CHAPTER

8

Electrochemistry

EXERCISE I (JEE MAIN)

Electrode Potential

1. A metal rod is dipped in a solution of its ions. Its electrode potential is independent of

(a) temperature of the solution

(b) concentration of the solution

(c) area of the metal exposed

(d) nature of the metal

2. Indicator electrode is

(a) SHE

(b) Calomel electrode

(c) Ag/AgCl electrode

(d) Quinhydrone electrode

3. The position of some metals in the electrochemical series in decreasing electropositive character is given as: Mg > Al > Zn > Cu > Ag. What will happen if a copper spoon is used to stir a solution of aluminium nitrate?

(a) The spoon will get coated with aluminium.

(b) An alloy of copper and aluminium is formed.

(c) The solution becomes blue.

(d) No chemical change will take place.

4. Four colourless salt solutions are placed in separate test tubes and a strip of copper is placed in each. Which solution finally turns blue?

(a) $AgNO_3$ (b) $Pb(NO_3)_2$

(c) $Zn(NO_3)_2$ (d) $Cd(NO_3)_2$

5. The metal that cannot be obtained on reduction of its oxide by aluminium is

(a) K (b) Mn

(c) Cr (d) Fe

6. Beryllium is placed above magnesium in the group II. Beryllium dust, therefore, when added to $MgCl_2$ solution will

(a) have no effect

(b) precipitate Mg metal

(c) precipitate MgO

(d) lead to dissolution of Be metal

7. A standard hydrogen electrode has zero electrode potential because

(a) hydrogen is easiest to oxidize

(b) this electrode potential is assumed to be zero

(c) hydrogen atom has only one electron

(d) hydrogen is the lightest element

8. The standard reduction potential values of three metallic cations, X, Y and Z are +0.52, –3.03 and –1.18 V, respectively. The order of reducing power of the corresponding metals is

(a) Y > Z > X

(b) X > Y > Z

(c) Z > Y > X

(d) Z > X > Y

9. A 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 reduction potential of $Z^- > Y^- > X$, then,

(a) Y^- will oxidize X and not Z^-
(b) Y^- will oxidize Z^- and not X
(c) Y^- will oxidize both X and Z^-
(d) Y^- will reduce both X and Z^-

10. 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:

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

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

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

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

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

(a) MnO_4^- can be used in aqueous HCl
(b) $Cr_2O_7^{2-}$ can be used in aqueous HCl
(c) MnO_4^- can be used in aqueous H_2SO_4
(d) $Cr_2O_7^{2-}$ can be used in aqueous H_2SO_4

11. The decreasing order of standard electrode potential of Mg, K, Ba and Ca, is

(a) K, Ca, Ba, Mg (b) Ba, Ca, K, Mg
(c) Ca, Mg, K, Ba (d) Mg, Ca, Ba, K

12. A metal having negative reduction potential, when dipped in the solution of its own ions, has a tendency to

(a) remain as metal atoms
(b) become electrically positive
(c) become electrically negative
(d) be deposited from the solution

13. The calomel electrode is reversible with respect to

(a) Hg_2^{2+} (b) H^+
(c) Hg^{2+} (d) Cl^-

14. Which one of the following does not get oxidized by bromine water?

(a) Fe^{2+} to Fe^{3+} (b) Cu^+ to Cu^{2+}
(c) Mn^{2+} to MnO_4^- (d) Sn^{2+} to Sn^{4+}

15. In salt bridge, normally KCl is used because

(a) it is a strong electrolyte.
(b) it is good conductor of electricity.
(c) K^+ and Cl^- ions have nearly same ionic mobility.
(d) it is an ionic compound.

16. By how much would the oxidizing power of MnO_4^-/Mn^{2+} couple change if the H^+ ions concentration is decreased 100 times at 25°C?

(a) increases by 189 mV
(b) decreases by 189 mV
(c) will increase by 19 mV
(d) will decrease by 19 mV

17. The solution of $CuSO_4$, in which copper rod is immersed, is diluted to 10 times. The reduction electrode potential

(a) increases by 0.0295 V
(b) decreases by 0.0295 V
(c) increases by 0.059 V
(d) decreases by 0.059 V

18. The standard reduction potential of oxygen in acidic solution is +1.23 V. What is the standard reduction potential of oxygen in basic solution?

(a) +0.404 V (b) −0.404 V
(c) +2.056 V (d) −2.056 V

19. 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

(a) 0.184 V (b) 0.827 V
(c) 0.521 V (d) 0.490 V

20. The electrode potential of hydrogen electrode in neutral solution and 298 K is

(a) −0.413 V (b) zero
(c) −0.826 V (d) +0.413 V

21. Electrode potential will be more for hydrogen electrode at pH (at the same temperature)

(a) 4 (b) 3 (c) 2 (d) 5

22. Saturated solution of KNO_3 is used to make 'salt bridge' because

(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

23. The standard reduction potentials of Pt|$Cr_2O_7^{2-}$, Cr^{+3}; Pt|MnO_4^-, Mn^{+2}; Pt|Ce^{+4}, Ce^{+3} in the presence of acid are 1.33 V, 1.51 V and 1.61 V, respectively, at 25°C. The decreasing order of oxidizing power is

(a) $Cr_2O_7^{2-} > MnO_4^- > Ce^{+4}$
(b) $MnO_4^- > Cr_2O_7^{2-} > Ce^{+4}$
(c) $Ce^{+4} > MnO_4^- > Cr_2O_7^{2-}$
(d) $MnO_4^- > Ce^{+4} > Cr_2O_7^{2-}$

24. The standard reduction potentials at 25°C of Li^+|Li, Ba^{2+}|Ba, Na^+|Na and Mg^{2+}|Mg are −3.05, −2.73, −2.71 and −2.37 V, respectively. Which is the strongest reducing agent?

(a) Li (b) Ba
(c) Na (d) Mg

25. Some standard electrode potentials are given:

$Fe^{2+} + 2e^- \rightarrow Fe;\ E° = -0.440$ V
$Fe^{3+} + 3e^- \rightarrow Fe;\ E° = -0.036$ V

The standard electrode potential for: $Fe^{3+} + e^- \rightarrow Fe^{2+}$, is

(a) −0.476 V (b) −0.404 V
(c) +0.988 V (d) +0.772 V

26. The dissociation constant for CH_3COOH is 1.8×10^{-5} at 298 K. The electrode potential for the half-cell: Pt | H_2 (1 bar) | 0.5 M – CH_3COOH, at 298 K is (log 2 = 0.3; log 3 = 0.48; 2.303 *RT*/*F* = 0.06)

(a) −0.3024 V (b) −0.1512 V
(c) +0.3024 V (d) +0.1512 V

27. At 25°C, the solubility product of CuCl is 2.0×10^{-7} and $E^\circ_{Cl^- \mid CuCl \mid Cu}$ is 0.128 V. The value of $E^\circ_{Cu^+|Cu}$ is (log 2 = 0.3; 2.303 *RT*/*F* = 0.06)

(a) +1.08 V (b) +0.53 V
(c) +1.682 V (d) +0.878 V

28. At 25°C, the solubility product of $Pb(OH)_2$ (s) is [Given: $E^\circ_{Pb^{2+}|Pb} = -0.13$ V; $E^\circ_{OH^-|Pb(OH)_2|Pb} = -0.55$ V and $\frac{2.303\ RT}{F} = 0.06$]

(a) 1.36×10^{-5} (b) 1.0×10^{-7}
(c) 1.0×10^{-14} (d) 1.25×10^{-15}

29. The standard potentials of MnO_4^- | Mn^{2+} and MnO_2 | Mn^{2+} electrodes in acid solution are 1.51 and 1.23 V, respectively. Standard electrode potential for the electrode, MnO_4^-| MnO_2 in acid solution is

(a) +1.697 V (b) +5.09 V
(c) +0.28 V (d) +1.37 V

30. The following reactions represent the reduction of IO_3^- ion into I^- ion in acidic and basic medium. Predict in which medium IO_3^- ion will act as a better oxidizing agent?

$IO_3^- + 6H^+ + 6e^- \rightarrow I^- + 3H_2O;\ E° = +0.907$ V
$IO_3^- + 3H_2O + 6e^- \rightarrow I^- + 6OH^-;\ E° = +0.260$ V

(a) Acid medium (b) Basic medium
(c) Equally in both (d) Not predictable

Galvanic Cell

31. The correct cell diagram for the following reaction and *E*° for the cell is

$2AgBr(s) + H_2(g) \rightarrow 2Ag(s) + 2H^+ + 2Br^-$
$E°_{AgBr|Ag|Br-} = +0.10$ V.

(a) (Pt) H_2 | H^+ || Br^- | AgBr | Br_2 (Pt); *E*° = 0.10 V
(b) (Pt) H_2 | H^+ || Br^- | AgBr | Br_2 (Pt); *E*° = −0.10 V
(c) (Pt) Br_2 | AgBr | Br^- || H^+ | H_2 (Pt); *E*° = 0.10 V
(d) (Pt) Br_2 | AgBr | Br^- || H^+ | H_2 (Pt); *E*° = −0.10 V

32. In an experimental set-up for the measurement of EMF of a half-cell using a reference electrode and a salt bridge, when the salt bridge is removed, the voltage

(a) remains the same
(b) increases to maximum
(c) decreases half the value
(d) drops to zero

33. After some time, the voltage of an electrochemical cell becomes zero. This is because

(a) their electrode potential becomes zero.
(b) their reduction potential become equal but have opposite sign.
(c) their reduction potential become equal and have the same sign.
(d) the ions of the electrolyte in the salt bridge stop moving.

34. The cell reaction for the given cell is spontaneous if Pt, Cl_2 (P_1 atm) | Cl^- | Cl_2 (P_2 atm), Pt

(a) $P_1 > P_2$ (b) $P_1 < P_2$
(c) $P_1 = P_2$ (d) $P_1 = 1$ atm

35. Which one of the following statements is incorrect regarding an electrochemical cell?

(a) The electrode on which oxidation takes place is called anode.
(b) Anode is the negative pole.
(c) The direction of the current is same as that of the direction of flow of electrons.
(d) The flow of current is partly due to flow of electrons and partly due to flow of ions.

36. When an electric current is drawn from a galvanic cell

(a) EMF suddenly increases.
(b) EMF gradually increases and attains a maximum value.
(c) EMF decreases and finally falls to zero.
(d) EMF must remain constant.

37. Identification of anode and cathode in an electrochemical cell is made by the use of

(a) Galvanometer (b) Salt bridge
(c) Voltmeter (d) Potentiometer

38. For the cell Zn | Zn^{2+} || Cu^{2+} | Cu, if the concentration of both, Zn^{2+} and Cu^{2+} ions are doubled, the EMF of the cell

(a) doubles (b) reduces to half
(c) remains same (d) becomes zero

39. The standard EMF of a galvanic cell can be calculated from

(a) the size of the electrode
(b) the pH of the solution
(c) the amount of metal in the anode
(d) the $E°$ values of the half-cells

40. The value of equilibrium constant for a feasible cell reaction must be

(a) <1 (b) Zero
(c) = 1 (d) >1

41. If the cell reaction is spontaneous then

(a) $\Delta G° = -$ve (b) $E°_{red} = -$ve
(c) $E°_{red} = +$ve (d) $\Delta G = -$ve

42. Which of the following pair of metals, when coupled, will give maximum EMF for a voltaic cell?

(a) Fe and Cu (b) Pb and Au
(c) Cu and Au (d) Ca and Cu

43. When a lead storage battery is charged

(a) PbO_2 dissolves.
(b) the lead electrode becomes coated with lead sulphate.
(c) sulphuric acid is regenerated.
(d) the amount of acid decreases.

44. Use of lithium metal as an electrode in high energy density batteries is due to

(a) lithium is the lightest element.
(b) lithium has the highest oxidation potential.
(c) lithium is quite reactive.
(d) lithium does not corrode readily.

45. A depolarizer used in dry cell batteries is

(a) NH_4Cl (b) MnO_2
(c) KOH (d) Na_3PO_4

46. Which is correct about fuel cells?

(a) Cell continuously run as long as fuels are supplied.
(b) These are more efficient and free from pollution.
(c) These are used to provide power and drinking water to astronauts in space programme.
(d) All of these

47. When a lead storage battery is discharged

(a) SO_2 is evolved
(b) lead sulphate is consumed
(c) lead is formed
(d) sulphuric acid is consumed

48. For a cell reaction involving a two-electron change, the standard EMF of the cell is found to be 0.295 V at 25°C. The equilibrium constant of the reaction at 25°C will be

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

49. The E_{Cell} for Ag(s) | AgI (satd) || Ag^+ (0.10 M) | Ag (s) is +0.413 V. What is the value of K_{sp} of AgI?

(a) 1.0×10^{-8} (b) 1.0×10^{-7}
(c) 1.0×10^{-14} (d) 1.0×10^{-16}

50. Assuming that hydrogen behaves as an ideal gas, what is the EMF of the cell at 25°C if $P_1 = 600$ mm and $P_2 = 420$ mm: Pt | H_2 (P_1) | HCl | H_2 (P_2) | Pt? [Given: 2.303 $RT/F = 0.06$, log 7 = 0.85]

(a) −0.0045 V (b) −0.0 V
(c) +0.0045 V (d) +0.0015 V

51. For the electrochemical cell, M | M^+ || X^- | X, $E^\circ_{M^+|M} = 0.44$ V and $E^\circ_{X|X^-} = 0.33$ V. From this data, one can deduce that

(a) $M + X \rightarrow M^+ + X^-$ is the spontaneous reaction
(b) $M^+ + X^- \rightarrow M + X$ is the spontaneous reaction
(c) $E_{cell} = 0.77$ V
(d) $E_{cell} = -0.77$ V

52. The EMF of the cell: Zn | Zn^{2+} (0.01 M) || Fe^{2+} (0.001 M) | Fe at 298 K is 0.2905 V, then the value of equilibrium constant for the cell reaction is

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

53. For the cell reaction: $4Br^- + O_2 + 4H^+ \rightleftharpoons 2Br_2 + 2H_2O$; $E^\circ = 0.18$ V. The value of (log K_C) at 298 K is [2.303 $RT/F = 0.06$]

(a) 12 (b) 6
(c) 18 (d) 3

54. The standard EMF for the cell reaction: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ is 1.10 volts at 25°C. The EMF of the cell reaction when 0.1 M Cu^{2+} and 0.1 M Zn^{2+} solutions are used at 25°C is

(a) 1.10 V (b) 1.041 V
(c) −1.10 V (d) −1.041 V

55. For the cell: Ni | Ni^{2+} || Cu^{2+} | Cu; $E^\circ = 0.77$ V. By which of the following activity, E_{cell} will increase?

(a) On decreasing $[Ni^{+2}]$
(b) On decreasing $[Cu^{+2}]$
(c) On increasing mass of Ni electrode
(d) On increasing mass of Cu electrode

56. The standard EMF of a Daniel cell at 298 K is E_1. When the concentration of $ZnSO_4$ is 1.0 M and that of $CuSO_4$ is 0.01 M, the EMF becomes E_2 at 298 K. The correct relationship between E_1 and E_2 is

(a) $E_1 = E_2$ (b) $E_2 = 0$
(c) $E_1 > E_2$ (d) $E_1 < E_2$

57. For a reaction $A(s) + 2B^+ \rightarrow A^{2+} + B(s)$; K_C has been found to be 10^{12}. The EMF of the cell is

(a) 0.354 V (b) 0.708 V
(c) 0.534 V (d) 0.453 V

58. An electrochemical cell is set up as follows:

Pt | H_2(g) (1 atm) | 0.001 M HCl || 0.1 M HA | H_2(g) (1 atm) | Pt

EMF of this cell is zero because (pK_a of HA = 5)

(a) molar concentrations of acids are different
(b) Temperature is constant
(c) pH of two solutions are same
(d) both are standard hydrogen electrodes

59. The reaction: $H_2(g) + 2AgCl(s) \rightarrow 2H^+(aq) + 2Cl^-(aq) + 2Ag(s)$ occurs in the galvanic cell

(a) Ag | AgCl (s) | KCl(aq) | $AgNO_3$(aq) | Ag
(b) Pt | H_2(g) | HCl(aq) | $AgNO_3$(aq) | Ag
(c) Pt | H_2(g) | HCl(aq) | AgCl(s) | Ag
(d) Pt | H_2(g) | KCl(aq) | AgCl(s) | Ag

60. The standard reduction potentials in acidic conditions are 0.77 V and 0.53 V, respectively, for Fe^{3+} | Fe^{2+} and I_3^- | I^- couples. The equilibrium constant for the reaction: $2Fe^{3+} + 3I^- \rightleftharpoons 2Fe^{2+} + I_3^-$, is (2.303 $RT/F = 0.06$)

(a) 2×10^8 (b) 10^8
(c) 10^4 (d) 10^{-8}

61. The following electrochemical cell has been set up: Pt(s)|Fe^{3+}, Fe^{2+} (a = 1) || Ce^{4+}, Ce^{3+} (a = 1) | Pt(s); $E^\circ(Fe^{3+}|Fe^{2+}) = 0.77$ V; E° $(Ce^{4+}|Ce^{3+}) = 1.61$ V. If an ammeter is connected between the two platinum electrodes, predict the direction of flow of current. Will the current increase or decrease with time?

(a) Ce electrode to Fe electrode, decrease
(b) Ce electrode to Fe electrode, increase
(c) Fe electrode to Ce electrode, decrease
(d) Fe electrode to Ce electrode, increase

62. For the reaction: H_2 (1 bar) + 2AgCl(s) $\rightleftharpoons$ 2Ag(s) + $2H^+$ (0.1 M) + $2Cl^-$ (0.1 M); $\Delta G^0 = -48{,}250$ J at 25°C. The EMF of cell in which the given reaction takes place is

(a) 0.25 V (b) 0.37 V
(c) 0.13 V (d) 0.0.49 V

63. 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. The concentration of hydrogen ions at the positive electrode is

(a) 10^{-6} M (b) 10^{-3} M
(c) 10^{-4} M (d) 10^{-5} M

64. The standard potentials of OCl^-/Cl^- and Cl^-/Cl_2 are 0.94 V and −1.36 V, respectively. The *E*° value of OCl^-/Cl_2 will be

(a) 3.24 V (b) −0.42 V
(c) −2.30 V (d) 0.52 V

65. From the following *E*° values for the half-cells:

(i) $D \rightarrow D^{2+} + 2e^-;\ E° = -1.5$ V
(ii) $B^+ + e^- \rightarrow B;\ E° = -0.5$ V
(iii) $A^{3-} \rightarrow A^{2-} + e^-;\ E° = 1.5$ V
(iv) $C^{2+} + e^- \rightarrow C^+;\ E° = +0.5$ V

Which combination of two half-cells would result in a cell with largest potential?

(a) i and iii (b) i and iv
(c) iii and iv (d) ii and iv

Electrolysis

66. Which of the following statements does not differentiate between electrochemical cell and electrolytic cell?

(a) Spontaneous or non-spontaneous nature of the chemical process.
(b) Chemical reactions occurring at the electrodes
(c) Positive and negative nature of anode.
(d) EMF measurement.

67. The electrode through which electrons enter the electrolytic solution is

(a) cathode
(b) anode
(c) may be anode or cathode
(d) both, anode and cathode

68. Which process occurs in the electrolysis of an aqueous solution of nickel chloride at nickel anode?

(a) $Ni \rightarrow Ni^{2+} + 2e^-$ (b) $Ni^{2+} + 2e^- \rightarrow Ni$
(c) $2Cl^- \rightarrow Cl_2 + 2e^-$ (d) $2H^+ + 2e^- \rightarrow H_2$

69. If mercury is used as a cathode during the electrolysis of an aqueous NaCl solution, the ions discharged at cathode are

(a) H^+ (b) Na^+
(c) OH^- (d) Cl^-

70. Electrochemical equivalent is more for

(a) Hydrogen (b) Silver
(c) Copper (d) Zinc

71. The electrolytic bath used in gold plating of copper articles contains

(a) Molten gold
(b) Copper sulphate(aq)
(c) $AuCl_3$(aq)
(d) $AuCl_3$ + NaCN(aq)

72. Copper can be deposited from acidified copper sulphate and alkaline cuprous cyanide. If the same current is passed for a definite time

(a) the amount of copper deposited from acidic copper sulphate will be higher
(b) the amount of copper deposited from alkaline cuprous cyanide will be higher
(c) the same amount of copper will be deposited
(d) copper will not deposit in either case

73. In the electrolytic cell, flow of electrons is from

(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

74. Electrolytic cell is used to convert

(a) Chemical energy to electrical energy
(b) Electrical energy to chemical energy
(c) Chemical energy to mechanical energy
(d) Electrical energy to mechanical energy

75. Faraday's law of electrolysis fails when

(a) temperature is increased
(b) inert electrodes are used
(c) a mixture of electrolytes is used
(d) in none of these cases

76. Using same quantity of current, which among Na, Mg and Al is deposited more (by mass) during electrolysis of their molten salts?

(a) Na (b) Mg
(c) Al (d) All in same

77. A certain current liberated 0.50 g of hydrogen in 2 h. How many grams of copper can be liberated by the same current flowing for the same time in a copper sulphate solution? (Cu = 63.5)

(a) 12.7 g (b) 15.88 g
(c) 31.75 g (d) 63.5 g

78. A current of 3.7 A is passed for 6 h between nickel electrodes in 0.50 L of 2 M solution of $Ni(NO_3)_2$. The molarity of Ni^{2+} at the end of electrolysis is

(a) 1.172 M (b) 0.172 M
(c) 0.586 M (d) 2 M

79. The current efficiency of an electrodeposition of copper metal in which 9.8 g of copper is deposited by a current of 3 A for 10000 s, from aqueous copper sulphate solution, is about

(a) 60% (b) 99%
(c) 92% (d) 75%

80. On passing electricity through dilute H_2SO_4 solution, the mass of substances liberated at the cathode and anode are in the ratio of

(a) 1:8 (b) 8:1
(c) 1:32 (d) 1:16

81. The electrochemical equivalents of two substances are E_1 and E_2. The current that must pass to deposit the same amount at the cathodes in the same time must be in the ratio of

(a) $E_1:E_2$ (b) $E_2:E_1$
(c) $(E_1 - E_2):E_2$ (d) $E_1:(E_2 - E_1)$

82. The same quantity of electricity is passed through one molar solution of H_2SO_4 and one molar solution of HCl. The amount of hydrogen evolved from H_2SO_4 as compared to that from HCl is

(a) the same
(b) twice as such
(c) one half as such
(d) dependent on size of electrode

83. In the electrolysis of acidified $AgNO_3$ solution using Pt-electrodes, the anode reaction is

(a) $2NO_3^- \rightarrow 2NO_2 + O_2 + 2e^-$
(b) $NO_3^- \rightarrow NO + \frac{1}{2}O_2 + e^-$
(c) $2H_2O \rightarrow 4H^+ + O_2 + 4e^-$
(d) $Pt \rightarrow Pt^{3+} + 3e^-$

84. Two platinum electrodes were immersed in a solution of $CuSO_4$ and electric current was passed through the solution. After some time, it was found that colour of $CuSO_4$ disappeared with the evolution of gas at the electrode. The colourless solution contains

(a) platinum sulphate
(b) copper sulphate
(c) copper hydroxide
(d) sulphuric acid

85. A solution containing 1.0 M each of $Cu(NO_3)_2$, $Mg(NO_3)_2$, $AgNO_3$, $Hg(NO_3)_2$ is being electrolysed using inert electrodes. The values of standard electrode potential are: $Ag^+ | Ag = 0.80$ V, $Hg^{2+} | Hg = 0.79$ V, $Cu^{2+} | Cu = 0.34$ V, $Mg^{2+} | Mg = -2.37$ V. With increasing voltage, the sequence of deposit of metals on the cathode will be

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

86. During the electrolysis of an aqueous salt solution, the pH in the space near one of the electrode was increased and the other one was decreased. The salt solution was

(a) NaCl (very dilute) (b) $ZnCl_2$
(c) NaCl (Conc.) (d) $Cu(NO_3)_2$

87. Two electrolytic cells, one containing acidified ferrous chloride and another acidified ferric chloride, are connected in series. The mass ratio of iron deposited at cathodes in the two cells will be

(a) 3:1 (b) 2:3
(c) 1:1 (d) 3:2

88. A galvanic cell is set up from a zinc bar weighing 100 g and 1.0 L of 1.0 M copper sulphate solution. How long would the cell run if it is assumed to deliver a steady current of 1.0 A? (Zn = 65.4)

(a) 53.6 h (b) 26.8 h
(c) 81.97 h (d) 40.99 h

89. An ion is a reduced to the element when it absorbs 6×10^{20} electrons. The number of equivalents of the ion is

(a) 0.10 (b) 0.01
(c) 0.001 (d) 0.0001

90. In the lead storage battery, the anode reaction is $Pb(s) + HSO_4^- + H_2O \rightarrow PbSO_4(s) + H_3O^+ + 2e^-$. How many grams of Pb will be used up to deliver 1 A for 100 h? (Pb = 208)

(a) 776 g (b) 388 g
(c) 194 g (d) 0.1 g

91. The copper anode of a cell containing silver nitrate solution weighs 60.0 g. After passing current for some time, it is found that 3.24 g of silver if deposited on the platinum cathode. What is the final weight of the anode? (Ag = 108, Cu = 64)

(a) 0.96 g (b) 60 g
(c) 59.04 g (d) 60.96 g

92. The quantity of electricity required for the reduction of 1 mole of Fe_2O_3 to Fe is

(a) 1F (b) 0.33F
(c) 3F (d) 6F

93. Three faradays of electricity is passed through molten Al_2O_3, aqueous solutions of $CuSO_4$ and molten NaCl. The amounts of Al, Cu and Na deposited at the cathodes will be in the molar ratio of

(a) 1:2:3 (b) 3:2:1
(c) 1:1.5:3 (d) 6:3:2

94. Electrolysis of a solution of HSO_4^- ions produces $S_2O_8^{2-}$. Assuming 75% current efficiency, what current should be employed to achieve a production rate of 1 mole of $S_2O_8^{2-}$ per hour?

