted into Y is 193 kJ.



Energy consumed in converting one mole of M to M^3

$$nE \ F \quad 2 \quad 96500 \quad 0.25\ J \quad \frac{96500}{2}\ J$$
$$193 \quad 10^3 \quad n \ \frac{96500}{2} \qquad n \quad 4\ mol$$