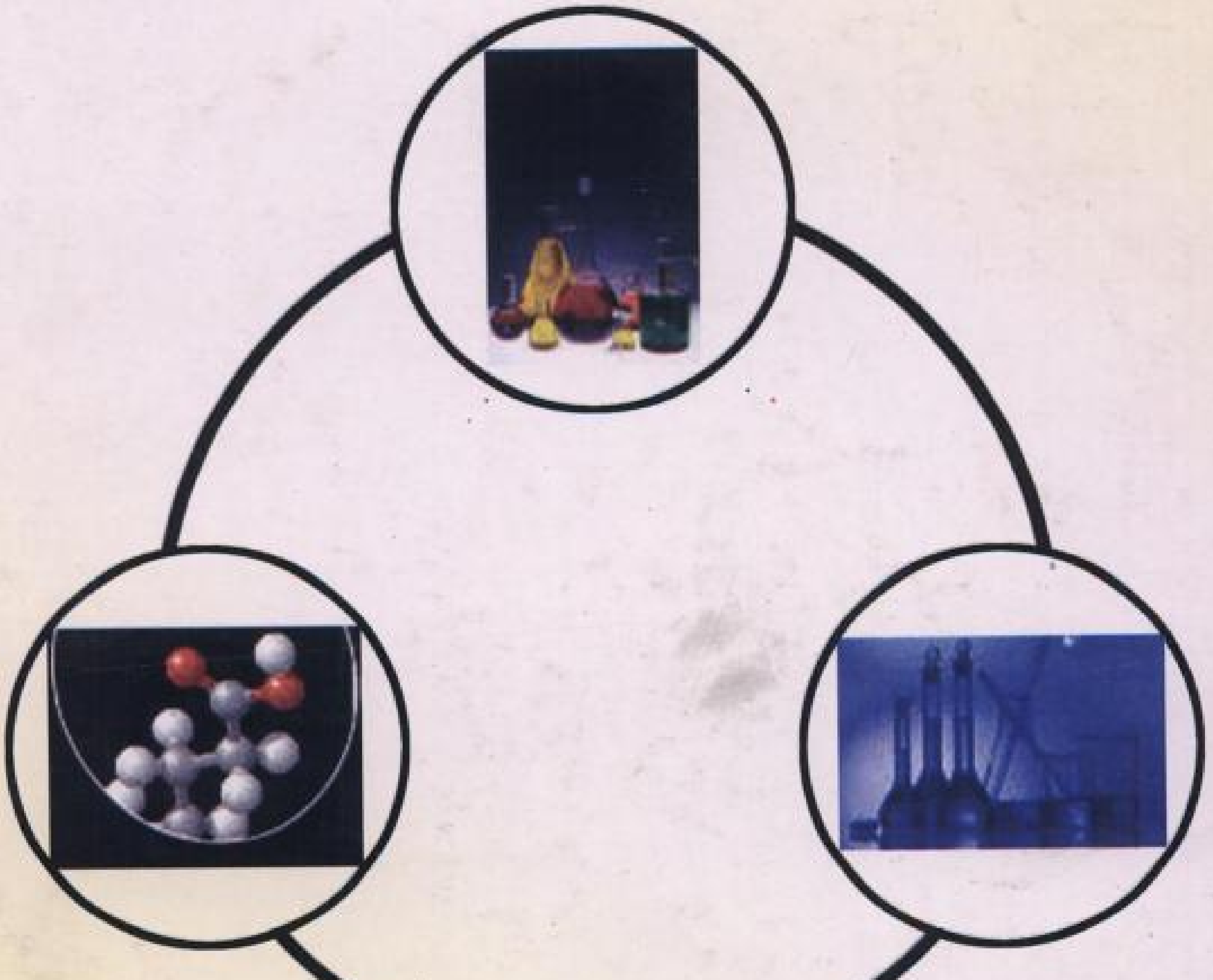
Comprehensive

MCQ's in CHEMISTRY

For Engineering & Medical Entrance Examinations



GOLDEN BELLS

Comprehensive

MCQs

in

CHEMISTRY

[*for various Engineering & Medical Entrance Examinations*]

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CHEMISTRY

1 SOME BASIC CONCEPTS (Atoms, Molecules and Chemical Arithmetic)

Important Terms, Facts and Formulae

SIGNIFICANT FIGURES

(*i*) All non-zero digits as well zeros between the non-zero digits are significant.

(*ii*) Zeros to the left of the first non-zero digit are not significant.

(*iii*) If a number ends in zeros but these zeros are to the right of the decimal point, then these zeros are significant.

(*iv*) If a number ends in zero but these zero are not to the right of a decimal point, these zeros may or may not be significant. It depends how the number is expressed in the exponential form *e.g.* 10500 may be written as 1.05×10^4, 1.050×10^4 or 1.0500×10^4. These have 3, 4 and 5 significant figures respectively.

(*v*) The result of addition or subtraction should be reported to the same number of decimal places as that of the term with least number of decimal places.

(*vi*) The result of multiplication or division should be reported to the same number of significant figures as possessed by the least precise term.

(*vii*) If a calculation involves a number of steps, the result should contain the same number of significant figures as that of the least precise number, other than the exact numbers.

MATTER

Anything that occupies *space*, *possesses mass* and the presence of which can be felt by any one or more of our five senses is called *matter*. It exists in three states *i.e. Solids, Liquids* and *Gases*.

The fourth state of matter is known as **plasma state** and is found only at a high temperature.

CHEMICAL CLASSIFICATION OF MATTER

Matter may be **heterogeneous** (non-uniform composition) or homogeneous (uniform composition). Homogeneous matter comprises of **solutions** (non-fixed composition) and **pure substances** or (fixed composition). Pure subsstances are further classified as (*i*) **Elements** (cannot be decomposed and (*ii*) **Compounds** (can be decomposed by chemical reactions).

A **mixture** is formed by mixing two or more elements or compounds in any proportion. It may be homogeneous or heterogeneous.

PURIFICATION TECHNIQUES

The different methods used are as follows :

(*i*) **Filtration**

(*ii*) **Distillation :** It may be

  (*a*) *Simple distillation*

  (*b*) *Fractional distillation*

(*iii*) **Extraction**

(*iv*) **Fractional crystallization**

(*v*) **Gravity separation**

(*vi*) **Magnetic separation**

(*vii*) **Sublimation**

(*viii*) **Chromatography.**

CHEMICAL EQUATION

It is a brief representation of a chemical change in terms of *symbol* and *formulae* of reactants and products.

LAWS OF CHEMICAL COMBINATION

- **Law of Conservation of Mass.** Total mass of reactants = Total mass of products
- **Law of definite proportions** (*Joseph Proust 1799*)
  A chemical compound always contains same elements combined together in the same proportion by mass.
- **Law of multiple proportions** (*John Dalton*)
  When two elements combine to form two or more compounds, the masses of one of the element which combine with fixed mass of the other bear a simple whole number ratio.
- **Law of Reciprocal proportions** (*Richter 1792*)
  When two elements combine separately with fixed mass of the third element, then the ratio of the masses in which they do so is either same or some whole

16. Which of the following illustrates the law of conservation of mass ?

(*a*) Mixing of 10 g of sulphur and 2 g of sand does not show a change in mass

(*b*) The mass of platinum wire before and after heating remains constant

(*c*) 2.2 g of propane and 8 g of oxygen produces 10.2 g of gaseous mixture

(*d*) 2.8 g of CO and 1.6 g of oxygen gave only 2.24 L of CO_2 at S.T.P.

17. The mole percent of oxygen present in gaseous mixture containing 14.0 g nitrogen and 32 g oxygen is

(*a*) 50
(*b*) 33.3
(*c*) 66.6
(*d*) 40.

18. The number of moles of oxygen present in one litre of air if its volume content is 21% at S.T.P. is

(*a*) 9.375×10^{-3}
(*b*) 9.375
(*c*) 0.063
(*d*) 0.05.

19. For a reaction, $A + 2B \longrightarrow C$. The amount of C formed by starting the reaction with 5 moles of A and 8 moles of B is

(*a*) 5 mol
(*b*) 8 mol
(*c*) 16 mol
(*d*) 4 mol.

20. A compound contains 10^{-2}% of phosphorus. If atomic mass of phosphorus is 31, the molecular mass of the compound having one phosphorus atom per molecule is

(*a*) 31
(*b*) 31×10^2
(*c*) 31×10^4
(*d*) 31×10^3.

21. 12 g of Mg (at. mass 24) react with dilute mineral acid to produce maximum hydrogen equal to

(*a*) 0.5 mol
(*b*) 1.5 mol
(*c*) 1.5 g
(*d*) 1 g-atom.

22. What is not correct about 1 mol of ethyne ?

(*a*) It contains 2 g-atom of hydrogen

(*b*) It contains 1.2×10^{23} C atoms

(*c*) It weighs is 26 g

(*d*) It contains 24 g of carbon.

23. Which of the following does not have same percentage of carbon as in ethene ?

(*a*) 2-Butene
(*b*) Cyclohexane
(*c*) Cylohexene
(*d*) 2-Methyl but-2-ene.

24. The correct arrangement of the following in order of increasing mass is

I. nitrogen molecule
II. oxygen atom
III. 1 avogram
IV. 1×10^{-10} g-atom of copper.

(*a*) I > II > III > IV
(*b*) I < II < III < IV
(*c*) III < II < I < IV
(*d*) II < III < I < IV.

25. Which of the following ionic compound contains largest number of ions ?

(*a*) 11.1 g of $CaCl_2$
(*b*) 0.1 mol of KI
(*c*) 0.1 mol of $AlPO_4$
(*d*) 0.1 mol of $SrCO_3$.

26. The number of oxygen atoms in 0.2 mole of decahydrate sodium carbonate is

(*a*) 1.56×10^{24}
(*b*) 1.56×10^{23}
(*c*) 1.56×10^{25}
(*d*) 3.12×10^{24}.

27. The mass of nitrogen in 1 kg of ammonium nitrate is

(*a*) 700 g
(*b*) 3.5×10^{-1} kg
(*c*) 350 g
(*d*) 35 g.

28. The mass of carbon (II) oxide which contains 6.02×10^{23} oxygen atoms is

(*a*) 2.8 g
(*b*) 28 g
(*c*) 14 g
(*d*) 1.4 g.

29. The number of PH_3 molecules in 8.5 g of phosphine is approximately

(*a*) 1×10^{23}
(*b*) 1.5×10^{23}
(*c*) 2×10^{23}
(*d*) 2.5×10^{23}.

30. A sample of AlF_3 contains 3×10^{25} F^- ions. The number of Al^{3+} in the sample would be

(*a*) 3×10^{25}
(*b*) 1×10^{25}
(*c*) 1.5×10^{25}
(*d*) 2×10^{25}.

31. A certain gaseous mixture contains methane and sulphur dioxide in ratio of 1 : 8 by mass. The ratio of the number of molecules is

(*a*) 1 : 8
(*b*) 1 : 2
(*c*) 1 : 1
(*d*) 2 : 1.

32. x L of nitrogen at N.T.P. contains 3×10^{22} molecules. The number of molecules in $\frac{x}{2}$ L of ozone at N.T.P. will be

(*a*) 3×10^{22}
(*b*) 1.5×10^{22}
(*c*) 1.5×10^{21}
(*d*) 1.5×10^{11}.

83. On reduction with hydrogen 3.6 g of an oxide of metal leaves 3.2 g of metallic residue. If the atomic mass of metal is 64, the formula of metal oxide is

(*a*) M_2O_3 (*b*) M_2O

(*c*) MO (*d*) MO_2.

84. Among the pairs of compounds given below which pair contains compounds with different percentage of carbon ?

(*a*) propene and propane (*b*) butane and isobutane

(*c*) acetylene and benzene (*d*) propene, cyclopropane.

85. The mole fraction of solute in 1 molal aqueous solution is

(*a*) 0.0176 (*b*) 1.8

(*c*) 0.05 (*d*) 0.98.

QUESTION BANK

Level II

Choose the correct answer from the four alternatives given in each of the following questions :

1. 10 g of a sample of silver which is contaminated with silver sulphide produced 11.2 mL of hydrogen sulphide at S.T.P. by treatment with excess of hydrochloric acid. The mass of silver sulphide in the sample is (Ag = 108 ; S = 32)

(*a*) 1.24 g (*b*) 124 mg

(*c*) 5×10^{-2} mol (*d*) 62 mg.

2. Dehydration of sucrose, $C_{12}H_{22}O_{11}$ by concentrated H_2SO_4 gives purest form of carbon. The amount of carbon which can be obtained from 34.2 g of sucrose is

(*a*) 14.4 g (*b*) 12 g-atom

(*c*) 3.2 g-atoms (*d*) 14.4 g-atom.

3. 142 g of chlorine represents

(*a*) Two g-molecules of chlorine

(*b*) 4 moles of chlorine atoms

(*c*) Two moles of Cl atoms

(*d*) Both *a*, *b*.

4. 2.0 g of a tri-atomic gaseous element was found to occupy a volume of 448 ml at 76 cm of Hg and 273 K. The mass of its atom is

(*a*) 80 amu (*b*) 5.53×10^{-23} g

(*c*) 33.3 g (*d*) 5.53 amu.

5. 5 L of 0.1 M solution of sodium carbonate contains

(*a*) 53 g of Na_2CO_3

(*b*) 5×10^2 milli moles of Na_2CO_3.

(*c*) 106 g of Na_2CO_3

(*d*) Both *a*, *b*.

6. Total number of g-molecules of SO_2Cl_2 in 13.5 g of sulphuryl chloride is

(*a*) 0.1 (*b*) 0.2

(*c*) 0.3 (*d*) 0.4.

7. Total number of protons in 10 g of calcium carbonate is

(*a*) 1.5707×10^{24} (*b*) 2.0478×10^{24}

(*c*) 3.01×10^{24} (*d*) 4.0956×10^{24}.

8. 2 g of oxygen contains number of atoms equal to that in

(*a*) 0.5 g of hydrogen (*b*) 4 g of sulphur

(*c*) 7 g of nitrogen (*d*) 2.3 g of sodium.

9. The number of moles of sodium oxide present in 620 g of it are

(*a*) 1 mol (*b*) 10 mol

(*c*) 18 mol (*d*) 100 mol.

10. 3.5 g of CO gas at 0°C and 760 mm pressure contains molecules equal to

(*a*) $3.5 \times 6.02 \times 10^{23}$ (*b*) $28 \times 6.02 \times 10^{23}$

(*c*) 7.525×10^{22} (*d*) 1.25×10^{22}.

11. The number of moles of helium that occupies 2.24 litre at 0°C and 1 atm pressure is

(*a*) 1.0 (*b*) 0.1

(*c*) 10 (*d*) 1×10^{-2}.

12. The number of molecules in 8.96 L of a gas at 0°C and 1 atm pressure is approximately

(*a*) 6.02×10^{23} (*b*) 12.04×10^{23}

(*c*) 18.06×10^{23} (*d*) 24.08×10^{22}.

13. In the reaction,

$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI,$$

68. In a reaction, $3Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2$, the equivalent mass of iron (atomic mass = 56) is

(*a*) 21 (*b*) 56
(*c*) 112 (*d*) 42.

69. During synthesis of ammonia from its constituent elements, the volume of the product relative to the total volume of the reacting species is

(*a*) one-fourth (*b*) three-fourth
(*c*) one-half (*d*) one-eighth.

70. Which of the following contains largest number of atoms ?

(*a*) 1 g of C_2H_4 (*b*) 1 g of ozone
(*c*) 1 g of oxygen (*d*) 1 g of helium.

71. 50 ml of samples of distilled water, ordinary tap water and boiled tap water requires 2 ml, 26 ml and 10 ml of soap solution respectively to form permanent lather. The ratio of permanent hardness to temporary hardness in tap water is

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

72. 300 ml of 3.0 M NaCl is added to 200 ml of 4.0 M $BaCl_2$ solution. The concentration of Cl^- ions in the resulting solution is

(*a*) 7 M (*b*) 1.6 M
(*c*) 1.8 M (*d*) 5 M.

73. 60 g of a compound on analysis gave 24 g of C, 4 g of H and 32 g of O. The empirical formula of the compound is

(*a*) $C_2H_4O_2$ (*b*) CH_2O_2
(*c*) $C_2H_2O_2$ (*d*) CH_2O.

74. Two oxides of a metal contain 50% and 40% of metal (M) respectively. If the formula of first oxide is MO, the formula of 2nd oxide will be

(*a*) MO_2 (*b*) M_2O_3
(*c*) M_2O (*d*) M_2O_5.

75. 4 g of hydrogen is ignited with 4 g of oxygen, the amount of water formed is

(*a*) 2.5 g (*b*) 0.5 g
(*c*) 4.5 g (*d*) 8 g.

76. A solution containing 0.1 mol of a metal chloride MCl_x requires 500 mol of 0.8 M $AgNO_3$ solution for complete precipitation. The value of *x* is

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

ANSWERS

QUESTION BANK (Level I)

1. (*d*) **2.** (*d*) **3.** (*b*) **4.** (*b*) **5.** (*a*) **6.** (*c*) **7.** (*b*) **8.** (*d*)
9. (*c*) **10.** (*c*) **11.** (*b*) **12.** (*d*) **13.** (*a*) **14.** (*c*) **15.** (*d*) **16.** (*c*)
17. (*c*) **18.** (*a*) **19.** (*d*) **20.** (*c*) **21.** (*a*) **22.** (*b*) **23.** (*c*) **24.** (*c*)
25. (*a*) **26.** (*a*) **27.** (*c*) **28.** (*b*) **29.** (*b*) **30.** (*b*) **31.** (*b*) **32.** (*b*)
33. (*c*) **34.** (*b*) **35.** (*a*) **36.** (*c*) **37.** (*c*) **38.** (*c*) **39.** (*c*) **40.** (*d*)
41. (*d*) **42.** (*a*) **43.** (*d*) **44.** (*b*) **45.** (*b*) **46.** (*b*) **47.** (*b*) **48.** (*b*)
49. (*c*) **50.** (*a*) **51.** (*a*) **52.** (*d*) **53.** (*b*) **54.** (*c*) **55.** (*a*) **56.** (*a*)
57. (*a*) **58.** (*a*) **59.** (*a*) **60.** (*a*) **61.** (*a*) **62.** (*b*) **63.** (*d*) **64.** (*a*)
65. (*d*) **66.** (*c*) **67.** (*b*) **68.** (*b*) **69.** (*a*) **70.** (*c*) **71.** (*a*) **72.** (*b*)
73. (*c*) **74.** (*b*) **75.** (*a*) **76.** (*d*) **77.** (*c*) **78.** (*a*) **79.** (*b*) **80.** (*b*)
81. (*c*) **82.** (*d*) **83.** (*b*) **84.** (*a*) **85.** (*a*).

QUESTION BANK (Level II)

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

Moles of Mg $= \frac{2.4}{24} = 0.1$ mol.

From the equation,

HCl L. Reagent and moles of magnesium left

$$= 0.1 - 0.05 = 0.05.$$

73. (*a*) 50 ml of 0.5 M $Ca(OH)_2 = 0.025$ mol of $Ca(OH)_2$

The eqn. is $Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$

1 mol of $Ca(OH)_2$ gives $CaCO_3 = 100$ g

0.025 mol of $Ca(OH)_2$ gives $CaCO_3 = 100 \times 0.025 = 2.5$ g

74. (*b*) $\frac{1}{8}S_8 + O_2 \longrightarrow SO_2 \xrightarrow{+\frac{1}{2}O_2} SO_3 \xrightarrow{BaCl_2} BaSO_4$

32 g of sulphur produce $BaSO_4 = 1$ mol

∴ 16 g of sulphur produce $BaSO_4 = 0.5$ mol.

75. (*a*) The equation is

$$3BaCl_2 + 2Na_3PO_4 \longrightarrow Ba_3(OP_4)_2 + 6NaCl$$

Limiting reagent is 0.2 mol sodium phosphate.

76. (*d*) $2KI + HgCl_2 \longrightarrow KCl + HgI_2$

$2KI + HgI_2 \longrightarrow K_2HgI_4$

For producing 1 mol of K_2HgI_4, KI required = 4 mol

For producing 0.4 mol of K_2HgI_4,

KI required $= 4 \times 0.4 = 1.6$ mol.

77. (*c*) This is in accordance with law of definite proportions

78. (*a*) $2Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 + O_2$

2 mol 32 g

Lead nitrate required for producing 48 g of O_2

$$= \frac{2 \times 48}{32} = 3 \text{ mol.}$$

79. (*b*) The ionic equation is

$$H_2S + Cu^{2+} \longrightarrow CuS + 2H^+$$

34 g 63.5 g ppt.

80. (*b*) If atomic mass of O is 16 mol, mass of $H_2O = 18$

If atomic mass of O is 100 mol. mass of H_2O

$$= \frac{18 \times 100}{116} = 112.6.$$

81. (*c*) Neutrons in 1 molecule of $H_2O = 16$

Neutrons is 1.8 g of water

$$= \frac{1.8 \times 6.02 \times 10^{23} \times 16}{18} = 9.632 \times 10^{23}.$$

82. (*d*) 1 mol of Cu^{2+} ions has charge
= that on 2 mol of electrons = 2F

0.1 mol of Cu^{2+} has charge $= 2 \times 0.1$ F = 0.2F.

83. (*b*) Mass of oxygen which gets displaced from metal oxide = 0.4 g

Now, 0.4 g of oxygen combines with metal = 3.2 g

8 g of oxygen combines with metal $= \frac{3.2}{0.4} \times 8 = 64$ g

∴ GEW of metal = 64 g

Valency of metal $= \frac{\text{GAM}}{\text{GEW}} = \frac{64 \text{ g}}{64 \text{ g}} = 1.$

Hence, formula of oxide is M_2O.

84. (*a*) The compounds whose empirical formulae are different will have different percentage compositions.