(a) 71.5 A (b) 35.7 A
(c) 53.0 A (d) 143 A

95. The number of Faradays required to produce 1 g-atom of Mg from $MgCl_2$ is

(a) 1 (b) 2
(c) 0.5 (d) 4

96. Passage of 96,500 coulomb of electricity liberates ________ L of O_2 at 273°C and 2 atm during electrolysis.

(a) 5.6 (b) 16.8
(c) 22.4 (d) 11.2

97. An electrolytic cell contains a solution of Ag_2SO_4 and platinum electrodes. A current is passed until 1.6 g of O_2 has been liberated at anode. The amount of silver deposited at cathode would be

(a) 108.0 g (b) 1.6 g
(c) 10.8 g (d) 21.6 g

98. When 12,000 coulombs of electricity is passed through the electrolyte, 3.0 g of a metal of atomic mass 96.5 g/mol is deposited. The electro-valency of the metal cation in the electrolyte is

(a) +4 (b) +3
(c) +2 (d) –4

99. How many electrons flow when a current of 5 A is passed through a solution for 200 s?

(a) 6.022×10^{23} (b) 6.24×10^{21}
(c) 6.024×10^{21} (d) 6.022×10^{20}

100. The current of 9.65 A flowing for 10 min deposits 3.0 g of a metal. The equivalent weight of the metal is

(a) 10 (b) 30
(c) 50 (d) 96.5

101. If a current of 1.0 A is drawn from the Daniel cell for 96.5 min, the cathode will gain in weight by (Cu = 63.5, Zn = 65.4)

(a) 1.905 g (b) 1.962 g
(c) 3.81 g (d) 3.924 g

102. The current required to produce oxygen at the rate of 2.8 ml (0°C, 1 atm) per second during electrolysis of acidulated water is

(a) 48.25 A/s (b) 24.12 A/s
(c) 96.5 A/s (d) 0.0048 A/s

103. Sodium amalgam is prepared by electrolysis of aqueous NaCl using 10 g mercury as cathode. How many Faraday of electricity is required to prepare 18.7% Na-amalgam, by weight, with a current efficiency of 50%?

(a) 0.1 F (b) 0.2 F
(c) 0.05 F (d) 0.16 F

104. Element A (atomic mass = 112) and element B (atomic mass = 27) form chlorides. Solutions of these chlorides are electrolysed separately and it is found that when the same quantity of electricity is passed, 5.6 g of A was deposited while only 0.9 g of B was deposited. The valency of B is 3. The valency of A is

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

105. The same current was passed successively through solution of zinc–ammonium sulphate and nickel–ammonium sulphate rendered alkaline with ammonia. The weights of zinc and nickel deposited in a certain time were found to be 22.89 g and 20.55 g, respectively. Given that the chemical equivalent weight of zinc is 32.7, what is the chemical equivalent weight of nickel?

(a) 58.71 (b) 29.36
(c) 14.39 (d) 36.42

Conductance

106. Which of the following solutions have highest resistance?

(a) 1N – NaCl (b) 0.05N – NaCl
(c) 2N – NaCl (d) 0.1N – NaCl

107. Variation of molar conductance of an electrolytic solution with temperature is that it

(a) increases with increase of temperature
(b) decreases with increase of temperature
(c) first increases then decreases
(d) is not affected by temperature

108. Which pure substance will not conduct electricity?

(a) Molten NaCl (b) Molten KOH
(c) Liquefied HCl (d) Liquid Hg

109. The correct order of molar conductance at infinite dilution of LiCl, NaCl and KCl is

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

110. The molar conductance of a strong electrolyte at infinite dilution

(a) tends to a finite value, which is above that at higher concentration
(b) tends to a finite value, which is below that at higher concentration
(c) tends to zero
(d) tends to a finite value, which is equal to that at high concentration

111. The best conductor of electricity is a 0.1 M solution of

(a) Boric acid (b) Sulphuric acid
(c) Acetic acid (d) Propanoic acid

112. The specific conductance of AgCl solution in water was determined to be $1.8 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$ at 298 K. The molar conductances at infinite dilution, of Ag^+ and Cl^- are 67.9 and 82.1 $\Omega^{-1}\ cm^2\ mol^{-1}$, respectively. What is the solubility of AgCl in water?

(a) 1.2×10^{-8} M (b) 1.44×10^{-10} M
(c) 1.2×10^{-5} M (d) 1.44×10^{-16} M

113. Equivalence conductance at infinite dilution of NH_4Cl, NaOH and NaCl are 129.8, 217.4 and 108.9 $\Omega^{-1}\ cm^2\ mol^{-1}$, respectively. If the equivalent conductance of 0.01 N solution of NH_4OH is 9.532 $\Omega^{-1}\ cm^2\ mol^{-1}$, then the degree of dissociation of NH_4OH at this temperature is

(a) 0.04% (b) 2.1%
(c) 4.0% (d) 44.7%

114. The resistance of 1 M – CH_3COOH solution is 250 Ω, when measured in a cell of cell constant 125 m^{-1}. The molar conductivity, in $\Omega^{-1}\ m^2\ mol^{-1}$ is

(a) 5.0×10^{-4} (b) 500
(c) 2×10^{-3} (d) 200

115. How does the electrical conductivity of 20 ml of 0.2 M – $MgSO_4$ change when 0.5 M – $Ba(OH)_2$ solution is gradually added in it, to excess?

(a) decreases continuously
(b) increases continuously
(c) increases and then decreases
(d) decreases and then increases

116. The equivalent conductivity (in $\Omega^{-1}\ cm^2\ eq^{-1}$) of 1.0 M – H_2SO_4 solution of specific conductance $2.6 \times 10^{-1}\ cm^{-1}$, is

(a) 1.3×10^2 (b) 6.5×10^1
(c) 1.3×10^{-1} (d) 2.6×10^2

117. The molar conductance of a 0.01 M solution of acetic acid was found to be 16.30 $\Omega^{-1}\ cm^{-1}\ mol^{-1}$ at 25°C. The ionic conductances of hydrogen and acetate ions at infinite dilution are 349.8 and 40.9 $\Omega^{-1}\ cm^{-1}\ mol^{-1}$, respectively, at the same temperature. What percentage of acetic acid is dissociated at this concentration?

(a) 0.04172% (b) 4.172%
(c) 41.72% (d) 0.4172%

118. The distance between two electrodes of a cell is 2.5 cm and area of each electrode is 5 cm^2. The cell constant is

(a) 0.5 m^{-1} (b) 12.5 cm^3
(c) 2.0 cm (d) 50 m^{-1}

119. The molar conductivity of NH_4Cl, OH^- and Cl^- at infinite dilution is 150, 200 and 75 Ω^{-1} cm^2 mol^{-1}, respectively. If the molar conductivity of a 0.01 M–NH_4OH solution is 22 Ω^{-1} cm^2 mol^{-1}, then its degree of dissociation is

(a) 0.146 (b) 0.063
(c) 0.080 (d) 0.293

120. Calculate the ionic product of water at 25°C from the following data:

Conductivity of water = 5.5×10^{-6} mho m^{-1}
$\lambda°_{H^+} = 0.035$ mho m^2 mol^{-1}
$\lambda°_{OH^-} = 0.020$ mho m^2 mol^{-1}

(a) 2×10^{-14} M^2 (b) 1×10^{-7} M
(c) 1×10^{-8} M^2 (d) 1×10^{-14} M^2

121. Calculate K_a of acetic acid if its 0.05 M solution has molar conductivity of 7.814×10^{-4} Ω^{-1} m^2 mol^{-1} at 25°C. Given: Λ°_{m} for $CH_3COOH = 3.907 \times 10^{-2}$ Ω^{-1} m^2 mol^{-1}.

(a) 2×10^{-5} (b) 1.8×10^{-5}
(c) 4×10^{-4} (d) 0.02

122. Equal volumes of 0.015 M – CH_3COOH and 0.015 M – NaOH solutions are mixed together. What would be the molar conductivity of mixture if conductivity of CH_3COONa is 6.3×10^{-4} S cm^{-1}?

(a) 0.84 S cm^2 mol^{-1} (b) 8.4 S cm^2 mol^{-1}
(c) 84 S cm^2 mol^{-1} (d) 42 S cm^2 mol^{-1}

123. Calculate Λ^{∞}_{m} (in Ω^{-1} cm^2 mol^{-1}) for $SrCl_2$ at 25°C, from the following data:

Conc.	0.25 M	1.0 M
Λ_m (in Ω^{-1} cm^2 mol^{-1})	260	250

(a) 270 (b) 265
(c) 240 (d) 275

124. The resistance of a solution A is 50 Ω and that of solution B is 100 Ω, both solutions being taken in the same conductivity cell. If equal volumes of solution A and B are mixed, what will be the resistance of the mixture using the same cell? Assume that there is no increase in the degree of dissociation of A and B on mixing.

(a) 150 Ω (b) 75 Ω
(c) 33.33 Ω (d) 66.67 Ω

125. In a conductivity cell, the two platinum electrodes, each of area 10 cm^2 are fixed 1.5 cm apart. The cell contained 0.05 N solution of a salt. If the two electrodes are just half dipped into the solution which has a resistance of 50 Ω, the equivalent conductance of the salt solution, in Ω^{-1} cm^2 eq^{-1}, is

(a) 120 (b) 60
(c) 240 (d) 3000

EXERCISE II (JEE ADVANCED)

Section A (Only one Correct)

1. A student made the following observations in the laboratory:

(I) Clean copper metal did not react with 1 M – $Pb(NO_3)_2$ solution.

(II) Clean lead metal dissolves in 1 M – $AgNO_3$ solution and crystals of Ag metal appeared.

(III) Clean silver metal did not react with 1 M – $Cu(NO_3)_2$ solution.

The order of decreasing reducing character of the three metals is

(a) Cu > Pb > Ag (b) Cu > Ag > Pb
(c) Pb > Cu > Ag (d) Pb > Ag > Cu

2. We have an oxidation–reduction system: $[Fe(CN)_6]^{3-} + e^- \rightleftharpoons [Fe(CN)_6]^{4-}$; $E° = +0.36$ V. The ratio of concentrations of oxidized and reduced from at which the potential of the system becomes 0.24 V, is [Given: 2.303 $RT/F = 0.06$)

(a) 2:1 (b) 1:2
(c) 1:20 (d) 1:100

3. The standard reduction potential for the process: $[Co(H_2O)_6]^{3+} + e^- \rightarrow [Co(H_2O)_6]^{2+}$ is 1.8 V. The standard reduction potential for the process: $[Co(NH_3)_6]^{3+} + e^- \rightarrow [Co(NH_3)_6]^{2+}$ is 0.1 V. Which of the complex ion, $[Co(H_2O)_6]^{2+}$ or $[Co(NH_3)_6]^{2+}$ can be oxidized to the corresponding cobalt (III) complex, by oxygen, in basic medium, under standard condition? [Given: $E^{\circ}_{O_2|OH^-} = 0.4$ V]

(a) $[Co(H_2O)_6]^{2+}$ (b) $[Co(NH_3)_6]^{2+}$
(c) both (d) none of these

4. The standard reduction potential for the reactions: $Ag^+ + e^- \rightarrow Ag$ and $Ag(NH_3)_2^+ + e^- \rightarrow Ag + 2NH_3$ are +0.79 V and +0.37 V, respectively. From these values and the Nernst equation, what should be K_f for the $Ag(NH_3)_2^+$ ion? [Given: 2.303 $RT/F = 0.06$]

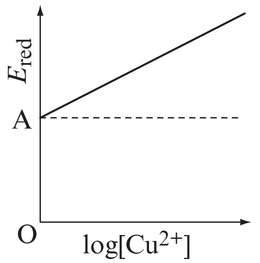
(a) 1.0×10^{-7} (b) 1.0×10^{7}
(c) 2.15×10^{19} (d) 4.64×10^{-20}

5. The overall formation constant for the reaction of 6 mole of CN^- with cobalt (II) is 1×10^{19}. What is the formation constant for the reaction of 6 moles of CN^- with cobalt (III)? Given that

$Co(CN)_6^{3-} + e^- \rightarrow Co(CN)_6^{4-}$; $E° = -0.83$ V
$Co^{3+} + e^- \rightarrow Co^{2+}$; $E° = +1.81$ V
and 2.303 $RT/F = 0.06$.

(a) 1.0×10^{63} (b) 1.0×10^{25}
(c) 1.0×10^{-25} (d) 1.0×10^{-63}

6. For the process: $Cu^{2+} + 2e^- \rightarrow Cu$; $\log[Cu^{2+}]$ vs. E_{red} graph is shown in the figure, where OA = 0.34 V. The electrode potential of the half-cell of $Cu|Cu^{2+}$ (0.1 M) will be [2.303 $RT/F = 0.06$]



(a) −0.31 V (b) +0.31 V
(c) −0.37 V (d) +0.37 V

7. Tell which of the following statements accurately describes the effect of adding CN^- to the cathode of a cell with a cell reaction: $Cd + 2Ag^+ \rightarrow 2Ag + Cd^{2+}$, $E° = 1.2$ V

(a) $E°$ increases because $Cd(CN)_4^{2-}$ forms
(b) $E°$ decreases because $Cd(CN)_4^{2-}$ forms
(c) $E°$ increases because $Ag(CN)_2^-$ forms
(d) $E°$ decreases because $Ag(CN)_2^-$ forms

8. For a electrochemical cell $Zn \mid Zn^{2+}$ (C_1 M) $\|$ Cu^{2+} (C_2 M) $\mid$ Cu, the decrease in free energy at a given temperature is a function of

(a) $\ln C_1$ (b) $\ln C_2$
(c) $\ln C_2 \cdot C_1$ (d) $\ln C_1/C_2$

9. Select the correct option if it is known that K_{sp} (AgCl) > K_{sp} (AgBr) > K_{sp} (AgI)

(a) $E^{\circ}_{I^-|AgI|Ag} > E^{\circ}_{Br^-|AgBr|Ag} > E^{\circ}_{Cl^-|AgCl|Ag}$

(b) $E^{\circ}_{I^-|AgI|Ag} < E^{\circ}_{Br^-|AgBr|Ag} < E^{\circ}_{Cl^-|AgCl|Ag}$

(c) $E^{\circ}_{I^-|AgI|Ag} < E^{\circ}_{Cl^-|AgCl|Ag} < E^{\circ}_{Br^-|AgBr|Ag}$

(d) $E^{\circ}_{I^-|AgI|Ag} = E^{\circ}_{Br^-|AgBr|Ag} = E^{\circ}_{Cl^-|AgCl|Ag}$

10. The EMF of a galvanic cell composed of two hydrogen electrodes is 272 mV. What is the pH of the solution in which the anode is immersed if the cathode is in contact with a solution of pH = 3?

(a) 3 (b) 6.7

(c) 7.6 (d) 1.6

11. At what pH does the potential (EMF) for the disproportionation of chlorine change from a negative value to a positive value, assuming 1.0 bar pressure and 1.0 M concentration for all species except hydrogen ion? Given:

$Cl_2 + 2e^- \rightarrow 2Cl^-$; $E^\circ = 1.36$ V

$2OCl^- + 4H^+ + 2e^- \rightarrow Cl_2 + 2H_2O$; $E^\circ = 1.63$ V.

[2.303 $RT/F = 0.06$]

(a) 4.5 (b) 1.5

(c) 2.25 (d) 9.0

12. The EMF of the cell: Hg(l) | Hg_2Cl_2(s), KCl sol. (1.0N) | Quinohydrone | Pt, is 0.210 V at 298 K. What is the pH of the quinohydrone solution, the potential of the normal calomel electrode is 0.279 V and E° for the quinohydrone electrode is 0.699 V, both at the same temperature. [2.303 $RT/F = 0.06$]

(a) 3.5 (b) 7.0

(c) 1.85 (d) −3.5

13. The potential (EMF) of a cell consisting of an anode of silver in 0.10 M – $AgNO_3$ solution and a cathode of Pt immersed in a solution of 1.6 M – $Cr_2O_7^{2-}$, 0.4 M – Cr^{3+} and 0.1 M – H^+ is ($E^\circ_{Ag^+|Ag} = 0.80$ V and $E^\circ_{Cr_2O_7^{2-}|Cr^{3+}} = 1.33$ V) [2.303 $RT/F = 0.06$]

(a) 0.46 V (b) 0.60 V

(c) 0.53 V (d) −0.17 V

14. The EMF of the cell: Zn–Hg (C_1M) | Zn^{2+}(aq) | Zn–Hg (C_2M) at 25°C, if the concentrations of the zinc amalgams are: C_1 = 10 g per 100 g of mercury, C_2 = 1 g per 100 g mercury, is

(a) 0.059 V (b) 0.0295 V

(c) 0.59 V (d) 0.295 V

15. What is the equilibrium constant of the reaction: $2Fe^{3+} + Au^+ \rightarrow 2Fe^{2+} + Au^{3+}$? Given $E^\circ_{Au^+|Au} = 1.68$ V, $E^\circ_{Au^{3+}|Au} = 1.50$ V, $E^\circ_{Fe^{3+}|Fe^{2+}} = 0.75$ V and 2.303 $RT/F = 0.06$.

(a) 1×10^{22} (b) 1×10^{-22}

(c) 1×10^{-11} (d) 1×10^{-72}

16. What is the EMF of the cell: Pt, H_2 (1 atm) | CH_3COOH (0.1 M) || (0.01 M) NH_4OH | H_2 (1 atm), Pt? Given: K_a for $CH_3COOH = 1.8 \times 10^{-5}$, K_b for $NH_4OH = 1.8 \times 10^{-5}$, 2.303 $RT/F = 0.06$, log 1.8 = 0.25)

(a) 0.465 V (b) −0.465 V

(c) −0.2325 V (d) −0.93 V

17. Two electrochemical cells are assembled in which the following reactions occur:

$V^{2+} + VO^{2+} + 2H^+ \rightarrow 2V^{3+} + H_2O$; $E^\circ_{Cell} = 0.616$ V

$V^{3+} + Ag^+ + H_2O \rightarrow VO^{2+} + Ag(s) + 2H^+$; $E^\circ_{Cell} = 0.439$ V

If $E^\circ_{Ag^+|Ag} = 0.799$ V, what is $E^\circ_{V^{3+}|V^{2+}}$?

(a) −0.256 V (b) +0.256 V

(c) +1.854 V (d) −1.854 V

18. The EMF of cell: H_2(g) | Buffer || Normal calomel electrode, is 0.70 V at 25°C, when barometric pressure is 760 mm. What is the pH of the buffer solution? $E^\circ_{Calomel} = 0.28$ V. [2.303 $RT/F = 0.06$]

(a) 3.5

(b) 7.0

(c) tending to zero

(d) tending to 14.0

19. What is the solubility product of a saturated solution of Ag_2CrO_4 in water at 298 K if the EMF of the cell: Ag | Ag^+ (satd. Ag_2CrO_4) || Ag^+ (0.1 M) | Ag is 0.162 V at 298 K? [2.303 $RT/F = 0.06$, log 2 = 0.3]

(a) 2.0×10^{-4} (b) 3.2×10^{-11}

(c) 8.0×10^{-12} (d) 4.0×10^{-12}

20. A Tl^+|Tl couple was prepared by saturating 0.10 M – KBr with TlBr and allowing Tl^+ ions form the insoluble bromide to equilibrate. This couple was observed to have a potential –0.444 V with respect to Pb^{2+} | Pb couple in which Pb^{2+} was 0.10 M. What is the K_{sp} of TlBr. [Given: $E^\circ_{Pb^{2+}|Pb} = -0.126$ V, $E^\circ_{Tl^+|Tl} = -0.336$ V, log 2.5 = 0.4, 2.303 $RT/F = 0.06$]

(a) 4.0×10^{-6} (b) 2.5×10^{-4}

(c) 4.0×10^{-5} (d) 6.3×10^{-3}

21. The EMFs of the cell obtained by combining separately Zn and Cu electrodes of a Daniel cell with normal calomel electrodes are 1.083 V and −0.018 V, respectively, at 25° C. If the potential of normal calomel electrode is −0.28 V, the EMF of the Daniel cell is

(a) 1.065 V (b) 1.101 V
(c) 0.803 V (d) 0.262 V

22. A hydrogen electrode placed in a buffer solution of CH_3COONa and CH_3COOH in the ratio's $x{:}y$ and $y{:}x$ has electrode potential values E_1 and E_2 volts, respectively, at 25°C. The pK_a value of acetic acid is

(a) $(E_1 + E_2)/\,0.118$ (b) $(E_2 - E_1)/\,0.118$
(c) $-(E_1 + E_2)/\,0.118$ (d) $(E_1 - E_2)/\,0.118$

23. The standard reduction potential at 25°C of the reaction $2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$ is −0.84 V. Calculate equilibrium constant for the reaction: $2H_2O \rightleftharpoons H_3O^+ + OH^-$ at 25°C. ($2.303\,RT/F = 0.06$)

(a) 10^{-14} (b) 10^{14}
(c) 10^{7} (d) 10^{-7}

24. The voltage of the cell given below is −0.61 V.

Pt | H_2 (1 bar) | $NaHSO_3$ (0.4 M), Na_2SO_3 (6.4×10^{-2} M) || Zn^{2+} (0.4 M) | Zn

If $E^\circ_{Zn^{2+}|Zn} = -0.76$ V, Calculate K_{a2} of H_2SO_4. ($2.303\,RT/F = 0.06$)

(a) 3.2×10^{-4} (b) 3.2×10^{-2}
(c) 3.2×10^{-3} (d) 6.4×10^{-7}

25. Estimate the cell potential of a Daniel cell having 1.0 M – Zn^{2+} and originally having 1.0 M – Cu^{2+} after sufficient ammonia has been added to the cathode compartment to make the NH_3 concentration 2.0 M. Given: $E^\circ_{Zn^{2+}|Zn} = -0.76$ V, $E^\circ_{Cu^{2+}|Cu} = +0.34$ V, K_f for $Cu(NH_3)_4^{2+} = 1 \times 10^{12}$ [$2.303\,RT/F = 0.06$].

(a) 1.10 V (b) 0.704 V
(c) 0.396 V (d) 1.496 V

26. The minimum mass of NaOH required to be added in RHS to consume all the H^+ present in RHS of the cell of EMF, +0.70 V at 25°C, before its use.

Zn | Zn^{2+} (0.01 M) || HCl (V = 500 ml) | H_2 (1 bar) | Pt

Given: $E^\circ_{Zn^{2+}|Zn} = -0.76$ V; $2.303\,RT/F = 0.06$

(a) 2.0 g (b) 4.0 g
(c) 0.2 g (d) 0.4 g

27. The EMF of the cell: Ag, AgCl in 0.1 M – KCl || satd. NH_4NO_3 || 0.1 M – $AgNO_3$, Ag is 0.42 V at 25°C. 0.1 M – KCl is 50% dissociated and 0.1 M – $AgNO_3$ is 40% dissociated. The solubility product of AgCl is ($2.303\,RT/F = 0.06$)

(a) 1.0×10^{-10} (b) 2.0×10^{-9}
(c) 1.0×10^{-9} (d) 2.0×10^{-10}

28. On the basis of information available from the reaction

$$4Al + 3O_2 \rightarrow 2Al_2O_3;\ \Delta G = -965\ \text{kJ/mol of } O_2$$

The minimum EMF required to carry out electrolysis of Al_2O_3 is

(a) 0.833 V (b) 2.5 V
(c) 5.0 V (d) 1.67 V

29. The theoretical efficiency of a hypothetical cell is about 84% which involves the following reaction

$$A(s) + B^{2+}(aq) \rightarrow A^{2+}(aq) + B(s);\ \Delta H = -285\ \text{kJ},$$

then, the standard EMF of the cell is

(a) 1.10 V (b) 1.24 V
(c) 2.48 V (d) 2.20 V

30. To a beaker containing 0.1 M – HCl, a little pure solid AgCl is added. Both a silver and a hydrogen electrode (P_{H_2} = 1.0 bar) are then placed in the solution. What is the approximate value of EMF measured between the electrodes at 25°C? (Given: $E^\circ_{Ag^+|Ag} = 0.80$ V and K_{sp} (AgCl) = 10^{-10}) [$2.303\,RT/F = 0.06$]

(a) 0.92 V (b) 0.32 V
(c) 1.28 V (d) 0.56 V

31. Although aluminium is above hydrogen in the electrochemical series, it is stable in air and water. Why?

(a) Aluminium is non-reactive metal.
(b) A layer of oxide is formed at metal surface, which prevent further reaction.
(c) The reaction is thermodynamically unfavourable, i.e., ΔG is not negative.
(d) Kinetically, the reaction has very low activation energy and hence do not occur.

32. When silver chloride is dissolved in a large excess of ammonia, practically all silver ion can be assumed to exist in form of a single ionic species $[Ag_x(NH_3)_y]^{x+}$. Compute the values of x and y using the two following cells:

Cell I: Ag | 4.0×10^{-4} M – AgCl, 1 M – NH_3 || 4×10^{-2} M – AgCl, 1 M – NH_3 | Ag; $E_{cell} = 0.118$ V at 298 K.

Cell II: Ag | 3×10^{-3} M – AgCl, 1 M – NH_3 || 3×10^{-3} M – AgCl, 0.1 M – NH_3 | Ag; $E_{cell} = 0.118$ V at 298 K.

(a) $x = 1, y = 2$
(b) $x = 1, y = 4$
(c) $x = 2, y = 4$
(d) $x = 1, y = 6$

33. When metallic copper is shaken with a solution of a copper salt, the reaction $Cu + Cu^{2+} \rightleftharpoons 2Cu^+$ proceeds. When equilibrium is established at 298 K, $[Cu^{2+}]/[Cu^+]^2 = 1.667 \times 10^6\ M^{-1}$. If the standard potential of the Cu^{2+} | Cu half-cell is +0.3376 V, what is the standard potential of Cu^+| Cu half-cell? (Given: 2.303 $RT/F = 0.06$, log 2 = 0.3, log 3 = 0.48)

(a) −0.3732 V
(b) 0.6752 V
(c) 0.5242 V
(d) 0.151 V

34. Zinc granules are added in excess to a 500 ml of 1.0 M nickel nitrate solution at 25°C until the equilibrium is reached. If the standard reduction potential of Zn^{2+}|Zn and Ni^{2+}|Ni are −0.75 V and −0.24 V, respectively, the concentration of Ni^{2+} in solution at equilibrium is (2.303 $RT/F = 0.06$)

(a) 1.0×10^{-17} M
(b) 1.0×10^{17} M
(c) 5×10^{-17} M
(d) 2×10^{-17} M

35. The EMF for the cell: Ag(s) | AgCl(s) | KCl(0.2 M) || KBr (0.001 M) | AgBr(s) | Ag(s) at 25°C is (K_{sp}(AgCl) = 2.0×10^{-10}; K_{sp}(AgBr) = 4.0×10^{-13}, 2.303 $RT/F = 0.06$, log 2 = 0.3)

(a) 0.024 V
(b) −0.024 V
(c) −0.24 V
(d) − 0.012 V

36. Two students use same stock solution of $ZnSO_4$ but different solutions 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. The concentration of $CuSO_4$ in the other cell is (2.303 $RT/F = 0.06$)

(a) 0.05 M
(b) 5.0 M
(c) 0.5 M
(d) 0.005 M

37. Two weak acid solutions HA_1 and HA_2 each with the same concentration and having pK_a values 3 and 5 are placed in contact with hydrogen electrodes (1 atm, 25°C) and are interconnected through a salt bridge. EMF of the cell is

(a) 0.0295 V
(b) 0.118 V
(c) 0.0885 V
(d) 0.059 V

38. Consider the reaction of extraction of gold from its ore:

$$Au(s) + 2CN^-(aq) + \frac{1}{4}O_2(g) + \frac{1}{2}H_2O(l) \rightarrow Au(CN)_2^-(aq) + OH^-(aq)$$

Use the following data to calculate ΔG^o for the above reaction.

