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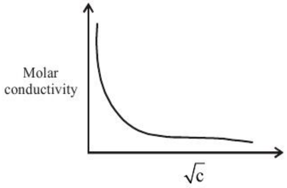
Electrochemistry

TOPIC 1 Conductance and Conductivity

1. The variation of molar conductivity with concentration of an electrolyte (X) in aqueous solution is shown in the given figure. **[Sep. 05, 2020 (II)]**



The electrolyte X is :

(a) HCl (b) NaCl

(c) KNO_3 (d) CH_3COOH

2. Let C_{NaCl} and C_{BaSO_4} be the conductances (in S) measured for saturated aqueous solutions of NaCl and $BaSO_4$, respectively, at a temperature T.

Which of the following is **false**? **[Sep. 03, 2020 (I)]**

(a) Ionic mobilities of ions from both salts increase with T

(b) $C_{BaSO_4}(T_2) > C_{BaSO_4}(T_1)$ for $T_2 > T_1$

(c) $C_{NaCl}(T_2) > C_{NaCl}(T_1)$ for $T_2 > T_1$

(d) $C_{NaCl} >> C_{BaSO_4}$ at a given T

3. The equation that is incorrect is: **[Jan. 07, 2020 (II)]**

(a) $\left(\Lambda_m^0\right)_{NaBr} - \left(\Lambda_m^0\right)_{NaCl} = \left(\Lambda_m^0\right)_{KBr} - \left(\Lambda_m^0\right)_{KCl}$

(b) $\left(\Lambda_m^0\right)_{KCl} - \left(\Lambda_m^0\right)_{NaCl} = \left(\Lambda_m^0\right)_{KBr} - \left(\Lambda_m^0\right)_{NaBr}$

(c) $\left(\Lambda_m^0\right)_{H_2O} = \left(\Lambda_m^0\right)_{HCl} + \left(\Lambda_m^0\right)_{NaOH} - \left(\Lambda_m^0\right)_{NaCl}$

(d) $\left(\Lambda_m^0\right)_{NaBr} - \left(\Lambda_m^0\right)_{NaI} = \left(\Lambda_m^0\right)_{KBr} - \left(\Lambda_m^0\right)_{NaBr}$

4. The decreasing order of electrical conductivity of the following aqueous solutions is : **[April 12, 2019 (II)]**

0.1 M Formic acid (A),

0.1 M Acetic acid (B),

0.1 M Benzoic acid (C).

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

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

5. Consider the statements S1 and S2 :

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

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

The correct option among the following is :

[April 10, 2019 (I)]

(a) Both S1 and S2 are wrong

(b) S1 is wrong and S2 is correct

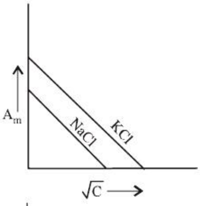
(c) Both S1 and S2 are correct

(d) S1 is correct and S2 is wrong

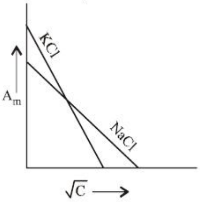
6. Which one of the following graphs between molar conductivity (A_m) versus $\sqrt{C}$ is correct?

[April 10, 2019 (II)]

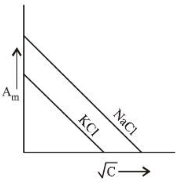
(a)



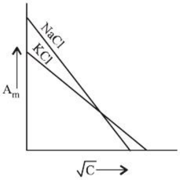
(b)



(c)



(d)



7. Λ_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 : **[Jan. 12, 2019 (II)]**

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

8. 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: **[2014]**

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

9. 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) **[2014]**

(a) $\lambda_C = \lambda_\infty + (B)C$ (b) $\lambda_C = \lambda_\infty - (B)C$
(c) $\lambda_C = \lambda_\infty - (B)\sqrt{C}$ (d) $\lambda_C = \lambda_\infty + (B)\sqrt{C}$

10. Resistance of 0.2 M solution of an electrolyte is 50 Ω. The specific conductance of the solution is 1.3 S m^{-1}. If resistance of the 0.4 M solution of the same electrolyte is 260 Ω, its molar conductivity is : **[2011RS]**

(a) 6.25×10^{-4} S m^2 mol^{-1} (b) 625×10^{-4} S m^2 mol^{-1}
(c) 62.5 S m^2 mol^{-1} (d) 6250 S m^2 mol^{-1}

11. 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]**

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

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

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 $H^+ (\lambda^\circ_{H^+})$.

12. The molar conductivities Λ^o_{NaOAc} and Λ^o_{HCl} at infinite dilution in water at 25ºC 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}

13. 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}

14. 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

15.

Electrolyte:	KCl	KNO_3	HCl	NaOAc	NaCl
Λ^∞ (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

16. 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}

17. Conductivity (unit Siemen's S) is directly proportional to area of the vessel and the concentration of the solution in it and is inversely proportional to the length of the vessel then the unit of the constant of proportionality is

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

TOPIC 2 Electrolysis and Types of Electrolysis

18. Potassium chlorate is prepared by the electrolysis of KCl in basic solution $6\,OH^- + Cl^- \rightarrow ClO_3^- + 3\,H_2O + 6\,e^-$

If only 60% of the current is utilized in the reaction, the time (rounded to the nearest hour) required to produce 10 g of $KClO_3$ using a current of 2 A is ______.

(Given : F = 96,500 C mol^{-1}; molar mass of $KClO_3$ = 122 g mol^{-1}) **[NV, Sep. 06, 2020 (I)]**

19. 250 mL of a waste solution obtained from the workshop of a goldsmith contains 0.1 M $AgNO_3$ and 0.1 M AuCl. The solution was electrolyzed at 2 V by passing a current of 1 A for 15 minutes. The metal/metals electrodeposited will be : **[Sep. 04, 2020 (II)]**

$$\left(E^0_{Ag^+/Ag} = 0.80\ V,\ E^0_{Au^+/Au} = 1.69\ V\right)$$

(a) only gold
(b) silver and gold in proportion to their atomic weights
(c) only silver
(d) silver and gold in equal mass proportion

20. An acidic solution of dichromate is electrolyzed for 8 minutes using 2A current. As per the following equation

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

The amount of Cr^{3+} obtained was 0.104 g. The efficiency of the process (in %) is (Take : F = 96000 C, At. mass of chromium = 52) ___________. **[NV, Sep. 03, 2020 (II)]**

21. 108 g of silver (molar mass 108 g mol^{-1}) is deposited at cathode from $AgNO_3$(aq) solution by a certain quantity of electricity. The volume (in L) of oxygen gas produced at 273 K and 1 bar pressure from water by the same quantity of electricity is _______. **[NV, Jan. 09, 2020 (I)]**

22. 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? **[April 9, 2019 (II)]**

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

23. The anodic half-cell of lead-acid battery is recharged using electricity of 0.05 Faraday. The amount of $PbSO_4$ electrolyzed in g during the process is : (Molar mass of $PbSO_4$ = 303 g mol^{-1}) **[Jan. 9, 2019 (I)]**

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

24. 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 = 10.8 u) **[2018]**

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

25. When 9.65 ampere current was passed for 1.0 hour into nitrobenzene in acidic medium, the amount of *p*-aminophenol produced is _______. **[Online April 16, 2018]**

(a) 109.0 g (b) 98.1 g (c) 9.81 g (d) 10.9 g

26. When an electric current is passes through acidified water, 112 mL of hydrogen gas at N.T.P. was collected at the cathode in 965 seconds. The current passed, in ampere, is : **[Online April 15, 2018 (I)]**

(a) 2.0 (b) 0.1 (c) 0.5 (d) 1.0

27. Given **[2017]**

$$E^o_{Cl_2/Cl^-} = 1.36V, E^o_{Cr^{3+}/Cr} = -0.74V,$$

$$E^o_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33V, E^o_{MnO_4^-/Mn^{2+}} = 1.51V.$$

Among the following, the strongest reducing agent is

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

28. Consider the following standard electrode potentials (E° in volts) in aqueous solution : **[Online April 8, 2017]**

Element	M^{3+}/ M	M^+/M
Al	–1.66	+0.55
Tl	+1.26	–0.34

Based on these data, which of the following statements is correct ?