85. (*a*) Moles of solute = 1 ; Moles of solvent $= \frac{1000}{18} = 55.5$

Mole fraction of solute $= \frac{1}{56.5} = 0.0176.$

QUESTION BANK (Level II)

1. (*b*) $Ag_2S + 2HCl \longrightarrow H_2S + 2AgCl$

248 g 22.4 L

11.2 ml of H_2S is produced from Ag_2S

$$= \frac{248 \times 11.2}{2240} = 0.124 \text{ g.}$$

Now 0.124 g of Ag_2S = 124 mg $= \frac{0.124}{248} = 5 \times 10^{-4}$ mols.

2. (*a*) 342 g of $C_{12}H_{22}O_{11}$ gives C = 144 g

34.2 g of $C_{12}H_{22}O_{11}$ gives C = 14.4 g

3. (*d*) 142 g of $Cl_2 = 142/71 = 2$ mol of Cl_2

It is also equal to four mole of Cl atoms.

4. (*b*) Mass 22400 ml of gas $= \frac{2 \times 22400}{448} = 100$

∴ Atomic mass $= \frac{100}{3} = 33.3$

Mass of one atom = 33.3 amu $= \frac{33.3}{6.02 \times 10^{23}}$

$$= 5.53 \times 10^{-23} \text{ g.}$$

5. (*d*) Amount of Na_2CO_3 in 0.1 M of 5L solution

$$= 0.1 \times 5 \times 106 = 53 \text{ g}$$

$$= \frac{53}{106} \times 1000 \text{ millimoles} = 5 \times 10^2.$$

2.1 GASEOUS STATE

Important Terms, Facts and Formulae

DIFFERENT STATES OF MATTER

- **Solids.** The substance is called solid if its melting point and boiling point are above room temperature. Matter in solid state has definite mass, definite volume as well as definite shape.
- **Liquids.** The substance is called liquid if its melting point is below room temperature but boiling point is above room temperature. Matter in liquid state has definite mass, definite volume but no definite shape.
- **Gases.** The substance is called gas if its melting and boiling points are below room temperature. Matter in gaseous state has definite mass but no definite volume and shape.
- **Plasma state.** It consists of gaseous mixture of electrons and positive ions. About 99% of matter in this universe is found to exist as plasma state.

GASEOUS STATE

Some measurable properties of the gases aong with their respective units are as under.

(*a*) **Mass.** Expressed in grams (*g*) or in mol (*n*).

(*b*) **Volume (V).** It is expressed in *litres (L), cubic metres* (m^3) or cm^3 or dm^3.

$$1\ \mathrm{m^3} = 10^3\ \mathrm{L} = 10^3\ \mathrm{dm^3} = 10^6\ \mathrm{cm^3}.$$

(*c*) **Pressure (P).** It is expressed in the units such as *atmospheres, millimetres (mm), centimetres (cm), torr, bar, etc*. The SI units of pressure are *pascals (Pa)* or *kilopascals (kPa)*.

$$\boxed{\begin{aligned} 1\ \text{atm} &= 101.3\ \text{kPa} = 101.3\ \text{Nm}^{-2} = 1.013\ \text{bar} \\ &= 76\ \text{cm Hg} = 760\ \text{mm or torr} \end{aligned}}$$

(*d*) **Temperature.** It is expressed in *Celcius scale* (°*C*) or in *Kelvin scale* (*K*)

$$T(K) = t(°C) + 273.$$

These are the generalisations developed from the quantitative studies of behaviour of the gases.

BOYLE'S LAW (Robert Boyle, 1662)

The volume of a definite mass of a gas is inversely proportional to its pressure at constant temperature.

- *Mathematical representation*

$$P \propto \frac{1}{V} \quad \text{or} \quad PV = \text{Constant (K) or } P_1V_1 = P_2V_2.$$

The constant **K** depends upon : *temperature, mass* and *nature of gas.*

- The law can be represented by means of plots of V *vs* P or PV *vs* P or $\frac{1}{V}$ *vs* P at constant temperature such plots are called **isotherms.**

CHARLE'S LAW (Jacques Charle's, 1787)

The volume of a given mass of a gas at constant pressure increases or decreases by $\frac{1}{273}$ *of its volume at 0°C for each degree rise or fall of temperature.*

- *Alternative statement.* The volume of a fixed mass of the gas at constant pressure is directly proportional to its temperature in Kelvin.
- *Mathematical representation.*

$$V \propto T \quad \text{or} \quad \frac{V}{T} = \text{Constant (K)} \quad \text{or} \quad \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

The value of **K** depends upon, *mass, pressure* and *nature of gas.*

- *Graphical interpretation.* The law can be represented by plotting V *vs* T at constant pressure. Such plot is called **isobars.**

PRESSURE–TEMPERATURE RELATIONSHIP (Amanton's or Gay Lussac's Law)

The pressure of a fixed mass of a gas at constant volume is directly proportional to the temperature in Kelvin.

- *Mathematical representation.* At constant volume and fixed number of moles

$$P \propto T \quad \text{or} \quad \frac{P}{T} = \text{Constant (K)} \quad \text{or} \quad \frac{P_1}{T_1} = \frac{P_2}{T_2}.$$

- Plot of P *vs* T at constant volume is a straight line passing through origin. Such a plot is known as **isochores.**

(*i*) **If a gas is** allowed to expand above its inversion temperature, heating effect is caused.

(*ii*) **If a gas is allowed** to expand below its inversion **temperature,** cooling effect is caused.

(*iii*) **Inversion temperature** is related to **the van der Waal's constants of a gas as**

$$T_i = \frac{2a}{Rb}.$$

MOLAR HEAT CAPACITIES OF GASES

1. Molar heat capacity at constant volume (C_v). It is the amount of heat required to raise the temperature of one mole of a gas through 1°C when its volume is kept constant. Mathematically,

$$C_v = \frac{3}{2}R.$$

2. Molar heat capacity at constant pressure (C_p). It is the **amount of heat required to raise the** temperature of one mole **of a gas through 1°C when** its pressure **is kept constant. Mathematically,**

$$C_p = \frac{5}{2}R.$$

Some Important Points

- $C_p - C_v = R$.
- Ratio $\frac{C_p}{C_v} = \gamma$.
- The value of γ is related to atomicity of gases as

Monoatomic gas	**Diatomic gas**	**Triatomic gas**
$\gamma = 1.66$	$\gamma = 1.40$	$\gamma = 1.33$

(*a*) increase in average molecular speed

(*b*) increased rate of collisions amongst molecules

(*c*) increase in molecular attraction

(*d*) decrease in mean free path.

45. A gas of volume 100 cc is kept in vessel at pressure 10^4 P maintained at temperature 24°C. If now the pressure is changed to 10^5 P at the same temperature, the volume of the gas becomes

(*a*) 10 cc
(*b*) 100 cc
(*c*) 1 cc
(*d*) 10^3 cc.

46. Equal masses of methane and hydrogen are mixed in an empty container at 25°C. The fraction of total pressure exerted by hydrogen is

(*a*) $\frac{1}{2}$
(*b*) $\frac{8}{9}$
(*c*) $\frac{1}{16}$
(*d*) $\frac{4}{9}$.

47. Five gram of each of the following gases at 87°C and 750 mm pressure are taken, which of them will have least volume ?

(*a*) HF
(*b*) HCl
(*c*) HBr
(*d*) HI.

48. The critical temperature of water is higher than that of O_2 because H_2O molecule has

(*a*) fewer electrons than O_2
(*b*) two covalent bonds
(*c*) V-shape
(*d*) dipole moment > 0.

49. One litre of gas weighs 2 g at 300 K and 1 atm pressure. If the pressure is made 0.75 atm, and temperature is brought down to 250 K, the gas will occupy a volume of

(*a*) 2 L
(*b*) 1.11 L
(*c*) 2.22 L
(*d*) 0.7 L.

50. In a closed room of 1000 m^3, a perfume bottle is opened up. The whole room after some time develops smell of perfume. This is due to which property of gases

(*a*) viscosity
(*b*) density
(*c*) diffusion
(*d*) none of these.

51. The density of Neon is highest at

(*a*) STP
(*b*) 0°C, 2 atm
(*c*) 273°C, 1 atm
(*d*) 273°C, 2 atm.

52. The number of moles of H_2 in 0.224 L of hydrogen at STP (assuming ideal gas behaviour) is

(*a*) 1
(*b*) 0.1
(*c*) 0.01
(*d*) 0.001.

53. Which of the following statement is false ?

(*a*) The product PV for fixed amount of gas is independent of temperature.

(*b*) Molecules of different gases have same KE at a given given temperature.

(*c*) The gas equation is not valid at high pressure and low temperature.

(*d*) The gas constant per molecule is known as Boltzmann Boltzmann constant.

54. The dimensions of pressure are same as that of

(*a*) Energy
(*b*) Energy per unit volume
(*c*) Force per unit area
(*d*) Force per unit volume.

55. The densities of two gases are in the ratio of 1 : 16. The ratio of their rates of diffusion is

(*a*) 16 : 1
(*b*) 4 : 1
(*c*) 1 : 4
(*d*) 1 : 16.

56. The molecular velocities of two gases at same temperature are u_1 and u_2. Their masses are m_1 and m_2 respectively, which of the following expression is correct

(*a*) $\frac{m_2}{u_1^2} = \frac{m_2}{u_2^2}$
(*b*) $m_1u_1 = m_2u_2$
(*c*) $m_1u_2 = m_2u_1$
(*d*) $m_1u_1^2 = m_2u_2^2$.

57. The ratio of the root mean square velocity of H_2 at 50 K and that of O_2 at 800 K is

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

58. X ml of H_2 gas effuses through the hole in a container in 5 seconds. The time taken for the effusion of same volume of gas specified below under identical conditions is

(*a*) 10 sec ; He
(*b*) 20 sec ; O_2
(*c*) 25 sec ; CO
(*d*) 55 sec ; CO_2.

59. The average kinetic energy per molecule of ideal gas at 25°C in S.I. units is

(*a*) 6.17×10^{-21} kJ
(*b*) 6.17×10^{-21} J
(*c*) 6.17×10^{-20} J
(*d*) 7.16×10^{-20} J.

60. Which of the following law lead us to arrive at the conclusion that *1 g-molecule* of each gas at S.T.P. occupies a volume of 22.4 L ?

(*a*) Dalton's law
(*b*) Law of combining volumes
(*c*) Avogadro's law
(*d*) Boyle's law.

4. The volume occupied by 10.0 g of oxygen at 0°C and 2 atm pressure will be approximately

(*a*) 20 L (*b*) 4.48 L

(*c*) 3.5 L (*d*) 1.5 L.

5. For X g of ideal gas V and V_0 are the volumes at t°C and 0°C respectively at 1 atm pressure so that $V/V_0 = (1 + \alpha t)$. Here, α is

(*a*) < 1 (*b*) < 0

(*c*) > 1 (*d*) $= 0$.

6. A pressure of 0.101325 bar when expressed in atmospheres represents

(*a*) 0.01 atm (*b*) 1 atm

(*c*) 0.1 atm (*d*) 10 atm.

7. Three gases X, Y, Z are enclosed in a container and have partial pressures as p_1, p_2, p_3 respectively at T kelvin. The total pressure at T kelvin will be

(*a*) always equal to $(p_1 + p_2 + p_3)$

(*b*) $< (p_1 + p_2 + p_3)$

(*c*) $> (p_1 + p_2 + p_3)$

(*d*) $= (p_1 + p_2 + p_3)$ only if the gases do not react chemically at T.

8. A sample of gas contains N_1 molecules and the total kinetic energy at − 123°C as E_1 ergs. Another sample of gas at 27°C has total kinetic energy as $2E_1$ ergs. Assuming gases to be ideal, the number of gas molecules in the 2nd sample will be

(*a*) N_1 (*b*) $\frac{N_1}{2}$

(*d*) $2N_1$ (*d*) $4N_1$.

9. Among the gases given below, the highest value of mean free path is for,

(*a*) N_2 (*b*) O_2

(*c*) H_2 (*d*) Cl_2.

10. If two gases have molecular masses M_A, M_B at temperature T_A and T_B such that, $T_A M_B = T_B M_A$. then which property has the same magnitude for two gases

(*a*) density (*b*) pressure

(*c*) K.E. per molecule (*d*) rms.

11. The state in which 99% matter of the universe exists is

(*a*) Plasma (*b*) Solid

(*c*) Gaseous (*d*) Liquid.

12. The temperature above which the gas cannot exist as liquid howsoever large the pressure may be, is

(*a*) Absolute zero (*b*) 0° Celcius

(*c*) Critical temperature

(*d*) Inversion temperature.

13. The density of a gas is given by the expression

(*a*) nP (*b*) P/RT

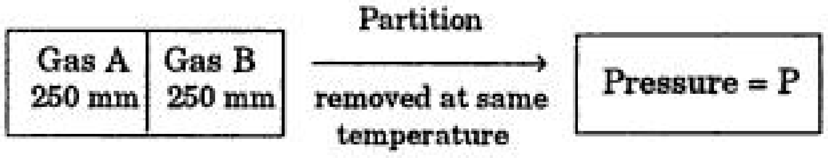
(*c*) PM/RT (*d*) M/V.

14. The compressibility factor for ideal gas at particular temperature

(*a*) equal to zero (*b*) < 0

(*c*) equal to 1 (*d*) can be > 1 or < 1.

15.



In the above experiment, the value of P is

(*a*) 250 mm (*b*) 500 mm

(*c*) 300 mm (*d*) 400 mm.

16. When ideal gas undergoes unstrained expansion, no cooling occurs because the molecules

(*a*) are above inversion temperature

(*b*) exert no attractive force on each other

(*c*) work equal to loss in kinetic energy

(*d*) collide without loss of energy.

17. Rate of diffusion of a gas is

(*a*) directly proportional to its density

(*b*) directly proportional to its molecular mass

(*c*) directly proportional to the square root of its molecular mass

(*d*) inversely proportional to the square root of its molecular mass.

18. The average velocity of an ideal gas molecules at 27°C is 0.3 m sec^{-1}. The average velocity at 927°C will be

(*a*) 0.6 m sec^{-1} (*b*) 0.3 m sec^{-1}

(*c*) 0.9 m sec^{-1} (*d*) 3.0 m sec^{-1}.

19. If a gas is expanded at constant temperature

(*a*) the pressure decreases

(*b*) the kinetic energy of molecules increases

(*c*) the kinetic energy of molecules decreases

(*d*) the number of molecules of the gas increases.

20. In van der Waal's equation of state the term which accounts for intermolecular forces is

(*a*) $(V - b)$ (*b*) RT

(*c*) $(P + a/V^2)$ (*d*) $(RT)^{-1}$.

71. A bottle of cold drink has 200 ml of liquid in which conc. of CO_2 is 0.1 molar. If CO_2 behaves as ideal gas, the volume of CO_2 at S.T.P. equivalent to the one in cold drink is

(*a*) 0.224 L (*b*) 0.448 L
(*c*) 0.112 L (*d*) 4.48 L.

72. In the outer space the pressure recorded is 5×10^{-14} torr. How much outer space could be compressed into 1 dm^3 box at a pressure of 1 atm ?

(*a*) 1.52×10^{16} dm^3 (*b*) 4.56×10^{16} dm^3
(*c*) 2.28×10^{16} dm^3 (*d*) 1.14×10^{16} dm^3.

73. Same gas is confined to two containers A and B. The pressure, volume and temperature (K) of gas in A are three times as compared to that in B. If the mass of gas in A is *x* g, then the mass in B would be

(*a*) *x* g (*b*) 0.3*x* g
(*c*) 0.5*x* g (*d*) 3*x* g.

74. Two flasks of equal capacity contain argon and chlorine gases respectively at room temperature. What is true about them ?

(*a*) Both contain same number of atom
(*b*) Cl atoms are half of the Ar atoms
(*c*) Cl atoms are double the number of Ar atoms
(*d*) Chlorine molecules are double the number of argon molecules.

75. Equal masses of CH_4 and O_2 are introduced in an empty container. The fraction of the total pressure exerted by oxygen is

(*a*) 1/3 (*b*) 1/2
(*c*) 2/3 (*d*) 91/298.

76. The temperature at which real gas exhibits ideal behaviour over a wide range of pressure is called

(*a*) Inversion temperature (*b*) Boyle temperature
(*c*) Reduced temperature (*d*) Critical temperature.

77. He atom is twice as heavy as H_2 molecule. The average kinetic energy of helium at 298 K is

(*a*) twice that of hydrogen
(*b*) same as that of hydrogen
(*c*) four times that of hydrogen
(*d*) half that of hydrogen.

78. An empty container was filled with equal masses of methane and hydrogen gases. The fraction of total pressure exerted by hydrogen is

(*a*) 1/2 (*b*) 8/9
(*c*) 1/9 (*d*) 16/17.

79. A sample of air saturated with water vapours recorded a pressure of 640 torr. If vapour pressure of water at that temperature is 40 torr and the sample contains N_2 and O_2 in the molar ratio of 3 : 1 besides water vapours. The partial pressure of N_2 in the sample is

(*a*) 540 torr (*b*) 450 torr
(*c*) 480 torr (*d*) 300 torr.

80. A balloon containing methane is pricked with a sharp needle and quickly plunged into a tank of hydrogen at same pressure. After sometime, the balloon will

(*a*) get enlarged
(*b*) get collapsed
(*c*) remain as before
(*d*) reduce to half of its original size.

81. The values of critical temperatures (T_c) and critical pressure (P_c) for some gases are given below. Which of the gases cannot be liquified at 100 K and 50 atm ?

Gases	A	B	C	D
P_c (atm)	2.2	14	35	45
T_c (K)	5.1	33	127	140

(*a*) D only (*b*) A only
(*c*) A and B (*d*) C and D.

82. The average K.E. of 14 g of nitrogen at 127°C (K = 8.31 J K^{-1} mol^{-1}) is

(*a*) 2.493 kJ (*b*) 4.2 kJ
(*c*) 3.8 kJ (*d*) 1.493 kJ.

83. Molecular velocities of two gases at same temperature are u_1 and u_2 and their masses are m_1 and m_2 respectively. Which relation is correct ?

(*a*) $m_1/u_1 = m_2/u_2$ (*b*) $m_1u_1 = m_2u_2$
(*c*) $m_1/u_1^2 = m_2/u_2^2$ (*d*) $m_1u_1{}^2 = m_2u_2{}^2$.

84. 10 g of each of the following gases were taken, HF, HCl, HBr, HI, under similar conditions, then

(*a*) all will have same volume
(*b*) HF will have largest volume
(*c*) HI will have largest volume
(*d*) HBr will have lowest volume.

85. The van der Waal constant '*b*' is equal to

(*a*) four times the volume of 1 mol of gas
(*b*) the molecular volume of 1 mol of gas
(*c*) four times the actual volume of molecules contained in 1 mol of gas
(*d*) twice the molecular volume of 1 mol of gas.

47. (*a*) Number of moles of HF is highest.

48. (*d*) Water has $u > 0$. Hence inter-particle forces in water are more.

49. (*b*) $V_2 = \frac{P_1V_1T_2}{T_1P_2} = \frac{1 \times 1 \times 250}{300 \times 0.75} = 1.11$ L.

50. (*a*) This is as per definition of diffusion.

51. (*b*).

52. (*c*) 22.4 L of Hydrogen = 1 mol = 0.224 L of Hydrogen
= 0.01 mol.

53. (*a*) The product PV depends on temperature and number of moles.

57. (*c*) $u_{H_2} : u_{O_2} = \sqrt{\frac{50}{2} \times \frac{32}{800}} = \sqrt{1} = 1.$

58. (*b*) Apply Graham's law.

59. (*b*) K.E. per molecule is given by $\frac{3RT}{2N_A}$.

60. (*c*) Avogadro's law help us to derive this conclusion.

61. (*b*) The compressibility factor for ideal gas = 1.

62. (*a*) Apply $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$.

67. (*a*) $V = \frac{730 \times 380}{760} = 365$ ml.

68. (*c*) Partial pressure of C = 10 – 4 = 6 atm

Number of moles of C = 6 moles

(Because 10 moles have pressure = 10 atm)

Mass of C = 6 × 2 = 12 g.

69. (*c*) $\sqrt{\frac{T_{H_2} \times M_{N_2}}{T_{N_2} \times M_{H_2}}} = \frac{\sqrt{7}}{1} = \frac{u_{H_2}}{u_{N_2}}$

or $\frac{T_{H_2} \times 28}{T_{N_2} \times 2} = 7$ or $T_{H_2} = \frac{1}{2} T_{N_2}$

70. (*b*) $z < 1$ or $PV < nRT$ or $PV < P_iV_i$

For the same pressure $V < V_i$.

71. (*c*) 1 L of steam = 1000 cm^3 of steam weighs
= 0.0006 × 1000 g = 0.6 g

Since density of liquid water = 1 g cm^{-3}

∴ Volume of 0.6 g of water = 0.6 × 1 = 0.6 cm^3.

72. (*d*) Among the given gases which are all non-polar Cl_2 has the largest molecular size and largest magnitude of van der Waal forces.

73. (*b*) $\left[P + a\left(\frac{1}{2}V\right)^2\right]\left[V - \frac{1}{2}b\right] = \frac{1}{2}RT$

or $\left(P + \frac{a}{4V^2}\right)(2V - b) = 2 \times \frac{RT}{2}$.

74. (*d*) V.D. of dry air is 14.4 which is more than that of moist air. Other gases have V.D. less than moist air (V.D. 9 – 14).

75. (*b*) 70 g of $N_2 = \frac{70}{28} = 2.5$ moles, Mass of 2.5 moles of CO
= 2.5 × 28 = 70 g.

76. (*a*) $PV = nRT$

$\therefore \quad T = \frac{PV}{nR} = \frac{1.5 \times 1}{1.5 \times 0.082} = 12.195$ K
$= 12.195 - 273 = -260.8$°C.

77. (*a*) NH_3 molecules are able to form H-bonds with water molecules.