$K_f[Au(CN)_2^-] = X$
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$; $E° = +0.41$ V
$Au^{3+} + 3e^- \rightarrow Au$; $E° = +1.50$ V
$Au^{3+} + 2e^- \rightarrow Au^+$; $E° = +1.40$ V

(a) $-RT \ln X + 1.29$ F
(b) $-RT \ln X - 1.29$ F
(c) $+RT \ln X + 2.11$ F
(d) $-RT \ln X - 2.11$ F

39. F_2 gas cannot be obtained by the electrolysis of any aqueous fluoride salt because

(a) F_2 is the strongest oxidizing agent
(b) F_2 easily combines with water
(c) F_2 readily combines with the electrodes
(d) F^- can never be oxidized

40. A volume of 100 ml of a buffer of 1 M – NH_3 and 1 M – NH_4^+ is placed in two half-cells connected by a salt bridge. A current of 1.5 A is passed through the cell for 20 min. If electrolysis of water takes place only and the electrode reactions are:

Right: $2H_2O + O_2 + 4e \rightarrow 4\ OH^-$
and Left: $2H_2O \rightarrow 4H^+ + O_2 + 4e$,
then, the pH of the

(a) right electrode will increase
(b) left electrode will increase
(c) both electrode will increase
(d) both electrode will decrease

41. When molten ICl_3 is electrolysed using platinum electrodes

(a) I_2 is evolved at cathode and Cl_2 at anode
(b) Cl_2 is evolved at cathode and I_2 at anode
(c) I_2 is evolved at cathode and both I_2 and Cl_2 at anode
(d) electrolysis does not take place

42. When electric current is passed through a cell having an electrolyte, positive ions move towards the cathode and negative ions towards the anode. If the cathode is pulled out of the solution, then the

(a) positive and negative ions will move towards the anode
(b) positive ions will start moving towards the anode, the negative ions will stop moving
(c) negative ions will continue to move towards the anode, the positive ions will start moving randomly
(d) positive and negative ions will start moving randomly

43. When 10^{-6} M – HCl is electrolysed

(a) O_2 is produced at the anode
(b) H_2 is produced at the anode
(c) Cl_2 is produced at the anode
(d) Cl_2 and O_2 are produced at the anode

44. A dilute aqueous solution of Na_2SO_4 is electrolysed using platinum electrodes. The products at the anode and cathode are, respectively,

(a) O_2, H_2 (b) $S_2O_8^{2-}$, Na
(c) O_2, Na (d) $S_2O_8^{2-}$, H_2

45. In the electrolysis of a fused salt, the mass of substance deposited on an electrode will not depend on

(a) temperature of bath
(b) current intensity
(c) time of electrolysis
(d) electrochemical equivalent of ions

46. When an electric current is passed through an aqueous solution of the following, the concentrations of cation as well as anion will not change for (assume constant volume of the electrolytic solution)

(a) CsCl (b) KNO_3
(c) $AgNO_3$ (d) HCl

47. Which of the following substances: Na, Hg, S, Pt and graphite can be used as electrodes in electrolytic cells having aqueous solution?

(a) Na, Pt and graphite (b) Na and Hg
(c) Hg, Pt and graphite (d) Na and S

48. An ammeter and a copper voltameter are connected in series in an electric circuit through which a constant direct current flows. The ammeter shows 0.5 A. If 0.635 g of Cu is deposited in 0.965 h, what is the percentage error of ammeter? (Cu = 63.5)

(a) 5 % (b) 10 %
(c) 9 % (d) 90 %

49. The same current is passed through acidulated water and stannous chloride solution. What volume of dry detonating gas at 0°C and 1 atm is evolved from water, when 1.20 g of tin is deposited from the other solution? (Sn = 120)

(a) 112 ml (b) 336 ml
(c) 224 ml (d) 672 ml

50. The preparation of LiOH by the electrolysis of a 35% solution of LiCl using a platinum anode led to a current efficiency of 80%. What weight of LiOH was formed by the passage of 2.5 A for 4825 s?

(a) 1.92 g (b) 2.40 g
(c) 0.96 g (d) 0.672 g

51. Assuming that copper contains only iron, silver and gold as impurities. After passage of 12.4 A for 4825 s, the mass of anode decreased by 20.00 g and the cathode increased by 19.05 g. The percentages of iron and copper in the original sample are, respectively, (Cu = 63.5, Fe = 56)

(a) 4.75%, 95.25% (b) 2.8%, 95.25%
(c) 95.25%, 4.75% (d) 95.25%, 1.91%

52. After electrolysis of an aqueous sodium chloride solution, it was found that the solution is being neutralized by 60 ml N – HCl solution. During the same period of electrolysis, 3.18 g of copper was deposited in a copper voltameter in series. What is the percentage of the theoretical yield of sodium hydroxide obtained? (Cu = 63.6)

(a) 40% (b) 60%
(c) 30% (d) 80%

53. A lead storage battery has initially 200 g of lead and 200 g of PbO_2 plus excess H_2SO_4. Theoretically, how long could this cell deliver a current of 10.0 A, without recharging, if it were possible to operate it so that the reaction goes to completion? (Pb = 208)

(a) 16083.33 s (b) 8041.67 s
(c) 44.68 s (d) 18557.7 s

54. A volume of 100 ml of 0.6 N–$CuSO_4$ solution is electrolysed between two platinum electrodes till the concentration in the residual liquid is 0.1 N, when a steady current of 5.0 A is used. How long should the current be passed to get the above change?

(a) 965 s
(b) 96500 s
(c) 1930 s
(d) 482.5 s

55. A constant current flowed for 2 h through a potassium iodide solution, oxidizing the iodide ion to iodine. At the end of the experiment, the iodine was titrated with 72 ml of 1.0 M–$Na_2S_2O_3$ solution. What was the average rate of current flow, in ampere?

(a) 0.965 A
(b) 1.93 A
(c) 0.483 A
(d) 0.0965 A

56. Anthracene, $C_{14}H_{10}$, can be oxidized to anthraquinone, $C_{14}H_8O_2$. What weight of anthraquinone can be produced by the passage of a current of 1 A of 40 min if the current efficiency is 96.5%?

(a) 0.862 g
(b) 0.832 g
(c) 0.624 g
(d) 0.738 g

57. Most of the copper used to make wire has been electrically refined by depositing it from copper salts solution (divalent) on to a cathode. What is the cost of electrical energy required per kg of copper if the cost of electricity is Rs 4.00 per kWh and the cell operates at 0.33 V? The electrochemical equivalent of copper is 0.00033 g/coulomb.

(a) Rs 11.11
(b) Rs 5.55
(c) Rs 2.22
(d) Rs 1.11

58. Electrolysis of an acetate solution produces ethane according to the reaction:

$$2CH_3COO^- \rightarrow C_2H_6(g) + 2CO_2(g) + 2e^-$$

What total volume of ethane and CO_2 would be produced at 0°C and 1 atm, if a current of 0.5 A is passed through the solution for 482.5 min? Assume current efficiency 80%.

(a) 1.344 L
(b) 2.688 L
(c) 4.032 L
(d) 1.792 L

59. To perform an analysis of a mixture of metal ions by electro-deposition, the second metal to be deposited must not being plating out until the concentration ratio of the second to the first is about 10^6. What must be the minimum difference in standard potential of the two metals which form dipositive ions in order for such an analysis to be feasible?

(a) 0.177 V
(b) 0.354 V
(c) 0.708 V
(d) 0.088 V

60. During the electrolysis of 0.1 M – $CuSO_4$ solution using copper electrodes, a depletion of Cu^{2+} occurs near the cathode with a corresponding excess near the anode, owing to inefficient stirring of the solution. If the local concentration of Cu^{2+} near the anode and cathode are, respectively, 0.12 M and 0.08 M, the back EMF developed at 298 K is (log 1.5 = 0.18, 2.303 RT/F = 0.06)

(a) 0.33 V
(b) 5.4 mV
(c) 2.7 mV
(d) 10.8 mV

61. The following galvanic cell:

Zn | $Zn(NO_3)_2$ (100 ml, 1 M) || $Cu(NO_3)_2$ (100 ml, 1 M) | Cu

was operated as an electrolytic cell as Cu as the anode and Zn as the cathode. A current of 0.4825 A was passed for 10 h and then the cell was allowed to function as galvanic cell. What would be the final EMF of the cell at 25°C? Assume that the only electrode reactions occurring were those involving Cu | Cu^{2+} and Zn | Zn^{2+}. Given: $E^\circ_{Cu^{2+}|Cu} = +0.34$ V, $E^\circ_{Zn^{2+}|Zn} = -0.76$ V, 2.303 RT/F = 0.06, log 1.9 = 0.28)

(a) 1.10 V
(b) 1.0616 V
(c) 1.1084 V
(d) 1.1768 V

62. At the Nangal fertilizer plant in Punjab, hydrogen is produced by the electrolysis of water. The hydrogen is used for the production of ammonia and nitric acid (by the oxidation of ammonia). If the average production of ammonium nitrate is 1152 kg/day, the daily consumption of electricity (in A /day) is

(a) 96,500
(b) 48,250
(c) 32,166.67
(d) 24,125

63. Lactic acid, $HC_3H_5O_3$, produced in 1 g sample of muscle tissue was titrated using phenolphthalein as indicator against OH^- ions which were obtained by the electrolysis of water. As soon as OH^- ions are produced, they react with lactic acid and at complete neutralization, immediately a pink colour is noticed. If electrolysis was made for 1158 s using 50.0 mA current to reach the end point, what was the percentage of lactic acid in muscle tissue?

(a) 5.4%
(b) 2.7%
(c) 10.8%
(d) 0.054%

64. H_2O_2 can be prepared by successive reactions:

$$2NH_4HSO_4 \rightarrow H_2 + (NH_4)_2S_2O_8$$

$$(NH_4)_2S_2O_8 + 2H_2O \rightarrow 2NH_4HSO_4 + H_2O_2$$

The first reaction is an electrolytic reaction and second is steam distillation. What amount of current would have to be used in first reaction to produce enough intermediate to yield 102 g pure H_2O_2 per hour. Assume current efficiency 50%.

(a) 643.33 A (b) 321.67 A
(c) 160.83 A (d) 1286.67 A

65. In an analytical determination of arsenic, a solution containing arsenious acid, H_3AsO_3, KI and a small amount of starch is electrolysed. The electrolysis produces free I_2 from I^- ions and the I_2 immediately oxidizes the arsenious acid to hydrogen arsenate ion, $HAsO_4^{2-}$.

$$I_2 + H_3AsO_3 + H_2O \rightarrow 2I^- + HAsO_4^{2-} + 4H^+$$

When the oxidation of arsenic is complete, the free iodine combines with the starch to give a deep blue colour. If during a particular run, it takes 96.5 s for a current of 1.68 mA to give an end point (indicated by the blue colour), how many g of arsenic are present in the solution. (As = 75)

(a) 6.3×10^{-4} g (b) 1.26×10^{-4} g
(c) 3.15×10^{-5} g (d) 6.3×10^{-5} g

66. Electrolysis of a solution of $MnSO_4$ in aqueous sulphuric acid is a method for the preparation of MnO_2 as per the reaction: $Mn^{2+}(aq) + 2H_2O \rightarrow MnO_2(s) + 2H^+(aq) + H_2(g)$. Passing a current of 19.3 A for 2 h gives only 52.2 g of MnO_2. The current efficiency is (Mn = 55)

(a) 8.33% (b) 83.33%
(c) 41.67% (d) 100%

67. Copper sulphate solution (250 ml) was electrolysed using a platinum anode and a copper cathode. A constant current of 2 mA was passed for 19.3 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.

(a) 9.6×10^{-5} M (b) 4.8×10^{-5} M
(c) 2.4×10^{-5} M (d) 1.2×10^{-5} M

68. 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?

(a) 0.3 F, 86.85 kJ (b) 0.6 F, 173.7 kJ
(c) 1.2 F, 347.4 kJ (d) 0.6 F, 173.7 kJ

69. Perdisulphuric acid, $H_2S_2O_8$ can be prepared by electrolytic oxidation of H_2SO_4, oxygen and hydrogen gases are by products. In such an electrolysis, 9.08 L of H_2 and 2.27 L of O_2 were generated at STP. What is the mass of $H_2S_2O_8$ formed?

(a) 0 (b) 77.6 g
(c) 38.8 g (d) 19.4 g

70. During the discharge of a lead storage battery, the density of sulphuric acid fell from 1.5 to 1.1 g/ml. Sulphuric acid of density 1.5 g/ml is 40% H_2SO_4, by weight, and that of density 1.1 g/ml is 10% H_2SO_4, by weight. The battery holds 3.6 L of the acid and the volume remained practically constant during the discharge. Calculate the number of ampere-hours which the battery should have been used. The electrode reactions are:

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

$$PbO_2 + 4H^+ + SO_4^{2-} + 2e \rightarrow PbSO_4 + 2H_2O$$

(a) 965 (b) 482.5
(c) 1930 (d) 241.25

71. A cell whose resistance, when filled with 0.1 M – KCl is 200 Ω, is measured to be 6400 Ω, when filled with 0.003 M – NaCl solution. What is the molar conductance of NaCl solution, in Ω^{-1} cm^2 mol^{-1} if the molar conductance of 0.1 M – KCl is 120 Ω^{-1} cm^2 mol^{-1}?

(a) 41.67 (b) 250
(c) 125 (d) 375

72. At 18°C, the ionic mobilities of NH_4^+ and CrO_4^{2-} ions are 6.6×10^{-8} and 5.4×10^{-8} m^2 volt^{-1} s^{-1} at infinite dilution. What is the molar conductance of ammonium chromate solution in Ω^{-1} m^2 mol^{-1}?

(a) 0.01795 (b) 0.01158
(c) 1.2×10^{-8} (d) 1.86×10^{-7}

73. At 25°C, the molar conductance at infinite dilution for HCl solution is 4.25 Ω^{-1} m^2 mol^{-1}, while its specific conductance is 382.5 Ω^{-1} m^{-1}. If the degree of dissociation is 90%, the molarity of solution is

(a) 0.9 M (b) 1.0 M
(c) 0.1 M (d) 1.1 M

74. A big irregular shaped vessel contained water, conductivity of which was 2.56×10^{-3} S^{-1}m^{-1}. 585 g of NaCl was then added to the water and conductivity after the addition of NaCl, was found to be 3.06×10^{-3} S^{-1}m^{-1}. The molar conductivity of NaCl at this concentration is 1.5×10^{-2} S^{-1}m^{2} mol^{-1}. The capacity of vessel if it is fulfilled with water, is

(a) 3×10^4 L
(b) 30 L
(c) 3×10^8 L
(d) 3×10^5 L

75. The molar conductivity of 0.10 M solution of $MgCl_2$ is 100 mho cm^2 mol^{-1}, at 25°C. A cell with electrodes that are 1.50 cm^2 in surface area and 0.50 cm apart is filled with 0.10 M – $MgCl_2$ solution. How much current will flow when the potential difference between the electrodes is 5 volts?

(a) 0.03 A
(b) 3.0 A
(c) 0.15 A
(d) 15 A

76. For Na$^+$, the value of symbol λ_m° is 50.0 Ω^{-1} cm^2 mol^{-1}. The speed of Na$^+$ ion in the solution, if in the cell, electrodes are 5 cm apart and to which a potential of 19.3 volt is applied is

(a) 2×10^{-3} cm/s
(b) 1×10^{-3} cm/s
(c) 2×10^{-4} cm/s
(d) 2×10^{-2} cm/s

77. The conductivity of a saturated solution of AgCl at 298 K was found to be 3.40×10^{-6} Ω^{-1} cm^{-1}; the conductivity of water used to make up the solution was 1.60×10^{-6} Ω^{-1} cm^{-1}. Determine the solubility of AgCl in water in mole per litre at 298 K. The equivalent conductivity of AgCl at infinite dilution is 150.0 Ω^{-1} cm^{-2} eq^{-1}.

(a) 1.44×10^{-10}
(b) 1.2×10^{-5}
(c) 3.33×10^{-5}
(d) 1.2×10^{-8}

78. 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

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

79. The conductivity of a saturated solution containing AgA ($K_{sp} = 3 \times 10^{-14}$) and AgB ($K_{sp} = 1 \times 10^{-14}$) is 3.75×10^{-8} Ω^{-1}cm^{-1}. If the limiting molar conductivity of Ag$^+$ and A$^-$ ion is 60 and 80 Ω^{-1} cm^2 mol^{-1}, respectively, the limiting molar conductivity of B$^-$ (in Ω^{-1} cm^2 mol^{-1}) is

(a) 135
(b) 67.5
(c) 270
(d) 190

80. The conductivity of saturated solution of $Ba_3(PO_4)_2$ is 1.2×10^{-5} Ω^{-1} cm^{-1}. The limiting equivalent conductivities of $BaCl_2$, K_3PO_4 and KCl are 160, 140 and 100 Ω^{-1} cm^2 eq^{-1}, respectively. The solubility product of $Ba_3(PO_4)_2$ is

(a) 10^{-5}
(b) 1.08×10^{-23}
(c) 1.08×10^{-25}
(d) 1.08×10^{-27}

Section B (One or More than one Correct)

1. Which of the following statement(s) differentiate between electrochemical cell and electrolytic cell?

(a) Spontaneous or non-spontaneous nature of the chemical process.
(b) Chemical reactions occurring at the electrodes.
(c) Positive and negative nature of anode.
(d) Dependence on Faraday's law.

2. Pick up the false statement(s):

(a) The net chemical change in a galvanic cell reaction is always redox reactions.
(b) In a galvanic cell made of copper and cadmium electrodes, cadmium electrode may act as anode.
(c) Standard potential increases with increasing concentration of the electrolyte.
(d) Calomel electrode is a reference electrode having 0.00 volt potential.

3. Consider the cell: Ag(s), AgCl(s) | KCl (0.1 M) | Hg_2Cl_2(s), Hg(l). The cell potential

(a) increases on increasing concentration of Cl$^-$ ions.
(b) decreases on decreasing concentration of Cl$^-$ ions.
(c) is independent of concentration of Cl$^-$ ions.
(d) is independent of amounts of AgCl and Hg_2Cl_2.

4. The passage of electricity in the Daniel cell when Zn and Cu electrodes are connected

(a) from Cu to Zn inside the cell
(b) from Cu to Zn outside the cell
(c) from Zn to Cu inside the cell
(d) from Zn to Cu outside the cell

5. From an electrolyte, one mole of electron will deposit at cathode

(a) 63.5 g of Cu (b) 24 g of Mg

(c) 11.5 g of Na (d) 9.0 g of Al

6. Which of the following statements is/are correct?

(a) The conductivity of molten NaCl is due to movement of Na^+ and Cl^- ions.

(b) Solid NaCl is good conductor of electricity.

(c) Molten sodium is a good conductor because of mobile electrons.

(d) Resistivity is reciprocal of molar conductivity of electrolyte.

7. Ionic conductance at infinite dilution of $A1^{3+}$ and SO_4^{2-} ions are 60 and 80 Ω^{-1} cm^2 eq^{-1}, respectively. The correct detail(s) regarding $Al_2(SO_4)_3$ is/are

(a) the molar conductance is 140 Ω^{-1} cm^2 mol^{-1}.

(b) the equivalent conductance is 140Ω^{-1} cm^2 eq^{-1}.

(c) the molar conductance is 840 Ω^{-1} cm^2 mol^{-1}.

(d) the molar conductance is 23.33Ω^{-1} cm^2 mol^{-1}.

8. The function(s) of salt bridge in a cell is/ are

(a) It maintains standard electrode potential of cell constant which depends on several factors.

(b) It completes the electrical circuit.

(c) It departs both the solutions from each other.

(d) It maintains the electrical neutrality of both electrolytic solutions.

9. The reactions taking place in the dry cell are:

Anode: $Zn \rightarrow Zn^{2+} + 2e^-$

Cathode: $2MnO_2 + 2NH_4^+ + 2e^- \rightarrow Mn_2O_3 + 2NH_3 + H_2O$

The minimum mass of reactants, if a dry cell is to generate 0.25A for 9.65 h, are (Mn = 55, Zn = 65.4) (neglect any other chemical reactions occurring in the cell)

(a) 2.943 g Zn (b) 7.83 g MnO_2

(c) 1.62 g NH_4^+ (d) 3.915 g MnO_2

10. EMF of the cell: Cd(s) | $CdCl_2.5H_2O$ (sat.) | AgCl(s) | Ag(s) is +0.70 V at 0°C and +0.60 V at 50°C. If ΔH^o and ΔS^o are temperature independent, then the correct information(s) regarding the cell reaction is/are

(a) $\Delta G° = -115.8$ kJ at 50°C

(b) $\Delta G° = 135.1$ kJ at 0°C

(c) $\Delta S° = -386$ J/K

(d) $\Delta H° = -221.178$ kJ

11. Two litre solution of a buffer mixture containing 1.0 M – NaH_2PO_4 and 1.0 M – Na_2HPO_4 is placed in two compartments (one litre in each) of an electrolytic cell. The platinum electrodes are inserted in each compartment and 1.25 A current is passed for 965 min. Assuming electrolysis of only water at each compartment, what will be pH in each compartment after passage of above charge? (pK_a for $H_2PO_4^- = 2.15$, log 7 = 0.85)

(a) Anode: 3.00 (b) Cathode: 3.00

(c) Anode: 1.30 (d) Cathode: 1.30

12. 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:

$V^{2+}(aq) + 2e^- \rightarrow V(s) \quad E° = -1.19$ V

$Fe^{3+}(aq) + 3e^- \rightarrow Fe(s) \quad E° = -0.04$ V

$Au^{3+}(aq) + 3e^- \rightarrow Au(s) \quad E° = +1.40$ V

$Hg^{2+}(aq) + 2e^- \rightarrow Hg(l) \quad E° = +0.86$ V

The pair(s) of metal that is(are) oxidized by NO_3^- in aqueous solution is(are)

(a) V and Hg (b) Hg and Fe

(c) Fe and Au (d) Fe and V

13. Among the following, the intensive property is (properties are)

(a) Molar conductivity (b) Electromotive force

(c) Resistance (d) Heat capacity

14. In a galvanic cell, the salt bridge

(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.

15. A lead storage cell is discharged which causes the H_2SO_4 electrolyte to change from a concentration of 40% by weight (density = 1.260 g/ml) to 28%, by weight. The original volume of solution was 1 L. Identify the correct statement(s):

(a) The overall cell reaction is: $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$.

(b) A total of 2.0 moles of H_2SO_4 is reacted.

(c) The total charge released from anode of the cell is 1.93×10^5 coulomb.

(d) The mass of electrolytic solution has decreased.

Section C (Comprehensions)

Comprehension I

Suppose that the S.H.E. was arbitrarily assigned a value of 1.00 V for $2H^+(aq) + 2e \rightarrow H_2(g)$. What would this do to the observed voltage under standard condition for each of the following: (Given: $E^\circ_{Zn^{2+}|Zn} = -0.76$ V, $E^\circ_{Cu^{2+}|Cu} = +0.34$ V when S.H.E. is 0.00 V)

1. $E^\circ_{Zn^{2+}|Zn}$

(a) +0.24 V (b) −0.76 V
(c) +1.76 V (d) −0.34 V

2. $E^\circ_{Cu^{2+}|Cu}$

(a) −0.76 V (b) +1.34 V
(c) +1.76 V (d) +0.34 V

3. Zn–Cu Cell

(a) +1.10 V
(b) −1.10 V
(c) 0.0 V
(d) Indeterminate

Comprehension II

The standard reduction potential of the $Ag^+|Ag$ electrode at 298 K is 0.80 V. The solubility product of AgI is 6.4×10^{-17} at 298 K. (2.303 $RT/F = 0.06$, log 2 = 0.3)

4. The potential of Ag^+ | Ag electrode in a saturated solution of AgI at 298 K is

(a) −0.314 V (b) +0.314 V
(c) −0.172 V (d) +0.172 V

5. The standard reduction potential of I^-|AgI|Ag electrode at 298 K is

(a) −0.314 V (b) +0.314 V
(c) −0.172 V (d) +0.172 V

6. The potential of I^- (0.04 M)|AgI|Ag electrode at 198 K is

(a) −0.088 V
(b) +0.088 V
(c) −0.172 V
(d) +0.172 V

Comprehension III

The Edison storage cell is represented as Fe(s) | FeO(s) | KOH(aq) | Ni_2O_3(s) | NiO(s) | Ni(s). The half-cell reactions are

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

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

7. What is the cell reaction?

(a) $Ni_2O_3(s) + Fe(s) \rightarrow 2\ NiO(s) + FeO(s)$
(b) $2NiO(s) + FeO(s) \rightarrow Ni_2O_3(s) + Fe(s)$
(c) $Ni_2O_3(s) + FeO(s) \rightarrow 2NiO(s) + Fe(s) + O_2$
(d) None of these

8. What is the standard cell EMF?

(a) 1.27 V
(b) 0.47 V
(c) −1.27 V
(d) −0.47 V

9. How does cell EMF depend on increasing the concentration of KOH?

(a) increases
(b) decreases
(c) remains unaffected
(d) none of these

10. What is the maximum amount of electrical energy that can be obtained from one mole of Ni_2O_3?

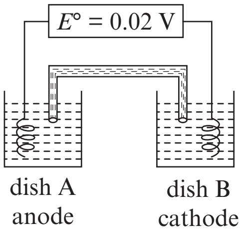
(a) 2.54 J (b) 245.11 kJ
(c) 122.56 kJ (d) 61.28 kJ

Comprehension IV

The cell potential for the unbalanced chemical reaction:

$$\mathbf{Hg_2^{2+}(aq) + NO_3^-(aq) + 3H_3O^+(aq) \rightarrow 2Hg^{2+}(aq) + HNO_2(aq) + 4H_2O(l)}$$

is measured under standard conditions in the electrochemical cell shown in the accompanying diagram.



11. In which dish, the solution is acidic?

(a) Dish A (b) Dish B
(c) Both (d) None

12. How many moles of electrons pass through the circuit when 0.60 mole of Hg^{2+} and 0.30 mole of HNO_2 are produced in the cell that contains 0.50 mole of Hg_2^{2+} and 0.40 mole of NO_3^- at the beginning of the reaction?

