2.2 Expressing Concentration of Solutions

VSA (1 mark)

1. Define the following term :
Molarity (1/5 AI 2014)

2. Define the following term :
Mole fraction (1/2 Delhi 2012, AI 2012, 2009)

3. What is meant by molality of a solution? (1/5 AI 2009)

4. State the main advantage of molality over molarity as the unit of concentration. (Delhi 2009C)

SA I (2 marks)

5. Calculate the molarity of 9.8% (*w/W*) solution of H_2SO_4 if the density of the solution is 1.02 g mL^{-1}.
(Molar mass of $H_2SO_4 = 98 \text{ g mol}^{-1}$) (2/5 Foreign 2014)

6. Differentiate between molarity and molality of a solution. How can we change molality value of a solution into molarity value? (Delhi 2014C)

7. Define :
(i) Mole fraction (ii) Molality (2/5 AI 2014 C)

8. A solution of glucose ($C_6H_{12}O_6$) in water is labelled as 10% by weight. What would be the molality of the solution?
(Molar mass of glucose = 180 g mol^{-1}) (2/5 AI 2013)

9. Differentiate between molarity and molality in a solution. What is the effect of temperature change on molarity and molality in a solution? (2/5 Delhi 2011, 2009, 2/5 AI 2011)

10. Differentiate between molarity and molality of a solution. Explain how molarity value of a solution can be converted into its molality? (Foreign 2011)

11. Define the term, 'molarity of a solution'. State one disadvantage in using the molarity as the unit of concentration. (2/3 AI 2010C)

12. An antifreeze solution is prepared from 222.6 g of ethylene glycol ($C_2H_4(OH)_2$) and 200 g of water. Calculate the molality of the solution. If the density of this solution be 1.072 g mL^{-1} what will be the molality of the solution? (Delhi 2007)

SA II (3 marks)

13. A solution of glucose (molar mass = 180 g mol^{-1}) in water is labelled as 10% (by mass). What would be the molality and molarity of the solution?
(Density of solution = 1.2 g mL^{-1}) (3/5 AI 2014)

2.3 Solubility

VSA (1 mark)

14. Gas (*A*) is more soluble in water than gas (*B*) at the same temperature. Which one of the two gases will have the higher value of K_H (Henry's constant) and why? (1/2 AI 2016)

15. Explain the following :
Henry's law about dissolution of a gas in a liquid. (1/5 AI 2012)

16. State the following :
Henry's law about partial pressure of a gas in a mixture. (1/5 Delhi, AI 2011)

SA I (2 marks)

17. State Henry's law and mention two of its important applications. (2/5, AI 2013C, 2012C)

18. Explain why aquatic species are more comfortable in cold water rather than in warm water. (Delhi 2012C)

19. State Henry's law correlating the pressure of a gas and its solubility in a solvent and mention two applications for the law. (Delhi 2008)

SA II (3 marks)

20. The partial pressure of ethane over a saturated solution containing 6.56×10^{-2} g of ethane is 1 bar. If the solution contains 5.0×10^{-2} g of ethane, then what will be the partial pressure of the gas? *(Delhi 2013C, AI 2012C)*

21. If N_2 gas is bubbled through water at 293 K, how many millimoles of N_2 gas would dissolve in 1 litre of water? Assume that N_2 exerts a partial pressure of 0.987 bar. Given that Henry's law constant for N_2 at 293 K is 76.48 k bar. *(AI 2012C)*

22. What concentration of nitrogen should be present in a glass of water at room temperature? Assume a temperature of 25°C, a total pressure of 1 atmosphere and mole fraction of nitrogen in air of 0.78.
[K_H for nitrogen = 8.42×10^{-7} M/mm Hg] *(3/5 AI 2009)*

2.4 Vapour Pressure of Liquid Solutions

VSA (1 mark)

23. Define Raoult's law. *(1/5 AI 2014C)*

24. State the following :
Raoult's law in its general form in reference to solutions. *(1/5 Delhi, 1/2 AI 2011)*

25. State 'Raoult's law' for a solution of volatile liquids. *(AI 2009C)*

SA I (2 marks)

26. State Raoult's law for the solution containing volatile components. What is the similarity between Raoult's law and Henry's law? *(Delhi 2014, AI 2013)*

27. State Raoult's law for a solution containing volatile components. Name the solution which follows Raoult's law at all concentrations and temperatures. *(2/5 Foreign 2014)*

28. State Raoult's law. How is it formulated for solutions of non-volatile solutes? *(Delhi 2012C)*

SA II (3 marks)

29. The vapour pressure of pure liquids *A* and *B* are 450 and 700 mm Hg respectively, at 350 K. Find out the composition of the liquid mixture if total vapour pressure is 600 mm Hg. Also find the composition of the vapour phase. *(3/5 AI 2013C)*

2.5 Ideal and Non-ideal Solutions

VSA (1 mark)

30. In non-ideal solution, what type of deviation shows the formation of maximum boiling azeotropes? *(1/2 AI 2016)*

31. Some liquids on mixing form 'azeotropes'. What are 'azeotropes'? *(Delhi 2014)*

32. Define the following term :
Azeotrope *(1/5 Foreign 2014)*

33. Define the following term :
Ideal solution
(1/5 AI 2013, 2012, 1/2 Delhi 2012)

34. How is it that alcohol and water are miscible in all proportions ? *(AI 2007)*

SA I (2 marks)

35. What is meant by positive deviations from Raoult's law? Give an example. What is the sign of $\Delta_{mix}H$ for positive deviation? *(Delhi 2015)*

36. Define azeotropes. What type of azeotrope is formed by positive deviation from Raoult's law? Give an example. *(Delhi 2015)*

37. What is meant by negative deviation from Raoult's law? Give an exmaple. What is the sign of $\Delta_{mix}H$ for negative deviation? *(Foreign 2015)*

38. Define azeotropes. What type of azeotrope is formed by negative deviation from Raoult's law? Give an example. *(Foreign 2015)*

39. What type of deviation is shown by a mixture of ethanol and acetone? Give reason. *(2/5 AI 2014)*

40. What is meant by positive and negative deviations from Raoult's law and how is the sign of $\Delta_{mix}H$ related to positive and negative deviations from Raoult's law? *(AI 2013 C)*

41. Explain why a solution of chloroform and acetone shows negative deviation from Raoult's law. *(2/5 Delhi 2011C)*

42. Non-ideal solutions exhibit either positive or negative deviations from Raoult's law. What are these deviations and why are they caused? Explain with one example for each type. *(Delhi 2010)*

43. What type of intermolecular attraction exists in each of the following pairs of compounds:
(i) *n*-hexane and *n*-octane
(ii) methanol and acetone *(Delhi 2010C)*

44. State Raoult's law for solutions of volatile liquids. Taking suitable examples explain the meaning of positive and negative deviations from Raoult's law. *(Delhi, AI 2008)*

45. What is meant by negative deviation from Raoult's law? Draw a diagram to illustrate the relationship between vapour pressure and mole fractions of components in a solution to represent negative deviation. *(AI 2008C)*

2.6 Colligative Properties and Determination of Molar Mass

VSA (1 mark)

46. What are isotonic solutions? *(Delhi 2014)*

47. Define the following term :
Molal elevation constant (K_b) *(1/5 AI 2014)*

48. How is the vapour pressure of a solvent affected when a non-volatile solute is dissolved in it? *(1/2 Delhi 2014C)*

49. Define the following term :
Osmotic pressure *(1/5 AI 2013)*

50. Define the following term :
Isotonic solutions *(1/2 Delhi 2012)*

51. Explain the following :
Boiling point elevation constant for a solvent. *(AI 2012)*

52. What is meant by colligative properties? *(1/5 AI 2009)*

53. State the condition resulting in reverse osmosis. *(AI 2007)*

SA I (2 marks)

54. (i) Out of 1 M glucose and 2 M glucose, which one has a higher boiling point and why?
(ii) What happens when the external pressure applied becomes more than the osmotic pressure of solution? *(2/5 Delhi 2016)*

55. Blood cells are isotonic with 0.9% sodium chloride solution. What happens if we place blood cells in a solution containing
(i) 1.2% sodium chloride solution?
(ii) 0.4% sodium chloride solution? *(2/5 Delhi 2016)*