78. (*d*) $Na_2CO_3 . x\,H_2O + 2HCl \longrightarrow NaCl + CO_2 + (x + 1)\,H_2O$

22.4 L of CO_2 at S.T.P. is produced from soda crystal

$= \frac{1.287 \times 22400}{100.8} = 286$ g

Now $286 = 106 + 18\,x$ or $x = \frac{286 - 106}{18} = 10$

Hence the sample is $Na_2CO_3 . 10H_2O$.

79. (*c*) 17 g of $NH_3 = \frac{17}{17}$ mole = 1 mol

which contains Avogadro number of molecule.

80. (*a*) 15 mm $= \frac{15 \times 101.3}{760}$ *k*Pa = 1.99 ≈ 2 *k*Pa

∴ The pressure is 101.3 + 2 = 103.3 *k*Pa.

81. (*c*) 1 litre of protium oxide (H_2O) weighs ≈ 1000 g (Density = 1) hence it has maximum number of molecules, *i.e.*,

$\frac{1000}{18} \times 6.02 \times 10^{23} = 3.3 \times 10^{25}$.

82. (*c*) On removing O_2 the pressure will be reduced to half of the original. Hence, the statement C is wrong.

83. (*a*) The maximum moles and hence maximum number of molecules are present in 2.7 g of NH_3.

(Mols $= \frac{2.7}{17} = 0.15$ mol)

84. (*c*) Consider 1 mol of water, the mass of which is 18 g

∴ Volume of liquid water at 100°C

$= \frac{18}{0.96}\ cm^3 = 18.75\ cm^3$.

Volume of 1 mole of water vapours

$= \frac{nRT}{P} = \frac{1 \times 0.082 \times 373}{1}$

= 30.586 L or 30586 cm^3.

The number of times the expansion has occured

$= \frac{30586}{18.75} = 1631.2$

80. (*a*) Rate of effusion of H_2 will be more than rate of effusion of CH_4.

81. (*c*) At the temperature above the critical temperature, the gas cannot be liquefied by applying pressure.

82. (*a*) Average K.E. = $3/2 \times nRT$

$$= \frac{3 \times 0.5 \times 0.082 \times 400}{2} \text{ J}$$

$$= 2493 \text{ J or } 2.493 \text{ kJ}.$$

83. (*d*) Average K.E. of both the gases will be same.

Thus, $\frac{1}{2} m_1 u_1^2 = \frac{1}{2} m_2 u_2^2$ or $m_1 u_1^2 = m_2 u_2^2$.

84. (*b*) The number of moles of HF will be largest. Hence it will occupy largest volume.

85. (*c*) It is a factual question.

86. (*b*) $V_2 = \frac{V_1}{T_1} \times T_2 = \frac{300 \times 270}{300} = 270$ mol.

87. (*a*) VD = 70 $\therefore$ Mol. mass = 140

$$n = \frac{\text{Mol. mass}}{\text{Empirical mass}} = \frac{140}{28} = 5$$

Hence mol. formula is C_5O_5.

88. (*a*) $\frac{r_{H_2}}{r_X} = \sqrt{\frac{M_x}{2}}$ or $\frac{6}{1} = \sqrt{\frac{M_x}{2}}$

or $M_x = \frac{6 \times 2 \times 2}{1} = 72.$

89. (*b*) No. of molecules of Ar, O_2 and O_3 are same. Now Ar is monoatomic, O_2 is diatomic and O_3 is triatomic. Hence atomic ratio is 1 : 2 : 3.

90. (*b*)

$$\begin{array}{lccccc} & A & + & B & \longrightarrow & C \\ & 2 \text{ vol.} & & 5 \text{ vol.} & & 2 \text{ vol.} \\ & 2n \text{ molecule} & & 5n \text{ molecules} & & 2n \text{ molecules} \\ \text{or} & 1 \text{ molecule} & & 5/2 \text{ molecules} & & 1 \text{ molecule} \\ & 2 \text{ atoms} & & 5 \text{ atoms} & & 1 \text{ molecule} \end{array}$$

Hence mol. formula of C is A_2B_5.

91. (*c*) $O_2 = 0.2$ mol ; $N_2 = \frac{11.2}{28} = 0.4$ mol ; He = 0.5 mol

Total moles = 0.2 + 0.4 + 0.5 = 1.1 mol.

Pressure due to 1.1 mol = 1.1 atm

Pressure due to 0.4 mol of N_2 = 0.4 atm

$$= 0.4 \times 760 \text{ torr} = 304 \text{ torr}.$$

92. (*b*) Mol. mass of Y = M $\therefore$ V.D. of Y = $\frac{M}{2}$

$$\text{V.D. of X} = 4 \times \frac{M}{2} = 2M$$

$\therefore$ Mol mass of X = $2 \times 2M = 4M$.

93. (*c*) $O_2 = \frac{21}{22.4}$ mol = 0.9375 mol,

$$N_2 = \frac{79}{22.4} = 3.526 \text{ moles}$$

Total moles = 0.9375 + 3.526 = 4.4635 ;

Total pressure = 740 mm

$$p_{O_2} = \frac{740 \times 0.9375}{4.463} = 155.4 \text{ mm.}$$

94. (*c*) $r_{H_2} : r_{D_2} = \sqrt{\frac{4}{2}} = \sqrt{2} : 1.$

95. (*c*) $T_2 = \frac{V_2}{V_1} \times T_1 = \frac{300}{250} \times 280 = 336$ K or 63°C.

96. (*c*) $P_A = \frac{300R}{V} n_{H_2}$; $P_B = \frac{600R}{V} n_{CH_4}$

$$P_A : P_B = \frac{n_{H_2}}{2n_{CH_4}}.$$

and negative ions are almost equal. **For example,** NaCl, KCl, CsCl and KBr.

- The presence of large number of Schottky defects in crystal results in significant decrease in its density.

(*ii*) ***Frenkel Defect.*** This type of defect is created when an ion leaves its correct lattice site and occupies an interstitial site. Frenkel defects are common in ionic compounds which have low co-ordination number and in which there is large difference in size between positive and negative ions. For example, ZnS, AgCl, AgBr and AgI.

- **Non-stoichiometric Defects**

These defects disturb the stoichiometry of the compound. These defects are either due to the presence of excess metal ions or excess non-metal ions.

(*i*) ***Metal Excess Defects due to Anion Vacancies.*** A compound may have excess metal ion if a negative ion is absent from its lattice site, leaving a '*hole*' which is occupied by electron to maintain electrical neutrality.

- This type of defects are found in crystals which are likely to possess Schottky defects.

The 'holes' occupied by electrons are called ***F-centres*** and are responsible for the colour of the compound and many other interesting properties.

(*ii*) ***Metal Excess Defects due to Interstitial Cations.*** Another way in which metal excess defects may occur is, if an extra positive ion is present in an interstitial site. Electrical neutrality is maintained by the presence of an electron in the interstitial site. This type of defects are exhibited by the crystals which are likely to exhibit 'Frenkel' defects.

(*iii*) ***Metal deficiency due to Cation Vacancies.*** The non-stoichiometric compounds may have metal deficiency due to the absence of a metal ion from its lattice site. The charge is balanced by an adjacent ion having higher positive charge. This type of defects are generally shown by compounds of transition metals.0

SOME MISCELLANEOUS IMPORTANT POINTS

- **Doping.** Addition of small amount of foreign impurity in the host crystal is termed as doping. It increases the electrical conductivity.
- **n and p type semiconductors.** Doping of group 14 elements with group 15 elements produces excess of electrons and doping of group 14 elements with group 13 elements produce holes (electron deficiency) in the crystals. Group 14 elements doped with group 15 elements are called *n* type semiconductors, symbol '*n*' indicating the flow of negative charge in them. Group 14 elements doped with group 13 elements are called *p* type semiconductors, symbol '*p*' indicating the flow of positive charge.
- **Diamagnetic substances** are weakly repelled by the magnetic field and do not have any unpaired electron.
- **Paramagnetic substances** are attracted by the magnetic field and have unpaired electrons. These lose magnetism in the absence of magnetic field.
- **Ferromagnetic substances** are attracted by the magnetic field and show permanent magnetism even in the absence of magnetic field *e.g.*, Fe, Co, Ni.
- **Antiferromagnetic substances** are those which are expected to possess paramagnetism or ferromagnetism on the basis of unpaired electrons but actually they possess zero net magnetic moment *e.g.*, MnO.
- **Ferrimagnetic substances** are those which are expected to possess large magnetism on the basis of the unpaired electrons but actually have small net magnetic moment *e.g.* Fe_3O_4, ferrites.
- **Piezoelectricity** is the electricity produced on applying mechanical stress on polar crystal.
- **Pyroelectricity** is the electricity produced on heating some polar crystals.
- **Super conductivity** is the property of the conductors where by they allow electricity to pass though them without any resistance. It was discovered by Kammerlingh Onnes in 1913. The temperature at which a substance starts behaving as super conductor is called *transition temperature*.

(*a*) 0% (*b*) 50%

(*c*) 100% (*d*) 25%.

50. A metal M has FCC arrangement and edge length of the unit cell is 400 pm. The atomic radius of 'M' is

(*a*) 100 pm (*b*) 200 pm

(*c*) 141 pm (*d*) 173 pm.

51. In a solid, oxide ions are arranged in CCP. Cations A occupy one-sixth of the tetrahedral voids and cations B occupy one-third of the octahedral voids. The formula of the compound is

(*a*) ABO_3 (*b*) AB_2O_3

(*c*) A_2BO_3 (*d*) $A_2B_2O_3$.

52. A binary solid AB having radius ratio 0.52 is most likely to have

(*a*) zinc blende structure (*b*) rock-salt structure

(*c*) fluorite structure (*d*) antifluorite structure.

53. In CCP arrangement of identical spheres, the coordination number of each sphere is

(*a*) 4 (*b*) 8

(*c*) 12 (*d*) 6.

54. For a cubic void the radius ratio is equal to

(*a*) 0.225 (*b*) 0.414

(*c*) 0.732 (*d*) 0.155.

55. In a unit cell of NaCl, the number of Na^+ ions present at the edge centres is

(*a*) 4 (*b*) 6

(*c*) 1 (*d*) 12.

56. In zinc blende structure, the number of formula units present in the unit cell is

(*a*) 4 (*b*) 6

(*c*) 1 (*d*) 8.

57. In which of the following arrangements, a metal would have least density ?

(*a*) BCC

(*b*) CCP

(*c*) HCP

(*d*) In all the three arrangements, the density would be same.

58. The number of octahedral voids in HCP arrangement of N spheres is

(*a*) 2 N (*b*) N

(*c*) 3 N (*d*) 4 N.

59. Na_2O has antifluorite structure. In Na_2O, the coordination number of oxide ions is

(*a*) 4 (*b*) 6

(*c*) 8 (*d*) 12.

60. In antifluorite structure, the percentage of octahedral voids occupied is

(*a*) 100% (*b*) 0%

(*c*) 50% (*d*) 25%.

61. The example, and general formula of sheet silicate respectively are

(*a*) Quartz, $(SiO_2)_n$ (*b*) Clay, $(Si_2O_5^{2-})_n$

(*c*) Asbestos, $(Si_2O_5^{2-})_n$ (*d*) Clay, $(SiO_3^{2-})_n$.

62. If the positions of Na^+ and Cl^- ions are interchanged in NaCl, the crystal lattice with respect to Na^+ and Cl^- is

(*a*) both fcc (*b*) both bcc

(*c*) fcc and bcc (*d*) bcc and fcc.

63. A mineral having the formula AB_2 crystallises in a cubic close packed lattice, with A atoms occupying the lattice points. The co-ordination number of A atoms, that of B atoms and fraction of tetrahedral voids occupied by B atoms are respectively

(*a*) 8, 4, 100% (*b*) 2, 6, 75%

(*c*) 3, 1, 25% (*d*) 6, 6, 50%.

64. The tetrahedral holes occupied in diamond are

(*a*) 50% (*b*) 25%

(*c*) 75% (*d*) 100%.

65. A compound alloy of gold and copper crystallises in a cubic lattice in which gold atoms occupy the lattice points at the corner of the cube and copper atoms occupy centres of each of the cube faces. The probable empirical formula of the compound alloy is

(*a*) Au_3Cu (*b*) $AuCu_3$

(*c*) Au_2Cu_3 (*d*) $AuCu_2$.

66. If '*a*' is edge length of a face centred cubic unit cell, then the distance of closest approach of two particles is

(*a*) 0.866*a* (*b*) 1.732*a*

(*c*) 1.414*a* (*d*) 0.707*a*.

67. In a body centred cubic unit cell of a metallic substance, the number of atoms per unit cell is

(*a*) 4 (*b*) 1

(*c*) 2 (*d*) 3.

68. An atom at the edge centre of the cubic unit cell contributes ...... to the particular unit cell.

(*a*) 1/2 (*b*) 1

(*c*) 1/8 (*d*) 1/4.

42. The number of NaCl units in a unit cell of its crystal

(*a*) 2
(*b*) 4
(*c*) 6
(*d*) 8.

43. The Edge length of face centred cubic unit cell is 508 pm. If the radius of cation is 110 pm, the radius of anion is

(*a*) 110 pm
(*b*) 144 pm
(*c*) 618 pm
(*d*) 398 pm.

44. The ratio of close packed atoms to tetrahedral holes in cubic close packing

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

45. In a metal M having BCC arrangement, edge length of the unit cell is 400 pm. The atomic radius of M is

(*a*) 100 pm
(*b*) 141 pm
(*c*) 173 pm
(*d*) 200 pm.

46. The co-ordination number of metal crystallising in hexagonal close packed structure is

(*a*) 12
(*b*) 4
(*c*) 8
(*d*) 6.

47. How many Cl^- ions are there around Na^+ ions in NaCl crystal ?

(*a*) 3
(*b*) 4
(*c*) 6
(*d*) 8.

48. The existence of a substance in more than one solid modification is known as

(*a*) isomorphism
(*b*) polymorphism
(*c*) amorphism
(*d*) allotropy.

49. Which of the following groups contain species which are solid at 283 K and one bar pressure ?

(*a*) NH_3, H_2O, C_2H_6
(*b*) Br_2, I_2, Cl_2
(*c*) SO_3, I_2, KCl
(*d*) Si, HCl, Hg.

50. A unit cell having dimensions $a \neq b \neq c$; $\alpha \neq \beta \neq \gamma \neq 90°$ is known as

(*a*) Monoclinic
(*b*) Triclinic
(*c*) Rhombohedral
(*d*) Orthorhombic.

51. The percentage of space occupied by spheres in a cubic close packing of spheres in three dimensions is

(*a*) 24%
(*b*) 52.4%
(*c*) 76%
(*d*) 74%.

52. Which of the following compounds is an example of molecular solid ?

(*a*) Diamond
(*b*) Dry ice
(*c*) Sodium chloride
(*d*) Zinc sulphide.

53. For an atomic crystal having body centred cubic unit cells, the number of atoms per unit cell is

(*a*) 4
(*b*) 8
(*c*) 9
(*d*) 2.

54. When a cation and an anion are missing leaving behind a pair of voids, the defect is known as :

(*a*) F-centre
(*b*) Schottky defect
(*c*) Frenkel defect
(*d*) None of these.

55. Edge length of a cube is 300 pm. Its body diagonal would be

(*a*) 600 pm
(*b*) 423 pm
(*c*) 519 pm
(*d*) 450 pm.

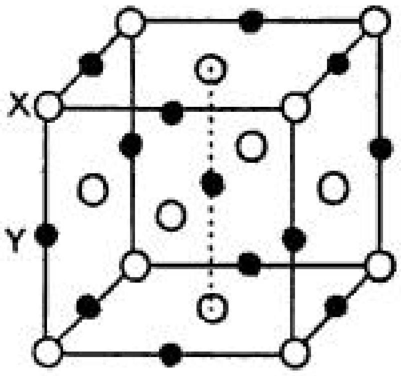
56. In zinc blende structure coordination number of cation is

(*a*) 6
(*b*) 4
(*c*) 8
(*d*) 12.

57. In fluorite structure the coordination number of cation is

(*a*) 4
(*b*) 6
(*c*) 8
(*d*) 12.

Consider the Fig. given for solid XY. Answer the following questions from 58-61.



58. The site Y represents

(*a*) tetrahedral void
(*b*) octahedral void
(*c*) triangular void
(*d*) cubical void.

59. The number of XY units per unit cell is

(*a*) 4
(*b*) 3
(*c*) 1
(*d*) 8.

60. Co-ordination number of Y is

(*a*) 3
(*b*) 4
(*c*) 6
(*d*) 8

61. Which of the following type of solid adopt above crystal structure ?

(*a*) CsCl
(*b*) CaF_2
(*c*) ZnS
(*d*) NaCl.

67-70. These are based on facts.

71. (*d*) In antifluorite structure *fcc* lattice sites are occupied by anions $(PtCl_6)^{2-}$.

72. (*a*) Anions $= \frac{8}{8} = 1$.

73. (*d*) The number of anions $= \frac{8}{8} + \frac{6}{2} = 4$

$\therefore$ Octahedral voids = 4 ; tetrahedral voids = 8 ;

Total voids = 12 ; Voids occupied by the ions = 3

$\therefore$ Fraction of voids occupied $= \frac{3}{12} = \frac{1}{4}$.

74-76. Questions based on facts and defintions.

QUESTION BANK (Level II)

4. (*a*) In zinc blende S^{2-} ions adopt *ccp* arrangement but Zn^{2+} occupy 50% of tetrahedral holes. In Na_2O. O^{2-} ions adopt *ccp* structure while Na^+ ions occupy all tetrahedral holes.

5. (*c*) Frenkel type defect is shown by crystals with low co-ordination number.

8. (*d*) $d = \frac{119 \times x}{N_0 \times a^3}$ or $n = \frac{2.75 \times N_0 \times a^3}{119}$

$$= \frac{2.75 \times 6.02 \times 10^{23} \times (654 \times 10^{-10})^3}{119} = 3.9 = 4.$$

9-18. The questions are based upon facts.

19. (*c*) Zn assumes *hcp* type crystal structure.

21. (*d*) $d = \dfrac{2 \times 39 \times 10^{-3}}{6.02 \times 10^{23} \times \left(\dfrac{4 \times 4.52 \times 10^{-3}}{2\sqrt{3}}\right)^3}$

$$= \frac{2 \times 39 \times 100}{6.02 \times 1.44} = 900 \text{ kg m}^3.$$

22. (*c*) Factual question.

23. (*d*) Question is based on properties of liquid crystal.

25. (*c*) Match Box has dimensions $a \neq b \neq c$; $\alpha = \beta = \gamma = 90$ which refers to orthorhombic.

27. (*b*) Applying the formula

$$N = \frac{Z \times A \times 100}{d \times a^3} = \frac{4 \times 100}{10 \times (2 \times 10^{-8})^3} = 5 \times 10^{24}.$$

31. (*b*) No. of atoms per unit cell = 2

$\therefore$ No. of atoms in 12.08×10^{23} unit cells $= 24.16 \times 10^{23}$.

35. (*b*) Density $= \frac{GMM \times 2}{N_0 \times a^3}$

$$= \frac{100 \times 2}{6.02 \times 10^{23} \times (400 \times 10^{-10})^3} = \frac{200}{38.528}$$

$= 5.188 \text{ g cm}^{-3}$.

37. (*b*) W atoms per unit cell $= \frac{8}{8} = 1$; Na atoms per unit cell = 1

O atoms per unit cell $= \frac{12}{4} = 3$

Hence formula = $NaWO_3$.

38-42. Questions based on facts.

43. (*b*) Edge length $= 2r^+ + 2r^-$ or $\frac{508}{2} = r^+ + r^-$

$\therefore$ $r^- = 254 - 110 = 144$ pm.

44-48. Questions based upon facts.

49. (*e*) SO_3, I_2 and KCl are solid at 10°C.

50-57. There are based on facts.

58. (*b*) Site Y is octahedral void.

59. (*a*) There are four X atoms and four Y atoms per unit cell. Hence, the formula units are Four.

60. (*c*) Y being octahedral void has co-ordination number = 6.

62. (*a*) Factual question.

63-67. Questions based upon facts.

68. (*b*) Anions in unit cell $= \frac{8}{8} + \frac{6}{2} = 4$;

Cations $= \left(\frac{12}{4} + 1\right) + 4 = 8$.

Hence the ratio of cations : anions = 2 : 1.

70. (*c*) No. of B atoms in the unit cell $= \frac{8}{8} = 1$

No. of A atoms in the unit cell $= \frac{2}{2} = 1$.

71. (*d*) The fraction of total volume occupied in simple cube

$$= \frac{\text{Volume of particles}}{\text{Volume of cube}} = \frac{4/3\,\pi\,(a/2)^3}{a^3} = \frac{\pi}{6}$$

72-74. Factual problems.

75. (*d*) The radius ratio $(r_+/r_-) = \frac{0.95}{1.81} = 0.54$. Hence co-ordination number of cation should be **six**. Thus, substance is likely to adopt rock salt structure.

76. (*c*) Factual question.

QUESTION BANK

Level I

Choose the correct answer from the four alternatives given in each of the following questions :

1. $^{23}_{11}Na$ and $^{24}_{12}Mg$ are

(*a*) Isotopes (*b*) Isobars
(*c*) Isodiaphers (*d*) Isotones.

2. The energy of a photon of radiation having wavelength 3000 Å is nearly

(*a*) 6.63×10^{-19} J (*b*) 6.63×10^{-18} J
(*c*) 6.63×10^{-16} J (*d*) 6.63×10^{-49} J.

3. The wavelength of the radio-waves having frequency 3 MHz would be

(*a*) 100 m (*b*) 300 m
(*c*) 100 nm (*d*) 300 nm.

4. The number of subshells in the fifth energy level is

(*a*) 4 (*b*) 11
(*c*) 9 (*d*) 5.