(a) Tl^+ is more stable than Al^{3+}
(b) Al^+ is more stable than Al^{3+}
(c) Tl^+ is more stable than Al^+
(d) Tl^{3+} is more stable than Al^{3+}

29. What will occur if a block of copper metal is dropped into a beaker containing a solution of 1M $ZnSO_4$? **[Online April 9, 2016]**

(a) The copper metal will dissolve with evolution of oxygen gas
(b) The copper metal will dissolve with evolution of hydrogen gas
(c) No reaction will occur
(d) The copper metal will dissolve and zinc metal will be deposited.

30. 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) **[2015]**

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

31. A variable, opposite external potential (E_{ext}) is applied to the cell $Zn|Zn^{2+}$ (1 M) || Cu^{2+} (1 M) | Cu, of potential 1.1 V. When $E_{ext} < 1.1$ V and $E_{ext} > 1.1$ V, respectively electrons flow from : **[Online April 10, 2015]**

(a) anode to cathode in both cases
(b) cathode to anode and anode to cathode
(c) anode to cathode and cathode to anode
(d) cathode to anode in both cases

32. The standard electrode potentials $\left(E^\circ_{M^+/M}\right)$ of four metals A, B, C and D are – 1.2 V, 0.6 V, 0.85 V and – 0.76 V, respectively. The sequence of deposition of metals on applying potential is: **[Online April 9, 2014]**

(a) A, C, B, D (b) B, D, C, A
(c) C, B, D, A (d) D, A, B, C

33. A current of 10.0 A flows for 2.00 h through an electrolytic cell containing a molten salt of metal X. This results in the decomposition of 0.250 mol of metal X at the cathode. The oxidation state of X in the molten salt is: (F = 96,500 C) **[Online April 9, 2014]**

(a) 1+ (b) 2+ (c) 3+ (d) 4+

34. Given

$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq); E^\circ = +0.77$ V
$Al^{3+}(aq) + 3e^- \rightarrow Al(s); E^\circ = -1.66$ V
$Br_2(aq) + 2e^- \rightarrow 2Br^-; E^\circ = +1.09$ V

Considering the electrode potentials, which of the following represents the correct order of reducing power? **[Online April 11, 2014]**

(a) $Fe^{2+} < Al < Br^-$ (b) $Br^- < Fe^{2+} < Al$
(c) $Al < Br^- < Fe^{2+}$ (d) $Al < Fe^{2+} < Br^-$

35. How many electrons would be required to deposit 6.35 g of copper at the cathode during the electrolysis of an aqueous solution of copper sulphate? (Atomic mass of copper = 63.5 u, N_A = Avogadro's constant): **[Online April 12, 2014]**

(a) $\frac{N_A}{20}$ (b) $\frac{N_A}{10}$ (c) $\frac{N_A}{5}$ (d) $\frac{N_A}{2}$

36. Electrode potentials (E°) are given below : **[Online April 9, 2013]**

$Cu^+/Cu = +0.52\,V$,

$Fe^{3+}/Fe^{2+} = +0.77\,V$,

$\frac{1}{2}I_2(s)/I^- = +0.54\,V$,

$Ag^+/Ag = +0.88\,V$.

Based on the above potentials, strongest oxidizing agent will be :

(a) Cu^+ (b) Fe^{3+} (c) Ag^+ (d) I_2

37. Given :

$$E^\circ_{\frac{1}{2}Cl_2/Cl^-} = 1.36\,V,\ E^\circ_{Cr^{3+}/Cr} = -0.74\,V,$$

$$E^\circ_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33\,V,\ E^\circ_{MnO_4^-/Mn^{2+}} = 1.51\,V$$

The correct order of reducing power of the species (Cr, Cr^{3+}, Mn^{2+} and Cl^-) will be : **[Online April 23, 2013]**

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

38. A solution of copper sulphate ($CuSO_4$) is electrolysed for 10 minutes with a current of 1.5 amperes. The mass of copper deposited at the cathode (at. mass of Cu = 63u) is: **[Online April 25, 2013]**

(a) 0.3892 g (b) 0.2938 g
(c) 0.2398 g (d) 0.3928 g

39. 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

40. A battery is constructed of Cr and $Na_2Cr_2O_7$. The unbalanced chemical equation when such a battery discharges is following:

$Na_2Cr_2O_7 + Cr + H^+ \rightarrow Cr^{3+} + H_2O + Na^+$

If one Faraday of electricity is passed through the battery during the charging, the number of moles of Cr^{3+} removed from the solution is **[Online May 7, 2012]**

(a) $\frac{4}{3}$ (b) $\frac{1}{3}$ (c) $\frac{3}{3}$ (d) $\frac{2}{3}$

41. The standard potentials of Ag^+/Ag, $Hg_2^{2+}/2Hg$, Cu^{2+}/Cu and Mg^{2+}/Mg electrodes are 0.80, 0.79, 0.34 and –2.37 V, respectively. An aqueous solution which contains one mole per litre of the salts of each of the four metals is electrolyzed. With increasing voltage, the correct sequence of deposition of the metals at the cathode is **[Online May 19, 2012]**

(a) Ag, Hg, Cu, Mg (b) Cu, Hg, Ag only
(c) Ag, Hg, Cu only (d) Mg, Cu, Hg, Ag

42. 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

43. Consider the following E° values

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

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

44. The $E^o_{M^{3+}/M^{2+}}$ 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? **[2004]**

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

45. 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

46. 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 **[2003]**

(a) 10.8 g (b) 21.6 g (c) 108 g (d) 1.08 g

47. Which of the following reaction is possible at anode? **[2002]**

(a) $2Cr^{3+} + 7H_2O \rightarrow Cr_2O_7^{2-} + 14H^+$

(b) $F_2 \rightarrow 2F^-$

(c) $(1/2)\,O_2 + 2H^+ \rightarrow H_2O$

(d) none of these.

48. 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.

TOPIC 3 Cells and Electrode Potential, Nernst Equation

49. For the given cell;

$Cu(s)|Cu^{2+}(C_1M)||Cu^{2+}(C_2M)|Cu(s)$

change in Gibbs energy (ΔG) is negative, if : **[Sep. 06, 2020 (II)]**

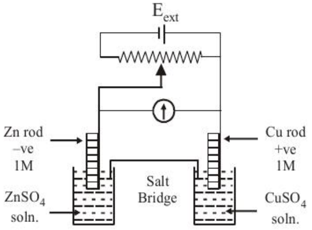
(a) $C_1 = C_2$ (b) $C_2 = \frac{C_1}{\sqrt{2}}$

(c) $C_1 = 2C_2$ (d) $C_2 = \sqrt{2}C_1$

50. An oxidation-reduction reaction in which 3 electrons are transferred has a ΔG^0 of 17.37 kJ mol^{-1} at 25°C. The value of E^0_{cell} (in V) is ______ $\times 10^{-2}$.

(1 F = 96,500 C mol^{-1}) **[NV, Sep. 05, 2020 (I)]**

51.



$E^o_{Cu^{2+}|Cu} = +0.34$ V; $E^o_{Zn^{2+}|Zn} = -0.76$ V

Identify the **incorrect** statement from the options below for the above cell : **[Sep. 04, 2020 (I)]**

(a) If $E_{ext} > 1.1$ V, e^- flows from Cu to Zn

(b) If $E_{ext} > 1.1$ V, Zn dissolves at Zn electrode and Cu deposits at Cu electrode

(c) If $E_{ext} < 1.1$ V, Zn dissolves at anode and Cu deposits at cathode

(d) If $E_{ext} = 1.1$ V, no flow of e^- or current occurs

52. The photoelectric current from Na (work function, $w_0 = 2.3$ eV) is stopped by the output voltage of the cell $Pt(s)|H_2(g, 1\text{ bar})|HCl(aq., pH = 1)|AgCl(s)|Ag(s)$.