56. Why does a solution containing non-volatile solute have higher boiling point than the pure solvent? Why is elevation of boiling point a colligative property? *(AI 2015)*

57. Calculate the mass of compound (molar mass = 256 g mol^{-1}) to be dissolved in 75 g of benzene to lower its freezing point by 0.48 K. (K_f = 5.12 K kg mol^{-1}). *(Delhi 2014)*

58. 18 g of glucose, $C_6H_{12}O_6$ (Molar mass = 180 g mol^{-1}) is dissolved in 1 kg of water in a sauce pan. At what temperature will this solution boil?
(K_b for water = 0.52 K kg mol^{-1}, boiling point of pure water = 373. 15 K) *(Delhi 2013)*

59. An aqueous solution of sodium chloride freezes below 273 K. Explain the lowering in freezing point of water with the help of a suitable diagram. *(Delhi 2013C)*

60. Define the terms osmosis and osmotic pressure. Is the osmotic pressure of a solution a colligative property? Explain. *(2/5 Delhi 2011)*

61. List any four factors on which the colligative properties of a solution depend. *(2/5 AI 2011C)*

62. Define the terms, 'osmosis' and 'osmotic pressure'. What is the advantage of using osmotic pressure as compared to other colligative properties for the determination of molar masses of solutes in solutions? *(AI 2010)*

63. Outer hard shells of two eggs are removed. One of the egg is placed in pure water and the other is placed in saturated solution of sodium chloride. What will be observed and why? *(AI 2010C)*

64. Find the boiling point of a solution containing 0.520 g of glucose ($C_6H_{12}O_6$) dissolved in 80.2 g of water.
[Given : K_b for water = 0.52 K/m] *(AI 2010C)*

65. Define the term 'osmotic pressure'. Describe how the molecular mass of a substance can be determined on the basis of osmotic pressure measurement. *(Delhi, AI 2008)*

SA II (3 marks)

66. Calculate the freezing point of the solution when 31 g of ethylene glycol ($C_2H_6O_2$) is dissolved in 500 g of water.
(K_f for water = 1.86 K kg mol^{-1}) *(AI 2015)*

67. A solution containing 15 g urea (molar mass = 60 g mol^{-1}) per litre of solution in water has the same osmotic pressure (isotonic) as a solution of glucose (molar mass = 180 g mol^{-1}) in water. Calculate the mass of glucose present in one litre of its solution. *(3/5 AI 2014)*

68. Calculate the boiling point elevation for a solution prepared by adding 10 g of $CaCl_2$ to 200 g of water. (K_b for water = 0.52 K kg mol^{-1}, molar mass of $CaCl_2$ = 111 g mol^{-1})
(2/3 Foreign 2014)

69. Define the following terms :
(i) Osmotic pressure
(ii) Colligative properties *(Foreign 2014)*

70. Some ethylene glycol, $HOCH_2CH_2OH$, is added to your car's cooling system along with 5 kg of water. If the freezing point of water-glycol solution is –15.0°C, what is the boiling point of the solution?
(K_b = 0.52 K kg mol^{-1} and K_f = 1.86 K kg mol^{-1} for water) *(Delhi 2014C)*

71. 1.00 g of a non-electrolyte solute dissolved in 50 g of benzene lowered the freezing point of benzene by 0.40 K. The freezing point depression constant of benzene is 5.12 K kg mol^{-1}. Find the molar mass of the solute. *(AI 2013, 2008)*

72. A 5% solution (by mass) of cane-sugar in water has freezing point of 271 K. Calculate the freezing point of 5% solution (by mass) of glucose in water if the freezing point of pure water is 273.15 K.
[Molecular masses : Glucose $C_6H_{12}O_6$: 180 amu; Cane-sugar $C_{12}H_{22}O_{11}$: 342 amu]
(3/5 AI 2013C)

73. A solution of glycerol ($C_3H_8O_3$) in water was prepared by dissolving some glycerol in 500 g of water. This solution has a boiling point of 100.42°C while pure water boils at 100°C. What mass of glycerol was dissolved to make the solution?
(K_b for water = 0.512 K kg mol^{-1})
(Delhi 2012, 2010, AI 2012)

74. 15.0 g of an unknown molecular material was dissolved in 450 g of water. The resulting solution was found to freeze at –0.34°C. What is the molar mass of this material?
(K_f for water = 1.86 K kg mol^{-1})
(Delhi 2012, 3/5, AI 2012, 2010)

75. A solution containing 30 g of non-volatile solute exactly in 90 g of water has a vapour pressure of 2.8 kPa at 298 K. Further 18 g of water is added to this solution. The new vapour pressure becomes 2.9 kPa at 298 K. Calculate
(i) the molecular mass of solute and
(ii) vapour pressure of water at 298 K.
(Delhi 2012C)

76. Calculate the boiling point of a solution prepared by adding 15.00 g of NaCl to 250.00 g of water. (K_b for water = 0.512 K kg mol^{-1}), (Molar mass of NaCl = 58.44 g)
(3/5 Delhi 2011)

77. A solution prepared by dissolving 8.95 mg of a gene fragment in 35.0 mL of water has an osmotic pressure of 0.335 torr at 25°C. Assuming the gene fragment is a non-electrolyte, determine its molar mass. *(3/5 Delhi, AI 2011)*

78. What would be the molar mass of a compound if 6.21 g of it dissolved in 24.0 g of chloroform to form a solution that has a boiling point of 68.04°C. The boiling point of pure chloroform is 61.7°C and the boiling point elevation constant, K_b for chloroform is 3.63°C/m.
(3/5 Delhi 2011)

79. What mass of NaCl must be dissolved in 65.0 g of water to lower the freezing point of water by 7.50°C? The freezing point depression constant (K_f) for water is 1.86°C/m. Assume van't Hoff factor for NaCl is 1.87.
(Molar mass of NaCl = 58.5 g mol^{-1}). *(AI 2011)*

80. The molecular masses of polymers are determined by osmotic pressure method and not by measuring other colligative properties. Give two reasons. *(3/5 AI 2011C)*

81. Calculate the boiling point of one molar aqueous solution (density 1.06 g mL^{-1}) of KBr.
[Given : K_b for H_2O = 0.52 K kg mol^{-1}, atomic mass : K = 39, Br = 80] *(3/5 AI 2011C)*

82. A solution prepared by dissolving 1.25 g of oil of winter green (methyl salicylate) in 99.0 g of benzene has a boiling point of 80.31°C. Determine the molar mass of this compound. (B.pt. of pure benzene = 80.10°C and K_b for benzene = 2.53°C kg mol^{-1}) *(Delhi 2010)*

83. What mass of ethylene glycol (molar mass = 62.0 g mol^{-1}) must be added to 5.50 kg of water to lower the freezing point of water from 0°C to – 10.0°C?
(K_f for water 1.86 K kg mol^{-1}) *(AI 2010)*

84. 100 mg of a protein is dissolved in just enough water to make 10.0 mL of solution. If this solution has an osmotic pressure of 13.3 mm Hg at 25°C, what is the molar mass of the protein? (R = 0.0821 L atm mol^{-1} K^{-1} and 760 mm Hg = 1 atm.) *(Delhi, 3/5, AI 2009)*

85. Calculate the amount of sodium chloride which must be added to one kilogram of water so that the freezing point of water is depressed by 3 K. [Given : K_f = 1.86 K kg mol^{-1}, atomic mass : Na = 23.0, Cl = 35.5] *(3/5, Delhi, AI 2009C)*

86. x g of a non-electrolytic compound (molar mass = 200) is dissolved in 1.0 L of 0.05 M NaCl aqueous solution. The osmotic pressure of this solution is found to be 4.92 atm at 27°C. Calculate the value of x. Assume complete dissociation of NaCl and ideal behaviour of the solution. (R = 0.082 L atm mol^{-1} K^{-1}) *(AI 2009C)*

87. Calculate the freezing point of a solution containing 18 g glucose, $C_6H_{12}O_6$ and 68.4 g sucrose, $C_{12}H_{22}O_{11}$ in 200 g of water. The freezing point of pure water is 273 K and K_f for water is 1.86 K m^{-1}. *(AI 2009C)*