5. The number of orbitals in the fourth energy level is

(*a*) 4 (*b*) 16
(*c*) 32 (*d*) 9.

6. The maximum number of electrons with clockwise spin that can be accommodated in a *f*-subshell its

(*a*) 14 (*b*) 7
(*c*) 5 (*d*) 10.

7. The maximum value of m for an electron in fourth energy level is

(*a*) + 4 (*b*) + 3
(*c*) + 5 (*d*) + 9

8. The maximum number of electrons that can be accommodated in fifth energy level is

(*a*) 10 (*b*) 25
(*c*) 50 (*d*) 32.

9. In chromium atom, in ground state, the number of occupied orbitals is

(*a*) 14 (*b*) 15
(*c*) 7 (*d*) 12.

10. The radius of the first orbit of hydrogen is 0.53 Å. The radius of second orbit would be

(*a*) 1.06 Å (*b*) 2.12 Å
(*c*) 0.53 Å (*d*) 0.26 Å.

11. The ratio of the radii of first orbits of H, He^+ and Li^{2+} is

(*a*) 1 : 2 : 3 (*b*) 6 : 3 : 2
(*c*) 1 : 4 : 9 (*d*) 9 : 4 : 1.

12. Which electronic transition in hydrogen atom is accompanied by maximum release of energy ?

(*a*) $n = 2$ to $n = 1$ (*b*) $n = 3$ to $n = 2$
(*c*) $n = 4$ to $n = 3$ (*d*) $n = 4$ to $n = 2$.

13. The ratio of radius of the nucleus to the radius of the atom is of the order of

(*a*) 10^5 (*b*) 10^6
(*c*) 10^{-5} (*d*) 10^{-8}.

14. A body of mass 10 mg is moving with a velocity of 100 ms^{-1}. The wavelength of the de Broglie wave associated with it would be

(*a*) 6.63×10^{-37} m (*b*) 6.63×10^{-31} m
(*c*) 6.63×10^{-34} m (*d*) 6.63×10^{-35} m.

15. Which of the following sets of the quantum numbers is permitted ?

(*a*) $n = 4, l = 2, m = +3, s = +\frac{1}{2}$

(*b*) $n = 3, l = 3, m = +3, s = +\frac{1}{2}$

(*c*) $n = 4, l = 0, m = 0, s = +\frac{1}{2}$

(*d*) $n = 4, l = 3, m = +1, s = 0$.

16. A subshell with $n = 6$, $l = 2$ can accommodate a maximum of

(*a*) 12 electrons (*b*) 36 electrons
(*c*) 10 electrons (*d*) 72 electrons.

17. An electron has spin quantum number, $s = +\frac{1}{2}$ and magnetic quantum number, $m = +1$. It cannot be present in

(*a*) *s*-orbital (*b*) *p*-orbital
(*c*) *d*-orbital (*d*) *f*-orbital.

18. The first use of quantum theory to explain the structure of atom was made by

74. The correct set of quantum numbers for the unpaired electron of chlorine atom is

	n	l	m
(*a*)	2	1	0
(*b*)	2	1	1
(*c*)	3	1	1
(*d*)	3	0	1.

75. The ion that is iso-electronic with CO is

(*a*) O_2^- (*b*) N_2^+

(*c*) CN^- (*d*) O_2^+.

76. The configuration $1s^2, 2s^2, 2p^5, 3s^1$ shows

(*a*) Ground state of fluorine

(*b*) Excited state of fluorine

(*c*) Excited state of argon atom

(*d*) Ground state of O^{2-} ion.

77. Which quantum number will determine the shape of the subshell ?

(*a*) Principal quantum number

(*b*) Azimuthal quantum number

(*c*) Magnetic quantum number

(*d*) Spin quantum number.

78. Which is correct statement about proton ?

(*a*) Proton is nucleus of deuterium

(*b*) Proton is alpha particle

(*c*) Proton is ionised hydrogen molecule

(*d*) Proton is ionised hydrogen atom.

79. The energy of an electron in nth orbit of hydrogen atom is

(*a*) $-\frac{13.6}{n^4}$ eV (*b*) $-\frac{13.6}{n^3}$ eV

(*c*) $-\frac{13.6}{n^2}$ eV (*d*) $-\frac{13.6}{n}$ eV.

80. The four quantum numbers of valence electron of potassium are

(*a*) $4, 0, 1, \frac{1}{2}$ (*b*) $4, 1, 0, \frac{1}{2}$

(*c*) $4, 0, 0, \frac{1}{2}$ (*d*) $4, 1, 1, \frac{1}{2}$

81. The frequency of a wave is $6 \times 10^{15}\ s^{-1}$. Its wave number would be

(*a*) $10^5\ cm^{-1}$ (*b*) $2 \times 10^{-5}\ cm^{-1}$

(*c*) 2×10^{-7} cm (*d*) $2 \times 10^5\ cm^{-1}$.

82. The energy of the second orbit of hydrogen is equal to the energy of

(*a*) Fourth orbit of He^+ (*b*) Fourth orbit of Li^{2+}

(*c*) Second orbit of He^+ (*d*) Second orbit of Li^{2+}.

83. The concept of dual radiation was introduced by

(*a*) Einstein (*b*) Stark

(*c*) de Broglie (*d*) Moseley.

84. The discharge tube experiment in which cathode rays are emitted has shown that

(*a*) All nuclei contain positive charge

(*b*) All forms of matter contain electrons

(*c*) Protons are positively charged

(*d*) Mass of proton and that of neutron are almost equal.

85. In Bohr's model of the atom, the electron does not fall into the positively charged nucleus because

(*a*) The electrons have dual character

(*b*) The electrons have wave character

(*c*) Quantum rules do not allow it

(*d*) The electrostatic attraction is balanced by mechanical forces.

86. Particles in cathode rays have same charge to mass ratio as

(*a*) α-particles (*b*) β-rays

(*c*) γ-rays (*d*) Protons.

87. Which of the following species has the same number of electrons in the outermost and penultimate shells ?

(*a*) O^{2-} (*b*) K^+

(*c*) Al^{3+} (*d*) F^-.

88. An electron is present in 4*f* sub-shell. The possible values of azimuthal quantum number for this electron are

(*a*) 0, 1, 2, 3 (*b*) 1, 2, 3, 4

(*c*) 3 (*d*) 4.

89. Which of the following radiations has the highest wave number ?

(*a*) X-rays (*b*) Microwaves

(*c*) I.R. rays (*d*) Radiowaves.

90. Bohr's model could explain successfully

(*a*) the spectrum of helium

(*b*) the spectrum of species containing only one electron

(*c*) the spectrum of multi-electron atoms

(*d*) the spectrum of hydrogen molecule.

(*a*) 3, 2, – 2, 1/2
(*b*) 3, 3, 1, – 1/2
(*c*) 3, 2, 1, 1/2
(*d*) 3, 1, 1, – 1/2.

41. The wave number of first line of Balmer series of hydrogen in 15200 cm^{-1}. The wave number of the first Balmer line of Li^{2+} ion is

(*a*) 15200 cm^{-1}
(*b*) 60800 cm^{-1}
(*c*) 76000 cm^{-1}
(*d*) 136,800 cm^{-1}.

42. Which one of the following pairs of atoms/atom-ion have identical ground state configuration ?

(*a*) Li^+ and He^+
(*b*) Cl^- and Ar
(*c*) Na and K
(*d*) F^+ and Ne.

43. For which one of the following sets of four quantum numbers, an electron will have the highest energy ?

(*a*) $n = 3, l = 2, m = 1, s = 1/2$
(*b*) $n = 4, l = 2, m = -1, s = 1/2$
(*c*) $n = 4, l = 1, m = 0, s = -\frac{1}{2}$
(*d*) $n = 5, l = 0, m = 0, s = -\frac{1}{2}$.

44. When α-particles are sent through a thin metal foil, most of them go straight through the foil because

(*a*) α-particles are lighter than electrons
(*b*) α-particles are positively charged
(*c*) Most part of the atom is empty space
(*d*) α-particles move with high velocity.

45. The radius of hydrogen atom in the ground state is 0.53 Å, the radius of $_3Li^{2+}$ in the similar state is

(*a*) 1.06 Å
(*b*) 0.265 Å
(*c*) 0.17 Å
(*d*) 0.53 Å.

46. An element, M has an atomic mass 19 and atomic number 9, its ion is represented by

(*a*) M^+
(*b*) M^{2+}
(*c*) M^-
(*d*) M^{2-}.

47. The number of nodal planes '*d*' orbital has is

(*a*) zero
(*b*) one
(*c*) two
(*d*) three.

48. Which of the following statements regarding spectral series is correct ?

(*a*) The lines in the Balmer series correspond to the electronic transition from the energy level higher than $n = 1$ energy level.
(*b*) Paschen series appear in the infrared region
(*c*) The lines of Lyman series appear in the visible region
(*d*) Transition from higher energy levels to 4th energy level produces Pfund series which fall in the infrared region.

49. Which of the following does not form a part of Bohr's model of hydrogen atom ?

(*a*) Energy of the electron in the orbit is quantized
(*b*) The electron in the orbit nearest to the nucleus has the lowest energy
(*c*) Angular momentum of the electron in the orbit is quantised
(*d*) The position and velocity of the electrons in the orbit cannot be determined simultaneously.

50. If the electron falls from $n = 3$ to $n = 2$, in hydrogen atom then emitted energy is

(*a*) 10.2 eV
(*b*) 12.09 eV
(*c*) 1.9 eV
(*d*) 0.65 eV.

51. The energy of an electron in the first orbit of H atom is – 13.6 eV. The possible value(s) of the excited state(s) for electron in Bohr orbits of hydrogen is(are)

(*a*) – 3.4 eV
(*b*) – 4.2 eV
(*c*) – 6.8 eV
(*d*) + 6.8 eV.

52. The electrons identified by quantum numbers n and l (*i*) $n = 4, l = 1$ (*ii*) $n = 4, l = 0$ (*iii*) $n = 3, l = 2$ (*iv*) $n = 3, l = 1$ can be placed in order of increasing energy, as

(*a*) (*iv*) < (*ii*) < (*iii*) < (*i*)
(*b*) (*ii*) < (*iv*) < (*i*) < (*iii*)
(*c*) (*i*) < (*iii*) < (*ii*) < (*iv*)
(*d*) (*iii*) < (*i*) < (*iv*) < (*ii*).

53. If wavelength of photon is 2.2×10^{-11} m, $h = 6.6 \times 10^{-34}$ Js, then momentum of photon is

(*a*) 3×10^{-23} kg ms^{-1}
(*b*) 3.33×10^{22} kg ms^{-1}
(*c*) 1.452×10^{-44} kg ms^{-1}
(*d*) 6.89×10^{43} kg ms^{-1}.

54. The first emission line in the atomic spectrum of hydrogen in the Balmer series appears at

(*a*) $\frac{5R}{36}$ cm^{-1}
(*b*) $\frac{3R}{4}$ cm^{-1}
(*c*) $\frac{7R}{144}$ cm^{-1}
(*d*) $\frac{9R}{400}$ cm^{-1}.

55. The angular part of wave function depends on quantum number(s)

(*a*) n and l
(*b*) l and m
(*c*) n only
(*d*) n, l and m.

56. If kinetic energy of a proton is increased nine times the wavelength of the de-Broglie wave associated with it would become

(*a*) 3 times
(*b*) 9 times

32. (*a*) Electrons having least mass have maximum e/m ratio.

33. (*b*) H.G.J. Moseley determined the atomic numbers by study of *X*-rays emitted by different electrons.

34. (*d*) $m = +2$ corresponds to a particular orbital. An orbital can accommodate only 2 electrons.

35. (*d*) Mn has atomic no. 25. Its electronic configuration is $[\text{Ar}]^{18}\, 3d^5\, 4s^2$.

36. (*c*) $n = 3, l = 2$ means 3*d*-sub-shell. In chromium atom there are five electrons is 3*d*-sub-sheil.

$$\text{Cr}[Z = 24] : [\text{Ar}]\, 3d^5\, 4s^1.$$

38. (*a*) Frequency is given by the relation

$$\nu = 3.29 \times 10^{15} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{Hz.}$$

For first line in Balmer series $n_1 = 2, n_2 = 3$.

39. (*c*) $\Delta E = h\nu$ or $\nu = \frac{h}{\Delta E}$ or $\nu \propto \frac{1}{\Delta E}$.

40. (*d*) The number of possible orientations is $(2l + 1)$.

$$(2 \times 3 + 1) = 7.$$

41. (*d*) $E = \frac{hc}{\lambda}, \frac{E_1}{E_2} = \frac{\lambda_2}{\lambda_1} = \frac{4000}{2000} = 2.$

42. (*b*) P : $1s^2, 2s^2, 2p_x^2, 2p_y^2, 2p_z^2, 3s^2, 3p_x^1, 3p_y^1, 3p_z^1$.

No. of sub-shell = 5(1*s*, 2*s*, 2*p*, 3*s*, 3*p*)

No. of orbitals = 9.

44. (*d*) An orbital can accommodate only two electrons.

45. (*c*) When $l = 2$, m_l cannot be -3, Value of m_l cannot be numerically greater than the value of l.

46. (*b*) Here 2*s* is not fully filled whereas filling 2*p* has started.

47. (*d*) Any orbital can accommodate only two electrons with opposite spin.

48. (*a*) Average distance of the electron from the nucleus is determined by n, hence it determines the size of the orbital.

49. (*d*) The maximum no. of electrons in an energy level

$$= 2n^2$$

For $n = 4$, $2n^2 = 32$.

50. (*b*) K.E. $\propto v \propto \frac{1}{\lambda}$.

52. (*b*) The maximum value of $l = (n - 1)$.

53. (*b*) For *g*-sub-shell, $l = 4$. The minimum value of n for which l can be 4 is equal to $(4 + 1)$ *i.e.*, 5.

58. (*a*) He^+ and H are both single electron species.

62. (*c*) $n = 3, l = 0, 1, 2$

$m = 0 ; +1, 0, -1 ; +2, +1, 0, -1, -2.$

64. (*a*) The energy difference between first and second energy levels is very large.

65. (*c*) During ionization, the electrons are first lost from 4*s* subshell.

68. (*d*) The last electron in Na is in 3*s*. For *s*-subshell $l = 0$.

69. (*c*) $\Delta x = \frac{h}{4\pi m \Delta v} = \frac{6.63 \times 10^{-27} \times 100}{4 \times 3.14 \times 9.1 \times 10^{-28} \times 3 \times 10^4 \times .011}$

$= 0.175$ cm.

72. (*b*) Orbital angular momentum

$$= \sqrt{l(l+1)} = \frac{h}{2\pi} = \sqrt{0(0+1)}\, \frac{h}{2\pi} = 0.$$

74. (*c*) The unpaired electron is chlorine is in 3*p* subshell. For 3*p* subshell, $n = 3$ and $l = 1$.

75. (*c*) CO and CN^-, both have 14 electrons each.

76. (*c*) Since the given configuration contains 10 electrons and one of the electrons is present in 3*s* orbital instead of 2*p*, it is excited state of argon.

80. (*c*) The valence electron in potassium is in 4*s* orbital.

81. (*d*) $\bar{\nu} = \frac{\nu}{C} = \frac{6 \times 10^{15}\ s^{-1}}{3 \times 10^{10}\ \text{cm s}^{-1}} = 2 \times 10^5\ \text{cm}^{-1}$.

82. (*a*) $E_{2(H)} = -\frac{B}{(2)^2}$

$$E_{x(He^+)} = -\frac{B \,.\, Z^2}{(x^2)} = \frac{-B\,(2)^2}{x^2}$$

$$-\frac{B}{(2)^2} = -\frac{B(2)^2}{x^2} \quad x = 4.$$

86. (*b*) Cathode rays as well as β-rays consist of electrons.

87. (*b*) K^+ and Cl^- have $(17 + 1) = 18$ electrons, which are distributed as 2, 8, 8.

88. (*c*) For *f*-sub shell, $l = 3$.

90. (*b*) Bohr's model could explain spectrum of hydrogen atom and hydrogen-like species such as He^+, Li^2, etc.

91. (*c*) $r_n = \frac{n^2 h^2}{4\pi^2 km Ze^2}$

$$r_n \propto n^2$$

$$r_n = n^2 r_1$$

$$r_2 = (2)^2 r_1 = 4r_1.$$

96. (*d*) There would be 10 electrons with $l = 2$. $l = 2$ corresponds to *d*-subshell.

97. (*b*) $v_n \propto \frac{1}{n}$.

99. (*b*) $\text{KE} = h(\nu - \nu_0)$

$$\frac{\text{KE}}{h} = \nu - \nu_0$$

4 SOLUTIONS

Important Terms, Facts and Formulae

SOLUTION AND ITS COMPONENTS

- **Solution.** *A homogeneous mixture of two or more pure substances whose composition may be altered within certain limits,* is called **solution.**
- **Solvent and Solute.** In general, for binary solution *the component of the solution whose physical state is same as that of solution* is called **solvent** while the other components are called **solute.** However, if physical state of the components is same as that of solution, then the *component in excess* is taken to be **solvent.**

VAPOUR PRESSURE OF A LIQUID

The pressure exerted by the vapours above the liquid surface in equilibrium with the liquid at a given temperature is called vapour pressure of the liquid.

The vapour pressure of a liquid depends on :

(*i*) *Nature of liquid.* Liquids, which have weak intermolecular forces, are volatile and have greater vapour pressure.

(*ii*) *Temperature.* Vapour pressure increases with increase in temperature.

- The effect of temperature on vapour pressure is mathematically given by the following form of clausius Clapyron's equation

$$\log \frac{p_2}{p_1} = \frac{\Delta H_{vap}}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

where p_2 and p_1 are vapour pressures at the temperature T_2 and T_1 and ΔH_{vap} is enthalpy of vaporisation of liquid.

VAPOUR PRESSURE OF SOLUTION AND LOWERING OF VAPOUR PRESSURE.

The vapour pressure of the solution containing non-volatile solute is less than that of the pure solvent.

The difference between the vapour pressure of solvent ($p_A°$) and that of solution (p) is represented by $\Delta p \ (= p_A° - p)$ and is called **lowering of vapour pressure.**

- **Raoult's Law** states that the vapour pressure of a solution containing non-volatile solute is equal to product of mole fraction of the solvent and vapour pressure of pure solvent.

In case of solution containing two components A (*volatile solvent*) and B (*non-volatile solute*) the vapour pressure of solution is given as

$$\boxed{p_A = p_A° \cdot x_A}$$

- **Vapour Pressure of the Solution of Miscible Liquids.** The total vapour pressure of the solution of two miscible liquids is given by the sum of their partial pressures. Thus, if p is the total vapour pressure of the solution, then

$$p = p_A + p_B = p_A° x_A + p_B° x_B$$

$$= p_A° x_A + p_B° (1 - x_A) \quad \because \quad x_A + x_B = 1$$

$$= (p_A° - p_B°)\, x_A + p_B° \qquad ...(i)$$

Similarly, it can also be shown that

$$p = (p_B° - p_A°)\, x_B + p_A° \qquad ...(ii)$$

Both the equations (*i*) and (*ii*) can be compared to ($y = mx + c$) which represents a straight line. This implies that the total vapour pressure p is a linear function of x_B (or x_A).

- **Relative Lowering of Vapour Pressure ($\Delta p / p_A°$).** The term relative lowering of vapour pressure is defined as the *ratio of the lowering of vapour pressure to the vapour pressure of pure solvent.*

Relative lowering of vapour pressure is equal to mole fraction of the solute.

$$\frac{p_A° - p_A}{p_A°} = x_B \quad \text{or} \quad \boxed{\frac{\Delta p}{p_A°} = x_B}$$

IDEAL AND NON-IDEAL SOLUTIONS

1. **Ideal Solutions.** *The solutions are said to be* **ideal** if they *fulfill the following conditions :*

QUESTION BANK

Level I

Choose the correct answer from the four alternatives given in each of the following questions :

1. The molarity of 6% (W/V) solution of acetic acid is

(*a*) 0.01 M (*b*) 0.1 M

(*c*) 1 M (*d*) 0.5 M.

2. The normality of 1 M solution of Na_2CO_3 is

(*a*) 1 N (*b*) 0.5 N

(*c*) 2 N (*d*) 3 N.

3. A non-volatile electrolyte, dissolved in equimolal proportion as non-volatile non-electrolyte, produces

(*a*) same colligative effect (*b*) lower colligative effect

(*c*) higher colligative effect (*d*) no colligative effect.

4. 18% (W/V) solution of urea (Mol. mass = 60) is

(*a*) 1 M (*b*) 2 M

(*c*) 0.3 M (*d*) 3 M.

5. The density of 5 molal solution of urea is 1.3 g cm^{-3}. Concentration of this solution in terms of molarity would be

(*a*) 5 M (*b*) > 5 M

(*c*) < 5 M (*d*) Cannot be predicted.

6. The enthalpy change on mixing water and ethanol at room temperature is

(*a*) Zero

(*b*) Positive

(*c*) Negative

(*d*) Depends on proportion of alcohol in the solution.

7. Two liquids A and B form an ideal solution. At 300 K the vapour pressure of a solution of 1 mole of A and x moles of B is 550 mm. If the vapour pressures of pure A and B are 400 mm and 600 mm respectively, then x is

(*a*) 1 (*b*) 2

(*c*) 3 (*d*) 4.

8. The number of moles of sodium hydroxide present in 2.5 L of 0.5 M aqueous solution is

(*a*) 1.25 (*b*) 0.5

(*c*) 12.5 (*d*) 5.

9. The molality of 2% (w/w) aqueous solution of sodium chloride is

(*a*) 0.17 m (*b*) 0.7 m

(*c*) 1 m (*d*) 0.34 m.

10. The molarity of decinormal aqueous solution of sodium hydroxide is

(*a*) M/5 (*b*) M/10

(*c*) M/2 (*d*) M/100.