The pH of aq. HCl required to stop the photoelectric current from K($w_0 = 2.25$ eV), all other conditions remaining the same, is ___________ $\times 10^{-2}$ (to the nearest integer).

Given, **[NV, Sep. 03, 2020 (I)]**

$$2.303\frac{RT}{F} = 0.06\text{ V}; E^0_{AgCl|Ag|Cl^-} = 0.22\text{ V}$$

53. The Gibbs energy change (in J) for the given reaction at $[Cu^{2+}] = [Sn^{2+}] = 1$ M and 298 K is :

$Cu(s) + Sn^{2+}(aq.) \rightarrow Cu^{2+}(aq.) + Sn(s)$;

$(E^0_{Sn^{2+}|Sn} = -0.16\text{ V}, E^0_{Cu^{2+}|Cu} = 0.34\text{ V},$

Take F = 96500 C mol^{-1}) **[NV, Sep. 02, 2020 (I)]**

54. For the disproportionation reaction

$2Cu^+(aq) \rightleftharpoons Cu(s) + Cu^{2+}(aq)$ at 298 K, ln K (where K is the equilibrium constant) is ________ $\times 10^{-1}$.

Given **[NV, Sep. 02, 2020 (II)]**

$(E^0_{Cu^{2+}/Cu^+} = 0.16\text{ V}; E^0_{Cu^+/Cu} = 0.52\text{ V}; \frac{RT}{F} = 0.025)$

55. What would be the electrode potential for the given half cell reaction at pH=5?

____________.

$2H_2O \rightarrow O_2 + 4H^{\oplus} + 4e^-$; $E^0_{red} = 1.23$V

(R = 8.314 J mol^{-1} K^{-1}; Temp = 298 K; oxygen under std. atm. pressure of 1 bar) **[NV, Jan. 08, 2020 (I)]**

56. For an electrochemical cell

$Sn(s)|Sn^{2+}(aq, 1M)||Pb^{2+}(aq, 1M)|Pb(s)$ the ratio $\frac{[Sn^{2+}]}{[Pb^{2+}]}$

when this cell attains equilibrium is_______.

[NV, Jan. 08, 2020 (II)]

57. Given that the standard potentials (E^0) of Cu^{2+}/Cu and Cu^+/Cu are 0.34 V and 0.522 V respectively, the E^0 of Cu^{2+}/Cu^+ is: **[Jan. 07, 2020 (I)]**

(a) +0.182 V (b) +0.158 V

(c) –0.182 V (d) –0.158 V

58. The standard Gibbs energy for the given cell reaction in kJ mol^{-1} at 298 K is: **[April 9, 2019 (I)]**

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

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

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

(a) –384 (b) 384 (c) 192 (d) –192

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

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

Given that **[April 8, 2019 (II)]**

$E^0_{Ag^+/Ag} = x$ V; $E^0_{Fe^{2+}/Fe} = y$ V; $E^0_{Fe^{3+}/Fe} = z$ V

(a) $x - z$ (b) $x - y$

(c) $x + 2y - 3z$ (d) $x + y - z$

60. The standard electrode potential E^0 and its temperature coefficient $\left(\frac{dE^0}{dT}\right)$ for a cell are 2 V and -5×10^{-4} VK^{-1} at 300 K respectively. The cell reaction is:
$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu$
The standard reaction enthalpy ($\Delta_r H^0$) at 300 K in kJ mol^{-1} is,
[Use R = 8 JK^{-1} mol^{-1} and F = 96,000 C mol^{-1}]
[Jan. 12, 2019 (I)]
(a) –412.8 (b) –384.0 (c) 192.0 (d) 206.4

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

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

If $E^o_{Zn^{2+}/Zn} = -0.76V$, which cathode will give a maximum value of E°_{cell} per electron transferred? **[Jan. 11, 2019 (I)]**
(a) Ag^+/Ag (b) Fe^{3+}/Fe^{2+}
(c) Au^{3+}/Au (d) Fe^{2+}/Fe

62. Given the equilibrium constant : **[Jan. 11, 2019 (II)]**
K_C of the reaction :
$Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$ is 10×10^{15} calculate the E^0_{cell} of this reaction at 298 K

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

(a) 0.04736 mV (b) 0.4736 mV
(c) 0.4736 V (d) 0.04736 V

63. In the cell
Pt(s) | H_2(g, 1bar) / HCl(aq)||AgCl(s)/Ag(s)|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: **[Jan. 10, 2019 (II)]**

$$\left\{\text{Given}: \frac{2.303RT}{F} = 0.06\text{ V at } 298\text{ K}\right\}$$

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

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

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

at 300 K is approximately
(R = 8JK^{-1} mol^{-1}, F = 96000 C mol^{-1}) **[Jan. 9, 2019 (II)]**
(a) e^{-80} (b) e^{-160} (c) e^{320} (d) e^{160}

65. What is the standard reduction potential (E°) for $Fe^{3+} \rightarrow Fe$?
Given that : **[Online April 8, 2017]**

$$Fe^{2+} + 2e^- \rightarrow Fe;\ E^o_{Fe^{2+}/Fe} = -0.47V$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+};\ E^o_{Fe^{3+}/Fe^{2+}} = +0.77V$$

(a) –0.057 V (b) +0.057 V
(c) +0.30 V (d) –0.30 V

66. To find the standard potential of M^{3+}/M electrode, the following cell is constituted : Pt/M/M^{3+}(0.001 mol L^{-1})/Ag^+(0.01 mol L^{-1})/Ag **[Online April 9, 2017]**
The emf of the cell is found to be 0.421 volt at 298 K. The standard potential of half reaction $M^{3+} + 3e \longrightarrow M$ at 298 K will be : (Given $\overset{\circ}{E}_{Ag^+/Ag}$ at 298 K = 0.80 Volt)
(a) 0.38 Volt (b) 0.32 Volt
(c) 1.28 Volt (d) 0.66 Volt

67. At 298 K, the standard reduction potentials are 1.51 V for $MnO_4^- | Mn^{2+}$, 1.36 V for $Cl_2 | Cl^-$, 1.07 V for $Br_2 | Br^-$, and 0.54 V for $I_2 | I^-$. At pH = 3, permanganate is expected to oxidize : $\left(\frac{RT}{F} = 0.059V\right)$
[Online April 11, 2015]
(a) Cl^-, Br^- and I^- (b) Br^- and I^-
(c) Cl^- and Br^- (d) I^- only

68. Given below are the half-cell reactions:

$$Mn^{2+} + 2e^- \rightarrow Mn;\ E^\circ = -1.18\text{ V}$$

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

The E° for $3Mn^{2+} \rightarrow Mn + 2Mn^{3+}$ will be: **[2014]**
(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

69. Given : $E^\circ_{Cr^{3+}/Cr} = -0.74\text{ V}$; $E^\circ_{MnO_4^-/Mn^{2+}} = 1.51\text{ V}$

$$E^\circ_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33\text{ V};\ E^\circ_{Cl/Cl^-} = 1.36\text{ V}$$

Based on the data given above, strongest oxidising agent will be : **[2013]**
(a) Cl (b) Cr^{3+} (c) Mn^{2+} (d) MnO_4^-

70. Given

$$E^\circ_{Cu^{2+}/Cu} = 0.34V,\ E^\circ_{Cu^{2+}/Cu^+} = 0.15V$$

Standard electrode potential for the half cell Cu^+/Cu is **[Online May 26, 2012]**
(a) 0.38 V (b) 0.53 V (c) 0.19 V (d) 0.49 V

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

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

The potential difference needed for electrolytic reduction of Al_2O_3 at 500 °C is at least **[2010]**
(a) 4.5 V (b) 3.0 V (c) 2.5 V (d) 5.0 V

72. Given:

$$E^o_{Fe^{3+}/Fe} = -0.036V,$$

$$E^o_{Fe^{2+}/Fe} = -0.439V$$

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

73. Given $E^\circ_{Cr^{3+}/Cr} = -0.72$ V,

$E^\circ_{Fe^{2+}/Fe} = -0.42$ 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

74. The cell, $Zn\,|\,Zn^{2+}(1\ M)\,||\,Cu^{2+}(1\ M)\,|\,Cu\ (E^\circ_{cell} = 1.10\ V)$ 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) $10^{37.3}$.