(a) 0.30 (b) 0.60
(c) 0.15 (d) 1.20

13. How long will it take to produce 0.10 mole of HNO_2 by this reaction if a current of 10 A passes through the cell?

(a) 965 s (b) 193 s
(c) 1930 s (d) 482.5 s

Comprehension V

A fuel cell is the device to convert the energy of a fuel into electrical energy without the use of heat engine, where the fuel is burnt directly. Such conversions are possible because the combustion reactions are essentially redox reactions and highly exothermic as well as highly exergonic. Electrical energy can be obtained indefinitely from a fuel cell as along as the outside supply of fuel is maintained. In hydrogen–oxygen fuel cell, the following reactions take place:

Anode reaction: $\mathbf{2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^-}$

Cathode reaction: $\mathbf{O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)}$

Overall reaction: $\mathbf{2H_2(g) + O_2(g) \rightarrow 2H_2O(l)}$

The overall reaction has a value of $\Delta H° = -285.8$ kJ and $\Delta G° = -237.39$ kJ at 25°C per mole of $H_2O(l)$.

14. What is the standard EMF of the cell?

(a) 0.615 V (b) 1.23 V
(c) 2.46 V (d) 0.74 V

15. What volume of gaseous H_2 (at STP), when combined with excess O_2 in the fuel cell, is needed to produce 23.739 kJ of useful work under standard conditions?

(a) 2.27 L (b) 4.54 L
(c) 1.13 L (d) 2.24 L

16. Suppose the concentration of hydroxide ion in the cell is doubled at 298 K. The cell voltage will be

(a) reduced by half
(b) increased by a factor of 2
(c) increased by a factor of 4
(d) unchanged

17. What is the approximate value of $\Delta S°$ for the fuel cell reaction at 25°C?

(a) -0.1624 JK^{-1} (b) -162.4 JK^{-1}
(c) $+162.4$ JK^{-1} (d) $+0.1624$ JK^{-1}

18. The theoretical efficiency of the fuel cell is given by

(a) 83.06% (b) 100%
(c) 67.53% (d) 97.88%

Comprehension VI

Billions of dollars are spent each year to replace or prevent the corrosion and subsequent destruction of government property such as ships, bridges, and metallic piping. Corrosion may result in decreased structural integrity and eventual ineffectuality. For example, a naval ship made from iron is highly susceptible to corrosion. One part of the hull acts as the anode, while another acts as the cathode, the iron hull itself connects the two parts, completing the circuit. Part of the metal hull begins oxidizing to Fe^{2+} in the presence of H_2O and O_2, the reduction reaction proceeds with an $E_{red} = 1.229$ V. It is there that Fe^{2+} ions migrate from the anode and are further oxidized as

$$2Fe^{2+}(aq) + \frac{1}{2}O_2(g) + (6 + x)H_2O(l) \rightarrow Fe_2O_3{\cdot}xH_2O(s) + 4H_3O^+(aq)$$

The Fe_2O_3, or rust, formed is only a small part of the problem. Pitting, or loss of solid metal, weaken the structure of the hull and may lead to serious damage and destruction of the hull. Using a sacrificial anode often successfully prevents corrosion. This metal, more easily oxidized than iron. Although the sacrificial anode eventually corrodes as well, the cost of replacing it is far less than that of replacing the iron hull.

Half-reaction	**Potential**
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	$E° = 1.229$ V
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	$E° = 0.771$ V
$Cu^+ + e^- \rightarrow Cu$	$E° = 0.521$ V
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	$E° = 0.401$ V
$Cu^{2+} + 2e^- \rightarrow Cu$	$E° = 0.342$ V
$Pb^{2+} + 2e^- \rightarrow Pb$	$E° = -0.126$ V
$Fe^{2+} + 2e^- \rightarrow Fe$	$E° = -0.447$ V
$Mn^{2+} + 2e^- \rightarrow Mn$	$E° = -1.185$ V
$Mg^{2+} + 2e^- \rightarrow Mg$	$E° = -2.372$ V

19. Which of the following reactions may occur at the anode of the iron hull?

(a) $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$

(b) $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$

(c) $O_2(g) + 4H_3O^+(aq) \rightarrow 6H_2O(l) + 4e^-$

(d) $2H_2O(l) \rightarrow 2OH - (aq) + H_2(g) + 2e^-$

20. What is the standard voltage generated by the corrosion reaction on the iron hull of a ship?

(a) −1.676 V (b) −0.782 V

(c) 1.782 V (d) 1.676 V

21. Which of the following materials could not serve as a sacrificial anode for lead?

(a) Copper (b) Iron

(c) Magnesium (d) Manganese

22. An ammeter reading shows a current of 0.50 A running through the iron hull. How many grams of Fe(s) are lost in 1.0 h?

(a) 0.261 g (b) 0.522 g

(c) 1.044 g (d) 0.783 g

23. A ship that has sunk to the bottom of the ocean may still exhibit corrosion. One difference in the corrosion reaction between ship above water and one that has sunk of the bottom of the ocean may be that

(a) the oxidation reaction of the sunken ship does not include H_2O as a reactant.

(b) the oxidation reaction of the sunken ship does not include O_2 as a reactant.

(c) the reduction reaction of the sunken ship does not include H_2O as a reactant.

(d) the reduction reaction of the sunken ship does not include O_2 as a reactant.

Comprehension VII

A current of 15.0 A is employed to plate nickel in a $NiSO_4$ solution. Both Ni and H_2 are formed at the cathode. The current efficiency with respect to formation of Ni is 60%. The density of nickel = 8.9 g/ml. (Ni = 58.7)

24. How much of nickel is plated on the cathode per hour?

(a) 16.43 g (b) 32.85 g
(c) 19.7 g (d) 9.85 g

25. What is the thickness of the plating if the cathode consists of a sheet of metal 4.0 cm^2, which is to be coated on both sides?

(a) 1.38 mm (b) 2.76 mm
(c) 0.69 mm (d) 23.0 mm

26. What volume of H_2 at 0°C and 1 atm is formed per hour?

(a) 6.27 L (b) 3.76 L
(c) 2.5 L (d) 5.01 L

27. At the end of the electrolysis, how many grams of the gaseous product appear at the anode?

(a) 4.48 g (b) 1.79 g
(c) 2.69 g (d) 7.46 g

Comprehension VIII

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

$$Ag^+ + e^- \rightarrow Ag;\ E°_{red} = 0.8\ V$$

$$C_6H_{12}O_6 + H_2O \rightarrow C_6H_{12}O_7\ \text{(Gluconic acid)} + 2H^+ + 2e;\ E°_{oxd} = -0.05\ V$$

$$Ag(NH_3)_2^+ + e^- \rightarrow Ag(s) + 2\ NH_3;\ E°_{red} = 0.337\ V$$

[Use 2.303 $RT/F = 0.0592$ and $F/RT = 38.92$ at 298 K]

28. $2Ag^+ + C_6H_{12}O_6 + H_2O \rightarrow 2Ag(s) + C_6H_{12}O_7 + 2H^+$. Find $\ln K$ of this reaction.

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

29. 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_{oxd} will increase by a factor of 0.65 from $E°_{oxd}$
(b) E_{oxd} will decrease by a factor of 0.65 from $E°_{oxd}$
(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 $E°_{red}$

30. 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 oxidizing agent than Ag^+
(c) In absence of ammonia, silver salt of gluconic acid is formed
(d) NH_3 has affected the standard reduction potential of glucose–gluconic acid electrode

Comprehension IX

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

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

Given: The standard reduction potential of the $Ag^+(aq)|Ag(s)$ couple is 0.80 V at 25°C.

$\Delta H°$ and $\Delta S°$ for the cell reaction remain unchanged in the range 15°C to 35°C.

31. The overall cell reaction is

(a) $H_2(g) + 2AgCl(s) \rightarrow 2HCl(aq) + 2Ag(s)$
(b) $H_2(g) + 2Ag^+(aq) \rightarrow 2H^+(aq) + 2Ag(s)$
(c) $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$
(d) $H_2(g) + Cl_2(g) \rightarrow 2HCl(aq)$

32. $\Delta H°$ for the cell reaction per mol of AgCl is

(a) −99,974 J (b) −49,987 J
(c) +99,974 J (d) +49,987 J

33. $\Delta S°$ for the cell reaction per mol of AgCl is

(a) −193 J/K (b) −96.5 J/K
(c) +96.5 J/K (d) +193 J/K

34. The solubility of AgCl in water at 25°C is ($2.303\,RT/F = 0.058$)

(a) 10^{-10} M (b) 10^{-12} M
(c) 10^{-5} M (d) 10^{-6} M

Comprehension X

For the reaction: $Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$. Given

Species	ΔG_f^o (kJ / mol) at 25°C
$Ag^+(aq)$	+77
$Cl^-(aq)$	–129
AgCl (s)	–109

$\mathbf{Ag^+ + e^- \rightarrow Ag;\ E° = 0.80\ V}$

$\mathbf{Zn^{2+} + 2e^- \rightarrow Zn;\ E° = –0.76\ V}$

35. The cell representations of the above reaction and $E°_{cell}$ are

(a) $Ag(s)\,|\,AgCl(s)\,|\,Cl^-(aq)\,||\,Ag^+(aq)\,|\,Ag(s)$; $E°_{cell} = 0.59$ V
(b) $Ag(s)\,|\,Ag^+(aq)\,||\,Cl^-(aq)\,|\,AgCl(s)\,|\,Ag(s)$; $E°_{cell} = 0.59$ V
(c) $Ag(s)\,|\,Cl^-(aq)\,||\,Ag^+(aq)\,|\,Ag$; $E°_{cell} = 0.59$ V
(d) $Ag(s)\,|\,Ag^+(aq)\,||\,Cl^-(aq)\,|\,AgCl(s)\,|\,Ag(s)$; $E°_{cell} = 1.18$ V

36. The solubility product of AgCl at 298 K is

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

37. A quantity of 6.539×10^{-2} g of metallic zinc is added to 100 ml of saturated solution of AgCl. The value of $\log\dfrac{[Zn^{2+}]}{[Ag^+]^2}$ is (Zn = 65.39)

(a) 5.288 (b) 52.88
(c) 528.8 (d) 26.44

38. How many moles of Ag will be precipitated in the above reaction?

(a) 10^{-3} (b) 2×10^{-3}
(c) 10^{-6} (d) 10^{-5}

Comprehension XI

A sample of water from a large swimming pool has a resistance of 10,000 Ω at 25°C, when placed in a conductivity cell. When filled with 0.02 M – KCl solution, the cell has a resistance of 100 Ω at 25°C. An amount of 585 g of NaCl was dissolved in the pool, which was thoroughly stirred. A sample of this solution gave a resistance of 8000 Ω. The molar conductivity of NaCl at this concentration is 125 Ω^{-1} cm^2 mol^{-1} and molar conductivity of 0.02 M – KCl is 200 Ω^{-1} cm^2 mol^{-1}.

39. Cell constant of the conductivity cell is
(a) 4 cm^{-1} (b) 0.4 cm^{-1}
(c) 40 cm^{-1} (d) 0.04 cm^{-1}

40. Conductivity of water (in Ω^{-1} cm^{-1}) is
(a) 0.4 (b) 0.04
(c) 0.0004 (d) 0.00004

41. Volume (in L) of water in the pool is
(a) 1,25,000 (b) 12,500
(c) 1250 (d) 125

Comprehension XII

Redox reactions play a pivoted 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 Daniel cell in which zinc goes into solution and copper gets deposited. Given below are a set of half-cell reactions (acidic medium) along with their $E°$ (V with respect to normal hydrogen electrode) values. Using this data, obtain the correct explanations to questions below:

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

42. Among the following, identify the correct statement?
(a) Chloride ion is oxidized by O_2
(b) Fe^{2+} is oxidized by iodine
(c) Iodide ion is oxidized by chlorine
(d) Mn^{2+} is oxidized by chlorine

43. While Fe^{3+} is stable, Mn^{3+} is not stable in acid solution because
(a) O_2 oxidizes Mn^{2+} to Mn^{3+}
(b) O_2 oxidizes both Mn^{2+} to Mn^{3+} and Fe^{2+} to Fe^{3+}
(c) Fe^{3+} oxidizes H_2O to O_2
(d) Mn^{3+} oxidizes H_2O to O_2

Comprehension XIII

The concentration of potassium ions inside a biological cell is at least 20 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

$$M(s) \mid M^+(aq; 0.05\ molar) \parallel M^+(aq; 1\ molar) \mid M(s)$$

For the above electrolytic cell, the magnitude of the cell potential, $|E_{cell}| = 70$ mV.

44. For the above cell
(a) $E_{cell} < 0; \Delta G > 0$ (b) $E_{cell} > 0; \Delta G < 0$
(c) $E_{cell} < 0; \Delta G° > 0$ (d) $E_{cell} > 0; \Delta G° < 0$

45. 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

Comprehension XIV

The electrochemical cell shown below is a concentration cell.

$M(s) \mid M^{2+}$ (saturated solution of a sparingly soluble salt, MX_2) $\parallel M^{2+}$ ($0.001\ \text{mol dm}^{-3}$) $\mid M(s)$

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

46. The value of ΔG (kJ mol^{-1}) for the given cell is (take $1\ F = 96500\ \text{C mol}^{-1}$)

(a) −5.7 (b) 5.7
(c) 11.4 (d) −11.4

47. The solubility product (K_{sp}; $\text{mol}^3\ \text{dm}^{-3}$) of MX_2 at 298 K based on the information available for the given concentration cell is (take $2.303 \times R \times 298/F = 0.059$)

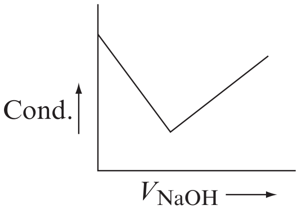
(a) 1×10^{-15} (b) 4×10^{-15}
(c) 1×10^{-12} (d) 4×10^{-12}

Comprehension XV

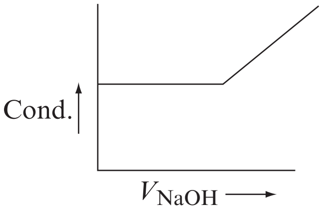
Conductance measurements are frequently employed to find the end points of acid–base and other titrations. The principle involved is that electrical conductance of a solution depends upon the number and mobility of ions. In the conductometric titrations, the conductance of the resulting solution is measured at different stages on adding some volume of the standard solution and then a graph is plotted from the experimental observations to get the end point. Conductometric titrations have several advantages. Coloured solutions, titration of weak acid and weak base, etc. cannot be titrated by normal methods, but can be titrated successfully by this method. Further, no special care is needed in titration because the end point is determined graphically.

48. Which of the following graph truly represents the titration of HCl solution against NaOH solution?

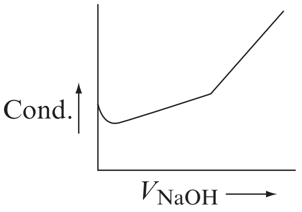
(a)



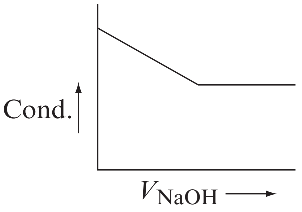
(b)



(c)

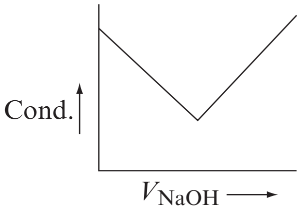


(d)

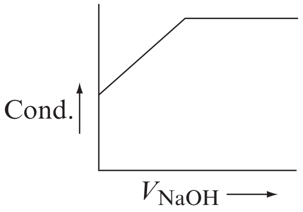


49. Which of the following graph truly represents the titration of CH_3COOH solution against NaOH solution?

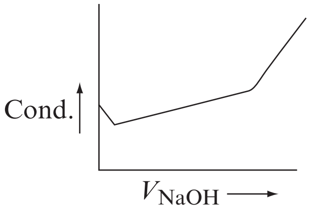
(a)



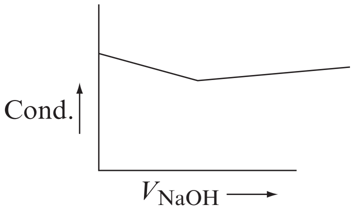
(b)



(c)

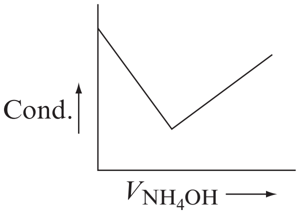


(d)

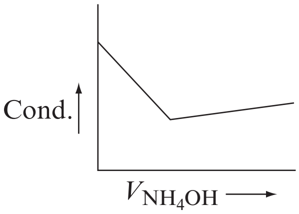


50. Which of the following graph truly represents the titration of HCl solution against NH_4OH solution?

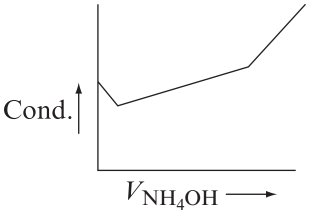
(a)



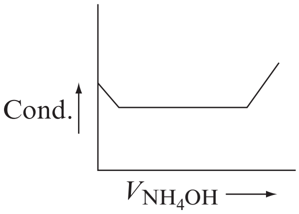
(b)



(c)

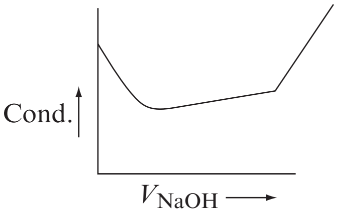


(d)

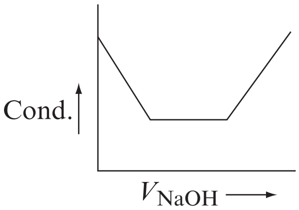


51. Which of the following graph truly represents the titration of a solution containing a mixture of HCl and CH_3COOH against NaOH solution?

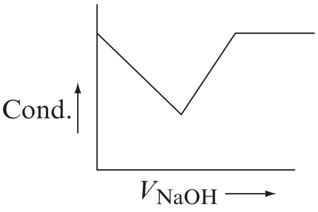
(a)



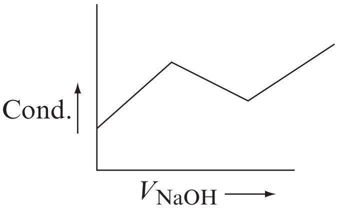
(b)



(c)

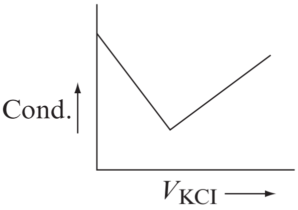


(d)

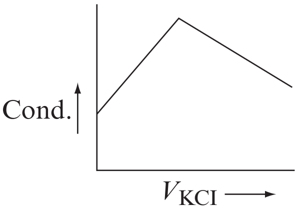


52. Which of the following graph truly represents the titration of $AgNO_3$ solution against KCl solution?

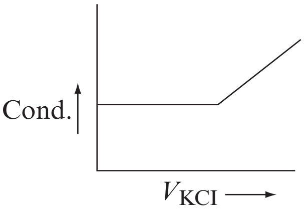
(a)



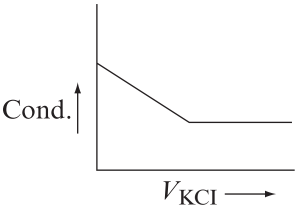
(b)



(c)

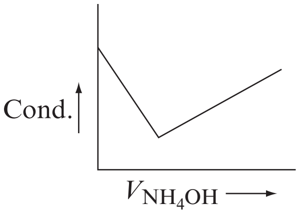


(d)

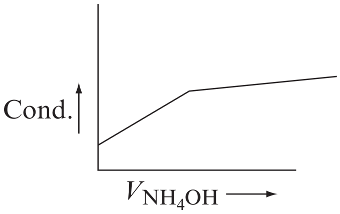


53. Which of the following graph truly represents the titration of CH_3COOH solution against NH_4OH solution?

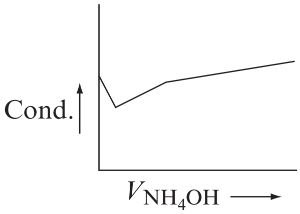
(a)



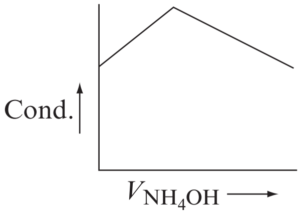
(b)



(c)



(d)



Section D (Assertion – Reason)

The following questions consist of two statements. Mark

(a) If both statements are CORRECT, and **Statement II** is the CORRECT explanation of **Statement I**.

(b) If both statements are CORRECT, and **Statement II** is NOT the CORRECT explanation of **Statement I**.

(c) If **Statement I** is CORRECT, but **Statement II** is INCORRECT.

(d) If **Statement I** is INCORRECT, but **Statement II** is CORRECT.

1. **Statement I:** Electrolysis of $CuCl_2(aq)$ gives 1 mole of Cu and 1 mole of Cl_2 by the passage of suitable charge.

   Statement II: Equal equivalents of Cu and Cl_2 are formed during the passage of same charge.

2. **Statement I:** Zinc metal can displace Ag metal from a solution containing the complex $[Ag((CN)_2]^-$.

   Statement II: $E^\circ_{Zn^{2+}, Zn}$ is greater than $E^\circ_{Ag^+, Ag}$.

3. **Statement I:** In electrolysis, the quantity of electricity needed for depositing 1 mole of silver is different from that required for 1 mole copper.

   Statement II: The atomic masses of silver and copper are different.

4. **Statement I:** In an electrochemical cell, anode and cathode are, respectively, negative and positive electrode.

   Statement II: At anode, oxidation takes place and at cathode reduction takes place.

5. **Statement I:** A metal having negative reduction potential when dipped in the solution of its own ions has a tendency to pass into the solution.

   Statement II: Metals having negative reduction potential have large hydration energy.

6. **Statement I:** Specific conductance decreases with dilution while molar conductance increases.

   Statement II: On dilution, number of ions per unit volume decreases but total number of ions increases considerably.

7. **Statement I:** When acidified zinc sulphate solution is electrolysed between zinc electrodes, it is zinc that is deposited at the cathode and evolution of hydrogen gas does not take place.

   Statement II: The electrode potential of zinc becomes less negative than hydrogen as the overvoltage for the hydrogen evolution on zinc is quite large.

8. **Statement I:** The conductivity of solutions of different electrolytes in the same solvent and at a given temperature is same.

   Statement II: The conductivity depends on the charge and size of the ions, the concentrations of ions and ease with which the ions move under potential gradient.

9. **Statement I:** Sodium ions are discharged in preference to hydrogen ions at a mercury cathode.

   Statement II: Na^+ is a strong reducing agent in comparison to H^+ ion.

10. **Statement I:** The conductivity of metals decreases while that of electrolytic solution increases with increase in temperature.

Statement II: Electrons in metals are very tightly held by the nucleus and are not free to move.

11. **Statement I:** An electrochemical cell can be set up only when the redox reaction is spontaneous.

Statement II: A reaction is spontaneous if free energy change at constant temperature and pressure is negative.

12. **Statement I:** In the Daniel cell, if concentrations of Cu^{2+} and Zn^{2+} ions are doubled, the EMF of cell does not change.

Statement II: If the concentration of ions in contact with the metal is doubled, the electrode potential will be doubled.

13. **Statement I:** KCl, NaCl, NH_4Cl, etc., cannot be used in the salt bridge of a cell containing silver ion.

Statement II: A salt bridge contains concentrated solution of an inert electrolyte like KCl, KNO_3, K_2SO_4, etc., in agar-agar.

14. **Statement I:** During electrolysis of aqueous sodium acetate solution, the molar ratio of gases formed at cathode and anode is 1:3.

Statement II: Acetate ion discharges at anode and H^+ ion, at cathode.

15. **Statement I:** Electrode potential of any electrode will change on changing any of its intensive properties.

Statement II: Any intensive property of system changes on changing any of its properties, whether intensive or extensive.

Section E (Column Match)

1. Match Column I with Column II

Column I	Column II (Electrolysis product using inert electrodes)
(A) Dilute solution of HCl	(P) O_2 evolved at anode
(B) Dilute solution of NaCl	(Q) H_2 evolved at cathode
(C) Concentrated solution of NaCl	(R) Cl_2 evolved at anode
(D) $AgNO_3$ solution	(S) Ag deposited at cathode

2. An aqueous solution of 'X' is added slowly to an aqueous solution of 'Y' as shown in List I. The variation in conductivity of these reactions is given in List II. Match List I with List II.

List I (X + Y)	List II
(A) $(C_2H_5)_3N + CH_3COOH$	(P) Conductivity decreases and then increases
(B) KI(0.1 M) + $AgNO_3$(0.01 M)	(Q) Conductivity decreases and then does not change much
(C) CH_3COOH + KOH	(R) Conductivity increases and then does not change much
(D) NaOH + HI	(S) Conductivity does not change much and then increases

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

$E^\circ(Fe^{3+}, Fe^{2+}) = +0.77$ V

$E^\circ(Fe^{2+}, Fe) = -0.44$ V

$E^\circ(Cu^{2+}, Cu) = +0.34$ V

$E^\circ(Cu^{+}, Cu) = +0.52$ V

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

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

$E^\circ(Cr^{3+}, Cr) = -0.74$ V

$E^\circ(Cr^{2+}, Cr) = -0.91$ V

Match E° of the redox pair in List I with the values given in List II.