11. Two beakers contain 1 L and 250 ml of pure water respectively. What is same in them ?

(*a*) number of moles (*b*) number of molecules

(*c*) molarity (*d*) mass.

12. According to Raoult's law, the relative lowering of vapour pressure of a solution of non-volatile solute is

(*a*) equal to mole fraction of solvent

(*b*) equal to mole fraction of solute

(*c*) directly proportional to mole fraction of solute

(*d*) equal to normality of the solution.

13. Which aqueous solution will have lowest vapour pressure at room temperature ?

(*a*) 0.1 M NaCl (*b*) 0.1 M glucose

(*c*) 0.1 M urea (*d*) 0.1 M $CaCl_2$.

14. At higher altitudes, water boils at temperature < 100°C because

(*a*) temperature at higher altitudes is low

(*b*) atmospheric pressure is low

(*c*) the proportion of heavy water increases

(*d*) atmospheric pressure becomes more.

15. An azeotropic solution of two liquids has boiling point lower than ether when it

(*a*) shows a negative deviation from Raoult's law

(*b*) shows a positive deviation from Raoult's law

(*c*) shows no deviation from Raoult's law

(*d*) is saturated.

16. A liquid is in equilibrium with its vapour at its boiling point. On the average, the molecules of the two phases will have

(*a*) same magnitude of interparticle forces

(*b*) same potential energy

(*c*) same total energy

(*d*) same free energy.

17. Ebullioscopic constant depends upon

(*a*) nature of solvent

(*b*) nature of solute

(*a*) 1 : 1 (*b*) 0.5 : 1
(*c*) 5 : 2 (*d*) 3 : 1.

71. The molal elevation constant of a liquid is the ratio of elevation in boiling point to

(*a*) molality (*b*) normality
(*c*) molarity (*d*) mole fraction of solvent.

72. A solution of benzoic acid dissolved in benzene will show a molecular mass closer to

(*a*) 122 (*b*) 244
(*c*) 61 (*d*) 366.

73. The correct relationship between the boiling points of very dilute solutions of $CaCl_2$ (t_1°C) and $AlCl_3$(t_2°C) having same molar concentration is

(*a*) $t_1 = t_2$ (*b*) $t_2 > t_1$
(*c*) $t_2 < t_1$ (*d*) $t_2 = 2t_1$.

74. Which of the following conditions is not satisfied by ideal solutions ?

(*a*) $\Delta H_{mix} = 0$ (*b*) $\Delta V_{mix} = 0$
(*c*) Obeyance of Raoult's law (*d*) $\Delta G_{mix} = 0$.

75. The value of k_b is given by $RT_b^2/1000X$. In this relation X is

(*a*) density of solution (*b*) ΔH_f° of solvent
(*c*) latent heat of vaporisation (*d*) ΔH_{vap}.

76. Osmotic pressure of 30% solution of glucose is 1.20 bar and that of 3.42% solution of cane sugar is 2.5 bar. The osmotic pressure of the mixture containing equal volumes of the two solutions will be

(*a*) 2.5 atm (*b*) 3.7 atm
(*c*) 1.85 atm (*d*) 1.3 atm.

77. Which inorganic precipitate acts a semi-permeable membrane ?

(*a*) Calcium sulphate (*b*) Barium oxalate
(*c*) Nickel phosphate (*d*) Copper ferrocyanide.

78. When mercuric iodide is added to the aqueous solution of KI, the

(*a*) freezing point is raised
(*b*) freezing point is lowered
(*c*) boiling point does not change
(*d*) freezing point does not change.

79. 0.6 g of a solute is dissolved in 0.1 L of a solvent which develops an osmotic pressure of 1.23 atm at 27°C. The molecular mass of the substance is

(*a*) 149.5 (*b*) 120
(*c*) 430 (*d*) None of these.

80. Isotonic solutions have the same

(*a*) Density (*b*) Molarity
(*c*) Normality (*d*) Mole fraction.

81. What is the freezing point of a solution containing 8.1 g HBr in 100 g water, assuming the acid to be 90% ionised. [K_f for water = 1.86 K kg mol^{-1}]

(*a*) 0.85°C (*b*) – 3.53°C
(*c*) 0°C (*d*) – 0.35°C.

82. The freezing point of a 0.08 molal aqueous solution of $NaHSO_4$ is – 0.372°C. The dissociation constant for the reaction,

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-} \text{ is}$$

(*a*) 4×10^{-2} (*b*) 8×10^{-2}
(*c*) 2×10^{-2} (*d*) 1.86×10^{-2}.

83. 3% aqueous solution of dextrose (mol. mass = 180) is isotonic with 2% aqueous solution of another non-electrolyte solute at 25°C. The molecular mass of the solute is

(*a*) 60 (*b*) 120
(*c*) 180 (*d*) 90.

84. The vapour pressure of the solution of two liquids A (p° = 80 mm) and B (p° = 120 mm) is found to be 100 mm when $x_A = 0.4$. The result shows that

(*a*) solution exhibits ideal behaviour
(*b*) solution shows positive deviations
(*c*) solution shows negative deviations
(*d*) solution will show positive deviations for lower concentrations and negative deviations for higher concentrations.

85. The relative lowering of vapour pressure produced by 4 m solution of glucose in water (v.p. of water = 22.5 mm) is

(*a*) 0.067 (*b*) 0.166
(*c*) 1.665 (*d*) unpredictable.

86. Equal volumes of 0.1 M aqueous solutions of $(NH_4)_2SO_4$ and $Ba(OH)_2$ are mixed. Which of the following species has largest concentration in the resulting solution ?

(*a*) Ba^{2+} (*b*) NH_2 (*aq*)
(*c*) NH_4^+ (*d*) $BaSO_4$.

87. Which of the following solutions has highest normality ?

(*a*) 8 g L^{-1} (KOH) (*b*) normal phosphoric acid
(*c*) 6 g per 100 ml (NaOH) (*d*) 0.5 M H_2SO_4.

88. 25 ml of semi-molar HNO_3 is mixed with 75 ml of pentimolar HNO_3 solution. The molarity of resulting solution is (*c*) No flow of water

(*d*) Direction of flow cannot be predicted.

3. 4.5% solution of glucose would be isotonic with respect to ...... solution of urea.

(*a*) 4.5% (*b*) 13.5%
(*c*) 1.5% (*d*) 9%.

4. 3% solution of glucose is isotonic with 1% solution of a non-volatile non-electrolyte substance. The molecular mass of the substance would be

(*a*) 180 (*b*) 360
(*c*) 420 (*d*) 60.

5. Which of the following change with increase in temperature

I. Molality II. Molarity
III. Mole fraction IV. Normality.

(*a*) I, II (*b*) II
(*c*) I, IV (*d*) II, IV.

6. Which of the following are not colligative properties ?

(*a*) Relative lowering of vapour pressure
(*b*) Surface tension
(*c*) Osmosis
(*d*) both *b* and *c*.

7. Which of the following solutions are expected to be isotonic with respect to 6% (W/V) solution of urea.

I. 18% solution of glucose
II. 0.1 M solution of NaCl
III. 0.1 M solution of sucrose
IV. 0.1 M solution of CH_3COOH.

(*a*) I, III (*b*) I, II, III
(*c*) II, IV (*d*) II, III.

8. Osmotic pressure of a solution of electrolyte does not depend on

I. Nature of solute II. Nature of solvent
III. Temperature IV. Molar conc. of solute.

(*a*) I (*b*) I, II
(*c*) II, III (*d*) III, IV.

9. Which of the following solutions exhibit positive deviation from Raoult's law ?

(*a*) $H_2O + C_2H_5OH$ (*b*) $C_6H_6 + C_6H_5CH_3$
(*c*) $H_2O + HCl$ (*d*) $CHCl_3 + (CH_3)_2CO$.

10. Which of the following statements are not true ?

I. Normality of a solution is always greater than molarity
II. Normality of a solution increases with increase in temperature
III. Normality of a solution may be equal to or greater than the molarity
IV. Normality × Eq. mass = Molarity × Mol mass.

(*a*) I, II (*b*) II, III
(*c*) III, IV (*d*) IV, I.

11. For which of the following solutes '*i*' is greater than 1 ?

(*a*) Urea (*b*) Sucrose
(*c*) Sodium chloride (*d*) glucose.

12. Solutions with same vapour pressures are called

(*a*) isotonic (*b*) isopeistic
(*c*) hypertonic (*d*) isomorphic.

13. For a solution containing non-volatile solute, the relative lowering of vapour pressure is 0.2. If the solution contains 5 moles in all, which of the following are true ?

I. Mole fraction of solute in the solution is 0.2
II. No. of moles of solute in the solution is 0.2
III. No. of moles of solvent in the solution is 4
IV. Mole fraction of solvent is 0.2.

(*a*) I, IV (*b*) II, III
(*c*) I, III (*d*) II, IV.

14. The normality of a 2.3 M sulphuric acid solution is

(*a*) 0.46 N (*b*) 0.23 N
(*c*) 2.3 N (*d*) 4.6 N.

15. The ebullioscopic constant for water is 0.513°C kg mol^{-1}. The aqueous solution of sugar containing 0.1 mole of it in 200 g of water will boil under a pressure of one atm at

(*a*) 100.513°C (*b*) 100.0513°C
(*c*) 100.256°C (*d*) 101.025°C.

16. A non-volatile electrolyte dissolved in an aqueous solution in same molal proportion as non-electrolyte produces

(*a*) same colligative effect (*b*) higher colligative effect
(*c*) lower colligative effect (*d*) no colligative effect.

17. The molal depression constant depends upon

(*a*) Nature of solute
(*b*) Nature of solvent
(*c*) $\Delta H_{solution}$
(*d*) Vapour pressure of solution.

18. Which of the following is not a colligative property

(*a*) ΔT_f (*b*) π
(*c*) $\Delta . T_b$ (*d*) K_b.

19. The weight of pure NaOH required to prepare 250 cm^3 of 0.1 N solution is

(*a*) 4 g (*b*) 1 g

(*c*) 2 g (*d*) 10 g.

20. Which of the following solutions will have the highest boiling point ?

(*a*) 1% of glucose in water (*b*) 1% sucrose in water

(*c*) 1% NaCl in water (*d*) 1% $CaCl_2$ in water.

21. Which is an example of colligative property ?

(*a*) boiling point (*b*) osmosis

(*c*) freezing point (*d*) osmotic pressure.

22. If 0.1 M solution of glucose and 0.1 M solution of urea are placed on two sides of the semipermeable membrane to equal heights, then it will be correct to say that

(*a*) There will be no net movement across the membrane

(*b*) Glucose will flow towards urea solution

(*c*) urea will flow towards glucose solution

(*d*) water will flow from urea solution to glucose solution.

23. An aqueous solution of glucose is 10% in strength. The volume in which 1 gm mole of it is dissolved will be

(*a*) 18 L (*b*) 9 L

(*c*) 0.9 L (*d*) 1.8 L.

24. A 500 g tooth paste sample has 0.2 g fluoride concentration. What is the concentration of fluoride in terms of ppm

(*a*) 250 (*b*) 200

(*c*) 400 (*d*) 1000.

25. How many grams of a dibasic acid (Molecular mass = 200) should be present in 100 ml of its aqueous solution to give decinormal strength ?

(*a*) 1 g (*b*) 2 g

(*c*) 10 g (*d*) 20 g.

26. The vapour pressure of a solution of 5 g of non-electrolyte in 100 g of water at a particular temperature is 2985 N/m^2. The vapour pressure of pure water is 3000 N/m^2. The molecular mass of solute is

(*a*) 180 (*b*) 120

(*c*) 60 (*d*) 392.

27. Osmotic pressure of a solution increases by

(*a*) decreasing the temperature

(*b*) increasing the volume

(*c*) increasing the number of molecules of the solute

(*d*) none of the above.

28. Acetic acid dissolved in benzene shows a molecular mass of

(*a*) 30 (*b*) 60

(*c*) 120 (*d*) 180.

29. Hydrochloric acid solutions A and B have concentrations 0.5 N and 0.1 N respectively. The volumes of solutions A and B required to make 2 litres of 0.2 N hydrochloric acid are

(*a*) 0.5 L of A + 1.5 L of B (*b*) 1.5 L of A + 0.5 L of B

(*c*) 1.0 L of A + 1.0 L of B (*d*) 0.75 L of A + 1.25 L of B.

30. Increasing the temperature of an aqueous solution will cause decrease in

(*a*) Molality (*b*) Molarity

(*c*) Mole fraction (*d*) % (W/V).

31. "Partial vapour pressure of a solution component is directly proportional to its mole fraction". This statement is known as

(*a*) Henry's law (*b*) Raoult's law

(*c*) Distribution law (*d*) Ostwald's dilution law.

32. An aqueous solution containing 1 g of urea boils at 100.25°C. The aqueous solution containing 3 g of glucose in the same volume will boil at

(*a*) 100.75°C (*b*) 100.5°C

(*c*) 100°C (*d*) 100.25°C.

33. Equal volumes of 0.1 M $AgNO_3$ and 0.2 M NaCl are mixed. The concentration of NO_3^- ions in the mixture will be

(*a*) 0.1 M (*b*) 0.05 M

(*c*) 0.2 M (*d*) 0.15 M.

34. How many grams of methanol would have to be added to water to prepare 150 ml of solution which is 2 M CH_3OH ?

(*a*) 9.6 (*b*) 2.4

(*c*) 9.6×10^3 (*d*) 4.3×10^2.

35. At 25°C, the highest osmotic pressure is exhibited by 0.1 M solution of

(*a*) $CaCl_2$ (*b*) KCl

(*c*) Glucose (*d*) Urea.

36. Which one of the following salts will have the same value of vant Hoff's factor (*i*) as that of $K_4[Fe(CN)_6]$.

(*a*) $Al_2(SO_4)_2$ (*b*) NaCl

(*c*) $Al(NO_3)_3$ (*d*) Na_2SO_4.

37. A solution containing 6.8 g of non-ionic solute in 100 g of water was found to freeze at – 0.93° C. If K_f for water is 1.86. The molecular mass of solute is

(*a*) 13.6 (*b*) 34
(*c*) 68 (*d*) 136.

38. The molarity of a solution obtained by dissolving 0.01 moles of NaCl in 500 ml of solution is

(*a*) 0.01 M (*b*) 0.005 M
(*c*) 0.02 M (*d*) 0.10 M.

39. 5.85 g of NaCl is dissolved in 500 ml of water. The molarity is

(*a*) 0.1 (*b*) 0.2
(*c*) 0.3 (*d*) 0.4.

40. In the phenomenon of osmosis, the semipermeable membrane allows the passage of

(*a*) solute particles (*b*) solvent molecules only
(*c*) both solute and solvent (*d*) none.

41. If 5.85 g of NaCl are dissolved in 90 g of water, the mole fraction of NaCl would be

(*a*) 0.1 (*b*) 0.01
(*c*) 0.2 (*d*) 0.0196.

42. Equivalent mass of crystalline oxalic acid is

(*a*) 90 (*b*) 63
(*c*) 53 (*d*) 45.

43. 4.0 g of caustic soda is dissolved in 100 cm^3 of solution. The normality of solution is

(*a*) 1 (*b*) 0.1
(*c*) 0.5 (*d*) 4.0

44. The osmotic pressure of 5% (mass-volume) solution of cane sugar at 150°C (mol. mass sugar = 342) is

(*a*) 4 atm (*b*) 5.07 atm
(*c*) 3.55 atm (*d*) 2.45 atm.

45. The molarity of the solution containing 7.1 g of Na_2SO_4 in 100 ml of aqueous solution is

(*a*) 2 M (*b*) 0.5 M
(*c*) 1 M (*d*) 0.05 M.

46. The volume of 0.1 M H_2SO_4 required to neutralise completely 40 ml of 0.2 M NaOH solution is

(*a*) 10 ml (*b*) 40 ml
(*c*) 20 ml (*d*) 80 ml.

47. The normal boiling point of water is 373 K (at 760 mm). Vapour pressure of water at 298 K is 23 mm. If enthalpy of vaporisation is 40.656 kJ mol^{-1}, the boiling point of water at 23 mm pressure will be

(*a*) 250 K (*b*) 298 K
(*c*) 51.6 K (*d*) 12.5 K.

48. The concentration units independent of temperature would be

(*a*) Normality (*b*) Mass-volume percent
(*c*) Molality (*d*) Molarity.

49. According to Raoult's law, the relative lowering of vapour pressure of solution is equal to the

(*a*) Mole fraction of solute (*b*) Moles of solute
(*c*) Mole fraction of solvent (*d*) Moles of solvent.

50. 12 g of urea is dissolved in 1 litre of water and 68.4 g of sucrose is dissolved in 1 litre of water. The lowering of vapours pressure of first solution is

(*a*) equal to that of second (*b*) greater than the second
(*c*) less than the second (*d*) double of the second.

51. Calculate the normality of 10 '*volume*' H_2O_2 solution.

(*a*) 1.7 N (*b*) 12 N
(*c*) 30.3 N (*d*) 0.0303 N.

52. Isotonic solutions have same

(*a*) Molar concentration (*b*) Molality
(*c*) Normality (*d*) None of these.

53. Which of the following methods is used for measuring the osmotic pressure of the solution ?

(*a*) Ostwald method (*b*) Berkley Hartley method
(*c*) Solvay method (*d*) Haber's method.

54. 2N HCl will have the same molar concentration as

(*a*) 0.5 N H_2SO_4 (*b*) 1.0 N H_2SO_4
(*c*) 2 N H_2SO_4 (*d*) 4 N H_2SO_4.

55. Vapour pressure of CCl_4 at 25°C is 143 mm Hg. 0.5 gm of a non-volatile solute (mol. mass 65) is dissolved in 100 ml CCl_4. Find the vapour pressure of the solution. (Density of CCl_4 = 1.58 g/cm^3).

(*a*) 141.93 mm (*b*) 94.39 mm
(*c*) 199.34 mm (*d*) 143.99 mm.

56. What is the molarity of H_2SO_4 solution that has a density of 1.84 gm/cc at 35°C and contains 98% by weight ?

(*a*) 4.18 M (*b*) 8.14 M
(*c*) 18.4 M (*d*) 18 M.

57. The relationship between osmotic pressure at 273 K when 10 g glucose (P_1), 10 g urea (P_2) and 10 g sucrose (P_3) are dissolved in 250 ml of water is

(*a*) $P_1 > P_2 > P_3$ (*b*) $P_3 > P_1 > P_2$
(*c*) $P_2 > P_1 > P_3$ (*d*) $P_2 > P_3 > P_1$.

58. The vapour pressure at a given temperature of an ideal solution containing 0.2 mol of a non-volatile solute and 0.8 mol of solvent is 60 mm of Hg. The vapour pressure of the pure solvent at the same temperature will be

(*a*) 120 mm of Hg (*b*) 150 mm of Hg
(*c*) 60 mm of Hg (*d*) 75 mm of Hg.

59. Lowering in vapour pressure is the highest for

(*a*) 0.2 M urea (*b*) 0.1 M glucose
(*c*) 0.1 M $MgSO_4$ (*d*) 0.1 M $BaCl_2$.

60. Vant Hoff factor for $Ca(NO_3)_2$ is

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

61. Which of the following has lowest freezing point ?

(*a*) 1% glucose (*b*) 1% sucrose
(*c*) 1% KCl (*d*) 1% $BaCl_2$.

62. Which is not affected by temperature ?

(*a*) Normality (*b*) Formality
(*c*) Molarity (*d*) Molality

63. Which of the following 0.10 m aqueous solutions will have lowest freezing point ?

(*a*) KCl (*b*) $Al_2(SO_4)_3$
(*c*) $C_6H_{12}O_6$ (*d*) $C_{12}H_{22}O_{11}$.

64. Molal depression constant for water is 1.86°C. The freezing point of a 0.05 molal solution of a non-electrolyte in water is

(*a*) – 1.86°C (*b*) – 0.93°C
(*c*) – 0.093°C (*d*) 0.93°C.

65. An aqueous solution freezes at – 0.186°C ($k_f = 1.86°$; $k_b = 0.512°$). What is the elevation in boiling point ?

(*a*) 0.186 (*b*) 0.512
(*c*) $\frac{0.512}{1.86}$ (*d*) 0.0512.

66. Which one of the following is a colligative property ?

(*a*) Surface tension (*b*) Osmotic pressure
(*c*) Viscosity (*d*) Refractive index.

67. Which of the following will have the highest boiling point at 1 atm pressure ?

(*a*) 0.1 M NaCl (*b*) 0.1 M Sucrose
(*c*) 0.1 M $BaCl_2$ (*d*) 0.1 M Glucose.

68. What will be the molality of a solution having 18 g of glucose (M. wt. 180) dissolved in 500 g of water ?

(*a*) 1 m (*b*) 0.5 m
(*c*) 0.2 m (*d*) 2 m.

69. What will be the osmotic pressure of 0.05 N solution of sucrose at 5°C ?

(*a*) 1.14 atm (*b*) 2.07 atm
(*c*) 1.05 atm (*d*) 3.05 atm.

70. A certain aqueous solution of $FeCl_3$ (formula mass = 162) has a density of 1.1 g/ml and contains 20.0% $FeCl_3$. Molar concentration of this solution is

(*a*) 0.028 (*b*) 1.36
(*c*) 1.27 (*d*) 1.47.

71. An ideal solution was obtained by mixing methanol and ethanol. If the partial vapour pressure of methanol and ethanol are 2.619 kPa and 4.556 kPa respectively, the composition of vapour (in terms of mole fraction) will be

(*a*) 0.635 MeOH, 0.365 EtOH
(*b*) 0.365 MeOH, 0.635 EtOH
(*c*) 0.574 MeOH, 0.326 EtOH
(*d*) 0.173 MeOH, 0.827 EtOH.

72. A 5% solution of cane sugar (MW = 342) is isotonic with 1% solution of substance X. The molecular weight of X is

(*a*) 171.2 (*b*) 68.4
(*c*) 34.2 (*d*) 136.2.