75. For a spontaneous reaction the ΔG, equilibrium constant (K) and E°_{cell} will be respectively **[2005]**

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

76. 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 $(F = 96{,}500\ C\ mol^{-1};\ R = 8.314\ JK^{-1}\ mol^{-1})$ **[2004]**

(a) 1.0×10^{10}
(b) 1.0×10^5
(c) 1.0×10^1
(d) 1.0×10^{30}

77. 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

78. 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 25ºC will be **[2003]**

(a) 29.5×10^{-2}
(b) 10
(c) 1×10^{10}
(d) 1×10^{-10}

79. 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
(c) 0.82 volt
(d) 2.14 volt

80. 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) $E = -(E_{right} + E_{left})$.

81. 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) $\frac{RT}{2F}\log_e\frac{P_2}{P_1}$
(c) $\frac{RT}{F}\log_e\frac{P_2}{P_1}$
(d) none of these.

TOPIC 4 Commercial Cells and Corrosion

82. Galvanization is applying a coating of: **[2016]**

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

83. Identify the correct statement : **[Online April 10, 2016]**

(a) Corrosion of iron can be minimized by forming a contact with another metal with a higher reduction potential
(b) Iron corrodes in oxygen free water
(c) Corrosion of iron can be minimized by forming an impermeable barrier at its surface
(d) Iron corrodes more rapidly in salt water because its electrochemical potential is higher

84. 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: **[2009]**

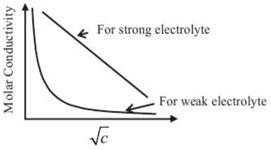
(a) 87%
(b) 90%
(c) 97%
(d) 80%

85. 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

Hints & Solutions

1. **(d)**



Among given electrolytes, CH_3COOH is weak electrolyte.

2. **(N)** Ionic mobility increases with increase in temperature, which increases the conductance of the solution, while conductance of NaCl solution is independant of temperature above 400°C. Because the temperature is not given, so none of the option is correct.

3. (d) $(\Lambda^0_m)_{NaBr} - (\Lambda^0_m)_{NaI}$

$$= \Lambda^0_m \overset{+}{Na} + \Lambda^0_m Br^- - (\Lambda^0_m \overset{+}{Na} + \Lambda^0_m I^-)$$
$$= \Lambda^0_m \overset{+}{Na} + \Lambda^0_m Br^- - \Lambda^0_m \overset{+}{Na} - \Lambda^0_m I$$
$$= \Lambda^0_m Br^- + \Lambda^0_m I^-$$

$(\Lambda^0_m)_{KBr} - (\Lambda^0_m)_{NaBr}$

$$= \Lambda^0_m K^+ + \Lambda^0_m Br^- - (\Lambda^0_m Na^+ + \Lambda^0_m Br^-)$$
$$= \Lambda^0_m K^+ + \Lambda^0_m Br^- - \Lambda^0_m \overset{+}{Na} - \Lambda^0_m Br^-$$
$$= \Lambda^0_m K^+ + \Lambda^0_m \overset{+}{Na}$$

$$\therefore (\Lambda^0_m)_{NaBr} - (\Lambda^0_m)_{NaI} \neq (\Lambda^0_m)_{KBr} - (\Lambda^0_m)_{NaBr}$$

4. **(a)** Order of acidic strength is

$HCOOH > C_6H_5COOH > CH_3COOH$

More the acidic strength more will be the dissociation of acid into ions and more will be the conductivity.

Thus, order of conductivity will be,

$$\underset{(A)}{HCOOH} > \underset{(C)}{C_6H_5COOH} > \underset{(B)}{CH_3COOH}$$

5. **(b)** Conductivity of an electrolyte is the conductance of 1 cm^3 of the given electrolyte. It increases with the increase in concentration of electrolyte due to increase in the number of ions per unit volume. Molar conductivity (λ_m) is the conductance of a solution containing 1 mole of the electrolyte. It increases with the decrease of concentration due to increase in the total volume having one mole of electrolyte. Thus, interionic attraction increses and degree of ionisation decreases. Therefore, (S_1) is wrong and (S_2) is correct.

6. **(a)** Since, KCl is more conducting than NaCl, therefore, graph (a) is correct.

7. **(c)** Given: $\Lambda^\circ_m(NaCl) = 126.4\ S\ cm^2\ mol^{-1}$, $\Lambda^\circ_m(HCl) = 425.9\ S\ cm^2\ mol^{-1}$ and $\Lambda^\circ_m(NaA) = 100.5\ S\ cm^2\ mol^{-1}$

$$\Lambda^\circ_m(HA) = \lambda^\circ_H + \lambda^\circ_{A^-}$$
$$= \lambda^\circ_{H^+} + \lambda^\circ_{Cl^-} + \lambda^\circ_{A^-} + \lambda^\circ_{Na^+} - \lambda^\circ_{Cl^-} - \lambda^\circ_{Na^+}$$
$$= \Lambda^\circ_m(HCl) + \Lambda^\circ_m(NaA) - \Lambda^\circ_m(NaCl)$$
$$\Lambda^\circ_m(HA) = 429.5 - 126.4 + 100.5 = 400\ S\ cm^2\ mol^{-1}$$
$$\kappa\,(HA) = 5 \times 10^{-5}\ S\ cm^{-1}$$
$$(HA) = \frac{\kappa(HA) \times 1000}{\text{Molality of HA}} = \frac{5 \times 10^{-5} \times 1000}{0.001} = 50\ S\ cm^2\ mol^{-1}$$
$$\alpha = \frac{\Lambda_m(HA)}{\Lambda^\circ_m(HA)} = \frac{50}{400} = 0.125$$

8. **(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, $R = \rho\frac{l}{a} = \frac{1}{\kappa} \times \frac{l}{a}$

$$\Rightarrow \frac{l}{a} = R \times \kappa = 50 \times 1.4 \times 10^{-2}\ cm^{-1}$$

For 0.5 M solution

$R = 280\ \Omega$

$\kappa = ?$

$$\frac{l}{a} = 50 \times 1.4 \times 10^{-2}\ cm^{-1}$$
$$\Rightarrow R = \rho\frac{l}{a} = \frac{1}{\kappa} \times \frac{l}{a}$$
$$\Rightarrow \kappa = \frac{1}{280} \times 50 \times 1.4 \times 10^{-2}$$
$$= \frac{1}{280} \times 70 \times 10^{-2}$$
$$= 2.5 \times 10^{-3}\ S\ cm^{-1}$$

Now, $\Lambda_m = \dfrac{\kappa \times 1000}{M}$

$$= \frac{2.5 \times 10^{-3}\ S\ cm^{-1} \times 1000\ cm^3/L}{0.5\ mol/L}$$
$$= 5\ S\ cm^2\ mol^{-1} = 5 \times 10^{-4}\ S\ m^2\ mol^{-1}$$

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

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

10. (a) $k = \frac{1}{R} \times \frac{l}{a}$

$$1.3 = \frac{1}{50} \times \frac{l}{a}$$

$$\frac{l}{a} = 65\,\text{m}^{-1}$$

$$\Lambda_m = \frac{k \times 1000}{\text{molarity}}$$

[molarity is in moles/litre but 1000 is used to convert litre into cm^3]

$$= \frac{\left(\frac{1}{260} \times 65\ \text{m}^{-1}\right) \times 1000\ \text{cm}^3}{0.4\ \text{mol}}$$

$$= \frac{65\ \text{m}^{-1}}{260 \times 0.4\ \text{mol}} \times \frac{1}{1000}\ \text{m}^3$$

$= 6.25 \times 10^{-4}\ \text{S m}^2\ \text{mol}^{-1}$

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

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

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

12. **(b)** $\overset{\circ}{\Lambda}_{CH_3COOH}$ is given by the following equation

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

Hence $\overset{\circ}{\Lambda}_{NaCl}$ is required.