88. Calculate the temperature at which a solution containing 54 g of glucose, ($C_6H_{12}O_6$), in 250 g of water will freeze.
(K_f for water = 1.86 K mol^{-1} kg) *(Delhi 2008)*

89. A solution containing 8 g of a substance in 100 g of diethyl ether boils at 36.86°C, whereas pure ether boils at 35.60°C. Determine the molecular mass of the solute. (For ether K_b = 2.02 K kg mol^{-1}) *(AI 2008)*

90. A 0.1539 molal aqueous solution of cane sugar (mol. mass = 342 g mol^{-1}) has a freezing point of 271 K while the freezing point of pure water is 273.15 K. What will be the freezing point of an aqueous solution containing 5 g of glucose (mol. mass = 180 g mol^{-1}) per 100 g of solution. *(AI 2007)*

2.7 Abnormal Molar Masses

VSA (1 mark)

91. Define the following term :
Van't Hoff factor *(1/5 Delhi 2012, AI 2009)*

SA I (2 marks)

92. What is van't Hoff factor? What types of values can it have if in forming the solution the solute molecules undergo
(i) Dissociation (ii) Association? *(2/5 AI 2014C)*

93. Assuming complete dissociation, calculate the expected freezing point of a solution prepared by dissolving 6.00 g of Glauber's salt, $Na_2SO_4 \cdot 10H_2O$ in 0.100 kg of water.
(K_f for water = 1.86 K kg mol^{-1}, atomic masses : Na = 23, S = 32, O = 16, H = 1) *(2/5, AI 2014C)*

94. A 1.00 molal aqueous solution of trichloroacetic acid (CCl_3COOH) is heated to its boiling point. The solution has the boiling point of 100.18°C. Determine the van't Hoff factor for trichloroacetic acid.
(K_b for water = 0.512 K kg mol^{-1}) *(Delhi 2012)*

95. What is van't Hoff factor? What possible value can it have if the solute molecules undergo dissociation? *(2/5 Delhi 2011C)*

SA II (3 marks)

96. Calculate the freezing point of solution when 1.9 g of $MgCl_2$(M = 95 g mol^{-1}) was dissolved in 50 g of water, assuming $MgCl_2$ undergoes complete ionization.
(K_f for water = 1.86 K kg mol^{-1}) *(Delhi 2016)*

97. When 2.56 g of sulphur was dissolved in 100 g of CS_2, the freezing point lowered by 0.383 K. Calculate the formula of sulphur (S_x).
(K_f the CS_2 = 3.83 K kg mol^{-1}, atomic mass of sulphur = 32 g mol^{-1}) *(3/5 Delhi 2016)*

98. Calculate the boiling point of solution when 4 g of $MgSO_4$ ($M = 120$ g mol^{-1}) was dissolved in 100 g of water, assuming $MgSO_4$ undergoes complete ionization.
(K_b for water = 0.52 K kg mol^{-1}) *(AI 2016)*

99. 3.9 g of benzoic acid dissolved in 49 g of benzene shows a depression in freezing point of 1.62 K. Calculate the van't Hoff factor and predict the nature of solute (associated or dissociated).
(Given : Molar mass of benzoic acid = 122 g mol^{-1}, K_f for benzene = 4.9 K kg mol^{-1}) *(Delhi 2015)*

100. Calculate the mass of NaCl (molar = 58.5 g mol^{-1}) to be dissolved in 37.2 g of water to lower the freezing point by 2°C, assuming that NaCl undergoes complete dissociation.
(K_f for water = 1.86 K kg mol^{-1}) *(Foreign 2015)*

101. Determine the osmotic pressure of a solution prepared by dissolving 2.5×10^{-2} g of K_2SO_4 in 2 L of water at 25°C, assuming that it is completely dissociated.
(R = 0.0821 L atm K^{-1} mol^{-1}, molar mass of K_2SO_4 = 174 g mol^{-1}) *(Delhi 2013)*

102. Calculate the amount of KCl which must be added to 1 kg of water so that the freezing point is depressed by 2 K (the K_f for water = 1.86 K kg mol^{-1}). *(Delhi 2012)*

103. Calculate the freezing point of an aqueous solution containing 10.50 g of $MgBr_2$ in 200 g of water. (Molar mass of $MgBr_2$ = 184 g mol^{-1})
(K_f for water = 1.86 K kg mol^{-1})
(3/5 Delhi 2011)

104. A 0.561 m solution of an unknown electrolyte depresses the freezing point of water by 2.93°C. What is van't Hoff factor for this electrolyte? The freezing point depression constant (K_f) for water is 1.86°C kg mol^{-1}. *(Foreign 2011)*

105. Phenol associates in benzene to a certain extent to form a dimer. A solution containing 20 g of phenol in 1.0 kg of benzene has its freezing point lowered by 0.69 K. Calculate the fraction of phenol that has dimerised
[Given K_f for benzene = 5.1 K m^{-1}]
(3/5 Delhi 2011C)

106. An aqueous solution containing 12.48 g of barium chloride in 1.0 kg of water boils at 373.0832 K. Calculate the degree of dissociation of barium chloride.
[Given K_b for H_2O = 0.52 K m^{-1};
Molar mass of $BaCl_2$ = 208.34 g mol^{-1}]
(3/5, Delhi 2011C)

107. A decimolar solution of potassium ferrocyanide $K_4[Fe(CN)_6]$ is 50% dissociated at 300 K. Calculate the value of van't Hoff factor for potassium ferrocyanide. *(Delhi 2010C)*

108. The boiling point elevation of 0.30 g acetic acid in 100 g benzene is 0.0633 K. Calculate the molar mass of acetic acid from this data. What conclusion can you draw about the molecular state of the solute in the solution?
[Given K_b for benzene = 2.53 K kg mol^{-1}]
(AI 2008C)

109. The freezing point of a solution containing 0.2 g of acetic acid in 20.0 g of benzene is lowered by 0.45°C. Calculate.
(i) the molar mass of acetic acid from this data
(ii) van't Hoff factor
[For benzene, K_f = 5.12 K kg mol^{-1}]
What conclusion can you draw from the value of van't Hoff factor obtained?
(AI 2008C)

LA (5 marks)

110. (i) The depression in freezing point of water observed for the same molar concentration of acetic acid, trichloroacetic acid and trifluroacetic acid increases in the order as stated above. Explain.
(ii) Calculate the depression in freezing point of water when 20.0 g of $CH_3CH_2CHClCOOH$ is added to 500 g of water.
[Given : $K_a = 1.4 \times 10^{-3}$, K_f = 1.86 K kg mol^{-1}]
(Delhi 2008C)

ELECTROCHEMISTRY

Electrochemistry : It is the study of production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to bring about non-spontaneous chemical transformations.

Differences between electrochemical cell and electrolytic cell :

Electrochemical cell (Galvanic or Voltaic cell)	Electrolytic cell
1. It is a device which converts chemical energy into electrical energy.	1. It is a device which converts electrical energy into chemical energy.
2. It is based upon the redox reaction which is spontaneous. *i.e.*, $\Delta G = -ve$	2. The redox reaction is non-spontaneous and takes place only when electrical energy is supplied. *i.e.*, $\Delta G = +ve$
3. Two electrodes are usually set up in two separate beakers.	3. Both the electrodes are suspended in the solution or melt of the electrolyte in the same beaker.
4. The electrolytes taken in the two beakers are different.	4. Only one electrolyte is taken.
5. The electrodes taken are of different materials.	5. The electrodes taken may be of the same or different materials.
6. The electrode on which oxidation takes place is called the *anode* (or –ve pole) and the electrode on which reduction takes place is called the *cathode* (or +ve pole)	6. The electrode which is connected to the –ve terminal of the battery is called the *cathode*; the cations migrate to it which gain electrons and hence, a reduction takes place, the other electrode is called the *anode*.
7. To set up this cell, a salt bridge/porous pot is used.	7. No salt bridge is used in this case.