List I	List II
(A) $E^\circ(Fe^{3+}, Fe)$	(P) −0.70 V
(B) $E^\circ(4H_2O \rightarrow 4H^+ + 4\,OH^-)$	(Q) −0.4 V
(C) $E^\circ(Cu^{2+} + Cu \rightarrow 2Cu^+)$	(R) −0.04 V
(D) $E^\circ(Cr^{3+}, Cr^{2+})$	(S) −0.83 V

4. Match the following

Column I	Column II
(A) Concentration cell	(P) $Ag \mid AgCl \mid Cl^- \parallel Ag^+ \mid Ag$
(B) Spontaneous cell reaction	(Q) $Ag \mid AgCl \mid Cl^- \parallel Br^- \mid AgBr \mid Ag$
(C) Non-spontaneous cell reaction	(R) $Ag \mid Ag^+ (0.1\ M) \parallel Ag^+ (1.0\ M) \mid Ag$
	(S) $Ag \mid AgCl \mid Cl^- (0.1\ M) \parallel Cl^- (1.0\ M) \mid AgCl \mid Ag$

Section F (Subjective)

Single-digit Integer Type

1. Percentage of aniline hydrochloride hydrolysed in its M/40 solution at 25°C is (Given: $E_{C_6H_5NH_2.HCl\,|\,H_2} = -0.18$ V, $2.303\,RT/F = 0.06$)

2. The standard reduction potential for $Cu^{2+}|Cu$ electrode is +0.34 V. The solubility product of $Cu(OH)_2$ is 1.0×10^{-19}. The pH of solution at which the reduction potential for the above electrode becomes 0.31 V, is ($2.303\,RT/F = 0.06$)

3. The reduction potential at 25°C for $Fe^{3+}|Fe^{2+}$ electrode is +0.718 V. If $E^\circ_{Fe^{2+}|Fe} = -0.44$ V and $E^\circ_{Fe^{3+}|Fe} = -0.04$ V, the ratio of molar concentrations of Fe^{2+} to Fe^{3+} ions in solution is ($2.303\,RT/F = 0.06$, log 5 = 0.7)

4. If $[Fe^{3+}]$ at equilibrium, when potassium iodide is added to a solution of Fe^{3+} initially at 0.50 M until $[I^-] = 1.0$ M, is $x \times 10^{-5}$ M, the value of x is (Given $E^\circ_{Fe^{3+}|Fe^{2+}} = 0.77$ V, $E^\circ_{I_2|I^-} = 0.53$ V, $2.303\,RT/F = 0.06$)

5. If it is desired to construct the following galvanic cell:

   $Ag(s)\ |\ Ag^+$ (saturated AgI) $\|\ Ag^+$ (saturated AgCl, $x \times 10^{-4}$ M Cl^-) $|\ Ag(s)$

   to have $E_{Cell} = 0.102$ V, what should be the value of x to get $[Cl^-]$, which must be present in the cathodic half-cell to achieve the desired EMF. Given K_{sp} of AgCl and AgI are 1.8×10^{-10} and 8.1×10^{-17}, respectively. ($2.303\,RT/F = 0.06$, log 2 = 0.3)

6. An alloy of lead (valency = 2)-thallium (valency = 1) containing 70% Pb and 30% Tl, by weight, can be electroplated onto a cathode from a perchloric acid solution. How many hours (approx.) would be required to deposit 5.0 g of this alloy at a current of 1.10 A? (Pb = 208, Tl = 204)

7. Iridium was plated from a solution containing $IrCl_6^{y}$ for 2.0 h with a current of 0.075 A. The Iridium deposited on the cathode weighed 0.36 g. If the oxidation state of Ir in $IrCl_6^{y}$ is x, then the value of $(x + y)$ is (Ir = 192)

8. The electrolysis of cold sodium chloride solution produces sodium hypochlorite by reacting NaOH and Cl_2 thoroughly. How long (in days) will a cell operate to produce 10 L of 7.45% (by mass) solution of NaClO if the cell current is 2.5 A? Assume that the density of solution is 1.0 g/ml.

9. A volume of 500 ml of 0.1 M – $CuSO_4$ solution is electrolysed for 5 min at a current of 0.161 A. If Cu is produced at one electrode and oxygen at the other, the approximate pH of the final solution is

10. A test for complete removal of Cu^{2+} ions from a solution of Cu^{2+} is to add NH_3(aq). A blue colour signifies the formation of complex $[Cu(NH_3)_4]^{2+}$ having $K_f = 1.1 \times 10^{13}$ and thus confirms the presence of Cu^{2+} in solution. 250 ml of 0.1 M – $CuSO_4$ is electrolysed by passing a current of 5 A for 1351 s. After passage of this charge, sufficient quantity of NH_3 is added to electrolysed solution maintaining $[NH_3] = 0.10$ M. If $[Cu(NH_3)_4]^{2+}$ is detectable up to its concentration as low as 1×10^{-5} M, would a blue colour be shown by the electrolysed solution on addition of NH_3. Mark '1', if the answer is 'yes' and mark '2', if the answer is 'no'.

11. By passing a certain amount of charge through NaCl solution, 9.08 L of chlorine gas were liberated at STP. When the same amount of charge is passed through a nitrate solution of metal M, 52.8 g of the metal was deposited. If the specific heat of metal is 0.032 Cal/°C-g, the valency of metal is

12. The electrode reactions for charging of a lead storage battery are:

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

    $$PbSO_4 + 2H_2O \rightarrow PbO_2 + SO_4^{2-} + 4H^+ + 2e$$

    The electrolyte in the battery is an aqueous solution of sulphuric acid. Before charging, the specific gravity of the liquid was found to be 1.10 (16% H_2SO_4 by wt.). After charging for $\frac{965}{9}$ h, the specific gravity of the liquid was found to be 1.42 (40% H_2SO_4 by weight). If the battery contained 2 L of the liquid and the volume remains constant during charge, the average current (in A) used for charging the battery is

13. A dilute solution of KCl was placed between two platinum electrodes, 12 cm apart, across which a potential of 1.93 volts was applied. How far (in cm) would the K^+ ion move in 20 h at 25°C? Ionic conductance of K^+ ion at infinite dilution at 25°C is 7.5×10^{-3} mho m^2 mol^{-1}.

14. In the refining of silver by electrolytic method, what will be the final mass (in gm) of 72.8 g silver anode (60% pure, by weight), if 9.65 A current is passed for 1 h? (Ag = 108)

15. The pH of 100 L of concentrated KCl solution after the electrolysis for 10 s using 9.65 A at 298 K is

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Four-digit Integer Type

1. The specific conductivity of a saturated solution of AgCl is 2.80×10^{-4} mho m^{-1} at 25°C. If $\lambda^\circ_{Ag^+} = 6.19 \times 10^{-3}$ mho m^2 mol^{-1} and $\lambda^\circ_{Cl^-} = 7.81 \times 10^{-3}$ mho m^2 mol^{-1}, the solubility of silver chloride (in order of 10^{-5} g l^{-1}) at 25°C, is

2. The electrode potential (in millivolts) of $2Ag(s) + S^{2-}(aq) \rightarrow Ag_2S(s) + 2e^-$ in a solution buffered at pH = 3 and which is also saturated with 0.1 M – H_2S, is (Given: for H_2S, $K_{a1} = 10^{-8}$; $K_{a2} = 10^{-13}$, K_{sp} of $Ag_2S = 4 \times 10^{-48}$, $E^\circ_{Ag^+|Ag} = 0.80$ V, log 2 = 0.3, 2.303 $RT/F = 0.06$)

3. An excess of liquid mercury is added to an acidified solution of 10^{-3} M – Fe^{3+}. It is found that 10% of Fe^{3+} remains at equilibrium at 25°C. The value of $E^\circ_{Hg_2^{2+}|Hg}$ (in mV), assuming that the only reaction that occurs is: $2Hg + 2Fe^{3+} \rightarrow Hg_2^{2+} + 2Fe^{2+}$, is (Given: $E^\circ_{Fe^{3+}|Fe^{2+}} = 0.7724$ V, log2 = 0.3, log3 = 0.48, 2.303 $RT/F = 0.06$)

4. Determine potential (in mV) of the cell: Pt | Fe^{2+}, Fe^{3+} || $Cr_2O_7^{2-}$, Cr^{3+}, H^+ | Pt in which $[Fe^{2+}] = 0.75$ M, $[Fe^{3+}] = 0.75$ M, $[Cr_2O_7^{2-}] = 2$ M, $[Cr^{3+}] = 4$ M and $[H^+] = 1$ M. Given:

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

$14\,H^+ + 6e + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$;
$E^\circ = 1.35$ V

2.303 $RT/F = 0.06$, log 2 = 0.3, log 3 = 0.48

5. An alloy weighing 2.70 mg of Pb–Ag was dissolved in desired amount of HNO_3 and volume was made 250 ml. A silver electrode was dipped in solution and E_{cell} of the cell:

Pt, H_2(1 bar) | H^+(1 M) || Ag^+ | Ag

was 0.50 V at 298 K. The percentage of lead in alloy is (Given: $E^\circ_{Ag^+|Ag} = 0.80$ V, Ag = 108, 2.303 $RT/F = 0.06$)

6. Given $E^\circ = 0.08$ V for Fe^{3+}(cyt b) | Fe^{2+} (cyt b) couple and $E^\circ = 0.20$ V for Fe^{3+}(cyb c_1) | Fe^{2+}(cyt c_1) couple, where E° represents the standard state reduction potentials at pH = 7.0 at 25°C and cyt is an abbreviation for cytochromes. The value of K_{eq} for the reaction

Fe^{3+} (cyt c_1) + Fe^{2+} (cyt b) $\rightleftharpoons$ Fe^{2+} (cyt c_1) + Fe^{3+} (cyt b)

is (2.303 $RT/F = 0.06$)

7. Calculate potential (in mV) of the cell: Cu | Mn(s) | $MnCl_2$(0.001 M), HCl(0.01 M) | O_2(0.25 bar) | Pt | Cu. Given, $E^\circ = -1.185$ V for the Mn^{2+} | Mn couple and 1.229 V for the O_2 | H_2O, H^+ couple. (2.303 $RT/F = 0.06$, log 2 = 0.3)

8. The temperature coefficient of the cell: Zn | $ZnCl_2$ | AgCl(s) | Ag is + 0.001 V/K. The entropy change (in J/K) accompanying this reaction, at 298 K is

9. For the reaction: $4Al(s) + 3O_2(g) + 6H_2O(l) + 4OH^-(aq) \rightleftharpoons 4Al(OH)_4^-(aq)$; $E^\circ_{cell} = 2.5$ V. If $\Delta_f G^\circ$ for $H_2O(l)$ and $OH^-(aq)$ are –280.0 and –156.25 kJ/mol, respectively, the magnitude of $\Delta_f G^\circ$ for $Al(OH)_4^-(aq)$ (in kJ/mol) is

10. In a Zn–MnO_2 Cell, the anode is made up of Zn and cathode of carbon rod surrounded by a mixture of MnO_2, Carbon, NH_4Cl and $ZnCl_2$ in aqueous base. If 8.7 g MnO_2 is present in cathodic compartment, how many days the dry cell will continue to give a current of 3.99×10^{-3} A?

11. An amount of 19 g of molten $SnCl_2$ is electrolysed for some time. Inert electrodes are used. 1.19 g of tin is deposited at the cathode. No substance is lost during electrolysis. If the ratio of the masses of $SnCl_2$ and $SnCl_4$ after electrolysis is $x : 261$, the value of x is (Sn = 119)

12. An object whose surface area is 80 cm^2 is to be plated with an even layer of gold 8.0×10^{-4} cm thick. The density of gold is 19.7 g/cm^3. The object is placed in a solution of $Au(NO_3)_3$ and a current of 2.4 A is applied. The time (in seconds) required for the electroplating to be completed, assuming that the layer of gold builds up evenly, is (Au = 197)

13. We have taken a saturated solution of AgBr. K_{sp} of AgBr is 12×10^{-14}. If 10^{-7} moles of $AgNO_3$ is added to 1 litre of this solution, find conductivity (specific conductance) of this solution in terms of 10^{-7} $S{\cdot}m^{-1}$ units. Given $\lambda^\circ(Ag^+) = 6 \times 10^{-3}$ S m^2 mol^{-1}, $\lambda^\circ(Br^-) = 8 \times 10^{-3}$ S m^2 mol^{-1}, $\lambda^\circ(NO_3^-) = 7 \times 10^{-3}$ $S{\cdot}m^2$ mol^{-1}.

14. On passing electricity through nitrobenzene solution, it is converted into azobenzene. The mass of azobenzene (in mg) produced, if the same quantity of electricity produces oxygen just sufficient to burn 96 g of fullerene (C_{60}), is

15. The conductivity of saturated solution of sparingly soluble salt, $Ba_3(PO_4)_2$, is 1.2×10^{-5} $ohm^{-1}cm^{-1}$. The limiting equivalent conductances of $BaCl_2$, K_3PO_4 and KCl are 160, 140 and 100 $ohm^{-1}cm^2$ eq^{-1}, respectively. The k_{sp} of $Ba_3(PO_4)_2$ (in the order of 10^{-25}) is

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Answer Keys

Exercise I

Electrode Potential

1. (c) 2. (d) 3. (d) 4. (a) 5. (a) 6. (a) 7. (b) 8. (a) 9. (a) 10. (a)
11. (d) 12. (b) 13. (a) 14. (c) 15. (c) 16. (b) 17. (b) 18. (a) 19. (c) 20. (a)
21. (c) 22. (c) 23. (c) 24. (a) 25. (d) 26. (d) 27. (c) 28. (c) 29. (a) 30. (a)

Galvanic Cell

31. (a) 32. (d) 33. (c) 34. (b) 35. (c) 36. (c) 37. (c) 38. (c) 39. (d) 40. (d)
41. (d) 42. (d) 43. (c) 44. (b) 45. (b) 46. (d) 47. (d) 48. (a) 49. (d) 50. (c)
51. (b) 52. (b) 53. (a) 54. (a) 55. (a) 56. (c) 57. (a) 58. (c) 59. (c) 60. (b)
61. (a) 62. (b) 63. (c) 64. (d) 65. (a)

Electrolysis

66. (b) 67. (a) 68. (a) 69. (b) 70. (b) 71. (d) 72. (b) 73. (c) 74. (b) 75. (d)
76. (a) 77. (b) 78. (d) 79. (b) 80. (a) 81. (b) 82. (a) 83. (c) 84. (d) 85. (a)
86. (a) 87. (d) 88. (a) 89. (c) 90. (b) 91. (c) 92. (d) 93. (c) 94. (a) 95. (b)
96. (a) 97. (d) 98. (a) 99. (b) 100. (c) 101. (a) 102. (a) 103. (b) 104. (b) 105. (b)

Conductance

106. (b) 107. (a) 108. (c) 109. (b) 110. (a) 111. (b) 112. (c) 113. (c) 114. (a) 115. (d)
116. (a) 117. (b) 118. (d) 119. (c) 120. (d) 121. (a) 122. (c) 123. (a) 124. (d) 125. (a)

Answer Keys Exercise II

Section A (Only one Correct)

1. (c) 2. (d) 3. (b) 4. (b) 5. (a) 6. (a) 7. (d) 8. (d) 9. (b) 10. (c)
11. (c) 12. (a) 13. (a) 14. (b) 15. (b) 16. (b) 17. (a) 18. (b) 19. (d) 20. (a)
21. (b) 22. (c) 23. (a) 24. (a) 25. (b) 26. (c) 27. (d) 28. (b) 29. (b) 30. (b)
31. (b) 32. (a) 33. (c) 34. (a) 35. (b) 36. (a) 37. (d) 38. (a) 39. (a) 40. (a)
41. (a) 42. (c) 43. (a) 44. (a) 45. (a) 46. (b) 47. (c) 48. (b) 49. (b) 50. (b)
51. (b) 52. (b) 53. (a) 54. (a) 55. (a) 56. (b) 57. (d) 58. (c) 59. (a) 60. (b)
61. (c) 62. (a) 63. (a) 64. (b) 65. (d) 66. (b) 67. (a) 68. (c) 69. (c) 70. (b)
71. (c) 72. (a) 73. (c) 74. (d) 75. (c) 76. (a) 77. (b) 78. (d) 79. (a) 80. (b)

Section B (One or More than one Correct)

1. (a), (c) 2. (a), (c), (d) 3. (c), (d) 4. (b), (c)
5. (d) 6. (a), (c) 7. (b), (c) 8. (b), (c), (d)
9. (a), (b), (c) 10. (a), (c) 11. (b), (c) 12. (a), (b), (d)
13. (a), (b) 14. (a), (b) 15. (a), (b), (c), (d)

Section C

Comprehension I

1. (a) 2. (b) 3. (a)

Comprehension II

4. (b) 5. (c) 6. (a)

Comprehension III

7. (a) 8. (a) 9. (c) 10. (b)

Comprehension IV

11. (b) 12. (b) 13. (c)

Comprehension V

14. (b) 15. (a) 16. (d) 17. (b) 18. (a)

Comprehension VI

19. (b) 20. (d) 21. (a) 22. (b) 23. (d)

Comprehension VII

24. (d) 25. (a) 26. (c) 27. (a)

Comprehension VIII

28. (b) 29. (a) 30. (d)

Comprehension IX

31. (a) 32. (b) 33. (b) 34. (c)

Comprehension X

35. (a) 36. (b) 37. (b) 38. (c)

Comprehension XI

39. (b) 40. (d) 41. (a)

Comprehension XII

42. (c) 43. (d)

Comprehension XIII

44. (b) 45. (c)

Comprehension XIV

46. (d) 47. (b)

Comprehension XV

48. (a) 49. (c) 50. (b) 51. (a)
52. (c) 53. (b)

Section D (Assertion – Reason)

1. (a) 2. (c) 3. (b) 4. (a) 5. (b) 6. (c) 7. (a) 8. (d) 9. (c) 10. (c)
11. (b) 12. (c) 13. (b) 14. (b) 15. (c)

Section E (Column Match)

1. A → P, Q; B → P, Q; C → Q, R; D → P, S
2. A → R; B → S; C → Q; D → P
3. A → R; B → S; C → P; D → Q
4. A → R, S; B → P, R; C → Q, S

Section F (Subjective)

Single-digit Integer Type

1. (4) 2. (5) 3. (5) 4. (5) 5. (4) 6. (1) 7. (0) 8. (9) 9. (3) 10. (2)
11. (3) 12. (2) 13. (9) 14. (8) 15. (9)

Four-digit Integer Type

1. (0287) 2. (0142) 3. (0815) 4. (0571) 5. (0090)
6. (0100) 7. (2633) 8. (0193) 9. (1300) 10. (0028)
11. (1520) 12. (0772) 13. (0055) 14. (0728) 15. (0108)

HINTS AND EXPLANATIONS

EXERCISE I (JEE MAIN)

Electrode Potential

1. Potential of electrode is independent from the area of electrode immersed in solution.

2. Informative.

3. Copper cannot reduce Al^{3+}.

4. Cu will reduce Ag^+ and itself becomes Cu^{2+}.

5. K is more active metal than Al.

6. Mg is better reducing agent.

7. Informative

8. Lower the reduction potential, strong is the reducing agent.

9. $Y^- + X \longrightarrow Y^{2-} + X^+$ is possible.

10. Mno_4^- Will also oxidize HCl.

11. Electrochemical series

12. $M^{n+}(aq) + ne^- \longrightarrow M(s); E = -ve, \Delta G = +ve$

Hence, reverse reaction is spontaneous.

13. $Hg_2Cl_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2Cl^-(aq)$

$$Hg_2^{2+}(aq) + 2e^- \rightleftharpoons 2Hg(l)$$

14. $E^\circ_{Mno_4^-/Mn^{2+}} > E^\circ_{Br_2/Br^-}$

15. Electrolyte used must have nearly same ionic mobility.

16. $MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$

$$\Delta E = -\frac{0.059}{5}\cdot\log\frac{1}{1\times[H^+]^8} = -\frac{0.059}{5}\cdot\log\frac{1}{(0.01)^8}$$

$= -0.1888$ V

17. $Cu^{2+} + 2e^- \rightleftharpoons Cu$

$$E = E^\circ - \frac{0.059}{2}\cdot\log\frac{1}{[Cu^{2+}]} = E^\circ - \frac{0.059}{2}\log\frac{1}{0.1}$$

$= E^\circ - 0.0295$ V

18. $O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$

$$E^\circ_{Basic} = E^\circ_{acidic} - \frac{0.059}{4}\cdot\log\frac{1}{(10^{-14})^4} = 0.404 \text{ V}$$

19. $$E_{Cu^+/Cu} = \frac{2\times E_{Cu^{2+}/cu} - 1\times E_{Cu^{2+}/Cu^+}}{2-1} = 0.521 \text{ V}$$

20. $2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$

$$E = E^\circ - \frac{0.059}{2}\cdot\log\frac{1}{(H^+)^2} = 0 - \frac{0.059}{2}\cdot\log\frac{1}{(10^{-7})^2}$$

$= -0.0413$

21. $E = -0.059.\ P^H$

22. Ionic mobility of ions in salt bridge should be same.

23. Higher reduction potential, stronger is the oxidizing agent.

24. Lower the reduction potential, stronger is the reducing agent.

25. $$E^\circ_{Fe^{3+}/Fe^{2+}} = \frac{3\times E^\circ_{Fe^{3+}/Fe} - 2\times E^\circ_{Fe^{2+}/Fe}}{3-2}$$

$= +0.772$ V

26. $H_2(g) \rightleftharpoons 2H + (aq) + 2e^-$

$$E_{H_2/CH_3COOH} = E_{H_2/H^+} = E^\circ_{H_2/H^+} - \frac{0.06}{2}\cdot\log\frac{(H^+)^2}{P_{H_2}}$$

$$= 0 - \frac{0.06}{2}\cdot\log\frac{\left(\sqrt{Ka\times C}\right)^2}{P_{H_2}}$$

$$= -\frac{0.06}{2}\cdot\log\frac{1.8\times10^{-5}\times0.5}{1}$$

$= +0.1512$ V

27. $E^\circ_{Cl^-/CuCl/Cu} = E^\circ_{Cu^+/Cu} - \frac{0.06}{1}\log\frac{1}{K_{sp}}$

or, $1.28 = E^\circ_{Cu^+/Cu} - \frac{0.06}{1}\cdot\log\frac{1}{2\times10^{-7}}$

$\Rightarrow\ E^\circ_{Cu^+/Cu} = 1.682\text{ V}$

28. $E^\circ_{OH^-/Pb(OH)_2/Pb} = E^\circ_{Pb^{2P}/Pb} - \frac{0.06}{2}\cdot\log\frac{1}{K_{sp}}$

or, $(-0.55) = (-0.13) - \frac{0.06}{2}\cdot\log\frac{1}{K_{sp}}$

$\therefore K_{sp} = 1.0\times10^{-14}$

29. $E_{MnO_4^-/MnO_2} = \frac{5\times E_{MnO_4^-/Mn^{2+}} - 2\times E_{MnO_2/Mn^{2+}}}{5-2}$

$= \frac{5\times1.51 - 2\times1.23}{3} = 1.697\text{ V}$

30. For stronger oxidizing agent, reduction potential should be high.

Galvanic Cell

31. Reduction occur at right electrode.

32. Circuit becomes incomplete.

33. $E_{Cell} = (ERP)_R - (ERP)_L = 0$

34. Net cell reaction is Cl_2 (P_2 atm) $\xrightarrow{\quad}$ Cl_2 (P_1 atm) for spontaneous reaction: $P_2 > P_1$

35. Theoretical

36. Theoretical

37. Theoretical

38. $E_{cell} = E^\circ_{cell} - \frac{RT}{2F}\cdot\ln\frac{[Zn^{2+}]}{[Cu^{2+}]}$

39. E°_{cell} is independent from size or amount of electrode as well as P^H of solution.

40. Theoretical

41. Theoretical

42. Ca and Cu are far away in the electrochemical series.

43. Reaction during charging of cell is 2Pb SO_4 (s) + $2H_2O$ (l) $\xrightarrow{\quad}$ Pb(s) + PbO_2 (s) + $2H_2$ SO_4 (aq)

44. Informative

45. Depolarizer is the term used for oxidizing agent in the cell.

46. Informative

47. Pb(s) + PbO_2 (s) + $2H_2SO_4$ (aq) $\xrightarrow{\quad}$ $2PbSO_4$ (aq) + $2H_2O$(l)

48. $E^\circ_{cell} = \frac{0.059}{n}\cdot\log K_{eq} \Rightarrow 0.295 = \frac{0.059}{2}\cdot\log K_{eq}$

$\therefore\quad K_{eq} = 10^{10}$

49. $L\cdot E: Ag\,(s) \rightleftharpoons Ag^+\left(c_1 = \sqrt{K_{SP}}\text{ M}\right) + e^-$

$R\cdot E: Ag^+\ (C_2 = 0.1\text{ M}) + e^- \rightleftharpoons Ag(s)$

$\therefore$ Net reaction: $Ag^+(C_2) \rightleftharpoons Ag^+(C_1)$

$E_{cell} = -\frac{0.059}{1}\cdot\log\frac{C_1}{C_2}$

$\Rightarrow 0.413 = -\frac{0.059}{1}\log\frac{\sqrt{K_{sp}}}{0.1}$

$\therefore K_{sp} = 1.0\times10^{-16}$

50. Net cell reaction = $H_2\,(P_1) \rightleftharpoons H_2\,(P_2)$

$E_{cell} = -\frac{0.06}{2}\cdot\log\frac{420}{600} = +0.0045\text{ V}$

51. $E^\circ_{cell} = 0.44 - 0.33 = 0.11\text{ V}$

52. Cell reaction: $Zn + Fe^{2+} \rightleftharpoons Zn^{2+} + Fe$

$E_{cell} = E^\circ_{cell} - \frac{0.059}{2}\cdot\log\frac{[Zn^{2+}]}{[Fe^{2+}]}$

or, $0.2905 = \frac{0.059}{2}\cdot\log K_{eq} - \frac{0.059}{2}\cdot\log\frac{0.01}{0.001}$

$\therefore K_{eq} = 10^{\left(\frac{0.32}{0.0295}\right)}$

53. $E^\circ_{cell} = \frac{0.06}{n}\cdot \log K_{eq} \Rightarrow 0.18 = \frac{0.06}{4}\cdot \log K_{eq}$

$\therefore \log K_c = 12$

54. $E_{cell} = E^\circ_{cell} - \frac{RT}{2F}\cdot \ln\frac{[Zn^{2+}]}{[Cu^{2+}]}$

55. $E_{cell} = E^\circ_{cell} - \frac{RT}{2F}\cdot \ln\frac{[Ni^{2+}]}{[Cu^{2+}]}$

56. $E_2 = E_1 - \frac{0.059}{2}\cdot \log\frac{1.0}{0.01} = E_1 - 0.059$

57. $E^\circ_{cell} = \frac{0.059}{2}\cdot \log 10^{12} = 0.354\ V$

58. $[H^+]_{HA} = \sqrt{K_a \cdot C} = \sqrt{10^{-5}\times 0.1} = 10^{-3}\ M$

59. Theoretical

60. $E^\circ_{cell} = \frac{0.06}{n}\cdot \log K_{eq}$

$\Rightarrow (0.77 - 0.53) = \frac{0.06}{2}\cdot \log K_{eq}$

$\therefore K_{eq} = 10^8$

61. Current flow from right electrode to left electrode in external circuit.

62. $\Delta G^\circ = -nF\cdot E^\circ_{cell} \Rightarrow -48250 = -2\times 96500\times E^\circ_{cell}$

$\therefore\ E^\circ_{cell} = 0.25\ V$

Now, $E_{cell} = E^\circ_{cell} - \frac{0.059}{2}\cdot \log\frac{[H^+]^2\,[Cl^-]^2}{P_{H_2}}$

$= 0.25 - \frac{0.059}{2}\cdot \log\frac{(0.1)^2\times(0.1)^2}{1} = 0.368\ V$

63. Net cell reaction: $H^+(C = ?) \rightleftharpoons H^+\ (10^{-6}\ M)$

$E_{cell} = -\frac{0.059}{1}\cdot \log\frac{10^{-6}}{c} = 0.118 \Rightarrow C = 10^{-4}\ M$

64. $E^\circ_{OCl^-/Cl_2} = \frac{2\times E^\circ_{OCl^-/Cl^-} - 1\times E^\circ_{Cl_2/Cl^-}}{2-1}$

$= \frac{2\times 0.94 - 1\times 1.36}{1}$

$= 0.52\ V$

65. For (i) & (iii); $E^\circ_{cell} = 3.0\ V$

Electrolysis

66. Oxidation occur at anode and reduction at cathode, in both.

67. Theoretical

68. Theoretical

69. Due to high over-voltage potential, reduction of H_2O becomes less favorable.

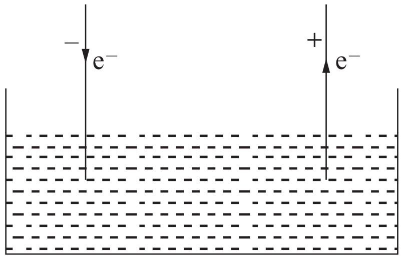
70. Electrochemical equivalent, $Z = \frac{E}{F}$ and E is maximum for silver.