13. **(b)** $R = 100\,\Omega$, $\kappa = \frac{1}{R}\left(\frac{l}{a}\right)$,

$\frac{l}{a}$ (cell constant) $= 1.29 \times 100\ \text{m}^{-1}$

Given, $R = 520\Omega$,

$C = 0.2\ \text{M} = 0.2 \times 1000\ \text{mol m}^{-3}$

Λ_m (molar conductivity) = ?

$\Lambda_m = K \times V$ (K can be calculated as cell constant is known.)

$$K = \frac{1}{R}\left(\frac{l}{a}\right)$$

Hence,

$$K = \frac{129\text{m}^{-1}}{520\ \Omega} = 0.248\ \text{Sm}^{-1}$$

$$\Lambda_m = \frac{K}{C} = \frac{0.248\ \text{Sm}^{-1}}{0.2 \times 1000\ \text{mol m}^{-3}}$$

$= 12.4 \times 10^{-4}\ \text{Sm}^2\ \text{mol}^{-1}$

14. **(a)** 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 acetic acid > acetic acid.

15. **(b)** $\Lambda^\infty_{HCl} = 426.2$ ....(i)

$\Lambda^\infty_{AcONa} = 91.0$ ....(ii)

$\Lambda^\infty_{NaCl} = 126.5$ ....(iii)

$\Lambda^\infty_{AcOH} = \text{(i)} + \text{(ii)} - \text{(iii)}$

$= [426.2 + 91.0 - 126.5] = 390.7$

16. **(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)

$\Lambda^\circ_{NaBr} = \lambda^\circ_{Na^+} + \lambda^\circ_{Br^-}$

$= 126 + 152 - 150 = 128\ \text{S cm}^2\ \text{mol}^{-1}$

17. **(b)** Given conductivity $\propto \frac{\text{area} \times \text{conc.}}{\text{length}}$

$$= \frac{\text{Km}^2\text{mol}}{\text{m} \times \text{m}^3}$$

$\therefore\ K = \text{Sm}^2\ \text{mol}^{-1}$

18. **(11)**

$$6OH^- + Cl^- \longrightarrow ClO_3^- + 3H_2O + 6e^-$$

For synthesis of 1 mole of ClO_3^-, 6F of charge is required.

$\because$ Current efficiency = 60%

$\therefore$ To synthesis 1 mole of ClO_3^-, 10F of charge is required.

To synthesis $\frac{10}{122}$ moles of $KClO_3$, charge $= \frac{10 \times 10}{122}$F

Q = I. t

$$t = \frac{100 \times 96500}{122 \times 2} = 39549.18\ \text{s}$$

$$= \frac{79098.365}{3600\,\text{s}} = 10.99\,\text{h}$$

$\therefore t = 11$ h.

19. **(a)** Millimoles of $Au^+ = 0.1 \times 250 = 25$

Mole of $Au^+ = \frac{25}{1000} = \frac{1}{40} = 0.025$

Similarly, moles of $Ag^+ = 0.025$

Charge passed $= I \times t = 1 \times 15 \times 60 = 900$ C

Moles of e^- passed $= \frac{900}{96500} = 0.0093$ mol.

Species with higher value of SRP will get deposited first at cathode.

$$\underset{0.025}{Au^+(aq)} + \underset{0.0093}{e^-} \longrightarrow Au(s)$$

So, only Au will get deposited.

20. **(60)**

Charge $(Q) = It = 2 \times 8 \times 60 = 960\,C$

$$\Rightarrow \frac{960}{96000} = 0.01F$$

$$Cr_2O_7^{2-} + 14H^+ + \underset{0.01\,F}{6e^-} \longrightarrow \underset{\frac{1}{3}\times 0.01\text{ mole}}{2Cr^{3+}} + 7H_2O$$

Theoritical mass of $Cr^{3+} = \frac{1}{3} \times \frac{960}{96000} \times 52 = 0.173\text{ g}$

So, efficiency $= \frac{W_{actual}}{W_{Theoritical}} \times 100 = \frac{0.104}{0.173} \times 100 = 60\%$

21. **(5.68)**

No. of moles of silver deposited.

$$= \frac{108}{108} = 1\text{ mol}$$

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

1 F charge is required to deposit 1 mole of Ag

$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$

2 F charge deposit → $\frac{1}{2}$ moles of oxygen

1 F charge will deposit → $\frac{1}{4}$ moles of oxygen

$$V_{O_2} = \frac{nRT}{P}$$

$$= \frac{1}{4} \times \frac{0.08314\,L\,bar\,K^{-1}mol^{-1} \times 273K}{1\,bar}$$

$$= \frac{1}{4} \times 22.7$$

$$V_{O_2} = 5.675\,L$$

22. **(c)** The reaction involved in the process is given below

$PbSO_4 \rightarrow Pb^{2+} + SO_4^{2-}$

$Pb^{2+} + H_2O \rightarrow PbO_2 + 4H^+ + 2e^-$

So, half cell reaction is

$PbSO_4 \rightarrow Pb^{4+} + 2e^-$

According to the reaction:

$PbSO_4 \rightarrow Pb^{4+} + 2e^-$

We require 2F for the electrolysis of 1 mol or 303 g of $PbSO_4$

∴ Amount of $PbSO_4$ electrolysed by 0.05F

$$= \frac{303}{2} \times 0.05 = 7.575\text{ g} \approx 7.6\text{ g}$$

23. **(a)** According to the Faraday's law of electrolysis, nF of current is required for the deposition of 1 mol

According to the reaction,

$$Ni(NO_3)_2 \longrightarrow Ni^{2+} + 2NO_3^-$$

2 F of current deposits = 1 mol

∴ 0.1 F of current deposits $= \frac{0.1}{2} = 0.05$ mol

24. **(c)** $B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O$

27.66 g of B_2H_6 (1 mole) requires 3 moles of oxygen (O_2) for complete burning.

Now the oxygen is produced by the electrolysis of H_2O.

On electrolysis : $2H_2O \xrightarrow{4F} 2H_2 + O_2$

1 mole O_2 is produced by 4F charge

∴ 3 mole O_2 will be produced by 12F charge.

∵ $Q = It$

$12 \times 96500\,C = I \times t$

$12 \times 96500\,C = 100 \times t$

$$t = \frac{12 \times 96500}{100}\text{ second}$$

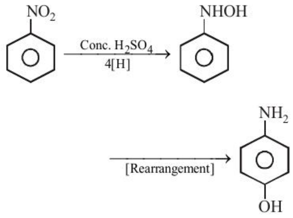
$$= \frac{12 \times 96500}{100 \times 3600}\text{ hour}$$

$= 3.2$ hours

25. **(c)** 9.65 ampere current was passed for 1.0 hour (3600 seconds)

Number of moles of electrons passed

$$= \frac{I(A) \times t(s)}{96500} = \frac{9.65A \times 3600s}{96500} = 0.36\text{ moles}$$



$$C_6H_5NO_2 + 4e^- + 4H^+ \longrightarrow p\text{-Aminophenol} + H_2O$$

$\because$ 4 moles of electrons reduces 1 mole of nitrobenzene to *p*-aminophenol.

$\therefore$ 0.36 moles of electrons will reduce $\frac{0.36}{4} = 0.09$ moles of nitrobenzene to *p*-aminophenol.

p-aminophenol molar mass = 109.14 g/mol

Mass of *p*-aminophenol obtained

= 109.14 g/mol × 0.09 mol = 9.81 g

26. **(d)** Reduction at cathode:

$2e^- + 2H_2O \rightarrow H_2 + 2OH^-$ (valence factor) $H_2 = 2$

At NTP 22400 mL of H_2 = 1 mole of H_2

$$112 \text{ mL of } H_2 = \frac{1}{22400} \times 112 = 0.005 \text{ mole of } H_2$$

$$\text{Moles of } H_2 \text{ produced} = \frac{I \times t}{96500} \times \text{molar ratio}$$

$$0.005 = \frac{I \times 965}{96500} \times \frac{1 \text{ mole of } H_2}{2 \text{ mole of } e^-}$$

$$I = 1.0 \text{ A}$$

27. **(a)** $E^\circ_{MnO_4^-/Mn^{2+}} = 1.51V$

$E^\circ_{Cl_2/Cl^-} = 1.36V$

$E^\circ_{C_2O_7^{2-}/Cr^{3+}} = 1.33V$

$E^\circ_{Cr^{3+}/Cr} = -0.74$

Since Cr^{3+} is having least reduction potential, so Cr is the best reducing agent.