Nernst equation : For a reduction reaction,

$M^{n+}{}_{(aq)} + ne^- \longrightarrow M_{(s)}$;

$$E_{cell} = E^\circ_{cell} - \frac{2.303RT}{nF}\log\frac{1}{[M^{n+}_{(aq)}]}$$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{1}{[M^{n+}_{(aq)}]}$$

- For concentration cell, EMF at 298 K is given by

$$E_{cell} = \frac{2.303RT}{nF}\log\frac{C_2}{C_1} \text{ where } C_2 > C_1$$

Applications of Nernst equation :

- **To calculate electrode potential of a cell :**

$$aA + bB \xrightarrow{ne^-} xX + yY$$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{[X]^x[Y]^y}{[A]^a[B]^b}$$

- **To calculate equilibrium constant :**

At equilibrium, $E_{cell} = 0$

$$E^\circ_{cell} = \frac{0.0591}{n}\log K_c \text{ at 298 K}$$

Relation between cell potential and Gibbs energy change :

$\Delta G^\circ = -nFE^\circ_{cell}$; $\Delta G^\circ = -2.303\, RT \log K_c$

Conductance in electrolytic solutions :

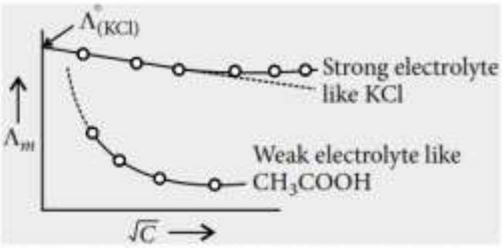
Property	Formula	Units	Effect of dilution
Conductance (G)	$\frac{1}{R} = \frac{a}{\rho l} = \frac{\kappa a}{l}$	Ohm^{-1} (Ω^{-1})/Siemens (S)	Increases as larger number of ions are produced.
Specific conductance (κ) or conductivity	$\frac{1}{\rho}$ or $G\frac{l}{a}$	$Ohm^{-1}\ cm^{-1}/S\ m^{-1}$	Decreases as number of ions per cm^3 decreases.
Equivalent conductivity (Λ_{eq})	$\kappa \times V$ or $\kappa \times \frac{1000}{N}$	$\Omega^{-1}\ cm^2\ eq^{-1}/S\ m^2\ eq^{-1}$	Increases with dilution due to large increase in V.
Molar conductivity (Λ_m)	$\kappa \times V$ or $\kappa \times \frac{1000}{M}$	$\Omega^{-1}\ cm^2\ mol^{-1}/S\ m^2\ mol^{-1}$	Increases with dilution due to large increase in V.

ELECTROCHEMISTRY

- **Limiting molar conductivity :** When concentration approaches zero *i.e.* ; at infinite dilution, the molar conductivity is known as *limiting molar conductivity* (Λ_m°).
- **Variation of molar conductivity with concentration :**

For a strong electrolyte it is shown by *Debye-Huckel Onsager equation* as follows :

$$\Lambda_m = \Lambda_m^\circ - A\sqrt{C}$$



Here, Λ_m° = Molar conductivity at infinite dilution (Limiting molar conductivity)

Λ_m = Molar conductivity at V-dilution

A = Constant which depends upon nature of solvent and temperature

C = Concentration

Plot of Λ_m against $C^{1/2}$ is a straight line with intercept equal to Λ_m° and slope equal to '$-A$'.

Thus, Λ_m^c decreases linearly with $\sqrt{C}$, when $C = 0$, $\Lambda_m^c = \Lambda_m^\circ$ and Λ_m° can be determined experimentally.

- **For weak electrolytes :** There is a very large increase in conductance with dilution especially near infinite dilution as no. of ions increases. Λ_m^c increases as C decreases but does not reach a constant value even at infinite dilution. Hence, their Λ_m° cannot be determined experimentally.
- **For a strong electrolyte :** there is only a small increase in conductance with dilution. This is because a strong electrolyte is completely dissociated in solution and so, the number of ions remain constant and on dilution, inter-ionic attractions decreases as ions move far apart.

- **Kohlrausch's law of independent migration of ions :** It states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.

$\Lambda_m^\circ = \upsilon_+\lambda_+^\circ + \upsilon_-\lambda_-^\circ$ where λ_+° and λ_-° are the limiting molar conductivities of the cation and anion respectively and υ_+ and υ_- are stoichiometric no. of cations and anions respectively in one formula unit of the electrolyte.

- **Applications of Kohlrausch's law :**
  - **Calculation of molar conductivity of weak electrolytes :**

$$\Lambda_m^\circ(CH_3COOH) = \lambda^\circ_{CH_3COO^-} + \lambda^\circ_{H^+}$$

$$= \left(\lambda^\circ_{H^+} + \lambda^\circ_{Cl^-}\right) + \left(\lambda^\circ_{CH_3COO^-} + \lambda^\circ_{Na^+}\right) - \left(\lambda^\circ_{Na^+} + \lambda^\circ_{Cl^-}\right)$$

$$= \Lambda_m^\circ(HCl) + \Lambda_m^\circ(CH_3COONa) - \Lambda_m^\circ(NaCl)$$

  - **Calculation of degree of dissociation :**

Degree of dissociation $(\alpha) = \dfrac{\Lambda_m^c}{\Lambda_m^\circ}$

$$= \frac{\text{Molar conductivity at concentration } c}{\text{Molar conductivity at infinite dilution}}$$

  - **Calculation of dissociation constant (K_c) of weak electrolyte :**

	$AB \rightleftharpoons$	A^+	$+ B^-$
Initial conc.	c	0	0
Conc. at equil.	$(c - c\alpha)$	$c\alpha$	$c\alpha$

$$K_c = \frac{c\alpha \times c\alpha}{(c - c\alpha)} = \frac{c\alpha^2}{(1-\alpha)}$$

- **Electrolysis :** It is the process of decomposition of an electrolyte by passing electricity through its aqueous solution or molten state.
  - **Faraday's first law of electrolysis :** The amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte (solution or melt).

$w \propto Q$ or $w = ZQ = Z \times I \times t$ where Z is electrochemical equivalent of the substance deposited and $Z = \dfrac{\text{Eq. wt. of substance}}{96500}$.

  - **Faraday's second law of electrolysis :** The amounts of different substances liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their chemical equivalent weights.

$\dfrac{w_1}{w_2} = \dfrac{E_1}{E_2}$ where E is the equivalent weight.

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Products of electrolysis :

Electrolyte	Products		Reactions involved	
	At cathode	At anode	At cathode	At anode
Molten NaCl	Na metal	Cl_2 gas	$Na^+_{(l)} + e^- \longrightarrow Na_{(l)}$	$Cl^-_{(l)} \longrightarrow \frac{1}{2}Cl_{2(g)} + e^-$
Aqueous NaCl	H_2 gas	Cl_2 gas	$H_2O_{(l)} + e^- \longrightarrow \frac{1}{2}H_{2(g)} + OH^-_{(aq)}$	$Cl^-_{(aq)} \longrightarrow \frac{1}{2}Cl_{2(g)} + e^-$
Dil. H_2SO_4	H_2 gas	O_2 gas	$H^+_{(aq)} + e^- \longrightarrow \frac{1}{2}H_{2(g)}$	$2H_2O_{(l)} \longrightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-$
Conc. H_2SO_4	H_2 gas	$S_2O_8^{2-}$	$H^+_{(aq)} + e^- \longrightarrow \frac{1}{2}H_{2(g)}$	$2SO^{2-}_{4(aq)} \longrightarrow S_2O^{2-}_{8(aq)} + 2e^-$

Some commercial cells :

- **Primary cells :** Cells once exhausted cannot be used again *e.g.*, dry cell and mercury cell.
- **Secondary cells :** Rechargeable cell which can be used again and again *e.g.*, nickel-cadmium cell and lead storage battery.
- **Fuel cells :** Cells which can convert the energy of combustion of fuels such as H_2, CO, CH_4, etc. into electrical energy *e.g.*, $H_2 - O_2$ fuel cell.