73. The vapour pressure of a solvent decreased by 10 mm of Hg when a non-volatile solute was added to the solvent. The mole fraction of solute in solution is 0.2. What would be the mole fraction of solvent if decrease in vapour pressure is 20 mm of Hg ?

(*a*) 0.8 (*b*) 0.6
(*c*) 0.4 (*d*) 0.2.

74. The freezing point of a solution prepared from 1.25 g of non electrolyte and 20 g of water is 271.9 K. If molal depression constant is 1.86 K mol^{-1} then molar mass of the solute will be

(*a*) 105.7 (*b*) 106.7
(*c*) 115.3 (*d*) 93.9.

75. 6 ml of 0.5 M HCl is mixed in 15 ml of 0.3 M H_2SO_4 and 15 ml of 0.2 M HNO_3. The normality of the acid mixture will be

(*a*) 0.10 (*b*) 0.25
(*c*) 0.32 (*d*) 0.42.

76. How many gram of diabasic acid (molecular mass = 200) should be present in 100 ml of the aqueous solution to give decinormal solution ?

(*a*) 1 g (*b*) 2 g
(*c*) 10 g (*d*) 20 g.

77. If 0.15 g of a solute, dissolved in 15 g of solvent, is boiled at temperature higher by 0.216°C than that of pure solvent, the molecular mass of the substance is (molal elevation constant for the solvent is 2.16 K/m)

(*a*) 1.01
(*b*) 10
(*c*) 10.1
(*d*) 100.

78. $p°$ and p are the vapour pressures of solvent and its solution and x_1 and x_2 are the moles of solute and solvent respectively, then

(*a*) $p = p°x_1$
(*b*) $p = p°x_2$
(*c*) $p = p° \dfrac{x_1}{x_1 + x_2}$
(*d*) $p = p° \dfrac{x_2}{x_1 + x_2}$.

79. For a solution of acetone in CS_2 the value of ΔS_{mix} is

(*a*) > 0
(*b*) < 0
(*c*) $= 1$
(*d*) $= 0$.

80. Which of the following liquid pairs show a positive deviation from Raoult's law ?

(*a*) Benzene—methanol
(*b*) Water—hydrochloric acid
(*c*) Water—nitric acid
(*d*) Acetone—chloroform.

81. Normality of 0.1 M sulphuric acid will be

(*a*) 0.033 N
(*b*) 0.3 N
(*c*) 0.15 N
(*d*) 0.2 N.

82. By studying the elevation in boiling point of aqueous solution of glucose the value of k_b for water is found to be 0.51 K kg^{-1} mol^{-1}. The value that can be expected from the aqueous solution of K_4 $[Fe(CN)_6]$ is

(*a*) 0.51
(*b*) 2×0.51
(*c*) 5×0.51
(*d*) 3×0.51.

83. Dissolution of 1 g of certain compound X in 250 g of water produces a depression in its freezing point by 0.124°C. If K_f for water is 1.86, the molecular mass of X will be

(*a*) 180
(*b*) 60
(*c*) 90
(*d*) 30.

84. If each of the following salts dissociates in aqueous solution to the extent of 90%, then the one with highest osmotic pressure would be

(*a*) decimolar solution of $Al_2(SO_4)_3$
(*b*) decimolar solution of Na_2SO_4
(*c*) decimolar solution of $BaCl_2$
(*d*) decimolar solution of NaCl.

85. Which of the following best describes the concentration of a solution formed by dissolving 4 g of NaOH in 1 kg of water

(*a*) 4 gL^{-1}
(*b*) 0.1 M
(*c*) 0.1 m
(*d*) 4 m.

86. 5% solution of sugar is isotonic with certain aqueous solution of acetic acid, the concentration of acetic acid is

(*a*) 0.15%
(*b*) unpredictable
(*c*) 0.877%
(*d*) 0.5%.

87. The molal cryoscopic constant for water is 18.6 K mol per 100 g. It can also be written as

(*a*) 186 K kg $molal^{-1}$
(*b*) 1.86 K mol per 10 g
(*c*) 18.6 K $molal^{-1}$
(*d*) 1.86 K $molal^{-1}$.

88. Which of following sequences is correct about the osmotic pressures of equimolar solutions of $BaCl_2$ (π_1), glucose (π_2) and NaCl (π_3).

(*a*) $\pi_1 = \pi_2 = \pi_3$
(*b*) $\pi_1 > \pi_2 > \pi_3$
(*c*) $\pi_1 > \pi_3 > \pi_2$
(*d*) $\pi_2 > \pi_3 > \pi_1$.

89. Vapour pressure of pure A is 70 mm of Hg at 25°C. It forms an ideal solution with B in which mole fraction of A is 0.8. If vapour pressure of solution is 84 mm of Hg at 25° C, the vapour pressure of pure B at 25°C is

(*a*) 1 atm
(*b*) 14 mm of Hg
(*c*) 140 mm of Hg
(*d*) 56 mm of Hg.

90. In a solution of A in B, A tetramerises as $4A \rightarrow A_4$. If degree of association is 30%, the Van't Hoff factor is approximately

(*a*) 0.775
(*b*) 1/4
(*c*) 4
(*d*) unpredictable.

91. The mole fraction of solute in 2.5 m aqueous solution is

(*a*) 0.043
(*b*) 0.43
(*c*) 55.5
(*d*) 0.55.

92. 50 g of some dental cream has 0.02 g of fluoride concentration. The concentration of fluorine in ppm is

(*a*) 250
(*b*) 200
(*c*) 400
(*d*) 1000.

93. H_2O and perchloric acid (b.p. 383 K) form constant boiling mixture at 71.6% of perchloric acid. The boiling point of the solution at this composition is

(*a*) > 373 but < 383 K
(*b*) < 373 K
(*c*) > than 383 K
(*d*) = 373 K.

94. An aqueous solution of a non-electrolyte containing 3.01×10^{23} molecules of solute in 250 g of water will freeze at : (K_f = 1.86 K kg mol^{-1})

(*a*) 273 K
(*b*) 271.14
(*c*) 269.28
(*d*) 274.1 K.

95. The relative lowering of vapour pressure of a solution containing 6 g of urea dissolved in 90 g of water is (*a*) 0.0196 (*b*) 0.05

(*c*) 1.50 (*d*) 0.01.

96. A 6% solution of urea is isotonic with

(*a*) 6% solution of glucose (*b*) 25% solution of glucose

(*c*) 0.1 M solution of glucose (*d*) 1 m solution of glucose.

97. When one mole of non-volatile solute is dissolved in three moles of solvent, the vapour pressure of the solution relative to the vapour pressure of the pure solvent is

(*a*) $\frac{1}{3}$ (*b*) $\frac{1}{4}$

(*c*) $\frac{3}{4}$ (*d*) 1.

98. In a binary solution containing non-volatile solute the mole fraction of the solute is 0.2 and the vapour pressure of the solution is 40 mm. The vapour pressure of the pure solvent is

(*a*) 30 mm (*b*) 48 mm

(*c*) 32 mm (*d*) 50 mm.

99. Which of the following aqueous solutions will have maximum lowering of vapour pressure ?

(*a*) 0.1 M NaCl (*b*) 0.1 M $FeCl_3$

(*c*) 0.1 M $Al_2(SO_4)_3$ (*d*) 0.1 M $BaCl_2$.

100. The freezing point of 1 per cent solution of urea in water will be

(*a*) 273 K (*b*) > 273 K

(*c*) < 273 K (*d*) cannot be predicted.

101. The values of observed and theoretical molecular masses of certain electrolyte XY are 65.4 and 114.45 respectively. The electrolyte XY in the solution has dissociation to the extent of

(*a*) 75% (*b*) 80%

(*c*) 50% (*d*) 90%.

102. After dissolving outer hard shell of an egg in dil. HCl, it is placed in concentrated solution of sodium chloride. What will happen to egg ?

(*a*) It gets cooked gradually with salty taste.

(*b*) It will swell.

(*c*) It will shrink.

(*d*) It will form homogeneous solution due to diffusion.

103. What should be done to prepare 0.40 M NaCl solution starting with 100 ml of 0.3 M NaCl solution. (Assume volume to remain same).

(*a*) Add 0.585 g NaCl

(*b*) Add 25 ml of water

(*c*) Add 20 ml of 0.2 M NaCl

(*d*) Evaporate 10 ml of water.

104. Certain azeotropic mixture boils at a temperature lower than the boiling point of either of component. This means that

(*a*) solution is saturated

(*b*) solution is ideal

(*c*) solution exhibits negative deviations from Raoult's law

(*d*) solution exhibits positive deviations from Raoult's law.

105. C_6H_5COOH dimerises when dissolved in benzene, the vant Hoff factor (i) is related to the degree of association (x) of the acid as

(*a*) $i = (1 - x)$ (*b*) $i = (1 + x)$

(*c*) $i = (1 - 0.5x)$ (*d*) $i = (1 + 0.5x)$.

106. Two solutions A and B have same vapour pressure at particular temperature. A and B are called

(*a*) isopiestic solutions (*b*) ideal solutions

(*c*) isotones of each other (*d*) isotonic solutions.

107. The vapour pressure of pure water is 92.5 mm at 300 K. The vapour pressure of 1 molal solution of X in water is

(*a*) 180

(*b*) 90.80

(*c*) 45.4

(*d*) unpredictable because mol. mass is not given.

108. At 300 K, the two solutions of glucose A and B with respective concentration 0.01 M and 0.001 M are separated by semipermeable membrane. How much external pressure need to be applied and on which solution so as to prevent osmosis ?

(*a*) 0.2463 atm pressure is applied on solution B

(*b*) 0.2217 atm pressure is applied on solution A

(*c*) 0.0246 atm pressure is applied on solution B

(*d*) 0.0217 atm pressure is applied on solution A.

109. The ratio of the values of colligative property of two equimolal solutions of KCl and glucose in water is approximately

(*a*) 2 : 1 (*b*) 3 : 2

(*c*) 1 : 2 (*d*) 5 : 2.

110. A solution containing 28 g of phosphorus in 315 g CS_2 (b.p. 46.3°C) boils at 47.98°C. If K_b for CS_2 is 2.34 K kg mol^{-1}. The formula of phosphorus is (at. mass of P = 31)

(*a*) P_6 (*b*) P_4

(*c*) P_3 (*d*) P_2.

111. On cooling the dilute aqueous solution of sucrose below its freezing point what will be observed

(*a*) ice will start separating out

(*b*) sugar will crystallise out

(*c*) solution will freeze as such with same composition

(*d*) water and sugar in frozen part will be present in the stoichiometric ratio of 1 : 1.

112. At certain temperature, the osmotic pressure of an aqueous solution of urea was found to be 405 mm. How many times the solution should be diluted in order to exhibit the osmotic pressure of 81 mm at the same temperature ?

(*a*) 2 times (*b*) 4 times

(*c*) 8 times (*d*) 5 times.

113. The mass of solute 'A' (mol. mass = 75 g mol^{-1}) that should be added to 180 g of pure water in order to lower its vapour pressure to 4/5th of its original value is

(*a*) 180 g (*b*) 90 g

(*c*) 150 g (*d*) 75 g.

114. Which of the following statements about the molal elevation constant, K_b is true ?

(*a*) It depends upon the nature of solute

(*b*) Its units are K kg mol^{-1}

(*c*) Its value depends upon conc. of the solution

(*d*) Its value is independent of the nature of solvent.

ANSWERS

QUESTION BANK (Level I)

1. (*c*)	**2.** (*c*)	**3.** (*c*)	**4.** (*d*)	**5.** (*a*)	**6.** (*c*)	**7.** (*c*)	**8.** (*a*)
9. (*d*)	**10.** (*b*)	**11.** (*c*)	**12.** (*b*)	**13.** (*d*)	**14.** (*b*)	**15.** (*b*)	**16.** (*d*)
17. (*a*)	**18.** (*c*)	**19.** (*b*)	**20.** (*c*)	**21.** (*a*)	**22.** (*b*)	**23.** (*d*)	**24.** (*b*)
25. (*c*)	**26.** (*b*)	**27.** (*a*)	**28.** (*d*)	**29.** (*d*)	**30.** (*d*)	**31.** (*b*)	**32.** (*b*)
33. (*b*)	**34.** (*a*)	**35.** (*d*)	**36.** (*c*)	**37.** (*c*)	**38.** (*b*)	**39.** (*c*)	**40.** (*a*)
41. (*c*)	**42.** (*d*)	**43.** (*b*)	**44.** (*b*)	**45.** (*b*)	**46.** (*c*)	**47.** (*a*)	**48.** (*b*)
49. (*d*)	**50.** (*b*)	**51.** (*b*)	**52.** (*a*)	**53.** (*b*)	**54.** (*b*)	**55.** (*b*)	**56.** (*a*)
57. (*d*)	**58.** (*b*)	**59.** (*d*)	**60.** (*b*)	**61.** (*b*)	**62.** (*a*)	**63.** (*c*)	**64.** (*c*)
65. (*b*)	**66.** (*a*)	**67.** (*c*)	**68.** (*a*)	**69.** (*d*)	**70.** (*d*)	**71.** (*a*)	**72.** (*b*)
73. (*b*)	**74.** (*d*)	**75.** (*c*)	**76.** (*c*)	**77.** (*d*)	**78.** (*a*)	**79.** (*b*)	**80.** (*b*)
81. (*b*)	**82.** (*a*)	**83.** (*b*)	**84.** (*c*)	**85.** (*a*)	**86.** (*b*)	**87.** (*c*)	**88.** (*b*)
89. (*d*)	**90.** (*c*)	**91.** (*c*)	**92.** (*a*)	**93.** (*c*)	**94.** (*b*)	**95.** (*c*)	**96.** (*b*)
97. (*a*)	**98.** (*b*)	**99.** (*c*)	**100.** (*b*).				

QUESTION BANK (Level II)

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

81. (*d*) **82.** (*a*) **83.** (*b*) **84.** (*a*) **85.** (*c*) **86.** (*b*) **87.** (*d*) **88.** (*c*)
89. (*c*) **90.** (*a*) **91.** (*a*) **92.** (*c*) **93.** (*c*) **94.** (*c*) **95.** (*a*) **96.** (*c*)
97. (*b*) **98.** (*d*) **99.** (*c*) **100.** (*c*) **101.** (*a*) **102.** (*c*) **103.** (*a*) **104.**(*d*)
105. (*c*) **106.** (*a*) **107.** (*b*) **108.** (*b*) **109.** (*a*) **110.** (*d*) **111.** (*a*) **112.** (*d*)
113. (*c*) **114.** (*b*).

HINTS/SOLUTIONS

QUESTION BANK (Level I)

1. (*c*) 6% (W/V) solution contains 60 gL^{-1}

$$\text{Molarity} = \frac{\text{Strength per litre}}{\text{Eq. mass}} = \frac{60}{60} = 1\text{ M.}$$

2. (*c*) Eq. mass of $Na_2CO_3 = \frac{\text{Molecular mass}}{2}$

Normality × Eq. mass = Molarity × Molecular mass

$$\text{Normality} = \frac{1 \times M}{M/2} = 2.$$

3. (*c*) Colligative effect is directly proportional to the number of solute particles. An electrolyte dissociates in solution producing more number of solute particles.

4. (*d*) 180% (W/V) solution contains 180 g of solute per litre

$$\text{Molarity} = \frac{180}{60} = 3\text{ M.}$$

5. (*a*) Mass of solute = 5 × 60 = 300 g

Mass of solvent = 1000 g ; Mass of solution = 1300 g

$$\text{Volume of solution} = \frac{1300}{1.3} = 1000\text{ cm}^3 \text{ or } 1\text{ L.}$$

Thus, the 5 molal solution contains 5 moles of solute in 1 L of solution and hence is 5 M.

6. (*c*) Factual question.

7. (*c*) $P_A^\circ X_A + P_B^\circ X_B = 550$ mm

$$400\left(\frac{1}{1+x}\right) + 600\left(\frac{x}{1+x}\right) = 550 \Rightarrow x = 3$$

8. (*a*) Moles = V(L) × molarity = 2.5 × 0.5 = 1.25.

9. (*d*) $\text{Molality} = \frac{2 \times 1000}{58.5 \times 100} = 0.341$ m.

11. (*c*) The molarity of pure water is always 55.5 M.

12. (*b*) Factual question.

13. (*d*) $CaCl_2$ solution will have maximum number of solute particles due to ionisation as

$$CaCl_2 \longrightarrow Ca^{2+} + 2Cl^-.$$

14. (*b*) Vapour pressure becomes equal to the atmospheric pressure at low temperature because atmospheric pressure is low.

15. (*b*) A solution showing positive deviation has higher vapour pressure and lower boiling point.

16. (*d*) At equilibrium ΔG, *i.e.*, $(G_P - G_R)$ is zero.

18. (*c*) If vapour pressure is lowered, the freezing point will also get lowered.

19. (*b*) NaCl ionises as ($NaCl \longrightarrow Na^+ + Cl^-$). Hence elevation in boiling point of solution is almost double the elevation for glucose solution.

20. (*c*) Factual question.

21. (*a*) Solubility of NaCl increases by rise in temperature.

22. (*b*) Concentration of $F = \frac{0.2}{500} \times 10^6 = 4 \times 10^2$ ppm.

23. (*d*) Mass of solvent is not known, which is required to calculate mole fraction of solute/solvent.

24. (*b*) Due to trimerisation the number of solute particle will be reduced to one-third.

25. (*c*) $N_1V_1 + N_2V_2 + N_3V_3 = N_4V_4$

$0.2 \times 50 + 0.1 \times 50 + 0.2 \times 100 = N_4 \times 200$

$$N_4 = \frac{35}{200} = 0.175\text{ N.}$$

26. (*b*) 0.8 mole are present in = 1000 ml

$$0.1 \text{ mole would be present in} = \frac{1000}{0.8} \times 0.1 = 125\text{ ml.}$$

27. (*a*) No. of milli equivalents = 100 × 0.6 = 60

$$\text{No. of milli moles} = \frac{60}{3} = 20 \quad (\because \text{ Eq. mass = Mol. mass/3})$$

28. (*d*) $M_1V_1 + M_2V_2 = M_3V_3$

$6 \times 250 + 2 \times 750 = 2.5 \times V_3$

$$V_3 = \frac{3000}{2.5} = 1200\text{ ml}$$

Volume of water = 1200 − (250 + 750) = 200 ml.

29. (*d*) Suppose 1000 cm^3 of solution

$$\text{Mass of solute} = \frac{1000 \times 15}{100} = 150\text{ g}$$

Mass of solution = 1000 × 1.1 = 1100 g

Mass of solvent = 950 g

$$\text{Molality} = \frac{150}{950} = \frac{1000}{98} = 1.6.$$

30. (*d*) 0.3 M HNO_3 = 0.3 N HNO_3

0.3 M H_2SO_4 = 0.6 N H_2SO_4

$N_1V_1 + N_2V_2 = N_3V_3$

$0.3 \times 100 + 0.6 \times 200 = N_3 \times 300 \Rightarrow N_3 = 0.5.$

31. (*b*) Total mole of KOH in 6 L = $(4 \times 0.2 + 2 \times 0.5) = 1.8$

$\therefore$ molarity $= \frac{1.8 \text{ mol}}{6\text{L}} = 0.3$ M.

32. (*b*) $\frac{10}{M} = \frac{5}{180}$ $\therefore$ $M = \frac{10 \times 180}{5} = 360.$

33. (*b*) $X_{\text{Benzene}} = \frac{2}{5}, X_{\text{liquid}} = \frac{3}{5}$

$p_{\text{Benzene}} = \frac{2}{5} \times 266 = 106.4, p_{\text{liquid}} = \frac{3}{5} \times 236 = 141.6$

$$p = 141.6 + 106.4 = 248.$$

34. (*a*) Dissociation increases the number of solute particles. Hence, observed molecular mass decreases and Van't Hoff factor becomes > 1.

35. (*d*) $i = \frac{58.5}{31.8} = 1.84$

$$\alpha = \frac{1.84 - 1}{2 - 1} = 0.84 \text{ or } 84\%.$$

36. (*c*) The conc. of urea and glucose will be same, KCl and $CaCl_2$ being electrolytes will cause a change in the concentration of solute particles.

37. (*c*) Conc. being same, the osmotic pressure of two solutions will also be equal.

38. (*b*) Calculate moles of each in 100 g of solution.

Glucose $= \frac{6}{180}$; Urea $= \frac{6}{60}$; Sucrose $= \frac{6}{342}$ molar concentration of urea is maximum. Hence urea solution will have highest value of ΔT_f.

40. (*a*) Factual question.

41. (*c*) $m = \frac{0.15 \times 1000}{M \times 15}$

$$\Delta T_b = K_b \times m = \frac{K_b \times 0.15 \times 1000}{M \times 15}$$

or $M = \frac{2.16 \times 0.15 \times 1000}{0.216 \times 15} = 100.$

42. (*d*) Mass of solution = 100 g (say)

Volume of solution $= \frac{100}{0.6}$ ml

Mass of solute = 35 g $\therefore$ Moles of solute $= \frac{35}{35} = 1$

Equivalents of solute = 1

$$\text{Normality} = \frac{1}{100/0.6} \times 1000 = 6.$$

43. (*b*) Concentration of $Mg^{2+} = \frac{0.01}{1000} \times 10^6 = 10$ ppm.

45. (*b*) $\frac{4.9 \times 10^{-3}}{10^3} \times 10^6 = 4.9$ ppm.

46. (*c*) $1 \times 10 = V \times 2.5$ or $V = \frac{1 \times 10}{2.5} = 4$ L

Water required = 4 − 1 = 3 L.

47. (*a*) Volume of 100 g of solution $= \frac{100}{d}$ ml

$\therefore$ $M = \frac{20 \times d \times 1000}{100 \times 98}$

or $d = \frac{2.55 \times 100 \times 98}{20 \times 1000} = 1.249 \approx 1.25.$

48. (*b*) Factual question.