28. **(c)** (i) $\underset{\text{Most stable}}{Al^{3+}} \xrightarrow{E^\circ=-1.66} Al \xleftarrow{E^\circ=+0.55} \underset{\text{Less stable}}{Al^{+}}$

(ii) $\underset{\text{Less stable}}{Tl^{3+}} \xrightarrow{E^\circ=+1.26} Tl \xleftarrow{E^\circ=-0.34} \underset{\text{More stable}}{Tl^{+}}$

Tl^+ has negative electrode potential (E° = –0.34) means, it does not prefer to convert into Tl but reverse must be preferred that's why it is more stable than Tl^{3+} (E° = +1.26). In Al, Al^{3+} is more stable (E° = –1.66) than Al^+ (E° = +0.55) and also from Tl^+ due to more negative value of E°. Therefore, by comparison it confirms that Tl^+ is more stable than Al^+.

29. **(c)** No reaction will occur as the Zn is placed above Cu in electrochemical series. Hence there will be no$_2$ displacement reaction.

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

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

= 63.5g

31. **(c)** EMF of galvanic cell = 1.1 volt

If E_{ext} < EMF then electrons flow steadily from anode to cathode, while if E_{ext} > EMF then electrons flow from cathode to anode as polarity is changed.

32. **(c)** As the value of reduction potential decreases the reducing power increases i.e.

C < B < D < A

(0.85). (0.6). (–0.76) (– 1.2)

33. **(c)** According to Faraday's first law of electrolysis

$$W = \frac{E \times i \times t}{96500}$$

Where E = equivalent weight

$$= \frac{\text{mol. mass of metal}(M)}{\text{oxidation state of metal } (x)}$$

Substituting the value in the formula

$$W = \frac{M}{x} \times \frac{i \times t}{96500}$$

$$\text{or} \quad x = \frac{M}{W} \times \frac{i \times t}{96500} = \frac{10 \times 2 \times 60 \times 60}{96500 \times 0.250} = 3$$

$$\left[\text{Given : no. of moles} = \frac{W}{M} = 0.250\right]$$

Hence oxidation state of metal is (+3)

34. **(d)** Reducing character decreases down the series. Hence the correct order is

$Al < Fe^{2+} < Br^-$

35. **(c)** $Cu \longrightarrow Cu^{2+} + 2e^-$

i.e, to deposit 1 mole of Cu at cathode from $Cu^{2+}\,SO_4^{2-}$ solution = 2 moles of electrons are required

$$\text{i.e, To deposit } 6.35g = \frac{6.35}{63.5} \times 2 = \frac{2}{10} = \frac{1}{5} \text{mol}$$

$$\text{Thus total no. of electrons required} = \frac{N_A}{5}$$

36. **(c)** Higher the value of reduction potential stronger will be the oxidising agent, hence based on the given values Ag^+ will be strongest oxidizing agent.

37. **(a)** Lower the value of reduction potential higher will be reducing power hence the correct order will be

$Mn^{2+} < Cl^- < Cr^{3+} < Cr$

38. **(b)** W = Zit

where Z = Electrochemical equivalent

$$\text{Eq. wt. of copper} = \frac{63}{2} = 31.5$$

$$Z = \frac{31.5}{96500}$$

$$W = Zit = \frac{31.5}{96500} \times 1.5 \times 10 \times 60 = 0.2938g$$

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

Since ΔG° = – nFE°

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

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

$$E^\circ_{cell} = E^\circ_{Ni^{2+}/Ni} - E^\circ_{Zn^{2+}/Zn}$$

$$= -0.23 - (-0.76) = +0.53 \text{ (positive)}$$

40. **(c)** Reduction half reaction :

$$Cr_2O_7^{2-} + 6e^- + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O$$

Oxidation half reaction :

$$Cr \longrightarrow Cr^{3+} + 3e^-$$

Overall reaction :

$$Cr_2O_7^{2-} + Cr + 14H^+ + 3e^- \longrightarrow 3Cr^{3+} + 7H_2O$$

3F of electricity = 3 moles of Cr^{3+}

1F of electricity = $\frac{3}{3}$ moles of Cr^{3+}

41. **(c)** More the reduction potential, more is the deposition of metals at cathode. Cation having E° value less than – 0.83V (reduction potential of H_2O) will not deposit from aqueous solution. Hence correct order of deposition of the metal at the cathode is

$$Ag > Hg > Cu$$

42. **(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

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

ALTERNATE SOLUTION

We know, $Q = \frac{mFz}{M}$

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

43. **(a)** $Fe^{3+} + e^- \rightarrow Fe^{2+}$; $Sn^{2+} + 2e^- \rightarrow Sn(s)$;

for $Sn(s) + 2Fe^{3+}(aq) \rightarrow 2Fe^{2+}(aq) + Sn^{2+}(aq)$

∴ Standard potential for the given reaction

or $E^\circ_{cell} = E^\circ_{Sn/Sn^{2+}} + E^\circ_{Fe^{3+}/Fe^{2+}}$

$$= 0.14 + 0.77 = 0.91\ V$$

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

45. **(d)**

A	B	C
+0.5V	–3.0V	–1.2V

Note: The higher the negative value of reduction potential, the more is the reducing power.

Hence B > C > A.

46. **(a)** When 96500 coulomb of electricity is passed through the electroplating bath the amount of Ag deposited = 108g

∴ when 9650 coulomb of electricity is passed deposited Ag.

$$= \frac{108}{96500} \times 9650 = 10.8\ g$$

47. **(a)** $2Cr^{3+} + 7H_2O \rightarrow Cr_2O_7^{2-} + 14H^+$

O.S. of Cr changes from +3 to +6 by loss of electrons. At anode oxidation takes place.

48. **(d)** Pure metal always deposits at cathode.

49. **(d)** For the concentration cell, $E^o_{cell} = 0$

Anode : $Cu(s) \longrightarrow Cu^{2+}\ (aq)_A$

Cathode : $Cu^{2+}(aq)_e \longrightarrow Cu\,(s)$

Overall : $\underset{(C_2M)}{Cu^{2+}(aq)_C} \longrightarrow \underset{(C_1M)}{Cu^{2+}\,(aq)_A}$

As $\Delta G = -nFE$

If $\Delta G = -ve$, then E_{cell} is $+v_e$.

$$E_{cell} = E^o_{cell} - \frac{RT}{2F}\ln\frac{C_1}{C_2}$$

$$E_{cell} = 0 - \frac{RT}{2F}\ln\frac{C_1}{C_2}$$

$$E_{cell} = \frac{RT}{2F}\ln\frac{C_2}{C_1}$$

So, $C_2 > C_1$.

Thus, $C_2 = \sqrt{2}C_1$ relation is correct.

50. **(– 6)**

$$\Delta G^o = -nFE^o_{cell}$$

$$17.37 \times 10^3 = -3 \times 96500 \times E^o_{cell}$$

$$E^o_{cell} = -0.06\ V \simeq -6.0 \times 10^{-2}\ V$$

51. **(b)** $E^o_{cell} = E^o_{Cu^{2+}|Cu} - E^o_{Zn^{2+}|Zn} = 1.1\,V$

So, if $E_{ext.} = 1.1$ V no electron will flow

At, $E_{ext.} > 1.1$ V cell act as electrolytic cell and electron will flow from Cu to Zn.

At, $E_{ext.} < 1.1$ V cell act as electrochemical cells so Zn dissolve and Cu deposit.