Dry cell, lead accumulator and fuel cell :

	Dry cell	Lead storage battery	Fuel cell
Anode	Zinc	Lead	Porous carbon containing catalysts (H_2 passed)
Cathode	Graphite	Lead dioxide	Porous carbon containing catalysts (O_2 passed)
Electrolyte	MnO_2 + C (touching cathode) $NH_4Cl + ZnCl_2$ (touching anode)	H_2SO_4 (38%)	Conc. aqueous KOH
Anode reaction	$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$	$Pb_{(s)} + SO^{2-}_{4(aq)} \longrightarrow PbSO_{4(s)} + 2e^-$	$H_{2(g)} + 2OH^-_{(aq)} \longrightarrow 2H_2O_{(l)} + 2e^-$
Cathode reaction	$MnO_{2(s)} + NH^+_{4(aq)} + e^- \longrightarrow MnO(OH)_{(s)} + NH_{3(g)}$	$PbO_{2(s)} + SO^{2-}_{4(aq)} + 4H^+ + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O_{(l)}$	$O_{2(g)} + 2H_2O_{(l)} + 4e^- \longrightarrow 4OH^-_{(aq)}$

Corrosion : The slow eating away of metals when exposed to the atmosphere is called *corrosion*.

Corrosion of iron (Rusting) : It is an electrochemical phenomenon which occurs in the presence of moisture and oxygen.

At anode : $2Fe_{(s)} \longrightarrow 2Fe^{2+}{}_{(aq)} + 4e^-$

At cathode : $O_{2(g)} + 4H^+{}_{(aq)} + 4e^- \longrightarrow 2H_2O_{(l)}$

Overall reaction : $2Fe_{(s)} + O_{2(g)} + 4H^+{}_{(aq)} \longrightarrow 2Fe^{2+}{}_{(aq)} + 2H_2O_{(l)}$.

Methods used for prevention of corrosion : Barrier protection, sacrificial protection, anti-rust solutions.

ELECTROCHEMISTRY

3.1 Electrochemical Cells

SA I (2 marks)

1. Define electrochemical cell. What happens if external potential applied becomes greater than E°_{cell} of electrochemical cell? *(2/5, AI 2016)*

3.2 Galvanic Cells

VSA (1 mark)

2. Represent the galvanic cell in which the reaction
$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$ takes place. *(1/3, Delhi 2013C)*

3. What is the necessity to use a salt bridge in a Galvanic cell? *(Delhi 2011C)*

SA I (2 marks)

4. On the basis of standard electrode potential values stated for acid solutions, predict whether Ti^{4+} species may be used to oxidise Fe^{II} to Fe^{III}.
Reactions :
$Ti^{4+} + e^- \rightarrow Ti^{3+}$; + 0.01
$Fe^{3+} + e^- \rightarrow Fe^{2+}$; + 0.77 *(AI 2007)*

5. Two half-reactions of an electrochemical cell are given below :
$MnO^-_{4(aq)} + 8H^+_{(aq)} + 5e^- \rightarrow Mn^{2+}_{(aq)} + 4H_2O_{(l)}, E^\circ = + 1.51 V$
$Sn^{2+}_{(aq)} \rightarrow Sn^{4+}_{(aq)} + 2e^-,\ E^\circ = + 0.15 V$
Construct the redox equation from the standard potential of the cell and predict if the reaction is reactant favoured or product favoured. *(Delhi 2011, AI 2010, 2009)*

6. Given that the standard electrode potential (E°) of metals are :
$K^+/K = -2.93$ V, $Ag^+/Ag = 0.80$ V,
$Cu^{2+}/Cu = 0.34$ V,
$Mg^{2+}/Mg = -2.37$ V, $Cr^{3+}/Cr = -0.74$ V,
$Fe^{2+}/Fe = -0.44$ V.
Arrange these metals in an increasing order of their reducing power *(AI 2010)*

7. Formulate the galvanic cell in which the following reaction takes place :
$Zn_{(s)} + 2Ag^+_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)}$
State :
(i) Which one of its electrodes is negatively charged.
(ii) The reaction taking place at each of its electrode.
(iii) The carriers of current within this cell. *(Delhi 2008)*

SA II (3 marks)

8. A cell is prepared by dipping copper rod in 1 M copper sulphate solution and zinc rod in 1 M zinc sulphate solution. The standard reduction potential of copper and zinc are 0.34 V and −0.76 V respectively.
(i) What will be the cell reaction?
(ii) What will be the standard electromotive force of the cell?
(iii) Which electrode will be positive? *(Delhi 2011C)*

9. Depict the galvanic cell in which the reaction $Zn_{(s)} + 2Ag^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)}$ takes place. Further show :
(i) Which of the electrode is negatively charged?
(ii) The carriers of the current in the cell.
(iii) Individual reaction at each electrode. *(Delhi 2010C)*

3.3 Nernst Equation

SA I (2 marks)

10. Calculate $\Delta_r G^\circ$ for the reaction :
$Mg_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Mg^{2+}_{(aq)} + Cu_{(s)}$
Given $E^\circ_{cell} = +2.71$ V, 1 F = 96500 C mol^{-1} *(2/3,AI 2014)*

11. Equilibrium constant (K_c) for the given cell reaction is 10. Calculate E°_{cell}.
$A_{(s)} + B^{2+}_{(aq)} \rightleftharpoons A^{2+}_{(aq)} + B_{(s)}$ *(2/3,Foreign 2014)*

12. The standard electrode potential (E°) for Daniell cell is +1.1 V. Calculate the ΔG° for the reaction.
$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$
(1 F = 96500 C mol^{-1}) *(AI 2013)*

13. The standard electrode potential for Daniell cell is 1.1 V. Calculate the standard Gibbs energy for the cell reaction.
($F = 96{,}500\ C\ mol^{-1}$) *(Delhi 2013C)*

14. A zinc rod is dipped in 0.1 M solution of $ZnSO_4$. The salt is 95% dissociated at this dilution at 298 K. Calculate the electrode potential.
[$E^\circ_{Zn^{2+}/Zn} = -0.76$ V] *(Delhi 2012C)*

15. Determine the value of equilibrium constant (K_c) and ΔG° for the following reactions :
$Ni_{(s)} + 2Ag^+_{(aq)} \rightarrow Ni^{2+}_{(aq)} + 2Ag_{(s)}$, $E^\circ = 1.05$ V
($1\ F = 96500\ C\ mol^{-1}$)
(Delhi 2011, Foreign 2011)

16. Calculate the emf for the given cell at 25° C :
$Cr|Cr^{3+}$ (0.1 M) || Fe^{2+} (0.01 M)| Fe
Given :
$E^\circ_{Cr^{3+}/Cr} = -0.74$ V, $E^\circ_{Fe^{2+}/Fe} = -0.44$V
(2/5, Delhi 2009C)

SA II (3 marks)

17. Calculate e.m.f. of the following cell at 298 K
$2Cr_{(s)} + 3Fe^{2+}(0.1M) \rightarrow 2Cr^{3+}(0.01M) + 3Fe_{(s)}$
Given : $E^\circ_{(Cr^{3+}|Cr)} = -0.74$ V, $E^\circ_{(Fe^{2+}|Fe)} = -0.44$ V
(Delhi 2016)

18. Calculate E°_{cell} for the following reaction at 298 K.
$2Al_{(s)} + 3Cu^{2+}(0.01M) \rightarrow 2Al^{3+}(0.01M) + 3Cu_{(s)}$
Given : $E_{cell} = 1.98$ V *(3/5, AI 2016)*

19. Calculate emf of the following cell at 25°C:
$Fe|Fe^{2+}(0.001\ M)||H^+(0.01\ M)|H_{2(g)}(1\ bar)|Pt_{(s)}$
$E^\circ(Fe^{2+}|Fe) = -0.44$ V, $E^\circ(H^+|H_2) = 0.00$ V
(Delhi 2015)

20. Calculate the emf of the following cell at 25°C
$Zn|Zn^{2+}$ (0.001 M) || H^+(0.01M)| $H_{2(g)}$ (1 bar) | $Pt_{(s)}$
$E^\circ_{(Zn^{2+}/Zn)} = -0.76$ V, $E^\circ_{(H^+/H_2)} = 0.00$ V
(Foreign 2015)