49. (*d*) 0.1 $Ca(NO_3)_2$ and 0.1 M Na_2SO_4 would produce same conc. of ions, on dissociation, in solution.

50. (*b*) $p_{\text{Benzene}} = 160 \times 0.2 = 32$ mm,

$p_{\text{Toluene}} = 68 \times 0.8 = 54.4$ mm

$$p = 32 + 54.4 = 86.4 \text{ mm}.$$

51. (*b*) $m = \frac{34.2 \times 10^3}{181.8 \times 342} = 0.55$ m.

52. (*a*) Mass $= \frac{m \times 100 \times 58.5}{1000} = \frac{0.1 \times 58.5}{10} = 0.585$ g.

53. (*b*) $\Delta S_{\text{mix.}}$ is always > 0.

54. (*b*) Non-electrolyte does not dissociate, but it can undergo association depending upon its nature.

56. (*a*) Benzene osmosis of water will occur into the egg shell increasing its size.

58. (*b*) $\pi = CRT$, for same value of C, $\pi \propto T$.

59. (*d*) **Deliquescence** is a phenomenon by virtue of which a crystalline substance on standing in air forms a solution by absorbing water vapours from the atmosphere. For deliquescence to occur the substance should be very soluble in water and its saturated solution should have low vapour pressure as compared to the pressure of water vapours in air at particular temperature.

60. (*b*) The molar conc. of 10% aq. solution of glucose is lower than that of 10% aqueous solution of urea. Hence $\pi_1 < \pi_2$.

61. (*b*) Freezing point will be highest of ΔT_f will be lowest. ΔT_f will be lowest for $C_6H_{12}O_6$ because other substances will undergo dissociation in aqueous solutions.

62. Freezing point will become less than 273 K.

64. (*c*) H_3PO_4 is a tribasic acid. Hence, the normality is 3 times the molarity.

65. (*b*) $\pi = CRT$ or $\pi \propto C$.

66. (*a*) $N_1V_1 = N_2V_2 \Rightarrow 10 \times 10 = 0.1 \times V_2$

$V_2 = 1000$ ml

Volume of water required = 1000 – 10 = 990 ml.

67. (*c*) In order to produce same lowering in vapour pressure for same solvent, the mole fraction of solute should be same.

Thus, $$\frac{W_B' M_A}{M_B' W_A'} = \frac{W_B M_A}{M_B W_A}$$

or $$W_B' = \frac{W_B M_B' W_A'}{M_B W_A} = \frac{1 \times 180 \times 1}{60 \times 50} = 6 \text{ g}.$$

68. (*a*) The solutions with same molality will also have same mole fraction. However their molarities, normalities, etc. may differ because of difference in densities.

69. (*d*) During distillation of immiscible liquids the mass of the component in the distillate is directly proportional to the product of its molar mass and its vapour pressure. Thus

$$\frac{W_A}{W_B} = \frac{M_A \cdot p_A}{M_B \cdot p_B} = \frac{18 \times 5}{137 \times 1} = \frac{190}{137} \quad \text{or} \quad \frac{1}{1.52}.$$

70. (*d*) $Ba(NO_3)_2$ dissociates into three particles and has $i = 3$ while $i = 1$ for sugar. Hence their colligative properties will be in the ratio of 3 : 1.

71. (*a*) $\Delta T_f = k_f m$ or $k_f = \Delta T_f / m$.

72. (*b*) C_6H_5COOH, (benzoic acid dimerises in benzene.) Hence it exhibits molecular mass corresponding to $(C_6H_5COOH)_2$ *i.e.*, 244.

73. (*b*) Elevation of boiling point in case of $AlCl_3$ is relatively larger than that of $CaCl_2$.

74. (*d*) $\Delta G_{mix} < 0$ in case of ideal solutions.

76. (*c*) On mixing equal volumes of the two solutions the individual concentrations of the two solutes will become half and hence their individual osmotic pressures would become half of the initial values.

The osmotic pressure will be sum of the osmotic pressures of individual components as per Dalton's law of partial pressure.

Osmotic pressure $= \dfrac{1.20 + 2.50}{2} = 1.85$ bar.

77. (*d*) Factual question.

78. (*a*) $2KI + HgI \longrightarrow K_2[HgI_4]$

Due to formation of above complex, the no. of ions in the solution decreases. Hence, depression in freezing point decreases and freezing point gets raised.

79. (*b*) Concentration $C = \dfrac{0.6}{0.1 \times M}$

i.e. $\pi = CRT \Rightarrow 1.23 = \dfrac{0.6 \times 0.082 \times 300}{0.1 \times M}$; M = 120.

80. (*b*) Isotonic solutions have same molar concentration.

81. (*b*) $m = \dfrac{8.1 \times 1000}{81 \times 100} = 1$

$$\alpha = \frac{i-1}{m-1} \quad \text{or} \quad i = \alpha(m-1) + 1 = 0.9(2-1) + 1 = 1.9$$

$$\Delta T_f = iK_f \times m = 1.9 \times 1.86 \times 1 = 3.53$$

Freezing point $= 0 - \Delta T_f = -3.53$°C.

82. (*a*) $\Delta T_f = K_f \times m$ or $m = \dfrac{\Delta T_f}{K_f} = \dfrac{0.372}{1.86} = 0.2$

$$\begin{array}{cccc} NaHSO_4 \longrightarrow & Na^+ & + & HSO_4^- \\ & 0.08 & & 0.08 \end{array}$$

$$\begin{array}{ccccc} HSO_4^- & \rightleftharpoons & H^+ & + & SO_4^{2-} \\ (0.08 - x) & & x & & x \end{array}$$

$$(0.08 - x) + x + x = 0.2$$

$$x = 0.04$$

$$K_a = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} = 0.04.$$

83. (*b*) $\dfrac{3}{180} = \dfrac{2}{M}$

$$M = \frac{180 \times 2}{3} = 120.$$

84. (*c*) Pressure expected from Raoult's law

$= 80 \times 0.4 + 120 \times 0.6 = 32 + 72 = 104$ mm

Pressure observed = 100 mm

Since observed pressure is less than the expected value from Raoult's law such a solution will show negative deviations from Raoult's law.

85. (*a*) $\dfrac{\Delta p}{P^\circ} = \dfrac{4}{4 + 55.5} = \dfrac{1}{59.5} = 0.067.$

86. (*b*) $(NH_4)_2SO_4 + Ba(OH)_2 \longrightarrow 2NH_3(aq) + 2H_2O + BaSO_4.$

87. (*c*) Normality of each of the solution is given below :

(*i*) 8/56 = 0.142 N (*ii*) 1 N

(*iii*) $\dfrac{6 \times 1000}{40 \times 100} = 1.5$ N (*iv*) $0.5 \times 2 = 1$ N.

88. (*b*) $M_{(resulting)} = \dfrac{25 \times \frac{1}{2} + 75 \times \frac{1}{5}}{100} = 0.275$ M.

89. (*d*) Molarity of mixture of 6 M and 3 M HCl

$$= \frac{350 \times 6 + 650 \times 3}{1000} = 4.05 \text{ M}$$

Now, apply dilution formula

$$M_1V_1 = M_2V_2 \quad \text{or} \quad V_2 = \frac{4.05 \times 1000}{3} = 1350 \text{ ml}$$

Volume of water to be added = 1350 – 1000 = 350 ml.

90. (*c*) Azeotropic solutions keeps on distilling at constant composition and cannot be separated into constituents liquids by simple distillation.

91. (*c*) $\alpha = \dfrac{i-1}{\dfrac{1}{m}-1} = \dfrac{i-1}{\dfrac{1}{2}-1}$

$\dfrac{\alpha}{2} = 1 - i$ or $i = 1 - \dfrac{\alpha}{2}$.

92. (*a*) Assuming complete dissociation of particles the solute particles concentration is as

0.001 M $MgCl_2$ = 0.003 M

0.001 M NaCl = 0.002 M

0.001 M urea = 0.001 M

0.01 M NaCl = 0.01 M

Thus correct increasing order of boiling points is 0.001 M urea < 0.001 NaCl < 0.001 $MgCl_2$ < 0.01 M NaCl.

93. (*c*) $\alpha = \dfrac{(1-i)}{\left(1-\dfrac{1}{m}\right)}$ $\alpha = 2(1-i) = 2(1-0.52) = \mathbf{0.96}$.

94. (*b*) For the application of Raoult's law, the solution should be dilute and the solute should not undergo any association or dissociation.

95. (*c*) The relative lowering of vapour pressure will be least for glucose. The other solutes being ionic will ionise to increase particle concentration in solution.

97. (*a*) This is as per statement of Raoult's law.

98. (*b*) Such a solution may exhibit positive or negative deviations depending upon the nature of A and B.

99. (*c*) Factual question.

100. (*c*) In cyclohexanol-ethanol the solute-solvent interactions will be weaker than solute-solute and solvent-solvent interactions.

QUESTION BANK (Level II)

1. (*c*) $\Delta T_b = i\, k_b \times m = 2 \times 0.53 \times 1 = 1.06$

Freezing point = 0 − 1.06 = − 1.06° C.

2. (*b*) Solution B having greater vapour pressure would have lower concentration of solute.

3. (*c*) $\dfrac{4.5}{180} = \dfrac{x}{60} \Rightarrow x = 1.5\%$.

4. (*d*) $\dfrac{3}{180} = \dfrac{1}{M} \quad \therefore \; M = 60$.

5. (*d*) Molarity and normality depend upon volume of the solution. Volume of the solution changes with change in temperature.

6. (*d*) Factual question.

7. (*a*) Like urea, glucose and sucrose are also molecular solutes which do not undergo association or dissociation in solution and hence produce same no. of particles in the solution.

8. (*c*) $\pi = CRT$.

9. (*a*) Factual question.

10. (*a*) (*a*) Normality may be equal to or greater than molarity.

(*b*) Normality of a solution decreases with increase in temperature.

11. (*a*) Sodium chloride and sodium sulphate are ionic compounds. They dissociate in solution producing more no. of particles.

13. (*c*) Mole fraction of solvent = 1 − 0.2 = 0.8

Moles of solvent = 0.8 × 5 = 4.

14. (*a*) N × Eq. mass = M × Mol. mass

$$\text{Normality} = \frac{M \times \text{Mol. mass}}{\text{Eq. mass}} = \frac{2.3 \times 98}{49} = 4.6 \text{ N}.$$

15. (*c*) Molality $= \dfrac{0.1}{200} \times 1000 = 0.5$

$\Delta T_b = k_b \times m = 0.513 \times 0.5 = 0.2565$

$T_b = (100 + 0.256)$.

16. (*b*) Electrolytes dissociate in solution producing higher conc. of particles and hence produce higher colligative effect.

19. (*b*) No. of equivalents of NaOH = N × V

$$= \frac{0.1 \times 250}{1000}$$

$$\text{Mass of NaOH} = \frac{0.1 \times 250 \times 40}{1000} = 1 \text{ g}.$$

20. (*c*) 1% solution of NaCl has maximum concentration of particles in the solution.

22. (*a*) Since both are non-electrolytes and have same molar conc., both solutions would have same osmotic pressure.

23. (*d*) Strength of solution is 10% or 100 g/litre.

The volume of solution containing 180 g of the solute

$$= \frac{1000}{100} \times 180 = 1800 \text{ ml or } 1.8 \text{ L}$$

24. (*c*) ppm (fluoride) $= \dfrac{0.2}{500} \times 10^6 = 400$.

25. (*a*) Eq. mass of the acid $= \dfrac{200}{2} = 100$

1000 ml of 0.1 N solution contains $= \dfrac{100}{10}$ or 10 g solute

100 ml of 0.1 N solution contain $= \dfrac{10 \times 100}{1000} = 1$ g.

26. (*a*) $$\frac{\Delta P}{P_A^{\circ}} = X_B$$

$$\frac{15}{3000} = \frac{5 \times 18}{M \times 100} \quad \text{or} \quad M = \frac{5 \times 18 \times 3000}{15 \times 100} = 180.$$

27. (*c*) Osmotic pressure, being a colligative property increases with increase in no. of solute molecules.

28. (*c*) Acetic acid dimerises in benzene.

29. (*a*) $N_1V_1 + N_2V_2 = N_3V_3$

$$0.5 \times 0.5 + 0.1 \times 1.5 = 0.2 \times 2$$

$$0.25 + 0.15 = 0.4.$$

30. (*b*) Molarity depends on volume of the solution and volume of solution increases with increase in temperature and hence molarity decreases.

31. (*b*) Factual question.

32. (*d*) Moles of urea $= \frac{1}{60}$; Moles of glucose $= \frac{3}{180} = \frac{1}{60}$

Since, both the solutions have same molar concentration they would have nearly equal boiling points.

33. (*b*) $[NO_3^-] = [AgNO_3]$

After mixing, $[AgNO_3] = \frac{0.1}{2} = 0.05.$

34. (*a*) 2 M solution contains (2×32) g of CH_3OH per litre.

Mass of CH_3OH in 150 ml solution $= \frac{64}{1000} \times 150 = 9.6$ g.

35. (*a*) Among the given solutions 0.1 M $CaCl_2$ would contain maximum no. of particles. $CaCl_2$ gives three mole ions per mole.

36. (*a*) $K_4[Fe(CN)_6]$ and $Al_2(SO_4)_3$ both give 5 mole ions per mole of the compound.

37. (*d*) Mass of solute per 1000 g of solvent

$$= \frac{6.8}{100} \times 1000 = 68 \text{ g}$$

$$\text{Molality} = \frac{68}{M}$$

$$\Delta T_f = k_f \times m = 1.86 \times \frac{68}{M}$$

$$0.93 = \frac{1.86 \times 68}{M}$$

$$M = 136.$$

38. (*c*) Moles of solute per litre $= \frac{0.01}{500} \times 1000 = 0.02.$

39. (*b*) Moles of NaCl $= \frac{5.85}{58.5} = 0.1$

Volume of solution = 0.5 L

$$\text{Molarity} = \frac{\text{moles of solute}}{\text{Volume of solution}} = \frac{0.1}{0.5} = 0.2 \text{ M}.$$

40. (*b*) Factual question.

41. (*d*) Moles of NaCl $= \frac{5.85}{58.5} = 0.1$; Moles of water $= \frac{90}{18} = 5$

Mole fraction of NaCl $= \frac{0.1}{5 + 0.1} = 0.0196.$

42. (*b*)

$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} \cdot 2H_2O, \text{ Mol. mass} = 126$$

$$\text{Eq. mass} = \frac{\text{Mol. mass}}{\text{Basicity}} = \frac{126}{2}.$$

43. (*a*) Strength per litre = 40 g/litre

$$\text{Normality} = \frac{40 \text{ g/litre}}{40 \text{ g/eq}} = 1 \text{ N}.$$

44. (*b*) Strength per litre = 50 g/litre

$$\text{Molarity, } C = \frac{50}{342}$$

$$\pi = CRT = \frac{50}{342} \times 0.082 \times 423 = 5.07 \text{ atm}.$$

45. (*b*) Strength per litre = 71 g/litre, mol. mass of Na_2SO_4

= 142

$$\text{Molarity} = \frac{71}{142} = 0.5 \text{ M}.$$

46. (*b*) $2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O$

$$\frac{M_1V_1}{M_2V_2} = \frac{n_1}{n_2}$$

$$\frac{0.2 \times 40}{0.1 \times V} = \frac{2}{1}$$

$$V = 40 \text{ ml}.$$

47. (*b*) At boiling point vapour pressure of the liquid is equal to the atmospheric pressure. Conversely, the temperature at which vapour pressure becomes equal to the atmospheric pressure is the boiling point of the liquid.

50. (*a*) Conc. of urea $= \frac{12}{60} = 0.2$ M

Conc. of sucrose $= \frac{68.4}{342} = 0.2$ M.

51. (*a*) $\underset{(2 \times 34)\text{ g}}{2H_2O_2} \longrightarrow 2H_2O + \underset{22.4 \text{ L at N.T.P.}}{O_2}$

Strength per litre of 10 'volume' $H_2O_2 = \frac{68}{22.4} \times 10$

= 30.4 g/litre

$$\text{Normality} = \frac{\text{Strength per litre}}{\text{Eq. mass}} = \frac{30.4}{17} = 1.7 \text{ N}.$$

54. (*b*) In case of H_2SO_4 molar concentration is half of normality whereas in case of HCl, molar concentration is equal to normality

2N HCl = 2M HCl

4N H_2SO_4 = 2 M H_2SO_4.

55. (*a*) Mass of solvent = $V \times d = 100 \times 1.58 = 158$ g

Moles of solvent = $\frac{158}{154}$; Moles of solute = $\frac{0.5}{65}$

Mole fraction of solute = $\frac{0.5/65}{158/154} = 7.5 \times 10^{-3}$

$$\Delta P = P_A{}^{\circ}X_B$$

$$P_A = P_A{}^{\circ} - P_A{}^{\circ}X_B = 143 - 143 \times 7.5 \times 10^{-3}$$

$$= 143 - 1.07 = 141.93 \text{ mm.}$$

56. (*c*) Molarity = $\frac{10 \times d \times P}{\text{Mol. mass}}$

$$= \frac{10 \times 1.84 \times 98}{98} = 18.4 \text{ M.}$$

57. (*c*) Molar concentration would be inversely proportional to the molecular mass.

$$\pi = CRT$$

Urea having highest conc. would have highest osmotic pressure whereas sucrose would have least.

58. (*d*) $P_A = P_A{}^{\circ} X_A$

$$60 = P_A{}^{\circ}\left(\frac{0.8}{0.8 + 0.2}\right) = P_A{}^{\circ} = \frac{60}{0.8} = 75 \text{ mm.}$$

59. (*d*) 0.1 M $BaCl_2$ would give 0.3 mole particles per litre on dissociation which is maximum among the given choices.

60. (*c*) $Ca(NO_3)_2 \longrightarrow Ca^{2+} + 2NO_3^-$.

61. (*c*) Depression in freezing point (ΔT_f) would be maximum in case of 1% KCl as it contains maximum no. of particles in a given volume of solution.

63. (*b*) $Al_2(SO_4)_3$ gives maximum no. of particles on dissociation and ΔT_f would be maximum in this case.

64. (*c*) $\Delta T_f = k_f \times m = 1.86 \times 0.05 = 0.093°C$

Freezing point = $0 - 0.093 = -0.093°C$.

65. (*d*) $\Delta T_f = k_f \times m$; $\Delta T_b = k_b \times m$

$$\therefore \quad \frac{\Delta T_b}{\Delta T_f} = \frac{k_b}{k_f}$$

$$\Delta T_b = \Delta T_f \times \frac{k_b}{k_f} = \frac{0.186 \times 0.512}{1.86} = 0.0512°.$$

66. (*b*) Factual question.

67. (*c*) 0.1 M $BaCl_2$ would give maximum no. of particles in solution and hence elevation in boiling point would be maximum in this case.

68. (*c*) Mass of solute per 1000 g of water = $\frac{18}{500} \times 1000 = 36$ g

$$\text{Molality} = \frac{36}{180} = 0.2 \text{ m.}$$

69. (*a*) $\pi = CRT = 0.05 \times 0.082 \times 288 = 1.14$ atm.

[**Note.** In case of sucrose 0.05 N = 0.05 M]

70. (*b*) Molarity = $\frac{10 \times d \times p}{\text{Mol. mass}} = \frac{10 \times 1.1 \times 20}{162} = 1.36$ M.

71. (*b*) $P_{Total} = 2.619 + 4.556 = 7.175$ kPa

$$X_{MeOH} = \frac{P_{MeOH}}{P_{Total}} = \frac{2.619}{7.175} = 0.365$$

$$X_{EtOH} = 1 - 0.365 = 0.635.$$

72. (*b*) $\frac{5}{342} = \frac{1}{M}$; $M = \frac{342}{5} = 68.4$.

73. (*c*) $\frac{\Delta P}{P_A{}^{\circ}} = X_B$; $\frac{10}{P_A{}^{\circ}} = 0.2$;

$$\frac{20}{P_A{}^{\circ}} = X_B ; \quad \frac{20}{10} = \frac{X_B}{0.2} \quad \Rightarrow X_B = 0.4.$$

74. (*a*) $\Delta T_f = k_f \times m$

$$1.1 = 1.86 \times \frac{1.25 \times 1000}{M \times 20}$$

$$M = \frac{1.86 \times 1.25 \times 1000}{1.1 \times 20} = 105.7.$$

75. (*d*) 0.5 M HCl = 0.5 N HCl ; 0.2 M HNO_3 = 0.2 N HNO_3

0.3 M H_2SO_4 = 0.6 N H_2SO_4

$$N_1V_1 + N_2V_2 + N_3V_3 = N_4V_4$$

$$0.5 \times 6 + 0.6 \times 15 + 0.2 \times 15 = N_4 \times 36$$

$$N_4 = \frac{15}{36} = 0.42.$$

76. (*a*) Milliequivalents of acid = $NV = 0.1 \times 100 = 10$

Millimoles of acid = 5 ($\because$ Mol. mass = 2 Eq. mass)

Mass of acid = $5 \times 10^{-3} \times 200 = 1$ g.

77. (*d*) $\Delta T_b = k_b \times m$

$$0.216 = 2.16 \times \frac{0.15 \times 1000}{M \times 15} \Rightarrow M = 100.$$

78. (*d*) Mole fraction of solute = $\frac{x_2}{(x_1 + x_2)}$

$$p = p^{\circ} \times \text{mole fraction of solute.}$$

79. (*a*) ΔS_{mix} is always positive.

80. (*a*) The interparticle forces between solute and solvent molecules are weaker than solute-solute and solvent-solvent interactions.

81. (*d*) Normality = $\frac{\text{Molarity} \times \text{Mol. mass}}{\text{Eq. mass}} = \frac{0.1 \times 98}{49} = 0.2$ N.