71. Informative

72. $W = \frac{Q}{F}\times\frac{A}{n}$

For smaller n, w will be higher.

73. Cathode to anode in internal supply.



74. Informative

75. Informative

76. Equivalent weight is maximum for Na.

77. $n_{eq}H_2 = n_{eq}Cu \Rightarrow \frac{0.5}{1} = \frac{w}{63.5}\times 2$

$\Rightarrow w = 15.875$ gm

78. Ni will oxidize and Ni^{2+} will reduce resulting no change in Ni^{2+} Concentration.

79. $\frac{W}{E} = \frac{Q}{F} \Rightarrow \frac{9.8}{63.5} \times 2 = \frac{3 \times 10000}{96500} \times \eta \Rightarrow \eta = 0.99$

80. Cathode = H_2, anode = O_2 and $\frac{W_{H_2}}{W_{O_2}} = \frac{1}{8}$

81. $W = Z \cdot i \cdot t \Rightarrow Z \cdot i = \text{constant}$

$\therefore \quad \frac{i_1}{i_2} = \frac{Z_2}{Z_2} = \frac{E_2}{E_1}$

82. Theoretical

83. Informative

84. At cathode: $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

At anode: $2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$

Hence, solution becomes rich in H_2SO_4.

85. Reduction occur first for the species having higher reduction potential.

86. For very dilute NaCl solution,

Cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$; $P^H \uparrow$

Anode: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$; $P^H \downarrow$

87. $\frac{w_1}{w_2} = \frac{E_1}{E_2} = \frac{A/2}{A/3} = \frac{3}{2}$

88. n_{eq} of Zn $= \frac{100}{65.4} \times 2 = 3.058$

n_{eq} of $CuSO_4 = 1.0 \times 2 = 2.0$ (L.R.)

$\because \ n_{eq} = \frac{Q}{F} \Rightarrow 2 = \frac{1.0 \times t}{96500}$

$\Rightarrow t = 193000$ sec $= 53.6$ hr.

89. $n_{eq} = \frac{6 \times 10^{20}}{6 \times 10^{23}} = 10^{-3}$

90. $n_{eq} = \frac{Q}{F} \Rightarrow \frac{w}{208} \times 2 = \frac{1 \times 100 \times 3600}{96500}$

$\Rightarrow w \approx 388$ gm

91. n_{eq} Ag deposited = n_{eq}Cu dissolved

or, $\frac{3.24}{108} \times 1 = \frac{w}{64} \times 2 \Rightarrow w = 0.96$ gm

$\therefore$ Final mass of Cu anode = 60 – 0.96 = 59.04 gm

92. n_{eq} Fe_2O_3 reduced $= n \times n$-factor $= 1 \times 6$

$\therefore$ Charge needed = 6 F

93. Number of moles, $n = n_{eq}/n$-factor

$\therefore n_{Al} : n_{Cu} : n_{Na} = \frac{3}{3} : \frac{3}{2} : \frac{3}{1} = 2 : 3 : 6$

94. $2HSO_4^- \rightleftharpoons S_2O_8^{2-} + 2H^+ + 2e^-$

Now, $n_{eq} = \frac{Q}{F} \Rightarrow 1 \times 2 = \frac{i \times 3600 \times 0.75}{96500}$

$\therefore i = 71.48$ A

95. Number of Faradays required $= n_{eq} = 1 \times 2 = 2$

96. $n_{eq} = n \times n\text{-factor} = \frac{Q}{F}$

or, $\frac{1 \times V}{0.0821 \times 546} \times 4 = \frac{96500}{96500} \Rightarrow V = 5.6$ L

97. $n_{eq}Ag = n_{eq}O_2 \Rightarrow \frac{w}{108} \times 1 = \frac{1.6}{32} \times 4 \Rightarrow w = 21.6$ gm

98. $n_{eq} = \frac{Q}{F} \Rightarrow \frac{3}{96.5} \times n = \frac{12000}{96500} \Rightarrow n = 4$

99. Number of electrons

$= \frac{Q}{e} = \frac{5 \times 200}{1.602 \times 10^{-19}} = 6.24 \times 10^{21}$

100. $n_{eq} = \frac{Q}{F} \Rightarrow \frac{3.0}{E} = \frac{9.65 \times 10 \times 60}{96500} \Rightarrow E = 50$

101. Cu will deposit at cathode.

$n_{eq} = \frac{Q}{F} \Rightarrow \frac{w}{63.5} \times 2 = \frac{1 \times 96.5 \times 60}{96500} \Rightarrow w = 1.905$ gm

102. $n_{eq} = n \times n\text{-factor} = \frac{Q}{F}$

or, $\frac{2.8}{22400} \times 4 = \frac{i \times 1}{96500} \Rightarrow i = 48.25$ A/sec

103. Mass of Na deposited

$= \frac{18.7}{(100 - 18.7)} \times 10 = 2.623$ gm

Now, $n_{eq} = \frac{Q}{F} \Rightarrow \frac{2.623}{23} \times 1 = \frac{Q}{F} \times 0.5 \Rightarrow Q \approx 0.2$ F

104. n_{eq} A $= n_{eq}$ B

or, $\frac{5.6}{112} \times V_A = \frac{0.9}{27} \times 3$

$\therefore$ Valency of A, $V_A = 2$

105. n_{eq} Zn $= n_{eq}$ Ni $\Rightarrow \frac{22.89}{32.7} = \frac{20.55}{E_{Ni}}$

$\therefore E_{Ni} = 29.36$

Conductance

106. On dilution, conductance decreases and hence resistance increase.

107. Theoretical

108. HCl is molecular.

109. Radius of aq.ion : $K^+ < Na^+ < Li^+$

110. On dilution, $\wedge_m$ increases.

111. H_2SO_4 is strong electrolyte

112. For AgCl, $\wedge^\circ_m = \wedge_m = \lambda^\circ_{m(Ag^+)} + \lambda^\circ_m(Cl^-)$

$= 67.9 + 82.1 = 150 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$

Now, $\wedge_m = \dfrac{\kappa}{C} \Rightarrow 150 = \dfrac{1.8\times10^{-6}}{s}$

$\therefore S = 1.2 \times 10^{-8} \text{ mol cm}^{-3} = 1.2 \times 10^{-5} \text{ mol e}^{-1}$

113. $\wedge^\circ_{eq(NH_4OH)} = \wedge^\circ_{eq(NH_4Cl)} + \wedge^\circ_{eq(NaOH)} - \wedge^\circ_{eq(NaCl)}$

$= 129.8 + 217.4 - 108.9 = 238.3 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$

Now, $\alpha = \dfrac{\lambda_{eq}}{\lambda^\circ_{eq}} = \dfrac{9.532}{238.3} = 0.04 = 4\%$

114. $\wedge_m = \dfrac{\kappa}{C} = \dfrac{\frac{1}{250}\times125}{1\times10^3} = 5\times10^{-4} \text{ ohm}^{-1} \text{ m}^2 \text{ mol}^{-1}$

115. $MgSO_4(aq) + Ba(OH)_2 \text{ (added)} \longrightarrow Mg(OH)_2(s) + BaSO_4(s)$

First number of ions decreases and then increases.

116. $\wedge_{eq} = \dfrac{\kappa}{C} = \dfrac{2.6\times10^{-1}}{(1\times2)\times10^{-3}} = 1.3\times10^2 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$

117. $\alpha = \dfrac{\wedge_m}{\wedge^\circ_m} = \dfrac{16.30}{(349.8+40.9)} = 0.04172 \text{ or } 4.172\%$

118. Cell constant, $C = \dfrac{l}{A} = \dfrac{2.5}{5} = 0.5 \text{ cm}^{-1} = 50 \text{ m}^{-1}$

119. $\wedge^\circ_{m(NH_4OH)} = \wedge^\circ_{m(NH_4Cl)} - \wedge^\circ_{m(Cl^-)} + \wedge^\circ_{m(OH^-)}$

$= 150 - 75 + 200 = 275 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$

Now, $\alpha = \dfrac{\wedge_m}{\wedge^\circ_m} = \dfrac{22}{275} = 0.08$

120. $\wedge^\circ_{m(H_2O)} = \lambda^\circ_{m(H^+)} + \lambda^\circ_{m(OH^-)} = 0.035 + 0.020$

$= 0.055 \text{ mho m}^2 \text{ mol}^{-1}$

Now, $\wedge_m = \dfrac{\kappa}{C} \Rightarrow 0.055 = \dfrac{5.5\times10^{-6}}{C}$

$\therefore C = 10^{-4} \text{ mol m}^{-3} = 10^{-7} \text{ M} \Rightarrow K_w = C^2 = 10^{-14} \text{ M}^2$

121. $\alpha = \dfrac{\wedge_m}{\wedge^\circ_m} = \dfrac{7.814\times10^{-4}}{3.907\times10^{-2}} = 0.02$

Now, $K_a = \dfrac{\alpha^2 \cdot C}{1-\alpha} \simeq \alpha^2 \cdot C = (0.02)^2 \times 0.05$

$= 2\times10^{-5}$

122. $n_m = \dfrac{\kappa}{C} = \dfrac{6.3\times10^{-4}}{\frac{0.015}{2}\times10^{-3}} = 84 \text{ S cm}^2 \text{ mol}^{-1}$

123. $\wedge_m = \wedge^\circ_m - A\cdot\sqrt{C}$ (for strong electrolyte)

or, $260 = \wedge^\circ_m - A\times\sqrt{0.25}$ (1)

$250 = \wedge^\circ_m - A\times\sqrt{1.00}$ (2)

$\therefore \wedge^\circ_m = 270 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$

124. $\kappa_A = \dfrac{1}{50}\times G^* \text{ and } \kappa_B = \dfrac{1}{100}\times G^*$

Now, $G_{mix} = \dfrac{1}{G^*}\left(\dfrac{\kappa_A}{2} + \dfrac{\kappa_B}{2}\right) = \dfrac{3}{200} \text{ ohm}^{-1}$

$\therefore R = \dfrac{1}{G} = \dfrac{200}{3} \text{ohm}$

125. Conductivity of solution will remain uncharged but the cell constant becomes double.

$\kappa = G\times G^* = \dfrac{1}{50}\times\dfrac{1.5}{5} = \dfrac{3}{5}\times10^{-2} \text{ohm}^{-1}\text{cm}^{-1}$

$\therefore \wedge_{eq} = \dfrac{K}{C} = \dfrac{\frac{3}{5}\times10^{-2}}{0.05\times10^{-3}} = 120 \text{ ohm}^{-1}\text{cm}^2\text{eq}^{-1}$

EXERCISE II (JEE ADVANCED)

Section A (Only one Correct)

1. (I) Cu cannot reduce Pb

(II) Pb can reduce Ag

(III) Ag cannot reduce Cu.

Hence, reducing power: Pb > Cu > Ag

2. $$E = E° - \frac{0.06}{n} \cdot \log \frac{[R]}{[O]}$$

$$\Rightarrow 0.24 = 0.36 - \frac{0.06}{1} \log \frac{[R]}{[O]}$$

$$\therefore \frac{[O]}{[R]} = \frac{1}{100}$$

3. For the complex ion to get oxidised, its reduction potential should be low.

4. $$Ag^+ + 2NH_3 \rightleftharpoons Ag(NH)_3^+;$$

$$E° = 0.79 - 0.37 = 0.42 \text{ V}$$

$$\text{Now, } E° - \frac{0.06}{n} \cdot \log K_{eq} \Rightarrow 0.42 = \frac{0.06}{1} \cdot \log K_f$$

$$\Rightarrow K_f = 10^7$$

5. Given: $Co^{3+} + e^- \longrightarrow Co^{2+}$; $E° = 1.81$ V;

$$\Delta G°_1 = -1 \times F \times 1.81$$

$$Co(CN)_6^{3+} + e^- \longrightarrow Co(CN)_6^{4-} \quad E° = -0.83 \text{ V};$$

$$\Delta G°_2 = -1 \times F \times (-0.83)$$

$$Co^{2+} + 6CN^- \longrightarrow Co(CN)_6^{4-}; \; K_f = 10^{19};$$

$$\Delta G°_3 = -RT \times \ln 10^{19}$$

$$\text{Required } Co^{3+} + 6CN^- \longrightarrow Co(CN)_6^{3-} \quad K_f = ?;$$

$$\Delta G° = -RT \times \ln K_f$$

$$\text{Now, } \Delta G° = \Delta G°_1 - \Delta G°_2 + \Delta G°_3$$

$$\text{or, } -RT \cdot \ln K_f = (-1.81\,F) - 0.83\,F + (-RT \ln 10^{19})$$

$$\text{or, } RT \cdot \ln \frac{10^{19}}{K_f} = -2.64\,F$$

$$\Rightarrow \log \frac{10^{19}}{K_f} = -\frac{2.64\,F}{2.303\,RT} = -\frac{2.64}{0.06}$$

$$\therefore K_f = 10^{63}$$

6. $$E_{Cu^{2+}|Cu} = E°_{Cu^{2+}|Cu} - \frac{0.06}{2} \cdot \log \frac{1}{[Cu^{2+}]}$$

$$= E°_{Cu^{2+}|Cu} + 0.03 \log [Cu^{2+}]$$

$$= 0.34 + 0.03 \times \log(0.1) = 0.31 \text{ V}$$

$$\therefore E_{Cu/Cu^{2+}} = -0.31 \text{ V}$$

7. $$E_{cell} = E°_{cell} - \frac{RT}{2F} \cdot \ln \frac{[Cd^{2+}]}{[Ag^+]^2}$$

As CN– will form complex with Ag+ ion in the cathodic compartment, E_{cell} will decrease.

8. $$-\Delta G_{cell} = nF \cdot E_{cell} = nF\,[E°_{Cell} - \frac{RT}{nF} \cdot \ln \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$= nFE°_{Cell} - RT \cdot \ln \frac{C_1}{C_2}$$

9. $$E°_{X^-|Ag\,X|Ag} = E°_{Ag^+|Ag} - \frac{RT}{F} \cdot \ln \frac{1}{K_{sp}}$$

10. Cell reaction: $H^+(\text{cathode, } P^H = 3) \longrightarrow H^+$ (anode, $P^H = ?$)

$$E_{cell} = 0 - \frac{0.059}{1} \cdot \log \frac{[H^+]\text{anode}}{[H^+]\text{cathode}}$$

$$= 0.059\left[P^H_{anode} - P^H_{cathode}\right]$$

$$\text{or, } 0.272 = 0.059\,[P^H_{anode} - 3] \Rightarrow P^H_{anode} = 7.6$$

11. $Cl_2 + H_2O \rightleftharpoons Cl^- + ClO^- + 2H^+$;

$$E°_{cell} = 1.36 - 1.63 = -0.27 \text{ V}$$

$$\text{Now, } E_{cell} = E°_{cell} - \frac{0.06}{1} \log [H^+]^2$$

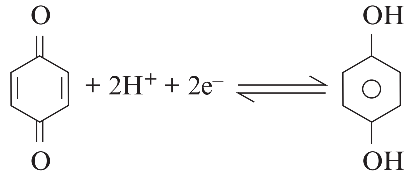
$$\text{or, } 0 = -0.27 + \frac{0.06}{1} \times 2P^H = 2.25$$

12. $$E_{cell} = E_{quinohydrone} - E_{calomel}$$

$$0.210 = E_{quinohydrone} - 0.279$$

$$\Rightarrow E_{quinohydrone} = 0.489 \text{ V}$$

Quinohydrone electrode is



(Quinone, Q) (Hydroquinone, H_2Q)

$$E = E^\circ - \frac{0.06}{2}\cdot\log\frac{1}{[H^+]} = E^\circ - 0.06\ P^H$$

or, $0.489 = 0.699 - 0.06.P^H \Rightarrow P^H = 3.5$

13. Anode: $Ag(s) \longrightarrow Ag^+(aq) + e^-\ 1\times 6$

Cathode:

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

Net:

$$6Ag(s) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \longrightarrow 6Ag^+(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$$

$$E_{cell} = E^\circ_{cell} - \frac{0.06}{n}\cdot\log\frac{[Ag^+]^6[Cr^{3+}]^2}{[Cr_2O_7^{2-}][H^+]^{14}}$$

$$= (1.33 - 0.80) - \frac{0.06}{6}\cdot\log\frac{(0.1)^6\times(0.4)^2}{1.6\times(0.1)^{14}} = 0.46\ V$$

14. Net cell reaction: $Zn - Hg(C_1M) \longrightarrow Zn - Hg(C_2M)$

$$E_{cell} = 0 - \frac{0.059}{2}\log\frac{C_2}{C_1} = -\frac{0.059}{2}\log\frac{1}{10} = 0.0295\ V$$

15. $E^\circ_{cell} = \dfrac{0.06}{2}\cdot\log K_{eq}$

$$\Rightarrow 0.75 - \frac{1.50\times3 - 1.68\times1}{3-1} = 0.03\log K_{eq}$$

$\therefore K_{eq} = 10^{-22}$

16. $[H^+]_{left} = \sqrt{Ka\cdot C} = \sqrt{1.8\times10^{-5}\times0.1} = C_1M$

$$[H^+]_{right} = \frac{K_w}{\sqrt{Kb\cdot C}} = \frac{10^{-14}}{\sqrt{1.8\times10^{-5}\times0.01}} = C_2M$$

Net cell reaction, assuming as concentration cell:

$$H^+(C_2M) \longrightarrow H^+(C_1M)$$

$$E_{cell} = 0 - \frac{0.06}{1}\cdot\log\frac{C_1}{C_2} = -0.465\ V$$

17. $E^\circ_{V^{2+}|V^{3+}} = 1\times0.616 + 1\times0.439 - 1\times0.799$

$= 0.256\ V$

$\therefore E^\circ_{V^{3+}|V^{2+}} = -0.256\ V$

18. $E_{cell} = E^\circ_{cell} - \dfrac{0.06}{n}\cdot\log\dfrac{[H^+]^2}{P_{H_2}}$

or, $0.70 = (0.28 - 0) - \dfrac{0.06}{2}\cdot\log\dfrac{[H^+]^2}{1} \Rightarrow P^H = 7.0$

19. Net cell reaction:

$$Ag^+(C_1 = 0.1\,M) \longrightarrow Ag^+\left(C_2 = 2\left(\frac{K_{sp}}{4}\right)^{1/3} M\right)$$

Now, $E_{cell} = 0 - \dfrac{0.06}{1}\cdot\log\dfrac{C_2}{C_1}$

$$\Rightarrow 0.162 = -0.06\cdot\log\frac{(2K_{sp})^{1/3}}{0.1}$$

$\therefore K_{sp} = 4\times10^{-12}$

20. $E_{Tl^+|Tl} - E_{Pb^{2+}|Pb} = -0.444\ V$

or, $\left(E_{Tl^+|Tl} - E_{Pb^{2+}|Pb}\right) - \dfrac{0.06}{2}\cdot\log\dfrac{[Pb^{2+}]}{[Tl^+]^2} = -0.444$

or, $[(-0.336) - (-0.126)] - 0.03\cdot\log\dfrac{0.1}{\left(\dfrac{K_{sp}}{0.1}\right)^2} = -0.444$

$\therefore K_{sp} = 4\times10^{-6}$

21. $E_{cell} = E_{Cu} - E_{Zn} = (E_{Cu} - E_{calomel}) - (E_{Zn} - E_{calomel})$

From question $E_{calomel} - E_{Zn} = 1.083\ V$

and $E_{calomel} - E_{Cu} = -0.018\ V$

22. The potential of hydrogen electrode at H_2(1 bar) may be expressed as $E = -0.059\ P^H$

Now, $E_1 = -0.059\left[P^{Ka} + \log\dfrac{x}{y}\right]$

and $E_2 = -0.059\left[P^{Ka} + \log\dfrac{y}{x}\right]$

$\therefore P^{Ka} = \dfrac{-(E_1 + E_2)}{0.118}$

23. For the given reaction, $E^\circ_{cell} = E^\circ_{given} - E^\circ_{hydrogen}$

$$\therefore (-0.84) - 0 = \frac{0.06}{1}\cdot \log K_{eq} \Rightarrow K_{eq} = 10^{-14}$$

24. Net cell reaction may be written as

$H_2 + Zn^{2+} \rightleftharpoons 2H^+ + Zn$

$$E_{cell} = E^\circ_{cell} - \frac{0.06}{n}\log\frac{[H^+]^2}{P_{H_2}\cdot[Zn^{2+}]}$$

$$\text{or, } (-0.61) = (-0.76) - \frac{0.06}{2}\cdot\log\frac{[H^+]^2}{1\times 0.4}$$

$\therefore [H^+] = 2\times 10^{-3}$ M

$$\text{Now, } K_{a_2} = \frac{[H^+][SO_3^{2-}]}{[HSO_3^-]} = \frac{(2\times10^{-3})\times(6.4\times10^{-2})}{0.4}$$

$= 3.2 \times 10^{-4}$

25.

$$Cu^{2+} + 4NH_3 \rightleftharpoons Cu(NH_3)_4^{2+},\ K_f = 10^{12}$$

	1.0 M	excess	
100%	0		1.0 M
Equ.	x	2.0 M	1.0 M

$$10^{12} = \frac{1.0}{x\times(2.0)^4} \Rightarrow x = \frac{10^{-12}}{16} = 6.25\times10^{-14}$$

Now, cell reaction: $Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu$

$$E_{cell} = E^\circ_{cell} - \frac{0.06}{2}\cdot\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$= [0.34 - (0.76)] - \frac{0.06}{2}\cdot\log\frac{1.0}{6.25\times10^{-14}} = 0.704 \text{ V}$$

26. Net cell reaction: $Zn + 2H^+ \rightleftharpoons Zn^{2+} + H_2$

$$E_{cell} = E^\circ_{cell} - \frac{0.06}{2}\log\frac{[Zn^{2+}]\cdot P_{H_2}}{[H^+]^2}$$

$$\text{or, } 0.70 = [0 - (-0.76)] - \frac{0.06}{2}\cdot\log\frac{0.01\times1}{[H^+]^2}$$

$\Rightarrow [H^+] = 0.01$ M

$$\text{Moles of HCl in RHS} = \frac{500\times0.01}{1000} = 5\times10^{-3}$$

$\therefore$ Mass of NaOH needed $= 5\times10^{-3}\times 40 = 0.2$ gm

27. On assuming concentration cell, the net cell reaction is $Ag^+ (C_1M, \text{Right}) \longrightarrow Ag^+ (C_2M, \text{left})$

$$\text{Now, } C_1 = 0.1\times\frac{40}{100} = 0.04 \text{ M}$$

$$\text{and } C_2 = \frac{K_{sp}}{[Cl^-]} = \frac{K_{sp}}{0.1\times\frac{50}{100}} = \frac{K_{sp}}{0.05} \text{ M}$$

$$\text{Now, } E_{cell} = 0 - \frac{0.06}{1}\log\frac{C_2}{C_1}$$

$$\text{or, } 0.42 = -\frac{0.06}{1}\log\frac{K_{sp}/0.05}{0.04} \Rightarrow K_{sp} = 2\times10^{-10}$$

28. $\Delta G_{cell} = -nFE_{cell} \Rightarrow -965\times3\times10^3 = -12\times96500 \times E_{cell}$

$\therefore E_{cell} = 2.5$ V

29. $$\text{Theoretical efficiency} = \frac{-\Delta G^\circ}{-\Delta H^\circ} \Rightarrow 0.84 = \frac{-\Delta G^\circ}{285}$$

$\therefore \Delta G^\circ = -0.84\times285 \text{ KJ} = -nF\cdot E^\circ_{cell}$

or, $0.84\times285\times10^3 = 2\times96500\times E^\circ_{cell}$

$\Rightarrow E^\circ_{cell} = 1.24$ V

30. Net cell reaction: $Ag(s) + H^+ + Cl^- \rightleftharpoons AgCl(s) + \frac{1}{2}H_2(g)$ But for E_{cell} calculation, reaction may be written as

$Ag(s) + H^+ \rightleftharpoons Ag^+ + \frac{1}{2}H_2$

$$\text{Now, } E_{cell} = E^\circ_{cell} - \frac{0.06}{1}\cdot\log\frac{[Ag^+]\cdot P_{H_2}^{1/2}}{[H^+]}$$

$$= [0 - 0.80] - \frac{0.06}{1}\cdot\log\frac{\left(\frac{10^{-10}}{0.1}\right)\times1^{1/2}}{0.1} = -0.32 \text{ V}$$

It means that actual reaction is in reverse direction and $E_{cell} = 0.32$ V

31. Informative

32.

$$x\,Ag^+ + y\,NH_3 \rightleftharpoons Ag(NH_3)_y^{x+}$$

	aM	bM	0	$b >> a$
Eqn.	?	bM	$\frac{a}{x}$M	

$$K_f = \frac{a/x}{[Ag^+]^x\cdot b^y} \Rightarrow [Ag^+] = \left(\frac{a}{K_f\cdot x\cdot b^y}\right)^{1/x}$$

Cell reaction: $Ag^+ (\text{Right}) \longrightarrow Ag^+ (\text{Left})$

$$\therefore E_{cell} = 0 - \frac{0.059}{1} \cdot \log \frac{[Ag^+]\text{Left}}{[Ag^+]\text{Right}}$$

Case-I: $0.118 = -0.059 \cdot \log\left(\frac{4\times10^{-4}}{4\times10^{-2}}\right)^{1/x} \Rightarrow x = 1$

Case-II: $0.118 = -0.059 \cdot \log\left(\frac{0.1}{1}\right)^{y/x} \Rightarrow y = 2$

33. $E°_{cell} = \frac{0.06}{1} \cdot \log K_{eq} = 0.06 \log \frac{1}{1.667\times10^6}$
$= -0.3732$ V