21. For the cell reaction
$Ni_{(s)}|Ni^{2+}_{(aq)}||Ag^+_{(aq)}|Ag_{(s)}$
Calculate the equilibrium constant at 25°C. How much maximum work would be obtained by operation of this cell?
$E^\circ_{(Zn^{2+}/Zn)} = -0.25$ V and $E^\circ_{Ag^+/Ag} = 0.80$V
(3/5, Delhi 2015C)

22. Calculate the standard cell potential of the galvanic cell in which the following reaction takes place :
$Fe^{2+}_{(aq)} + Ag^+_{(aq)} \rightarrow Fe^{3+}_{(aq)} + Ag_{(s)}$
Calculate the $\Delta_r G^\circ$ and equilibrium constant of the reaction also,
$\left(E^\circ_{Ag^+/Ag} = 0.80\ V;\ E^\circ_{Fe^{3+}/Fe^{2+}} = 0.77\ V\right)$
(3/5, Delhi 2015C)

23. Calculate the emf of following cell at 298 K :
$Mg_{(s)}$ | Mg^{2+}(0.1 M) || Cu^{2+}(0.01 M)|$Cu_{(s)}$
[Given : $E^\circ_{cell} = +2.71$ V, $1\ F = 96500\ C\ mol^{-1}$]
(3/5, Delhi 2014)

24. Estimate the minimum potential difference needed to reduce Al_2O_3 at 500°C. The Gibbs energy change for the decomposition reaction
$\frac{2}{3}Al_2O_3 \rightarrow \frac{4}{3}Al + O_2$ is 960 kJ.
($F = 96500\ C\ mol^{-1}$) *(3/5,Delhi 2014C)*

25. Calculate the emf of the following cell at 298 K :
$Fe_{(s)}|Fe^{2+}(0.001\ M)||H^+(1\ M)|H_{2(g)}$ (1 bar), $Pt_{(s)}$
(Given $E^\circ_{cell} = +0.44$ V) *(Delhi 2013)*

26. Calculate the emf of the following cell at 25°C :
$Ag_{(s)}|Ag^+(10^{-3}\ M)||Cu^{2+}\ (10^{-1}\ M)|Cu_{(s)}$
Given : $E^\circ_{cell} = +0.46$ V and $\log 10^n = n$.
(AI 2013)

27. In the button cell, widely used in watches, the following reaction takes place.
$Zn_{(s)} + Ag_2O_{(s)} + H_2O_{(l)} \rightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)} + 2OH^-_{(aq)}$
Determine E° and ΔG° for the reaction.
(Given : $E^\circ_{Ag^+/Ag} = +0.80$ V, $E^\circ_{Zn^{2+}/Zn} = -0.76$ V)
(3/5, Delhi 2012)

28. A voltaic cell is set up at 25°C with the following half cells :
Al/Al^{3+} (0.001 M) and Ni/Ni^{2+} (0.50 M)
Write an equation for the reaction that occurs when the cell generates an electric current and determine the cell potential.
$E^\circ_{Ni^{2+}/Ni} = -0.25$ V and $E^\circ_{Al^{3+}/Al} = -1.66$ V.
($\log 8 \times 10^{-6} = -5.09$) *(3/5, AI 2012, 2011, 3/5, Foreign 2011, 3/5, Delhi 2009)*

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29. The cell in which the following reaction occurs :
$2Fe^{3+}_{(aq)} + 2I^{-}_{(aq)} \rightarrow 2Fe^{2+}_{(aq)} + I_{2(s)}$
has E°_{cell} = 0.236 V at 298 K, Calculate the standard Gibbs energy and the equilibrium constant of the cell reaction.
(Antilog of 6.5 = 3.162×10^6 ; of 8.0 = 10×10^8 ; of 8.5 = 3.162×10^8)
(Delhi 2012C)

30. Calculate the potential for half-cell containing 0.10 M $K_2Cr_2O_{7(aq)}$, 0.20 M $Cr^{3+}_{(aq)}$ and 1.0×10^{-4} M $H^+_{(aq)}$. The half cell reaction is :
$Cr_2O^{2-}_{7(aq)} + 14H^+_{(aq)} + 6e^- \rightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$
and the standard electrode potential is given as E° = 1.33 V. *(3/5, AI 2011)*

31. For the cell
$Zn_{(s)} \mid Zn^{2+}$ (2 M) || Cu^{2+} (0.5 M) | $Cu_{(s)}$
(a) Write equation for each half-reaction.
(b) Calculate the cell potential at 25°C
Given :
$E^\circ_{Zn^{2+}/Zn} = -0.76$ V; $E^\circ_{Cu^{2+}/Cu} = +0.34$V
(Delhi 2011C)

32. Calculate the equilibrium constant, *K* for the reaction at 298 K,
$Zn_{(s)} + Cu^{2+}_{(aq)} \rightleftharpoons Zn^{2+}_{(aq)} + Cu_{(s)}$
Given : $\Delta G^\circ = -212.300$ kJ mol^{-1}
$E^\circ_{Zn^{2+}/Zn} = -0.76$ V; $E^\circ_{Cu^{2+}/Cu} = +0.34$ V
(AI 2011C)

33. A copper-silver cell is set up. The copper ion concentration is 0.10 M. The concentration of silver ion is not known. The cell potential when measured was 0.422 V. Determine the concentration of silver ions in the cell.
Given :
$E^\circ_{Ag^+/Ag} = +0.80$ V, $E^\circ_{Cu^{2+}/Cu} = +0.34$ V
(3/5, Delhi 2010, AI 2009)

34. A voltaic cell is set up at 25° with the following half cells :
Ag^+(0.001 M) | Ag and Cu^{2+} (0.10 M) | Cu
What would be the voltage of this cell?
(E°_{cell} = 0.46 V) *(AI 2009)*

35. A voltaic cell is set up at 25°C with the following half-cells :
Al | Al^{3+} (0.001 M) and Ni | Ni^{2+} (0.50 M)
Calculate the cell voltage
[$E^\circ_{Ni^{2+}|Ni} = -0.25$ V, $E^\circ_{Al^{3+}|Al} = -1.66$ V]
(3/5, Delhi 2009)

36. Calculate the equilibrium constant for the reaction
$Fe_{(s)} + Cd^{2+}_{(aq)} \rightleftharpoons Fe^{2+}_{(aq)} + Cd_{(s)}$
Given :
[$E^\circ_{Cd^{2+}|Cd} = -0.40$ V, $E^\circ_{Fe^{2+}|Fe} = -0.44$ V]
(3/5, Delhi 2009, 2009C, 3/5, AI 2009)

37. One half-cell in a voltaic cell is constructed from a silver wire dipped in silver nitrate solution of unknown concentration. Its other half-cell consists of a zinc electrode dipping in 1.0 M solution of $Zn(NO_3)_2$. A voltage of 1.48 V is measured for this cell. Use this information to calculate the concentration of silver nitrate solution used.
[$E^\circ_{Zn^{2+}|Zn} = -0.76$ V, $E^\circ_{Ag^+|Ag} = +0.80$ V]
(3/5, Delhi 2009)

38. Calculate the standard cell potential of a galvanic cell in which the following reaction takes place :
$2Cr_{(s)} + 3Cd^{2+}_{(aq)} \rightarrow 2Cr^{3+}_{(aq)} + 3Cd_{(s)}$
Calculate $\Delta_r G^\circ$ and equilibrium constant, *K* of the above reaction at 25°C.
Given :
$E^\circ_{Cr^{3+}/Cr} = -0.74$ V, $E^\circ_{Fe^{2+}/Fe} = -0.44$ V
(F = 96,500 C mol^{-1}) *(Delhi 2008C)*

39. (i) Formulate the electrochemical cell representing the reaction ;
$2Cr_{(s)} + 3Fe^{2+}_{(aq)} \longrightarrow 2Cr^{3+}_{(aq)} + 3Fe_{(s)}$
(ii) Calculate E°_{cell}.
(iii) Calculate E_{cell} at 25°C if
[Cr^{3+}] = 0.1 M and [Fe^{2+}] = 0.01 M
Given :
$E^\circ_{Cr^{3+}/Cr} = -0.74$ V, $E^\circ_{Fe^{2+}/Fe} = -0.44$ V
(3/5, AI 2008C)

LA (5 marks)

40. Calculate e.m.f and ΔG for the following cell
$Mg_{(s)} \mid Mg^{2+}$ (0.001 M) || Cu^{2+} (0.0001 M) | $Cu_{(s)}$
$E^\circ_{(Mg^{2+}/Mg)} = -2{\cdot}37$ V, $E^\circ_{(Cu^{2+}/Cu)} = +0.34$ V
(AI 2015)

41. Calculate the standard electrode potential of Ni^{2+}/Ni electrode if emf of the cell

$Ni_{(s)}|Ni^{2+}(0.01\,M)||Cu^{2+}(0.1\,M)|Cu_{(s)}$ is 0.059V.