52. **(142)**

Sodium metal :

$E = E_0 + (KE)_{max}$; $E^0_{cell} = 0.22$ V

Cell reaction

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

Anode : $\frac{1}{2}H_2(g) \longrightarrow H^+(aq) + e^-$

Overall : $AgCl(s) + \frac{1}{2}H_2(g) \longrightarrow Ag(s) + H^+(aq) + Cl^-(aq)$

$$E_{cell} = E^0_{cell} - \frac{0.06}{1}\log[H^+][Cl^-]$$

$$E_{cell} = 0.22 - \frac{0.06}{1}\log[10^{-1}][10^{-1}]$$

$$= 0.22 + 0.12 = 0.34\ V$$

$(KE)_{max} = E_{cell} = 0.34$ eV

So, $E = 2.3 + 0.34 = 2.64$ eV = Energy of photon incident

For potassium metal :

$E = E_0 + (KE)_{max}$

$2.64 = 2.25 + (KE)_{max}$

$(KE)_{max} = 0.39 = E_{cell}$

Cell reaction

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

Anode : $\frac{1}{2}H_2(g) \longrightarrow H^+(aq) + e^-$

Overall : $AgCl(s) + \frac{1}{2}H_2(g) \longrightarrow Ag(s) + H^+(aq) + Cl^-(aq)$

$$E_{cell} = E^0_{cell} - \frac{0.06}{1}\log[H^+][Cl^-]$$

$0.39 = 0.22 - 0.06 \log[H^+]^2$

$0.39 = 0.22 - 0.12 \log[H^+]$

$0.17 = 0.12 \times pH$

$pH = 17/12 = 1.4166 \simeq 1.42 = 142 \times 10^{-2}$

53. **(96500)**

$$E^0_{cell} = E^0_{Sn^{2+}/Sn} - E^0_{Cu^{2+}/Cu}$$

$$= -0.16 - 0.34 = -0.50\text{ V}$$

$$\Delta G^0 = -nE^0_{cell}$$

$$= -2 \times 96500 \times (-0.5) = 96500\text{ J}$$

54. **(144)**

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

$$E^o_{cell} = E^o_{Cu^+/Cu} - E^o_{Cu^{2+}/Cu^+} = 0.52 - 0.16 = 0.36\text{ V}$$

$$E^o_{cell} = \frac{RT}{nF}\ln K_{eq}$$

$$\Rightarrow 0.36 = \frac{0.025}{1}\ln K$$

$$\Rightarrow \ln K = 14.4 = 144 \times 10^{-1}$$

55. **(1.52)**

$$E = 1.23 - \frac{0.0591}{4}\log[H^+]^4$$

$= 1.23 + 0.0591 \times pH$

$= 1.23 + 0.0591 \times 5$

$= 1.23 + 0.2955$

$= 1.52$ V

56. **(2.15)**

At equilibrium state $E_{cell} = 0$; $E^0_{cell} = 0.01$ V

$Sn + Pb^{2+} \longrightarrow Sn^{2+} + Pb$

$$E = E^0_{cell} - \frac{0.06}{n}\log\frac{[P]}{[R]}$$

$$0 = 0.01 - \frac{0.06}{2}\log\frac{[Sn^{2+}]}{[Pb^{2+}]}$$

$$-0.01 = -\frac{0.06}{2}\log\frac{[Sn^{2+}]}{[Pb^{2+}]}$$

$$\frac{1}{3} = \log\frac{[Sn^{2+}]}{[Pb^{2+}]}$$

$$\frac{[Sb^{2+}]}{[Pb^{2+}]} = 10^{1/3} = 2.15$$

57. **(b)** $Cu^{2+} + 2e^- \longrightarrow Cu, \Delta G_1^\circ = -2F(0.34)$ ...(i)

$Cu^+ + e^- \longrightarrow Cu, \Delta G_2^\circ = -F(0.522)$ ...(ii)

Subtract (ii) from (i)

$Cu^{2+} + e^- \longrightarrow Cu^+, \Delta G_3^\circ = -F(E^0)$

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

$\Rightarrow -FE^\circ = -2F(0.34) + F(0.522)$

$\Rightarrow E^\circ = 0.68 - 0.522 = 0.158$ V

58. **(a)** $\Delta G^\circ = -nFE^\circ_{cell}$

$= -2 \times (96000) \times 2\text{ V} = -384000\text{ J/mol} = -384\text{ kJ/mol}$

59. **(c)** $Ag^+(aq) + Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + Ag(s)$

$$E^0_{cell} = E^0_{Ag^+/Ag} - E^0_{Fe^{3+}/Fe^{2+}}$$

$$\begin{tikzcd} Fe^{3+} \arrow[r] \arrow[rr, bend right, "z"'] & Fe^{2+} \arrow[r] \arrow[r, bend left, "y"] & Fe \end{tikzcd}$$

$$E^0_{Fe^{3+}/Fe^{2+}} = 3z - 2y$$

$E^0_{Ag^+/Ag} = x$ (given)

$\therefore E^0_{cell} = x - 3z + 2y$

60. **(a)** $\Delta G^\circ = \Delta_r H^\circ - T\Delta S^\circ$

$\Delta_r H^\circ = \Delta G^\circ + T\Delta S^\circ$

$$\Delta_r H^\circ = -nFE^\circ + TnF\frac{dE}{dT}$$

$$\Delta_r H^\circ = -nFE^\circ + nFT\frac{dE}{dT}$$

Cell reaction: $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

$$\Delta_r H^\circ = -nF\left(E^\circ - \frac{TdE^\circ}{dT}\right)$$

$\Delta_r H^\circ = -2 \times 96000(2 - 300 \times -5 \times 10^{-4})$

$\Delta_r H^\circ = -2 \times 96000(2 + 300 \times 5 \times 10^{-4})$

$= -2 \times 96000(2 + 0.15)$

$= -412.8 \times 10^3$ J/mol; $= -412.8$ kJ/mol

61. **(a)** $Zn + 2Ag^+ \longrightarrow 2Ag + Zn^{2+}$ $(n = 2e^-)$

$E^\circ_{cell} = (E^\circ_{R.P.})_{cathode} - (E^\circ_{R.P.})_{anode}$

$= 0.80 - (-0.76) = 1.56$ V for $2e^-$

$$\therefore E^\circ_{cell}\text{ for }1e^- = \frac{1.56}{2} = 0.78\text{ V}$$

62. **(c)** $E^0_{cell} = \frac{2.303RT}{nF}\log K_C$ or $E^0_{cell} = \frac{0.059V}{n}\log K_C$

$$= \frac{0.059V}{2}\log 10^{16} = 0.4736\,V$$

63. **(d)** Given that:

$Pt(s)\,|\,H_2(g, 1\text{ bar}) / HCl(aq)\,||\,AgCl(s) / Ag(s)\,|\,Pt(s)$

$E_{cell} = 0.92\,V$

Now, $E_{cell} = E^\circ_{H_2(g)/H^+(aq)} + E^\circ_{AgCl(s)/Ag(s),Cl^-} - \frac{0.06}{n}\log Q$