Now, $E°_{Cu^{2+}|Cu^+} - E°_{Cu^+|Cu} = -0.3732$ V (1)

and $E°_{Cu^{2+}|Cu} = \frac{1\times E°_{Cu^{2+}|Cu^+} + 1\times E°_{Cu^+|Cu}}{1+1}$
$= 0.3376$ V

or, $E°_{Cu^{2+}|Cu^+} + E°_{Cu^+|Cu} = 0.6752$ V (2)

From (1) and (2), $E°_{Cu^+|Cu} = 0.5242$ V

34. $Zn + Ni^{2+} \rightleftharpoons Zn^{2+} + Ni$

$E°_{cell} = \frac{0.06}{2} \log K_{eq}$

$\Rightarrow (-0.24) - (-0.75) = 0.03 \log K_{eq}$

$\therefore K_{eq} = 10^{17} \Rightarrow$ It means that Ni^{2+} will react almost completely and $[Zn^{2+}] \approx 1.0$ M

Now, $10^{17} = \frac{1.0}{[Ni^{2+}]} \Rightarrow [Ni^{2+}] = 10^{-17}$ M

35. Assuming the cell as concentration cell, the cell reaction may be written as

$$Ag^+\left(C_1 = \frac{4\times10^{-13}}{0.001} = 4\times10^{-10}\text{ M}\right)$$
$$\longrightarrow Ag^+\left(C_2 = \frac{2\times10^{-10}}{0.2} = 10^{-9}\text{ M}\right)$$

Now, $E_{cell} = 0 - \frac{0.06}{1} \cdot \log \frac{10^{-9}}{4\times10^{-10}} = -0.024$ V

36. $0.03 = \frac{0.06}{2} \cdot \log \frac{[Cu^{2+}]_{higher}}{[Cu^{2+}]_{lower}}$
$= 0.3 \cdot \log \frac{0.5}{[Cu^{2+}]_{lower}}$

$\therefore [Cu^{2+}]_{lower} = 0.05$ M

37. Cell reaction: $H^+(C_1, HA_1) \longrightarrow H^+(C_2, HA_2)$

$$E_{cell} = 0 - \frac{0.059}{1} \cdot \log\left(\frac{C_2}{C_1}\right) = 0.059 \cdot \log \sqrt{\frac{Ka_2}{Ka_1}}$$
$$= \frac{0.059}{2}(P^{K_{a1}} - P^{K_{a2}}) = 0.059 \text{ V}$$

38. $Au^+ + 2CN^- \rightleftharpoons Au\ (CN)_2^-$, $\Delta G°_1 = -RT \cdot \ln x$

$O_2 + 2H_2O + 4e^- \rightleftharpoons 40H^-$; $\Delta G°_2 = -4 \times F \times 0.41$

$Au^{3+} + 3e^- \rightleftharpoons Au$; $\Delta G°_3 = -3 \times F \times 1.50$

$Au^{3+} + 2e^- \rightleftharpoons Au^+$; $\Delta G°_4 = -2 \times F \times 1.40$

From $\Delta G°_1 + \frac{1}{4}\Delta G°_2 - \Delta G°_3 + \Delta G°_4, \Delta G°_{required}$
$= -RT \ln x + 1.29$ F

39. Informative

40. P^H of right electrode will increase due to formation of OH^- ion.

41. Informative

42. Theoretical

43. At low $[Cl^-]$, O_2 becomes anode product

44. Informative

45. Theoretical

46. In the electrolysis of aq. KNO_3, neither K^+ are NO_3^- participate in electrode reaction.

47. Na will react with water. S will not conduct electricity.

48. $\frac{w}{E} = \frac{Q}{F} \Rightarrow \frac{0.635}{63.5} \times 2 = \frac{i \times 0.965 \times 3600}{96500}$

$\Rightarrow i = \frac{2}{3.6}$ A

$\therefore$ % error $= \frac{\frac{2}{3.6} - 0.5}{\frac{2}{3.6}} = 10\%$

49. Detonating gas is mixture of H_2 and O_2

$n_{eq} S_n = n_{eq} H_2 = n_{eq} O_2 \Rightarrow \frac{1.2}{120} \times 2 = n_{H_2} \times 2 = n \quad \times 4$

$\therefore n_{H_2} = 0.01$ and $n_{O_1} = 0.005$

$\therefore$ Vol. of mixture of H_2 and $O_2 = 0.015 \times 22400$
$= 336$ ml

50. $$n_{eq} \text{ of Li OH } = \frac{Q}{F} \Rightarrow \frac{w}{24}\times 1 = \frac{2.5\times 4825\times 0.8}{96500}$$

51. $$n_{eq} \text{ Cu deposited at cathode } = \frac{Q}{F}$$

or, $$\frac{w}{63.5}\times 2 = \frac{12.4\times 4825}{96500} \Rightarrow w = 19.685 \text{ gm}$$

But the increase in mass of cathode is only 19.05 gm It represents that 20 gm of sample contains only 19.05 gm Cu.

$$\therefore \% \text{ of Cu} = \frac{19.05}{20}\times 100 = 95.25\%$$

Now, $$\frac{Q}{F} = n_{eq}\text{Cu} + n_{eq}\text{Fe} \text{ (oxidised at anode)}$$

or, $$\frac{12.4\times 4825}{96500} = \frac{19.05}{63.5}\times 2 + \frac{w}{56}\times 2 \Rightarrow w = 0.56 \text{ gm}$$

$$\therefore \text{Percentage of Fe} = \frac{0.56}{20}\times 100 = 2.8\%$$

52. Theoretical n_{eq} of NaOH formed $= n_{eq}$Cu

$$= \frac{3.18}{63.6}\times 2 = 0.1$$

Actual n_{eq} of NaOH formed $$= \frac{60\times 1}{1000} = 0.06$$

$$\therefore \text{Percentage yeild} = \frac{0.06}{0.1\times 100 = 60\%}$$

53. Cell reaction during discharge:

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

$$n_{Pb} \text{ taken} = \frac{200}{208} \text{ and } n_{PbO_2} \text{ taken} = \frac{200}{240}$$

Hence, PbO_2 is L.R.

Now, $$n_{eq}PbO_2 = \frac{Q}{F} \Rightarrow \frac{200}{240}\times 2 = \frac{10\times t}{96500}$$

$\Rightarrow t = 16083.33$ sec

55. $$\frac{Q}{F} = n_{eq} \text{ of } I^- = n_{eq}Na_2S_2O_3$$

or, $$\frac{i\times 2\times 3600}{96500} = \frac{72\times 1.0}{1000}\times 1 \Rightarrow i = 0.965 \text{ A}$$

56. $$C_{14}H_{10} + 2H_2O \longrightarrow C_{14}H_8O_2 + 6H^+ + 6e^-$$

$$n_{eq}\, C_{14}H_8O_2 = \frac{Q}{F} \Rightarrow \frac{w}{208}\times 6 = \frac{1\times 40\times 60\times 0.965}{96500}$$

$\therefore w = 0.832$ gm

57. Number of coulombs required $$= \frac{1000}{0.00033} \text{ per Kg Cu}$$

Energy required $$= \frac{1000}{0.00033}\times 0.33 = 10^6 \text{ J}$$

$\therefore$ Cost of electricity

$$= \frac{4}{10^3\times 3600}\times 10^6 = 1.11 \text{Rupee}$$

58. $$n_{eq}\, CH_3Coo^- \text{ oxidised} = \frac{Q}{F}$$

or, $$n\times 1 = \frac{0.5\times 482.5\times 60\times 0.8}{96500} \Rightarrow n = 0.12$$

$\therefore$ Moles of $(C_2H_6 + CO_2)$ produced

$$= \frac{3}{2}\times 0.12 = 0.18$$

and total volume = 0.18 × 22.4 = 4.032 L

59. $$\Delta E^\circ = \frac{0.059}{2}\cdot \log 10^6 = 0.177 \text{ V}$$

60. $$\text{Back EMF} = \frac{0.06}{2}\cdot \log\frac{0.12}{0.08} = 5.4\times 10^{-3} \text{ V}$$

61. Equivalent of charge used

$$= \frac{0.4825\times 10\times 3600}{96500} = 0.18 \text{ F}$$

Cell reaction during charge:

Cu +	$Zn^{2+} \longrightarrow$	Cu^{2+}	+ Zn
	$\frac{100\times 1}{1000} = 0.1$ mole	$\frac{100\times 1}{1000} = 0.1$ mole	
	= 0.2 eq	= 0.2 eq	
Final	0.2 – 0.1 8	= 0.2 + 0.18	
	= 0.02 eq	= 0.38 eq	
	= 0.01 mole	= 0.19 mole	

$$\therefore \text{Final } [Zn^{2+}] = \frac{0.01}{100}\times 1000 = 0.1 \text{ M}$$

and $$[Cu^{2+}] + \frac{0.19}{100}\times 1000 = 1.9 \text{ M}$$

Now, cell reaction as galvanic cell:

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

and $E_{cell} = E^{\circ}_{cell} - \frac{0.06}{n} \cdot \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$

$$= [0.34 - (-0.76)] - \frac{0.06}{2} \cdot \log \frac{0.1}{1.9} = 1.1084 \text{ V}$$

62. Reactions involved are

$2H_2O \xrightarrow{\text{electrolysis}} 2H_2 + O_2$

$N_2 + 3H_2 \longrightarrow 2NH_3$
$NH_3 + 2O_2 \longrightarrow HNO_3 + H_2O$
$NH_3 + HNO_3 \longrightarrow NH_4NO_3$

For 1 mole NH_4NO_3, 3 moles of H_2O should be electrolyzed. Hence for 1152 Kg NH_4NO_3, moles of H_2 needed $= 3 \times \frac{1152 \times 10^3}{80} = 4.32 \times 10^4$

Now, $n_{eq} H_2 = \frac{Q}{F} \Rightarrow 4.32 \times 10^4 \times 2 = \frac{i \times 24 \times 3600}{96500}$

$\therefore\ i = 96500$ A/day

63. $n_{eq}\ HC_3H_5O_3 = n_{OH^-} = \frac{Q}{F}$

or, $\frac{w}{90} \times 1 = \frac{50 \times 10^{-3} \times 1158}{96500} \Rightarrow w = 0.054$ gm

$\therefore$ % of lactice acid $= \frac{0.054}{1} \times 100 = 5.4\%$

64. $n_{H_2O_2}$ formed $= n_{(NH_4)_2S_2O_8} = n$

and $n_{eq} (NH_4)_2S_2O_8 = \frac{Q}{F}$

$\Rightarrow n \times 2 = \frac{102}{34} \times 2 = \frac{i \times 3600 \times 0.5}{96500}$

$[2SO_4^{2-} \longrightarrow S_2O_8^{2-} + 2e^-]$ $\quad \Rightarrow i = 321.67$ A

65. $n_{As} = n_{H_3AsO_3} = n$ and $n_{eq}\ H_3AsO_3 = n_{eq} I_2 = \frac{Q}{F}$

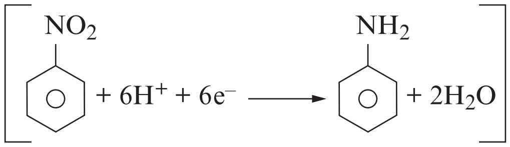
or, $\frac{w}{75} \times 2 = \frac{1.68 \times 10^{-3} \times 96.5}{96500} \Rightarrow w = 6.3 \times 10^{-5}$ gm

66. $\frac{W}{E} = \frac{Q}{F} \Rightarrow \frac{52.2}{87} \times 2 = \frac{19.3 \times 2 \times 3600 \times \eta}{96500}$
$\Rightarrow \eta = 0.8333$ or 83.33%

67. $n_{eq} Cu^{2+}$ reduced $= \frac{Q}{F} \Rightarrow n \times 2 = \frac{2 \times 10^{-3} \times 19.3 \times 60}{96500}$
$\therefore\ n = 1.2 \times 10^{-5}$

$\therefore\ [CuSO_4]_0 = \frac{(1.2 \times 10^{-5} \times 2)}{250} \times 1000 = 9.6 \times 10^{-5}$ M

68. $\frac{W}{E} = \frac{Q}{F} \Rightarrow \frac{12.3}{123} \times 6 = \frac{Q \times 0.5}{F} \Rightarrow Q = 1.2$ F



and Energy consumed = 1.2 F × 3.0 V = 347.4 KJ

69. n_{eq} H_2 (at cathode) $= n_{eq}$ O_2 $+$ n_{eq} $H_2S_2O_8$ (at anode)

or, $\frac{9.08}{22.7} \times 2 = \frac{2.27}{22.7} \times 4 + \frac{w}{194} \times 2 \ [2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^-]$
$\therefore\ w = 38.8$ gm

70. Initial mass of H_2SO_4,

$w_1 = 3600 \times 1.5 \times \frac{40}{100} = 2160$gm

Final mass of H_2SO_4,

$w_2 = 3600 \times 1.1 \times \frac{10}{100} = 396$ gm

$\therefore$ Moles of H_2SO_4 consumed $= \frac{w_1 - w_2}{98} = 18$

Now, $n_{eq}\ H_2SO_4 = \frac{Q}{F} \Rightarrow 18 \times 1 = \frac{(\text{amp-hr}) \times 3600}{96500}$

$\therefore$ Number of ampere-hr = 482.5

71. $\frac{\wedge_m(NaCl)}{\wedge_m(KCl)} = \frac{(\kappa/C)_{NaCl}}{(\kappa/C)_{KCl}} = \frac{\frac{1}{R_{NaCl}} \cdot G^* \cdot \frac{1}{C_{NaCl}}}{\frac{1}{R_{KCl}} \cdot G^* \cdot \frac{1}{C_{KCl}}}$

$$= \frac{(R \cdot C)_{KCl}}{(R \cdot C)_{NaCl}}$$

or, $\frac{\wedge_m(NaCl)}{120} = \frac{200 \times 0.1}{6400 \times 0.003}$

$\Rightarrow \wedge_{m(NaCl)} = 125\ \Omega^{-1}\ cm^{-1}\ mol^{-1}$

72. $\wedge^\circ_m[(NH_4)_2CrO_4] = 2\times\lambda^\circ_m(NH_4^+) + \lambda_m(CrO_4^{2-})$

$= (2 \times 6.6 \times 10^{-8} + 5.4 \times 10^{-8}) \times 96500$

$= 0.01795\ \Omega^{-1}\ m^2\ mol^{-1}$

73. $\wedge_m = \alpha \cdot \wedge^\circ_m = \dfrac{\kappa}{C}$

or, $0.9 \times 4.25 \times 10^{-2} = \dfrac{382.5}{C \times 10^3} \Rightarrow C = 0.1\ M$

74. $\wedge_m = \dfrac{K}{C} \Rightarrow 1.5 \times 10^{-2} = \dfrac{3.06\times10^{-3} - 2.56\times10^{-3}}{C}$

$\therefore\ C = \dfrac{1}{30}\, mol\ m^{-3} = \dfrac{1}{30}\times10^{-3}\, mol\cdot l^{-1} = \dfrac{585/58.5}{V}$

$\therefore\ V = 3 \times 10^5\ L$

75. $\wedge_m = \dfrac{\kappa}{C} = \dfrac{G\cdot G^*}{C} \Rightarrow 100 = \dfrac{\dfrac{1}{R}\times\dfrac{0.5}{1.5}}{0.1\times10^{-3}}$

$\Rightarrow\ R = \dfrac{100}{3}\, ohm$

Now, $V = IR \Rightarrow\ I = \dfrac{V}{R} = \dfrac{5}{100/3} = 0.15\ A$

76. Ionic mobility, $\mu^\circ = \dfrac{\text{speed of ion}}{\text{Pot. gradient}} = \dfrac{\lambda^\circ_m}{F}$

or, $\dfrac{\text{speed}}{\left(\dfrac{19.3}{5}\right)} = \dfrac{50}{96500} \Rightarrow \text{speed} = 2 \times 10^{-3}\ cm/s$

77. $\wedge_{eq} = \dfrac{\kappa}{C} \Rightarrow 150 \times \dfrac{3.4\times10^{-6} - 1.6\times10^{-6}}{5}$

$\therefore\ S = 1.2 \times 10^{-8}\ mol\ cm^{-3} = 1.2 \times 10^{-5}\ M$

78. $K = G \cdot G^* \Rightarrow \dfrac{\kappa}{1.4} = \dfrac{1/280}{1/50}$

$\Rightarrow \kappa = 0.25\ s\ m^{-1}$ for 0.5 M

Now, $\wedge_m = \dfrac{\kappa}{C} = \dfrac{0.25}{0.5\times10^3} = 5\times10^{-4} s\ m^2 mol^{-1}$

79. $Ag\,A(S) \rightleftharpoons \underset{(x+y)M}{Ag^+} + \underset{xM}{A^-}$

$Ag\,B(S) \rightleftharpoons \underset{(x+y)M}{Ag^+} + \underset{yM}{B^-}$

Now, $(x + y) \cdot x = 3 \times 10^{-14}$ and

$(x + y) \cdot y = 1 \times 10^{-14}$

$\therefore\ [Ag^+] = x + y = 2\times10^{-7} M,$

$[A^-] = x = 1.5\times10^{-7} M;$

$[B^-] = y = 0.5\times10^{-7} M$

Now,

$\kappa_{solution} = 3.75\times10^{-8} = 2\times10^{-7}\times10^{-3}\times60 + 1.5\times10^{-7}$
$\times10^{-3}\times80 + 0.5\times10^{-7}\times10^{-3}\ \overset{\circ}{\lambda}_B$

$\therefore\ \overset{\circ}{\lambda}_B = 135\ ohm^{-1}\ cm^2\ mol^{-1}$

80. $\overset{\circ}{\wedge}_{eq}\,[Be_3(Po_4)_2] = \overset{\circ}{\wedge}_{eq}\,[BeCl_2] + \overset{\circ}{\wedge}_{eq}\,[K_3Po_4]$
$- \overset{\circ}{\wedge}_{eq}\,[K\,Cl]$

$= 160 + 140 - 100 = 200\ ohm^{-1}\ cm^2\ eq^{-1}$

Now, $n_{eq} = \dfrac{\kappa}{C} \Rightarrow 200 = \dfrac{1.2\times10^{-5}}{C}$

$\Rightarrow\ C = 6 \times 10^{-8}\ eq\ cm^{-3}$

$= 6 \times 10^{-5}\ N$

$= 10^{-5}\ M$

Now, $K_{sp} = 108\,S^5 = 108\times(10^{-5})^5 = 1.08\times10^{-23}$

Section B (One or More than one Correct)

1. Net cell reaction is spontaneous in electrochemical cell but non-spontaneous in electrolytic cell. Cathode is +ve in electrochemical cell but –ve in electrolytic cell.

2. For the cell: Ag(s) | Ag Cl (s) | Cl− ‖ Ag^+ | Ag(s), the net cell reaction is $Ag^+ + Cl^- \rightleftharpoons Ag\,Cl\,(s)$.

3.

Left electrode: $Ag(s) + Cl^-(aq) \rightarrow Ag\,Cl\,(s) + e^-\ 1 \times 2$

Right electrode : $Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(l) + 2\,Cl^-(aq)$

Net reaction: $2Ag(s) + Hg_2Cl_2(s) \rightarrow 2Ag\,Cl(s) + 2Hg\,(l)$

4. Informative

5. $n_{eq}\ \text{Cu} = \frac{63.5}{63.5}\times 2 = 2;\ n_{eq}\ \text{Mg} = \frac{24}{24}\times 2 = 2$

$n_{eq}\ \text{Na} = \frac{11.5}{23}\times 1 = 0.5;\ n_{eq}\ \text{Al} = \frac{9}{27}\times 3 = 1$

6. Theoretical

7. $\wedge^\circ_{eq} = 60 + 80 = 140\ \text{ohm}^{-1}\ \text{cm}^2\ \text{eq}^{-1}$

$\wedge^\circ_m = 140 \times 6 = 840\ \text{ohm}^{-1}\ \text{cm}^2\ \text{eq}^{-1}$

8. Salt bridge does not change standard potential of any electrode.

9. Moles of electron involved

$$= \frac{0.25\times 9.65\times 3600}{96500} = 0.09$$

$\therefore$ Mass of Zn involved $= \frac{0.09}{2}\times 65.4 = 2.943$ gm

Mass of MnO_2 involved $= 0.09 \times 87 = 7.83$ gm

Mass of NH_4^+ involved $= 0.09 \times 18 = 1.62$ gm

10. Net cell reaction is

$Cd(s) + 2AgCl(s) \rightleftharpoons 2Ag(s) + Cd^{2+}(aq) + 2Cl^-(aq)$

$\Delta G^\circ_{50^\circ C} = -nFE^\circ = -2\times 96500\times 0.6 = -115800$ J

$\Delta G^\circ_{0^\circ C} = -nFE^\circ = -2\times 96500\times 0.7 = -135100$ J

$$\Delta S^\circ = nF\cdot\left(\frac{E^\circ_2 - E^\circ_1}{T_2 - T_1}\right) = 2\times 96500\times\frac{0.6-0.7}{50}$$

$= -386$ J/K

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

$= (-135100) + 273 \times (-386) = -240478$ J

11. Anode: $2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$

Cathode: $2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$

$n_{eq}\ H^+$ produced $= n_{eq}\ OH^-$ produced $= \frac{Q}{F}$

or, $n_{H^+}\times 1 = n_{OH^-} = \frac{1.25\times 965\times 60}{96500} = 0.75$

Anode: $HPO_4^{2-} + H^+ \rightleftharpoons H_2PO_4^-$

1.0 M 0.75 M 1.0 M

Final 0.25 M 1.75 M

$$\therefore\ P^H = P^{K_a} + \log\frac{[HPO_4^{2-}]_0}{[H_2PO_4^-]} = 2.15 + \log\frac{0.25}{0.75}$$

$= 1.30$

Cathode: $H_2PO_4^- + OH^- \rightleftharpoons HPO_4^{2-} + H_2O$

1.0 M 0.75 M 1.0 M

Final 0.25 M 0 1.75 M

$$\therefore\ P^H = P^{K_a} + \log\frac{[HPO_4^{2-}]_0}{[H_2PO_4^-]}$$

$$= 2.15 + \log\frac{1.75}{0.25} = 3.0$$

12. V, Fe and Hg will be oxidised by NO_3^-

13. Resistance and heat capacity depends on quantity.

14. Theoretical

15. Net cell reaction of discharge is

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

x mole x mole

Initial mass of H_2SO_4,

$$w_1 = 1000 \times 1.26 \times \frac{40}{100} = 504\ \text{gm}$$

Final mass of H_2SO_4,

$$w_2 = (1260 - 98x + 18x) \times \frac{28}{100}$$

$= (352.8 - 22.4x)$ gm

From reaction, $504 - 98x = 352.8 - 22.4x \Rightarrow x = 2$

Section C (Comprehensions)

Comprehension I

1. $E^\circ_{Cell} = E^\circ_{H^+/H_2} - E^\circ_{Zn^{2+}/Zn}$ because $E^\circ_{H^+/H_2}$ was higher

or, $0.76 = 1.00 - E^\circ_{Zn^{2+}/Zn} \Rightarrow E^\circ_{Zn^{2+}/Zn} = 0.24$ V

2. $E^\circ_{Cell} = E^\circ_{Cu^{2+}/Cu} - E^\circ_{H^+/H_2}$ because $E^\circ_{Cu^{2+}/Cu}$ was higher

or, $0.34 = E^\circ_{Cu^{2+}/Cu} - 1.00 \Rightarrow E^\circ_{Cu^{2+}/Cu} = 1.34$ V

3. $E^\circ_{Cell} = E^\circ_{Cu^{2+}/Cu} - E^\circ_{Zn^{2+}/Zn} = 1.34 - 0.24 = 1.10$ V

Comprehension II

4. $E_{Ag^+/Ag} = E^\circ_{Ag^+/Ag} - \frac{0.06}{1}\cdot\log\frac{1}{[Ag^+]}$

$= 0.80 - \frac{0.06}{1}.\log\frac{1}{\sqrt{K_{sp}}}$

$= +\ 0.314$ V

5. $E^\circ_{I^-|AgI|Ag} = E^\circ_{Ag^+/Ag} - \frac{0.06}{1}\cdot\log K_{sp} = -0.172V$

6. $E_{I^-|AgI|Ag} = E^\circ_{I^-/AgI/Ag} - \frac{0.06}{1}\cdot\log[I^-]$

$= -0.172 - 0.06\cdot\log 0.04 = -0.088$ V

Comprehension III

7. As(0.40) > (–0.87), reduction of $Ni_2O_3(s)$ will occur.

8. $E^\circ_{cell} = (0.40) - (-0.87) = 1.27$ V

9. Net cell reaction is independent from OH^- (aq)

10. $-\Delta G^\circ = nFE^\circ_{cell} = 2 \times 96500 \times 1.27 = 245110$ J

Comprehension IV

11. H_3O^+ is only needed in balancing cathode reaction:

$$NO_3^- + 3H_3O^+ + 2e^- \longrightarrow HNO_2 + 4H_2O$$

12. Moles of electron needed = 2 × moles of HNO_2 formed

13. $n_{eq}HNO_2 = \frac{Q}{F} \Rightarrow 0.1\times 2 = \frac{10\times t}{96500} \Rightarrow t = 1930$ sec

Comprehension V

14. $\Delta G^\circ = -nFE^\circ \Rightarrow -237.39\times 10^3 = -2\times 96500\times E^\circ_{cell}$

$\therefore E^\circ cell = 1.23$ V

15. Moles of H_2 needed $= \frac{23.739}{237.39} = 0.1$

$\therefore$ Volume of H_2 needed $= 0.1 \times 22.7 = 2.27$ L

16. E_{cell} is independent from $[OH^-]$

17. $\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$

$= \frac{(-285.8\times 10^3) - (-237.39\times 10^3)}{298}$

$= -162.4\ J/K^{-1}$

18. $\eta = \frac{(-\Delta G^\circ)}{(-\Delta H^\circ)} = \frac{237.39}{285.8} = 0.8306$ or 83.06%

Comprehension VI

19. Refer theory given is passage.

20. $E^\circ = E^\circ_{O_2/H_2O,\ H^+} - E^\circ_{Fe^{2+}/Fe} = 1.229 - (-0.447)$

$= 1.676$ V

21. $E^\circ_{Cu^{2+}/Cu} > E^\circ_{Pb^{2+}/Pb}$ and hence Cu will not oxidise easily.