[Given : $E^{\circ}_{Cu^{2+}/Cu} = +0.34$ V] *(Delhi 2009C)*

42. Calculate the cell emf and $\Delta_r G^{\circ}$ for the cell reaction at 25°C

$Zn_{(s)} \mid Zn^{2+}$ (0.1 M) $\|$ Cd^{2+} (0.01 M)$\mid Cd_{(s)}$

Given :

$E^{\circ}_{Zn^{2+}/Zn} = -0.763$ V, $E^{\circ}_{Cd^{2+}/Cd} = -0.403$ V

1 F = 96,500 C mol^{-1}, $R = 8.314$ J K^{-1} mol^{-1}

(AI 2009C)

3.4 Conductance of Electrolytic Solutions

VSA (1 mark)

43. Define limiting molar conductivity. Why conductivity of an electrolyte solution decreases with the decrease in concentration? *(1/2, Delhi 2015)*

44. State Kohlrausch's law of independent migration of ions. Write its one application. *(1/2, Foreign 2015)*

45. Define the following term :

Molar conductivity (Λ_m) *(1/5, Delhi 2015C)*

46. Define the following term :

Kohlrausch's law of independent migration of ions. *(1/5, Delhi 2015C)*

47. Define the following term : Limiting molar conductivity *(1/5, Delhi 2014)*

48. State and explain Kohlrausch's law. *(1/3, Delhi 2013C)*

49. Express the relation between conductivity and molar conductivity of a solution held in a cell? *(Delhi 2011)*

50. Express the relation among the conductivity of solution in the cell, the cell constant and the resistance of solution in the cell. *(Delhi 2011)*

51. Express the relation between the conductivity and the molar conductivity of a solution. *(AI 2008)*

SA I (2 marks)

52. Define the term degree of dissociation. Write an expression that relates the molar conductivity of a weak electrolyte to its degree of dissociation. *(2/5, Delhi 2015C)*

53. Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with concentration. *(2/5, AI 2015C)*

54. State Kohlrausch law of independent migration of ions. Why does the conductivity of a solution decrease with dilution? *(AI 2014)*

55. Define the terms conductivity and molar conductivity for the solution of an electrolyte. Comment on their variation with temperature. *(Delhi 2014C)*

56. The resistance of 0.01 M NaCl solution at 25°C is 200 Ω. The cell constant of the conductivity cell used is unity. Calculate the molar conductivity of the solution. *(2/3, AI 2014C)*

57. Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with change in temperature. *(AI 2014C)*

58. The conductivity of 0.20 M solution of KCl at 298 K is 0.025 S cm^{-1}. Calculate its molar conductivity. *(Delhi 2013, 2008, AI 2007)*

59. The conductivity of 0.001 M acetic acid is 4×10^{-5} S/cm. Calculate the dissociation constant of acetic acid, if molar conductivity at infinite dilution for acetic acid is 390 S cm^2/mol. *(2/3, Delhi 2013C, 2012C)*

60. Express the relation among cell constant, resistance of the solution in the cell and conductivity of the solution. How is molar conductivity of a solution related to its conductivity? *(AI 2012, 2010, 2/5,Delhi 2009)*

61. The molar conductivity of a 1.5 M solution of an electrolyte is found to be 138.9 S cm^2 mol^{-1}. Calculate the conductivity of this solution. *(AI 2012, 2010C)*

62. The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500 Ω. What is the cell constant if conductivity of 0.001 M KCl solution at 298 K is 0.146×10^{-3} S cm^{-1}? *(Delhi 2010C, 2009C, 2008, 2007)*

63. Define molar conductivity of a substance and describe how for weak and strong electrolytes, molar conductivity changes with concentration of solute. How is such change explained? *(2/5, Delhi 2009)*

64. Define the term molar conductivity. How is it related to conductivity of the related solution? *(2/5, Delhi 2009)*

65. State Kohlrausch's law of independent migration of ions. How can the degree of dissociation of acetic acid in a solution be calculated from its molar conductivity data? *(2/5, AI 2008C)*

66. Explain with examples the terms weak and strong electrolytes. *(Delhi 2007)*

SA II (3 marks)

67. The conductivity of 0.001 mol L^{-1} solution of CH_3COOH is 3.905×10^{-5} S cm^{-1}. Calculate its molar conductivity and degree of dissociation (α).
Given : $\lambda^\circ(H^+) = 349.6$ S cm^2 mol^{-1} and $\lambda^\circ(CH_3COO^-) = 40.9$ S cm^2 mol^{-1} *(3/5, AI 2016)*

68. The conductivity of 0·20 mol L^{-1} solution of KCl is 2.48×10^{-2} S cm^{-1}. Calculate its molar conductivity and degree of dissociation (α).
Given $\lambda^\circ(K^+) = 73.5$ S cm^2 mol^{-1} and $\lambda^\circ(Cl^-) = 76.5$ S cm^2 mol^{-1}. *(AI 2015)*

69. Resistance of a conductivity cell filled with 0.1 mol L^{-1} KCl solution is 100 Ω. If the resistance of the same cell when filled with 0.02 mol L^{-1} KCl solution is 520 Ω, calculate the conductivity and molar conductivity of 0.02 mol L^{-1} KCl solution. The conductivity of 0.1 mol L^{-1} KCl solution is 1.29×10^{-2} Ω^{-1} cm^{-1}. *(3/5, AI 2014)*

70. The value of Λ°_m of $Al_2(SO_4)_3$ is 858 S cm^2 mol^{-1}, while λ° SO_4^{2-} is 160 S cm^2 mol^{-1} calculate the limiting ionic conductivity of Al^{3+}. *(AI 2013C)*

71. The electrical resistance of a column of 0.05 M NaOH solution of diameter 1 cm and length 50 cm is 5.55×10^3 ohm. Calculate its resistivity, conductivity and molar conductivity. *(AI 2012)*

72. When a certain conductance cell was filled with 0.1 M KCl, it has a resistance of 85 ohms at 25°C. When the same cell was filled with an aqueous solution of 0.052 M unknown electrolyte, the resistance was 96 ohms. Calculate the molar conductance of the electrolyte at this concentration.
[Specific conductance of 0.1 M KCl $= 1.29 \times 10^{-2}$ ohm^{-1} cm^{-1}] *(AI 2012C)*

73. Calculate the degree of dissociation of acetic acid at 298 K, given that :
$\Lambda_m(CH_3COOH) = 11.7$ S cm^2 mol^{-1}
$\Lambda^\circ_m(CH_3COO^-) = 49.9$ S cm^2 mol^{-1}
$\Lambda^\circ_m(H^+) = 349.1$ S cm^2 mol^{-1} *(Delhi 2011C)*

74. The resistance of a conductivity cell when filled with 0.05 M solution of an electrolyte *X* is 100 ohms at 40°C. The same conductivity cell filled with 0.01 M solution of electrolyte *Y* has a resistance of 50 ohms. The conductivity of 0.05 M solution of electrolyte *X* is 1.0×10^{-4} S cm^{-1}. Calculate
(i) Cell constant
(ii) Conductivity of 0.01 M *Y* solution
(iii) Molar conductivity of 0.01 M *Y* solution *(3/5, AI 2008C)*

LA (5 marks)

75. (a) Define molar conductivity of a solution and explain how molar conductivity changes with change in concentration of solution for a weak and a strong electrolyte.
(b) The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500 Ω. What is the cell constant if the conductivity of 0.001 M KCl solution at 298 K is 0.146×10^{-3} S cm^{-1}? *(AI 2012)*