Cell reaction: $\frac{1}{2}H_2(g) \longrightarrow H^+(aq) + e^-$

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

Net cell reaction:

$$\frac{1}{2}H_2(g) + AgCl(s) \longrightarrow Ag(s) + H^+ + Cl^-(aq)$$

$$\therefore\ Q = \frac{[H^+][Cl^-]}{(P_{H_2})^{1/2}}$$

Here, 10^{-6} molal HCl solution is used

$$\text{So } Q = \frac{10^{-6} \times 10^{-6}}{1} = 10^{-12}$$

(assuming molality = molarity)

$$\text{Now, } 0.92 = E^\circ_{AgCl(s)/Ag(s),Cl^-} - \frac{0.06}{1}\log 10^{-12}$$

$$E^\circ_{AgCl(s)/Ag(s),Cl^-} = 0.92 + [0.06 \times (-12)]$$

$$= 0.92 - 0.72 = 0.20\,V$$

64. **(d)** We know that,

$$\ln K = \frac{nFE^\circ_{cell}}{RT}$$

$\Delta G = -nF\,E^\circ_{cell}$

$\Delta G = -RT\ln k$

Now,

After putting the given values, we get

$$\ln K = \frac{2 \times 96000 \times 2}{8 \times 300} = 160$$

$$\therefore\ K = e^{160}$$

65. **(a)** $\Delta G^\circ = -nFE^\circ$

(i) $Fe^{2+} + 2e^- \longrightarrow Fe;\quad E^0 = -0.47V;$

(ii) $\underline{Fe^{3+} + e^- \longrightarrow Fe^{2+}};\ E^0 = +0.77V;$

(iii) $Fe^{3+} + 3e^- \longrightarrow Fe$

(i) $\Delta G^0 = -nFE^0 = -2(-0.47)F = 0.94F$

(ii) $\underline{\Delta G^0 = -nFE^0 = -1(+0.77)F = -0.77F}$

(iii) On adding : $\Delta G^0 = +0.17\,F$

$$\Delta G^0 = -nFE^0$$

$$E^0 \text{ for } (Fe^{3+} \longrightarrow Fe) = \frac{\Delta G^0}{-nF} = \frac{0.17F}{-3F} = -0.057V$$

66. **(b)** Cell reaction :

$$M + 3Ag^+(aq) \longrightarrow M^{3+} + 3Ag(s)$$

$$E = E^0 - \frac{0.0591}{n}\log\frac{[\text{Reduced state}]}{[\text{Oxidised state}]}$$

$$0.421 = E^0 - \frac{0.0591}{3}\log\frac{0.001}{(0.01)^3}$$

$E^0 = 0.48$

$E^0 = E^0_{Ag^+/Ag} - E^0_{M^{3+}/M}$

$E^0_{M^{3+}/M} = 0.8V - 0.48V = 0.32$ volt

67. **(b)** $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

$$E = 1.51 - \frac{0.059}{5}\log\frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}$$

Taking Mn^{2+} and MnO_4^- in standard state i.e. 1 M,

$$E = 1.51 - \frac{0.059}{5} \times 8\log\frac{1}{[H^+]}$$

$$= 1.51 - \frac{0.059}{5} \times 8 \times 3 = 1.2268\,V$$

Hence at this pH, MnO_4^- will oxidise only Br^- and I^- as SRP of Cl_2/Cl^- is 1.36 V which is greater than that for MnO_4^-/Mn^{2+}.

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

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

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

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

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

(–ve value of EMF (i.e. $\Delta G = +ve$) shows that the reaction is non-spontaneous)

69. **(d)** Higher the value of standard reduction potential, stronger is the oxidising agent, hence MnO_4^- is the strongest oxidising agent.

70. **(b)** $Cu^{2+} + e^- \longrightarrow Cu^+$; $E_1^\circ = 0.15V; \Delta G_1^\circ = -n_1E_1^\circ F$

$Cu^{2+} + 2e \longrightarrow Cu$; $E_2^\circ = 0.34V; \Delta G_2^\circ = -n_2E_2^\circ F$

On subracting eq.(i) from eq. (ii) we get

$$Cu^+ + e^- \longrightarrow Cu \;;\quad \Delta G^\circ = \Delta G_2^\circ - \Delta G_1^\circ$$

$$-nE^\circ F = -(n_2E_2^\circ F - n_1E_1^\circ F)$$

$$E^\circ = \frac{n_2E_2^\circ F - n_1E_1^\circ F}{nF}$$

$$= \frac{2\times 0.34 - 0.15}{1} = 0.53\text{V}$$

71. **(c)** $\frac{2}{3}Al_2O_3 \rightarrow \frac{4}{3}Al + O_2$

The ionic reactions are

$$\frac{2}{3}\times(2Al^{3+}) + 4e^- \rightarrow \frac{4}{3}Al$$
$$\frac{2}{3}\times(3O^{2-}) \rightarrow O_2 + 4e^-$$

Thus, no. of electron transferred ⇒ n = 4

$\Delta G = -nFE$

or $E = \frac{\Delta G}{-nF} = \frac{966\times 10^3}{4\times 96500} = -2.5\text{ V}$

∴ The potential difference needed for the reduction = 2.5 V.

72. **(b)** Given

$Fe^{3+} + 3e^- \rightarrow Fe$,

$E^\circ_{Fe^{3+}/Fe} = -0.036\text{V}$ ...(i)

$Fe^{2+} + 2e^- \rightarrow Fe$,

$E^\circ_{Fe^{2+}/Fe} = -0.439\text{V}$ ...(ii)

we have to calculate

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

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

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

As we know that $\Delta G^\circ = -nFE^\circ$

Thus for reaction (iii)

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

$$-nFE_3^\circ = -nFE_1^\circ - (-nFE_2^\circ)$$
$$-nFE_3^\circ = nFE_2^\circ - nFE_1^\circ$$
$$-1FE_3^\circ = 2\times 0.439F - 3\times 0.036\,F$$
$$-1FE_3^\circ = 0.770\,F$$
$$\therefore\; E_3^\circ = -0.770\text{V}$$

73. **(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.]

$$= -0.42 - (-0.72) - \frac{0.059}{6}\log\frac{(0.1)^2}{(0.01)^3}$$
$$= -0.42 + 0.72 - \frac{0.059}{6}\log\frac{0.1\times 0.1}{0.01\times 0.01\times 0.01}$$
$$= 0.3 - \frac{0.059}{6}\log\frac{10^{-2}}{10^{-6}} = 0.3 - \frac{0.059}{6}\times 4$$
$$= 0.30 - 0.0393 = 0.26\text{ V}$$

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

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

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

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

$$\therefore\; \left(\frac{[Zn^{2+}]}{[Cu^{2+}]}\right) = 10^{37.3}$$

75. **(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 $\Delta G = -nFE^\circ_{cell}$.

E°_{cell} must be +ve to have ΔG –ve.

76. **(a)** $E_{cell} = E^\circ_{cell} - \frac{0.059}{n}\log K_c$

$$\text{or } 0 = 0.591 - \frac{0.0591}{1}\log K_c$$

$$\text{or } \log K_c = \frac{0.591}{0.0591} = 10 \text{ or } K_c = 1\times 10^{10}$$

77. **(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 thus the equilibrium shifts towards RHS.

78. **(c)** The equilibrium constant is related to the standard emf of cell by the expression

$$\log K = E^o{}_{cell} \times \frac{n}{0.059} = 0.295 \times \frac{2}{0.059}$$

$$\log K = \frac{590}{59} = 10 \text{ or } K = 1 \times 10^{10}$$

79. **(b)** $E_{cell} = E^\circ_{cell} + \frac{0.059}{n}\log\frac{[Cu^{2+}]}{[Zn^{2+}]}$

$$= 1.10 + \frac{0.059}{2}\log[0.1]$$

$$= 1.10 - 0.0295 = 1.07\,V$$

80. **(c)** E_{cell} = Reduction potential of cathode (right) – reduction potential of anode (left)

$$= E_{right} - E_{left}$$

81. **(d)** Oxidation half call:-

$$\underset{P_1}{H_2(g)} \longrightarrow 2H^+(1M) + 2e^-$$

Reduction half cell

$$2H^+(1M) + 2e^- \longrightarrow \underset{P_2}{H_2(g)}$$

The net cell reaction

$$\underset{P_1}{H_2(g)} \longrightarrow \underset{P_2}{H_2(g)}$$

$$E^o{}_{cell} = 0.00\,V;\ n = 2$$

$$\therefore\ E_{cell} = E^o{}_{cell} - \frac{RT}{nF}\log_e K$$

$$= 0 - \frac{RT}{nF}\log_e\frac{P_2}{P_1}$$

$$\text{or } E_{cell} = \frac{RT}{2F}\log_e\frac{P_1}{P_2}$$

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

83. **(c)** Corrosion of iron can be minimized by forming an impermeable barrier at its surface.

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

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

$$= -394.4 + 2(-237.2) - (-166.2) - 0$$

$$= -394.4 - 474.4 + 166.2 = -702.6\,kJ$$

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

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