22. $n_{eq}\ Fe = \frac{Q}{F} \Rightarrow \frac{w}{56}\times 2 = \frac{0.5\times 1.0\times 3600}{96500}$

$\Rightarrow w = 0.522$ gm

23. Theoretical

Comprehension VII

24. $n_{eq}\ Ni = \frac{Q}{F} \Rightarrow \frac{w}{58.7}\times 2 = \frac{15\times 3600\times 0.6}{96500}$

$\Rightarrow w = 9.85$ gm

25. $V = A\times t \Rightarrow \frac{9.85}{8.9} = (4.0\times 2)\times t \Rightarrow t = 0.138$ cm

26. $n_{eq}\ H_2 = \dfrac{Q}{F} \Rightarrow \dfrac{V_{H_2}}{22.4} \times 2 = \dfrac{15 \times 3600 \times 0.4}{96500}$

$\Rightarrow V_{H_2} = 2.5\ L$

27. Anode produced is only O_2 gas.

$n_{eq}\ O_2 = \dfrac{Q}{F} \Rightarrow \dfrac{w}{8} = \dfrac{15 \times 3600}{96500} \Rightarrow w = 4.477\ gm$

Comprehension VIII

28. $E°_{cell} = 0.8 - 0.05 = 0.75\ V$

Now, $E°_{cell} = \dfrac{RT}{nF} \cdot \ln K \Rightarrow 0.75 = \dfrac{1}{2 \times 38.92} \cdot \ln K$

$\Rightarrow \ln K = 58.38$

29. The oxidation reaction of glucose contains H^+ and

$E = E° - \dfrac{0.0592}{2} \cdot \log[H^+]^2$

$\Rightarrow E - E° = 0.0592\ P^H = 0.6512\ V$

30. Standard potential is independent from ammonia concentration.

Comprehension IX

31. Left electron: $H_2(g) \longrightarrow 2H^+(aq) + 2e^-$

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

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

32. $\Delta S° = nF \cdot \left(\dfrac{E_2 - E_1}{T_2 - T_1}\right) = 2 \times 96500 \times \dfrac{0.21 - 0.23}{20}$

$= -193\ J/K$

$\Delta G° = -nFE° = -2 \times 96500 \times 0.23 = -44390$ J at 15°C

Now, $\Delta H° = \Delta G° + T \cdot \Delta S° = (-44390) + 288 \times (-193)$

$= -99974\ J = -49987$ J/mole AgCl

33. $\Delta S° = -193\ J/K = -96.5$ J/K per mole AgCl

34. $\Delta G°_{298} = \Delta H° - T \cdot \Delta S° = (-49987) - 298 \times (-96.5)$

or, $-1 \times 96500 \times E° = -21230$

$\Rightarrow E° = 0.22\ V = E°_{Cl^-/AgCl/Ag}$

or, $E°_{Cl^-/AgCl/Ag} = E°_{Ag^+/Ag} + \dfrac{0.058}{1} \log K_{sp}$

or, $0.22 = 0.80 + \dfrac{0.058}{1} \log K_{sp} \Rightarrow K_{sp} = 1 \times 10^{-10}$

Hence, Solubility, $S = \sqrt{K_{sp}} = 10^{-5}\ M$

Comprehension X

35. Add Ag(s) in both sides of given reaction to get cell reaction. Now, for $E°_{cell}$

$\Delta G° = -nFE° \Rightarrow [-109] - [77 + (-129)] \times 10^3$

$= -1 \times 96500 \times E°_{cell}$

$\therefore E°_{cell} = 0.59\ V$

36. $E°_{cell} = \dfrac{0.059}{n} \log K_{eq} \Rightarrow 0.59 = \dfrac{0.059}{1} \cdot \log \dfrac{1}{K_{sp}}$

$\therefore K_{sp} = 10^{-10}$

37. $Zn(s) + 2Ag^+(aq)$ ¡ $Zn^{2+}(aq) + 3Ag(s)$; $E° = 0.80 - (-0.76)$

Now, $E° = \dfrac{0.059}{n} \cdot \log K_{eq}$

$\Rightarrow 1.56 = \dfrac{0.059}{2} \cdot \log \dfrac{[Zn^{2+}]}{[Ag^+]^2}$

$\therefore \log \dfrac{[Zn^{2+}]}{[Ag^+]^2} = 52.88$

38. Moles of Zn added $= \dfrac{6.539 \times 10^{-2}}{65.39} = 10^{-3}$

Moles of Ag^+ present $= \dfrac{10^{-5}}{1000} \times 100 = 10^{-6}$ (L.R.)

$\therefore$ Moles of Ag precipitated $= 10^{-6}$

Comprehension XI

39. For KCl: $\wedge_m = \dfrac{\kappa}{C} = \dfrac{G \cdot G^*}{C} \Rightarrow G^* = \wedge_m \cdot C/G$

or, $G^* = \wedge_m \cdot C \cdot R = 200 \times (0.02 \times 10^{-3}) \times 100 = 0.4$ cm^{-1}

40. $\kappa_{water} = G \cdot G^* = \dfrac{1}{10000} \times 0.4 = 4 \times 10^{-5}\, \Omega^{-1} cm^{-1}$

41. For NaCl: $\wedge_m = \dfrac{\kappa}{C} = \dfrac{G \cdot G^*}{C}$

$$\text{or, } 125 = \frac{\left(\dfrac{1}{8000} - \dfrac{1}{10000}\right) \times 0.4}{\left(\dfrac{585/58.5}{V}\right)}$$

$\Rightarrow V = 1.25 \times 10^8\ cm^3$

$= 1.25 \times 10^5$ L

Comprehension XII

42. $E^\circ_{Cl_2/Cl^-} > E^\circ_{I_2/I^-}$

43. $E^\circ_{Mn^{3+}/Mn^{2+}} > E^\circ_{O_2/H_2O,\, H^+}$

Comprehension XIII

44. Net reaction: $\underset{\text{Higher Conc.}}{M^+(1M)} \xrightarrow{\qquad} \underset{\text{Lower Conc.}}{M^+\ (0.05\ M)};$

$E_{cell} > 0$, $\Delta G_{cell} < 0$

45. $70\ mV = E^\circ - \dfrac{RT}{F} \cdot \ln \dfrac{0.05}{1}$ (1)

$$E_{req} = E^\circ - \frac{RT}{F} \cdot \ln \frac{0.0025}{1} = E^\circ - \frac{RT}{F} \cdot \ln \frac{(0.05)^2}{1} \quad (2)$$

and $E^\circ = 0$. Hence, $E_{req} = 140$ mV

Comprehension XIV

46. $\Delta G_{cell} = -nFE_{cell} = -2 \times 96500 \times 0.059 = -11387$ J

47. $E_{cell} = E^\circ_{cell} - \dfrac{0.059}{2} \cdot \log \dfrac{[M^{2+}]_{Left}}{[M^{2+}]_{Right}}$

or, $0.059 = 0 - \dfrac{0.059}{2} \cdot \log \dfrac{(K_{sp}/4)^{1/3}}{0.001}$

$\Rightarrow K_{sp} = 4 \times 10^{-15}$

Comprehension XV

48. $H^+ + Cl^- + \underset{\text{added}}{(NaOH)} \xrightarrow{\qquad} Na^+ + Cl^- + H_2O$

Conductance first decreases and H^+ ions are replaced by Na^+ ions. After equivalent point, conductance increase due to increase in number of ions.

49. CH_3COOH + (NaOH added) $\xrightarrow{\qquad} CH_3COO^- + Na^+ + H_2O$

As number of ions increases, conductance increases. slight decrease initially was due to some dissociated CH_3COOH. After equivalence point, in place of CH_3COO^- ion, number of OH^- ions increases and hence slope becomes greater.

50. $H^+ + Cl^- + (NH_4OH \text{ added}) \xrightarrow{\qquad}$
$NH_4^+ + Cl^- + H_2O$

As H^+ ions are replaced by NH_4^+ ions, conductance decreases. After equivalent point, it become almost constant as the dissociation of added NH4OH will be suppressed in presence of NH_4^+ ions.

51. HCl will neutralize first followed by CH_3COOH.

52. Ionic mobilities of Ag^+ and K^+ ions do not differ largely

53. First number of ions increases and then remain atmost constant.

Section D (Assertion – Reason)

1. $CuCl_2 \longrightarrow Cu + Cl_2$

2. $E^\circ_{Zn^{2+}/Zn} < E^\circ_{Ag^+/Ag}$ (informative)

3. Reason is different charges on ions.

4. Theoretical

5. Negative reduction potential means greater tendency to get oxidised.

6. Number of ions increases considerably only for weak electrolytes.

7. Informative

8. Theoretical

9. It is due to very high over voltage potential of hydrogen at mercury cathode.

10. Theoretical

11. Theoretical

12. $E = E^\circ - \frac{RT}{nF} \cdot \log Q$

13. Cl^- will combine with Ag^+ to precipitate AgCl.

14. At Cathode:

$$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$$

At Anode:

$$2CH_3COO^-(aq) \longrightarrow C_2H_6(g) + 2CO_2(g) + 2e^-$$

15. Theoretical

Section E (Column Match)

1. Informative

2. Theoretical

3. $$E^\circ_{Fe^{3+}|Fe} = \frac{1 \times E^\circ_{Fe^{3+},Fe^{2+}} + 2 \times E^\circ_{Fe^{2+}|Fe}}{1+2} = -0.037\ V$$

$$E^\circ_{(4H_2O \to 4H^+ + 4OH^-)} = 0.40 - 1.23 = -0.83\ V$$

$$E^\circ_{(Cu^{2+} + Cu \to 2Cu^+)} = E^\circ_{Cu^{2+}|Cu^+} - E^\circ_{Cu^+|Cu}$$

$$= \frac{0.34 - 0.52}{2-1} - 0.52 = -0.70\ V$$

$$E^\circ_{Cr^{3+},Cr^{2+}} = \frac{3 \times (-0.74) - 2 \times (-0.91)}{3-2} = -0.4\ V$$

4. For concentration cell, both half cell must have same configuration.

P. $Ag^+ + Cl^- \longrightarrow AgCl$ sponteneous,

$$K_{eq} = \frac{1}{K_{sp}} >> 1$$

Q. $Ag\,Br + Cl^- \longrightarrow AgCl + Br^-$;

$$K_{eq} = \frac{K_{sp}(Ag\,Br)}{K_{sp}(Ag\,Cl)} << 1, \text{ Non-Sponteneous}$$

R. $Ag^+(1.0\ M) \longrightarrow Ag^+(0.1\ M)$

Higher to lower concentration, spontaneous

S. $Cl^-(0.1\ M) \longrightarrow Cl^-(1.0\ M)$

Non–spontaneous

Section F (Subjective)

Single-digit Integer Type

1. $$E = E^\circ - \frac{0.06}{n} \cdot \log \frac{P_{H_2}}{[H^+]^2}$$

(assuming $2H^+ + 2e^- \to H_2$)

$$-0.18 = 0 - \frac{0.06}{2} \cdot \log \frac{1}{[H^+]^2} \Rightarrow [H^+] = 10^{-3} M$$

$$\underset{(C-x)M}{C_6H_5NH_3^+} + H_2O \rightleftharpoons C_6H_5NH_2 \quad \underset{xM}{H_3O^+}$$

$$h = \frac{x}{c} = \frac{10^{-3}}{1/40} = 0.04 \text{ or } 4\%$$

2. $E = E^\circ - \frac{0.06}{2}\cdot\log\frac{1}{[Cu^+]}$

$0.31 = 0.34 - \frac{0.06}{2}\cdot\log\frac{1}{[Cu^{2+}]}$

$\Rightarrow [Cu^{2+}] = 0.1\ M$

$\therefore\ [OH^-] = \sqrt{\frac{K_{sp}}{Cu^{2+}}} = \sqrt{\frac{10^{-19}}{0.1}} = 10^{-9} \Rightarrow p^H = 5$

3. $E^\circ_{Fe^{3+}|Fe^{2+}} = \frac{3\times E^\circ_{Fe^{3+}|Fe} - 2\times E^\circ_{Fe^{2+}|Fe}}{3-2}$

$= \frac{3\times(-0.04) - 2\times(-0.44)}{1} = 0.76\ V$

Now, $E_{Fe^{3+}|Fe^{2+}} = E^\circ_{Fe^{3+}|Fe^{2+}} - \frac{0.06}{1}\log\frac{[Fe^{2+}]}{[Fe^{3+}]}$

or, $0.718 = 0.76 - 0.06\ \log\frac{[Fe^{2+}]}{[Fe^{3+}]} \Rightarrow \frac{[Fe^{2+}]}{[Fe^{3+}]} = 5$

4.

	$2Fe^{3+}$ +	$2I^-$ →	$2Fe^{2+}$ +	I_2;
	0.5 M	excess		
100%	0		1.0 M	0.5 M
Equ.	CM		1.0 M	0.5 M

$E^\circ_{cell} = 0.77 - 0.53$

$= 0.24\ V;$

$K_{eq} = 10^8$

Now, $10^8 = \frac{(0.5)^2}{C^2\times(1.0)^2} \Rightarrow C = 5\times10^{-5}\ M$

5. Assuming the cell as concentration cell, net cell reaction is

$Ag^+\left(C_1 = \frac{K_{sp}(AgCl)}{[Cl^-]}\right) \longrightarrow Ag^+(C_2 = \sqrt{K_{sp(AgI)}})$

and $E_{cell} = O - \frac{0.06}{1}\log\frac{C_2}{C_1}$

or, 0.102

$= -0.06\cdot\ \log\frac{\sqrt{8.1\times10^{-17}}}{\left(\frac{1.8\times10^{-10}}{[Cl^-]}\right)} \Rightarrow [Cl^-] = 4\times10^{-4}\ M$

6. $n_{eq}\ Pb + n_{eq}\ Tl = \frac{Q}{F}$

$\Rightarrow \frac{5.0\times\frac{70}{100}}{208}\times2 + \frac{5.0\times\frac{30}{100}}{204}\times1 = \frac{1.1\times t}{96500}$

$\therefore\ t = 3597.4$ sec ; 1 hr

7. $n_{eq}\ I_r = \frac{Q}{F} \Rightarrow \frac{0.36}{192}\times x = \frac{0.075\times2\times3600}{96500} \Rightarrow x = 3$

Now, $x + 6(-1) = y \Rightarrow y = -3$

8. $2NaCl + 2H_2O \xrightarrow{\text{electrolysis}} 2NaOH + H_2 + Cl_2$

$2NaOH + Cl_2 \longrightarrow NaCl + NaClO + H_2O$

n_{NaClO} formed = n_{Cl_2} produced from electrolysis

or, $\frac{(10\times10^3\times1.0)\times\frac{7.45}{100}}{74.5}\times2 = \frac{2.5\times t}{96500}$

(n-factor of Cl_2 in electrolysis)

$\therefore\ t = 7.72\times10^5$ sec = 8.93 days ≈ 9 days

9. Cathode: $Cu^{2+} + 2e^- \longrightarrow Cu$

Anode $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

Moles of e^- used $= \frac{Q}{F} = \frac{0.161\times5\times60}{96500} \simeq 5\times10^{-4}$

Eq. of Cu^{2+} present $= \frac{500\times0.1}{1000}\times2 = 0.1$(excess)

$\therefore$ Moles of H^+ produced = Moles of e^- = 5×10^{-4}

$\therefore\ [H^+]_{final} = \frac{5\times10^{-4}}{500}\times1000 = 10^{-3}\ M \Rightarrow P^H = 3.0$

10. cathode: Cu^{2+} + $2e^- \longrightarrow Cu$

$\frac{250\times0.1}{1000}$ $\quad$ $\frac{5\times1351}{96500}$

$= 0.025$ mole $\quad$ $= 0.07$ mole

As Cu^+ will not remain finally in solution, no complex formation.

11. n_{eq} metal $= n_{eq}\ Cl_2 \Rightarrow \frac{52.8}{E} = \frac{9.08}{22.7}\times2 \Rightarrow E = 66$

At. wt. (approx) $= \frac{6.4}{0.032} = 200$

$\therefore$ valency $= \frac{\text{At. wt.}}{\text{Eq. wt}} = \frac{200}{66} \simeq 3$

13. Initial mass of H_2SO_4,

$$w_1 = 2000 \times 1.1 \times \frac{16}{100} = 352 \text{ gm}$$

Final mass of H_2SO_4,

$$w_2 = 2000 \times 1.42 \times \frac{40}{100} = 1136 \text{ gm}$$

Now, n_{eq} H_2SO_4 produced $= \dfrac{Q}{F}$

$$\text{or, } \frac{(1136-352)}{98} \times 1 = \frac{i \times \left(\frac{965}{9} \times 3600\right)}{96500} \Rightarrow i = 2A$$

13. Ionic mobility, $\mu = \dfrac{\lambda°_m}{F} = \dfrac{\text{Speed of ion}}{\text{Potential gradient}}$

$$\text{or, } \frac{7.5 \times 10^{-3}}{96500} = \frac{\text{distance} / 20 \times 3600}{1.93 / 0.12}$$

$\Rightarrow$ distance $= 0.09$ m $= 9$ cm

14. n_{eq} Ag oxidised $= \dfrac{Q}{F} \Rightarrow \dfrac{w}{108} \times 1 = \dfrac{9.65 \times 1 \times 3600}{96500}$

$\therefore w = 38.88$ gm

$\therefore$ Mass of anode dissolved $= 38.88 \times \dfrac{100}{60} \times 64.8$ gm

$\therefore$ Final mass of anode $= 72.8 - 64.8 = 8$ gm

15. Cathode: $2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$

Anode: $2ce^-(aq) \longrightarrow Cl_2(g) + 2e^-$

n_{eq} OH– produced $= \dfrac{Q}{F}$

$$\Rightarrow n_{OH^-} \times 1 = \frac{9.65 \times 10}{96500} = 10^{-3}$$

$$\therefore [OH^-]_{\text{final}} = \frac{10^{-3}}{100} = 10^{-5} \text{ M} \Rightarrow P^H = 9.0$$

Four digit integer type

1. $\Lambda°_{m(AgCl)} = \lambda°_{m(AgCl)} + \lambda°_{m(Cl^-)}$

$$= 6.19 \times 10^{-3} + 7.81 \times 10^{-3}$$

$$= 14.00 \times 10^{-3} \text{ohm}^{-1}\text{m}^2\text{mol}^{-1}$$

Now, $\Lambda_m = \dfrac{\kappa}{C} \Rightarrow 14 \times 10^{-3} = \dfrac{2.8 \times 10^{-4}}{S}$

$\Rightarrow S = 0.02 \text{ mol m}^{-3}$

$= 2 \times 10^{-5}$ M

$= 287 \times 10^{-5}$ g/L

2. $[S^{2-}] = Ka_1 \cdot Ka_2 \cdot \dfrac{[H_2S]}{[H^+]^2}$

$$= 10^{-8} \times 10^{-13} \times \frac{0.1}{(10^{-3})} = 10^{-16} \text{M}$$

$$\therefore [Ag^+] = \sqrt{\frac{K_{sp}}{[S^{2-}]}} = \sqrt{\frac{4 \times 10^{-48}}{10^{-16}}} = 2 \times 10^{-16} \text{M}$$

$$\text{Now, } E_{Ag^+/Ag} = 0.80 - \frac{0.06}{1} \log \frac{1}{2 \times 10^{-16}} = -0.142 \text{ V}$$

$\therefore$ Required potential $= 142$ mV

3.

$$\begin{array}{llll} & 2Hg(l) + 2Fe^{3+} & \rightleftharpoons & Hg_2^{2+} + 2Fe^{2+} \\ & \text{excess} \quad 10^{-3}\text{ M} & & \\ \text{Equ.} & \quad 10^{-3} - x & \frac{x}{2} & x \end{array}$$

$$= \frac{10}{100} \times 10^{-3} \text{M}$$

$\therefore x = 9 \times 10^{-4}$

$$\text{Now, } K_{eq} = \frac{\frac{x}{2} \times x^2}{(10^{-3} - x)^2} = \frac{\frac{9 \times 10^{-4}}{2} \times (9 \times 10^{-4})^2}{(1 \times 10^{-4})^2}$$

$$= \frac{9^3 \times 10^{-4}}{2}$$

$$\text{Now, } E°_{cell} = E°_{Fe^{3+}/Fe} - E°_{Hg_2^{2+}/Hg} = \frac{0.06}{2} \log K_{eq}$$

$$\text{or, } 0.7724 - E°_{Hg_2^{2+}/Hg} = \frac{0.06}{2} \cdot \log \frac{9^3 \times 10^{-4}}{2}$$

$$\therefore E°_{Hg_2^{2+}/Hg} = 0.815 \text{ V}$$

4. The cell reaction is

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

$$E_{cell} = E°_{cell} - \frac{0.06}{n} \cdot \log \frac{[Fe^{3+}]^6 [Cr^{3+}]^2}{[Fe^{2+}]^6 [Cr_2O_7^{2+}][H^+]^8}$$

$$= (1.35 - 0.77) - \frac{0.06}{6} \log \frac{(0.75)^6 \times (4)^2}{(0.75)^6 \times 2 \times (1)}$$

$$= 0.571 \text{ V}$$

5. Cell reaction: $H_2(g) + 2Ag^+ \rightarrow 2H^+ + 2Ag(s)$

$$E_{cell} = E°_{cell} - \frac{0.06}{2} \log \frac{[H^+]^2}{P_{H_2} \cdot [Ag^+]^2}$$

or, $0.50 = 0.80 - 0.03 \log \dfrac{1^2}{1 \times [Ag^+]^2}$

$\Rightarrow [Ag^+] = 10^{-5}$ M

$\therefore$ Mass of Ag in alloy

$$= \left(\frac{250 \times 10^{-5}}{1000}\right) \times 108 = 2.7 \times 10^{-4} \text{ gm}$$

$\therefore$ % of Pb in alloy

$$\frac{2.7 \times 10^{-3} - 2.7 \times 10^{-4}}{2.7 \times 10^{-3}} \times 100 = 90\%$$

6. $E^\circ_{cell} = \dfrac{0.06}{n} \log K_{eq} \Rightarrow (0.2 - 0.08) = \dfrac{0.06}{1} \log K_{eq}$

$\Rightarrow K_{eq} = 100$

7. Left electrode: $Mn(s) \rightarrow Mn^{2+} + 2e^-$

Right electrode: $2H_2O(l) \rightarrow O_2(g) + 4H^+ + 4e^-$

$\therefore$ Net cell reaction: $2Mn\,(s) + 2H_2O(l) \rightarrow 2Mn^{e+} + O_2(g) + 4H^+$

Now, $E_{cell} = E^\circ_{cell} - \dfrac{0.06}{4} \log \dfrac{[Mn^{2+}]^2 \cdot [H^+]^4 \cdot P_{O_2}}{1}$

$$= [1.229 - (-1.185)] - \frac{0.06}{4} \log \frac{(0.001)^2 \times (0.01)^4 \times 0.25}{1}$$

$= 2.633$ V

8. $\Delta S = nF \cdot \left(\dfrac{\partial E}{\partial T}\right)_P = 2 \times 96500 \times 0.001 = 193$ J/k

9. $\Delta_r G^\circ = -nFE^\circ = \Sigma\, \Delta_f G^\circ_{Products} - \Sigma\, \Delta_f G^\circ_{Reactants}$

or, $\dfrac{-12 \times 9600 \times 2.5}{1000} = \left[4 \times \Delta_f G^\circ_{Al(OH)_4^-}\right]$
$-[4 \times 0 + 3 \times 0 + 6 \times (-280) + 4 \times (-156.25)]$

$\therefore\ \Delta_f G^\circ_{Al(OH)_4^-} = -1300$ KJ/mol

10. $n_{eq}\, MnO_2 = \dfrac{Q}{F} \Rightarrow \dfrac{8.7}{87} \times 1 = \dfrac{3.99 \times 10^{-3} \times t}{96500}$

$\therefore\ t = 2.418 \times 10^6$ sec ≈ 28 days

11. $SnCl_2 \longrightarrow Sn^{2+} + 2Cl^-$

Cathode: $Sn^{2+} + 2e^- \longrightarrow Sn$

Anode: $2Cl^- \longrightarrow Cl_2 + 2e-$

$Cl_2 + SnCl_2 \longrightarrow SnCl_4$

Moles of $SnCl_2$ taken $= \dfrac{19}{190} = 0.1$

Moles of Sn produced $= \dfrac{1.19}{119} = 0.01$

= moles of Cl_2 produced

= moles of $SnCl_4$ formed

and moles of $SnCl_4$ left $= 0.1 - (0.01 + 0.01) = 0.08$

$$\therefore \frac{m_{SnCl_2}}{m_{SnCl_4}} = \frac{0.08 \times 190}{0.01 \times 261} = \frac{1520}{261}$$

12. n_{eq} Au $= \dfrac{Q}{F} \Rightarrow \dfrac{80 \times 8.0 \times 10^{-4} \times 19.7 \times 3}{197} = \dfrac{2.4 \times t}{96\,500}$

$\therefore\ t = 772$ sec

13.

$$\begin{array}{cccc} AgBr(s) & \rightleftharpoons & Ag^+ & + \quad Br^- \\ & & (10^{-7} + x)M & xM \end{array}$$

Now, $(10^{-7} + x)\, x = 12 \times 10^{-14} \Rightarrow x = 3 \times 10^{-7}$

Final solution: $[Ag^+] = 4 \times 10^{-7}$ M, $[Br^-] = 3 \times 10^{-7}$ M; $[NO_3^-] = 10^{-7}$ M

Now, $\kappa_{solution} = \lambda^\circ_m\,(Ag^+) \times [Ag^+] + \lambda^\circ_m(Br^-) \times [Br^-] + \lambda^\circ m\,(NO_3^-) \times [NO_3^-]$

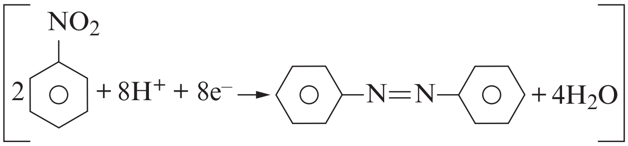
$= 6 \times 10^{-3} \times (4 \times 10^{-7} \times 10^3) + 8 \times 10^{-3} \times (3 \times 10^{-7} \times 10^3) + 7 \times 10^{-3}\, (10^{-7} \times 10^{-3})$

14. $C_{60} + 60O_2 \longrightarrow 60\, CO_2$

Moles of O_2 needed $= 60 \times n_{C_{60}} = 60 \times \dfrac{96}{60 \times 12} = 8$

$n_{eq}\, O_2 = n_{eq}$ azobenzene $\Rightarrow 8 \times 4 = \dfrac{w}{182} \times 8$

$\Rightarrow w = 728$ gm



15. $\Lambda^\circ_{eq[Ba_3(PO_4)_2]} = 160 + 140 - 100$

$= 200\ Ohm^{-1}\ cm^2\ eq^{-1}$

Now, $\wedge^\circ_{eq} = \wedge_{eq} = \dfrac{\kappa}{C} \Rightarrow 200 = \dfrac{1.2 \times 10^{-5}}{5}$

$\therefore\ S = 6 \times 10^{-8}$ eq/cm^3 $= 6 \times 10^{-5}$ N $= 10^{-5}$ M

$\therefore\ K_{sp} = 108\, S^5 = 10^8 \times 10^{-25}\ M^5$