76. (a) State Kohlrausch's law of independent migration of ions. Write an expression for the molar conductivity of acetic acid at infinite dilution according to Kohlrausch's law.
(b) Calculate Λ°_m for acetic acid.
Given that
$\Lambda^\circ_m(HCl) = 426$ S cm^2 mol^{-1}
$\Lambda^\circ_m(NaCl) = 126$ S cm^2 mol^{-1}
$\Lambda^\circ_m(CH_3COONa) = 91$ S cm^2 mol^{-1} *(Delhi 2010)*

77. Conductivity of 0.00241 M acetic acid is 7.896×10^{-5} S cm^{-1}. Calculate its molar conductivity if Λ°_m for acetic acid is 390.5 S cm^2 mol^{-1}. What is its dissociation constant? *(Delhi, AI 2008)*

3.5 Electrolytic Cells and Electrolysis

VSA (1 mark)

78. Following reactions occur at cathode during the electrolysis of aqueous silver chloride solution :

$Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}, \quad E^\circ = +0.80$ V

$H^+_{(aq)} + e^- \longrightarrow \frac{1}{2}H_{2(g)}, \; E^\circ = 0.00$ V

On the basis of their standard reduction electrode potential (E°) values, which reaction is feasible at the cathode and why? *(1/2, Delhi 2015)*

79. How much charge is required for the reduction of 1 mol of Zn^{2+} to Zn? *(Delhi 2015)*

80. Following reactions occur at cathode during the electrolysis of aqueous copper (II) chloride solution :

$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)} \qquad E^\circ = +0.34$ V

$H^+_{(aq)} + e^- \longrightarrow \frac{1}{2}H_{2(g)} \qquad E^\circ = 0.00$ V

On the basis of their standard reduction electrode potential (E°) values, which reaction is feasible at the cathode and why? *(1/2, Foreign 2015)*

81. State the Faraday's first law of electrolysis. *(Delhi 2015C)*

82. How much charge is required for the reduction of 1 mole of Cu^{2+} to Cu? *(Delhi 2007)*

SA I (2 marks)

83. State Faraday's first law of electrolysis. How much charge in terms of Faraday is required for the reduction of 1 mol of Cu^{2+} to Cu. *(2/5, Delhi 2014)*

84. A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5.0 ampere for 20 minutes. What mass of nickel will be deposited at the cathode?
(Given : At. mass of Ni = 58.7 g mol^{-1}, 1F = 96500 C mol^{-1}) *(Foreign 2014)*

85. Predict the products of electrolysis in each of the following :
(i) An aqueous solution of $AgNO_3$ with platinum electrodes.
(ii) An aqueous solution of H_2SO_4 with platinum electrodes. *(2/5, Delhi 2014C)*

86. How much electricity in terms of Faradays is required to produce 20 g of calcium from molten $CaCl_2$? *(2/3, Delhi 2013C)*

87. Silver is uniformly electrodeposited on a metallic vessel of surface area of 900 cm^2 by passing a current of 0.5 ampere for 2 hours. Calculate the thickness of silver deposited. Given : the density of silver is 10.5 g cm^{-3} and atomic mass of Ag = 108 amu. *(2/3, AI 2013C)*

88. How many coulombs are required to reduce 1 mole $Cr_2O_7^{2-}$ to Cr^{3+}? *(2/3, Delhi 2012C)*

89. How many moles of mercury will be produced by electrolysing 1.0 M $Hg(NO_3)_2$ solution with a current of 2.00 A for 3 hours? *(2/5, AI 2011)*

90. A solution of $CuSO_4$ is electrolysed for 10 minutes with a current of 1.5 amperes. What is the mass of copper deposited at the cathode? *(AI 2009)*

91. Explain why electrolysis of aqueous solution of NaCl gives H_2 at cathode and Cl_2 at anode. Write overall reaction.
Given :

$E^\circ_{Na^+/Na} = -2.71$ V, $E^\circ_{H_2O/H_2} = -0.83$ V,

$E^\circ_{Cl_2/Cl^-} = +1.36$ V, $E^\circ_{H^+/H_2/H_2O} = +1.23$ V

(2/5, Delhi 2009C)

92. Consider the reaction :
$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 8H_2O$
What is the quantity of electricity in coulombs needed to reduce 1 mol of $Cr_2O_7^{2-}$? *(AI 2008)*

93. Explain why electrolysis of an aqueous solution of NaCl gives H_2 at cathode and Cl_2 at anode.

$E^\circ_{Na^+/Na} = -2.71$ V, $E^\circ_{H_2O/H_2} = -0.83$ V

$E^\circ_{Cl_2/2Cl^-} = +1.36$ V,

$E^\circ_{2H^+/\frac{1}{2}O_2/H_2O} = +1.23$ V

(2/5, Delhi 2008C)

94. Predict the products of electrolysis obtained at the electrodes in each if the electrodes used are of platinum?
(i) An aqueous solution of $AgNO_3$.
(ii) An aqueous solution of H_2SO_4. *(AI 2007)*

SA II (3 marks)

95. Calculate the strength of the current required to deposit 1.2 g of magnesium from molten $MgCl_2$ in 1 hour.
[1 F = 96,500 C mol^{-1};
Atomic mass : Mg = 24.0] *(3/5, Delhi 2009C)*

96. A solution of $CuSO_4$ is electrolysed for 16 minutes with a current of 1.5 amperes. What is the mass of copper deposited at the cathode? *(AI 2007)*

LA (5 marks)

97. Three electrolytic cells *A*, *B* and *C* containing solutions of zinc sulphate, silver nitrate and copper sulphate, respectively are connected in series. A steady current of 1.5 ampere is passed through them until 1.45 g of silver is deposited at the cathode of cell *B*. How long did the current flow? What mass of copper and what mass of zinc were deposited on the concerned electrodes? (Atomic masses of Ag = 108, Zn = 65.4, Cu = 63.5) *(Delhi, AI 2008)*

3.6 Batteries

VSA (1 mark)

98. Define : Secondary batteries *(1/5, Delhi 2015C)*

SA I (2 marks)

99. From the given cells :
Lead storage cell, Mercury cell, Fuel cell and Dry cell
Answer the following :
(i) Which cell is used in hearing aids?
(ii) Which cell was used in Apollo Space Programme?
(iii) Which cell is used in automobiles and invertors?
(iv) Which cell does not have long life? *(Delhi 2016)*

100. What type of battery is mercury cell? Why is it more advantageous than dry cell? *(2/5, AI 2015)*

101. What type of a battery is the lead storage battery? Write the anode and the cathode reactions and the overall reaction occurring in a lead storage battery when current is drawn from it. *(2/5, Delhi 2012)*

102. Write the reactions taking place at cathode and anode in lead storage battery when the battery is in use. What happens on charging the battery? *(AI 2012C)*

103. What type of a battery is lead storage battery? Write the anode and cathode reactions and the overall cell reaction occurring in the operation of a lead storage battery. *(2/5, AI 2011, 2009, 2/5, Delhi 2009)*

104. Mention the reactions occurring at (i) anode, (ii) cathode, during working of a mercury cell. Why does the voltage of a mercury cell remain constant during its operation? *(Delhi 2011C)*

105. Write the anode and cathode reactions and the overall reaction occurring in a lead storage battery. *(2/5, Delhi 2010)*

SA II (3 marks)

106. What is a nickel-cadmium cell? State its one merit and one demerit over lead storage cell. Write the overall reaction that occurs during discharging of this cell. *(AI 2010C)*

3.7 Fuel Cells

VSA (1 mark)

107. Define : Fuel cell *(1/5, Delhi 2015C, 2014)*

108. Name the type of cell which was used in Apollo space programme for providing electrical power. *(1/3, AI 2014)*

SA I (2 marks)

109. Write two advantages of $H_2 - O_2$ fuel cell over ordinary cell. *(2/3, Foreign 2014)*

110. What are fuel cells? Explain the electrode reactions involved in the working of $H_2 - O_2$ fuel cell. *(2/3, Delhi 2013C, 2009)*