82. (*a*) K_b is independent of the nature of solute.

83. (*b*) $M = \frac{1.86 \times 1000}{0.124 \times 250} = 60$.

84. (*a*) The particle concentration will be highest in decimolar $Al_2(SO_4)_3$. In (*d*) $BaSO_4$ will be precipitated as

$$BaCl_2 + Na_2SO_4 \longrightarrow BaSO_4 + 2Na^+ + 2Cl^-.$$

85. (*c*) 4 g of NaOH = 4/40 = 0.1 mol dissolved in 1 kg of water. Thus, molality of solution is 0.1 m.

86. (*b*) Degree of dissociation of acetic acid is not given, hence answer is unpredictable.

87. (*d*) This is as per statement of cryoscopic constant.

88. (*c*) $BaCl_2$ ionises to give Ba^{2+} and $2Cl^-$, NaCl ionises to give Na^+ and Cl^-. Thus, particle concentration of $BaCl_2$ solution is 3 times that of glucose and particle concentration of NaCl is twice that of glucose. Hence $\pi_1 > \pi_3 > \pi_2$.

89. (*c*) Let vapour pressure of B be p_B

$\therefore\ 84 = 70 \times 0.8 + p_B \times 0.2 \quad \therefore\ p_B = 140$ mm.

90. (*a*) $\alpha = \frac{i-1}{1/m-1}$ or $0.3 = \frac{i-1}{1/4-1}$ $\therefore\ i = 0.775$.

91. (*a*) $x_B = \frac{2.5}{2.5+55.5} = 0.043$.

92. (*c*) Strength in ppm $= \frac{0.02}{50} \times 10^6 = 400$.

93. (*c*) H_2O and $HClO_4$ show negative deviation. Hence they form maximum boiling azeotrope.

$\therefore$ Boiling point will be greater than either of them.

94. (*c*) 3.01×10^{23} molecules $= \frac{3.01 \times 10^{23}}{6.02 \times 10^{23}} = 0.5$ mole

$\therefore\ \Delta T_f = 1.86 \times \frac{0.5 \times 100}{250} = 3.72$

$\therefore\ T_f = 273 - 3.72 = 269.28$ K.

95. (*a*) $\frac{\Delta p}{p^\circ} = x_2 = \frac{6/60}{6/60 + 90/18} = 0.0196$.

96. (*c*) 6% solution of glucose has molality

$$= \frac{6}{94} \times \frac{1000}{60} \approx 1.06 \text{ m}$$

Thus, it is isotonic with approx. 1 m solution of glucose.

97. (*b*) $\frac{\Delta P}{P^\circ}$ = Mole fraction of solute $= \frac{1}{1+3} = \frac{1}{4}$.

98. (*d*) $P_A = P_A^\circ X_A$

$40 = P_A^\circ \times 0.8$ or $P_A^\circ = 50$ mm.

99. (*c*) 0.1 M $Al_2(SO_4)_3$ would produce maximum conc. of ions in solution.

100. (*c*) Freezing point of solution is less than that of pure solvent.

101. (*a*) van't Hoff factor, $i = \frac{114.45}{65.4} = 1.75$

$$\alpha = \frac{i-1}{m-1} = \frac{1.75-1}{1} = 0.75$$

or $0.75 \times 100 = 75\%$.

102. (*c*) The shrinking is due to osmosis of fluid from the egg to the concentrated sodium chloride solution.

103. (*a*) Millimoles of KOH in 100 ml of 0.3 M solution

$= 0.3 \times 100 = 30$

Millimoles of KOH in 100 ml of 0.4 M solution

$= 0.4 \times 100 = 40$

Thus, 10 millimoles i.e., $10 \times 10^{-3} \times 58.5$ g = 0.585 g of NaCl has to be added to the solution.

105. (*c*) $x = \frac{i-1}{1/m-1}$ or $x = \frac{i-1}{1/2-1}$ or $i - 1 = x(0.5-1)$

or $i = 1 + x(-0.5) = (1 - 0.5x)$.

106. (*a*) Isopeistic solutions have same vapour pressure at particular temperature.

107. (*b*) $\frac{92.5 - P}{92.5} = \frac{1 \times 18}{1000}$

or $92.5 - P = \frac{92.5 \times 18 \times 1}{1000} = 1.665$

or $P = 92.5 - 1.665 = 90.8$ atm.

108. (*b*) $\pi_A = 0.01 \times 0.082 \times 300 = 0.2463$ atm ;

$\pi_B = 0.001 \times 0.082 \times 300 = 0.02463$ atm

The movement of solvent particles will occur from dilute solution (B) to A. Hence, the pressure of 10.2463 – 0.02463 = 0.2216 atm. should be applied on concentrated solution *i.e.*, solution A.

109. (*a*) It is due to dissociation of KCl into α particles K^+ and Cl^-.

110. (*d*) $M_B = \frac{k_f W_B \times 1000}{\Delta T_f \times W_A} = \frac{2.34 \times 28 \times 1000}{1.68 \times 315} = 123.80$

Atomicity of phosphorus $= \frac{123.80}{31} \approx 4$.

Hence formula is P_4.

111. (*a*) On cooling the dilute solution, the solvent will start crystallising. Hence, ice will separate first.

112. (*d*) $\pi_1 = C_1RT$; $\pi_2 = C_2RT$;

$\frac{\pi_1}{\pi_2} = \frac{C_1}{C_2}$ or $\frac{C_1}{C_2} = \frac{405}{81} = 5$ or $C_1 = 5C_2$.

Thus, C_1 should be 5 times the C_1. Hence, the solution has to diluted **5 times.**

113. (*c*) $\frac{\Delta P}{P} = \frac{W_B M_A}{M_B W_A}$ or $\frac{P - 4/5P}{P} = \frac{W_B \times 18}{75 \times 180}$

or $W_B = 150$ g.

5 CHEMICAL ENERGETICS AND THERMODYNAMICS

Important Terms, Facts and Formulae

THERMODYNAMICS

It is the *branch of science which deals with the quantitative relationship between heat and other forms of energies*. Thermodynamics does help us to predict the *feasibility of a chemical process* and also the *extent to which it occurs underparticular set of conditions*. However, thermodynamics cannot help us to know the speed or mechanism of the chemical process. Thermodynamics is primarily based on three fundamental laws.

Ist Law of Thermodynamics

Deals with equivalence of different forms of energies.

2nd Law of Thermodynamics

Deals with direction of the chemical change.

3rd Law of Thermodynamics

Deals with evaluation of entropy.

SOME IMPORTANT TERMS

- **System.** It is the part of universe selected for experimentation.
- **Surroundings.** The part of universe other than the system is referred to as **surroundings.**
- Surroundings and system are separated by real or imaginary boundaries.

  Types of System

  System capable of exchanging mass as well as energy with surrondings is called *open system*.

  System which can exchange energy but not mass with surroundings is called *closed system*.

  System which can neither exchange mass nor energy with surroundings is called *isolated system*.
- **Extensive Properties.** Properties of the system which depend upon the quantity of matter contained in it. Examples are : *mass, volume, energy, heat-capacity, enthalpy entropy free energy,* etc.
- **Intensive Properties.** Properties of the system which are independent of the quantity of matter contained in it. Examples are : *pressure, temperature, density, specific heat, viscosity, surface tension* etc.
- **State of System.** The conditions of existence of the system when its macroscopic properties have definite values refer to the *state of the system*.
- **State functions.** The thermodynamic parameters which depend on the initial and final state of the system but independent of the path are called *state functions.*
- **Thermodynamic process.** The operation which brings about the change in the state of the system. Various thermodynamic process are :

  (*i*) **Isothermal process.** The process occuring at constant temperature ($\Delta T = 0, \Delta E = 0$).

  (*ii*) **Isochoric process :** The process occuring at constant volume ($\Delta V = 0$).

  (*iii*) **Isobaric process.** The process occuring at constant pressure ($\Delta P = 0$).

  (*iv*) **Adiabatic process.** The process in which no heat enters or leaves the system ($\delta q = 0$).
- **Cyclic process.** A process in which, the system after undergoing a series of changes returns to the original state. $\Delta E_{cycle} = 0$; $\Delta H_{cycle} = 0$.
- **Reversible process.** A process that follows the reversible path, *i.e.,* a process occuring in infinite number of steps maintaining equilibrium conditions at each step. In a process following the reversible path, the opposing force is infinitessimally smaller than the driving force.
- **Irreversible process.** A process in which the changes are produced rapidly so that system no longer remains in equilibrium conditions. All, natural processes are irreversible.

MODES OF TRANSFERENCE OF ENERGY

Various modes of transference of energy between system and surroundings are :

(*i*) **Heat (q).** This mode of transference occurs if there is a difference of temperature between system and surroundings.

- It is a random form of energy.
- It is path dependent parameter.

- Units are **Joules** or **calories.**

  (*ii*) **Work (W).** This mode of transference of energy is possible, if the system involves gaseous substances and there is a difference of pressure between system and surroundings. Such a work is referred to as *pressure-volume work* (W_{PV}).
- **IUPAC conventions about heat and work**

  q = **+ ve** *if added to system* ;
  w = **+ ve** *if done on system*
  q = **– ve** *if given out by system* ;
  w = **– ve** *if done by system.*
- **Expression for pressure volume work**

  (*i*) *Work of irreversible expansion against constant pressure P under isothermal conditions*

  $$W_{PV} = -P\,\Delta V$$

  (*ii*) *Work of reversible expansion under isothermal conditions*

  $$W = -2.303\ nRT \log V_2/V_1$$

  or $$W = -2.303\ nRT \log P_1/P_2.$$
- Work done under reversible conditions is maximum work.
- **Units of work** : **ergs** in CGS system and **Joules** in SI system.

  ($1\ J = 10^{-7}$ ergs $= 1\ Nm = 1\ Kg\ m^2\ s^{-2}$).

INTERNAL ENERGY (E)

The energy associated with the substance under particular set of conditions.

- E is extensive property and state function.
- The absolute value cannot be determined.
- The change in internal energy (ΔE) can be experimentally determined and is given by the relation.

$$\boxed{\Delta E = E_2 - E_1 \quad \text{or} \quad \Sigma E_{(P)} - \Sigma E_R}$$

- For one mol of ideal gas $E = \frac{3}{2}RT$.
- For **exothermic reaction** **ΔE = – ve.**
- For **endothermic reactions** **ΔE = + ve.**
- ΔE represents the heat change taking place during the process occuring at constant temperature and constant volume.

FIRST LAW OF THERMODYNAMICS

- Energy can neither be created nor destroyed although it can be converted from one form to the other.

  Or
- Total energy of the universe is conserved during any physical or chemical process.
- Mathematically, it can be given by relation. **ΔE = q + W,** where ΔE is internal energy change, q is heat added to system and W is work added to system.
- For system performing only PV-work, the expression can be written as

$$\boxed{\Delta E = q - P\,\Delta V}$$

ENTHAPY (H)

It is the sum of internal energy and PV-energy of the system.

- It is also an extensive property and state function.
- It is mathematically given by the relation

$$\boxed{H = E + PV}$$

- Like E, absolute value of H also cannot be known. However ΔH can be determined experimentally.

$$\boxed{\Delta H = H_2 - H_1 \quad \text{or} \quad \Sigma H_P - \Sigma H_R}$$

- Enthalpy of one mole of ideal gas is $\frac{5}{2}RT$.
- For **exothermic reaction,** **ΔH = – ve.**
- For **endothermic reactions,** **ΔH = + ve.**
- ΔH represents the heat change taking place during the process occuring at constant temperature and constant pressure.

RELATIONSHIP BETWEEN ΔH and ΔE

ΔH and ΔE of a reaction are related as

$$\boxed{\Delta H = \Delta E + \Delta P\,\Delta V}$$

$$\boxed{\Delta H = \Delta E + \Delta n_{(g)}\,RT}$$

Here, $\Delta n_{(g)}$ = change in the number of gas moles.

ENTHALPY OR HEAT OF REACTION (ΔH)

It is the enthalpy change taking place during the reaction when the molar quantities of reactants consumed and those of the products formed are in accordance with the balanced chemical equation.

- Enthalpy of reaction varies with temperature according to KIRCHOFF'S equation given below :

$$\boxed{(\Delta H_2 - \Delta H_1) = (T_2 - T_1)\,[Cp_{(products)} - Cp_{(reactants)}]}$$

- Enthalpy of reaction expressed at the standard state conditions is called standard enthalpy of reaction (ΔH°).

VARIOUS FORMS OF ENTHALPY OF REACTION

1. **Enthalpy of formation.** It is the heat change taking place when one mole of a compound is obtained from its constituent elements. It is denoted as ΔH_f.

- Heat of formation expressed at the standard state conditions is called standard heat of formation (ΔH°_f), or simply standard enthalpy of compound denoted as H°.
- Standard enthalpy of free elements is taken to be zero.
- The value of ΔH°_f of the compound gives the idea of its chemical stability.

2. **Enthalpy of combustion.** It is the heat change taking place when one mole of a compound undergoes complete combustion in the atmosphere of oxygen.

- $\Delta H_{\text{comb.}}$ is always – ve because combustion processes are exothermic.
- Calorific value of fuel or food = $\dfrac{\Delta H_{\text{comb.}}}{\text{GMM}}$.

3. **Enthalpy of dissolution.** It is the heat change taking place when one mole of the substance is dissolved in large excess of solvent so that on further dilution no appreciable heat change occur.
4. **Enthalpy of hydration.** It is the heat change occuring when one mole of anhydrous substance undergoes complete hydration (*i.e.*, combine with the required number of water molecules to form hydrated salt in solid state).

- Hydration is exothermic process because it involves the bonding between the water molecules and central metal ion.

5. **Enthalpy of fusion.** It is the heat required to change one mole of the solid substance completely into liquid at the melting point.
6. **Enthalpy of vaporisation.** It is the heat required to change one mole of the liquid substance completely into vapours at the boiling point.

- **Troutons's rule.** It states that ratio of enthalpy of vaporisation of a liquid to its normal boiling point is approximately equal to 88 J $\text{mol}^{-1}\,\text{K}^{-1}$.

$$\boxed{\Delta H_{\text{vap}}/T_b \approx 88 \text{ J mol}^{-1}\text{ K}^{-1}}$$

7. **Enthalpy of neutralisation.** It is the heat change taking place when 1 gm-equivalent of an acid (or base is neutralised by 1 gm-equivalent of a base (or acid) in dilute solutions.

- *It may be remembered that heat of neutralisation of* **strong acid-strong base** *is always constant*
  i.e., $\Delta H = 57.1$ kJ. For example,
  $HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$; $\Delta H = -57.1$ kJ
- *Heat of neutralisation of* **strong acid-weak base** *or* **weak acid-strong base** *is not constant and numerically less than 57.1 kJ. This is because some heat is required to dissociate weak acid/or base completely into ions. This is called heat of ionisation of* **weak acid/or base.**

8. **Enthalpy of hydrogenation.** It is the enthalpy change occuring when 1 mole of an unsaturated organic compound is fully hydrogenated.

$$H_2C = CH_2(g) + H_2(g) \longrightarrow CH_3 - CH_3 \text{ ; } \Delta H = -x \text{ kJ}$$

9. **Enthalpy of transition.** It is a heat change occuring when one mole of the substance undergoes transition from one allotropic form to another. For example,

$$S(r) \longrightarrow S(m) \text{ ; } \Delta H = +2.5 \text{ kJ.}$$

LAWS OF THERMOCHEMISTRY

- **Lavoisier Laplace Law.** The enthalpy change taking place during the reaction is equal in magnitude but opposite in sign to the enthalpy change occuring in the reverse process.
- **Hess's law of constant heat summation.** It states that the enthalpy change taking during the process depends only on the initial and final states and is independent of the path by which the process is carried out.
- Hess's law helps us to :

  Calculate the enthalpies of many of the reactions which are practically not possible, such as *enthalpy of formation, enthalpy of transition, enthalpy of hydration, etc.*

BOND ENTHALPIES

- **Bond dissociation energy.** It is energy required to break the particular bond in a gaseous molecule. It is a definite quantity and is expressed in kJ mol^{-1}.
- In diatomic molecule, the term bond dissociation energy is same as **Bond Energy**.
- In polyatomic molecule, having more than one similar bonds, the term bond dissociation energy is not the same as bond energy.
- In fact bond energy, is average amount of energy required to break one mole of bonds of that type in gaseous molecule.
- ΔH of the reaction can be calculated from the knowledge of bond energies of reactants and products as

ΔH° = [Sum of bond energies of reactants] – [Sum of bond energies of products]

ENTROPY

It is the thermodynamics property which provides a measure of degree of disorder in the system. It is denoted by **S.**

- It is a *state function, extensive property*.
- It has unit, JK^{-1}.
- The change in entropy during the process is mathematically given by the ratio of heat absorbed by the system (q) in the reversible manner to the temperature (T) at which it is absorbed.

$$\Delta S = (S_2 - S_1) = q_{rev}/T$$

As evident, if $\Delta S > 0$, the process involves increase in randomness.

if $\Delta S < 0$, the process involves decrease in randomness.

- *Expressions of Entropy change during phase transitions*

Evaporation of liquid ;

$$\Delta S_{vap} = \Delta H_{vap}/T_b \text{ ; } T_b \text{ is boiling point}$$

Fusion of solid ;

$$\Delta S_{fusion} = \Delta H_{fusion} / T_f \text{ ; } T_f \text{ is freezing point.}$$

SPONTANEOUS PROCESS

The physical or chemical process which occurs in a particular direction under given set of conditions either of its own or after proper initiation, is called spontaneous process.

- All natural processes are spontaneous processes.
- Spontaneous process cannot reverse of their own under given set of conditions.

ENTROPY CRITERION OF SPONTANEITY

Any process, physical or chemical occuring in this universe will be spontaneous only if it involves increase in the entropy of the universe. For a process to be spontaneous

$$\boxed{\Delta S_{universe} > 0 \quad \text{or} \quad \Delta S_{syst.} + \Delta S_{surr.} > 0}$$

If, $\Delta S_{Total} = 0$; it refers to *equilibrium state*.

- **Limitation of ΔS Criterion.** During chemical changes, the entropy change of system can be easily known but, entropy changes of surroundings can not be easily known. Hence we require some thermodynamic parameter which should be able to provide criterion of spontaneity by studying its changes for system only. One such parameter is free energy (G) of system.

SECOND LAW OF THERMODYNAMICS

It states that *entropy of the universe always increases in the course of every spontaneous (natural) change.*

Or

The other statements of the 2nd law are :

- *The spontaneous flow of heat from a body at higher temperature to a body a lower temperature is accompanied by increase of entropy.*

Or

- *It is impossible for a cyclic process to transfer heat from a system at lower temperature to the one at higher temperature without applying some work.*

FREE ENERGY (G)

The energy freely available from the system at particular set of conditions which can be put into useful work is called *free energy*. Out of the total energy associated with system (H), a part of it is a random energy (TS) which is non-convertible into work. Thus, mathematically, free energy is given by the relation,

$$G = H - TS$$

Free energy is *state function, extensive property* and has units **J mole^{-1}** or **kJ mol^{-1}**.

- Change in free energy during the process is given by *Gibb's Helmholtz equation* as

$$\boxed{\Delta G = G_2 - G_1 = \Delta H - T\Delta S}$$

- Free energy change of the system is related to ΔS_{Total} as

$$\boxed{\Delta G_{syst.} = -T\,\Delta S_{Total}}$$

- Free energy change of the system at particular conditions represents the useful work obtainable from the system other than PV work.

$$-\Delta G_{T,P.} = -W_{net}.$$

CRITERION OF SPONTANIETY

The free energy criterion of spontaneity can be summed as follows :

$\Delta G_{T,P} < 0$	the process is spontaneous
$\Delta G_{T,P} = 0$	the process is in equilibrium state
$\Delta G_{T,P} > 0$	the process in non-spontaneous.

STANDARD FREE ENERGY OF FORMATION ($\Delta G°_f$)

The free energy change taking place during the formation of one mole of the compound from its constituting elements at the standard state.

- $\Delta G°_f$ of free elements at their standard state is taken to be zero.
- Standard free energy change ($\Delta G°$) is related to the standard free energies of reactants and products as

$$\boxed{\Delta G° = \Sigma\, \Delta G°_f\,(\text{Products}) - \Sigma\, \Delta G°_f\,(\text{Reactants})}$$

- $\Delta G°$ is related to $\Delta H°$ and $\Delta S°$ of reaction as

$$\boxed{\Delta G° = \Delta H° - T\,\Delta S°}$$

- $\Delta G°$ is also related to the equilibrium constant (K) as

$$\Delta G° = -\,2.303\ RT \log K.$$

THIRD LAW OF THERMODYNAMICS

The entropy of a substance at absolute zero (zero kelvin) is taken to be zero.

The importance of law lies in calculating absolute entropies of pure substances at different temperatures. This is possible by knowing the values of heat capacities (C_p) at number of temperatures between 0 K and T K.

$$\Delta S = \int_0^T C_p\, d \ln T = 2.303 \int_0^T C_p\, d \log T.$$

The plot C_p vs log T gives the value of integral.

- It should be noted that this law is true only for the substances which exist in perfect crystalline form at 0 K. However, if there are imperfections at 0 K, then entropy will be larger than zero.
- Glassy solids even at 0 K has entropy greater than zero.
- Solids having mixtures of isotopes do not have zero entropy at 0 K. For example, entropy of solid chlorine is not zero at 0 K.
- Crystals of CO, N_2O, NO, H_2O, etc. do not have perfect order even at 0 K thus their entropy is not equal to zero.

QUESTION BANK

Level I

Choose the correct answer from the four alternatives given in each of the following questions :

1. Carbon forms two oxides on combustion. Carbon (II) oxide and carbon (IV) oxide having values of their standard enthalpy of formation as -393.5 and -281.50 kJ mol^{-1} respectively. The value of $\Delta H_{combustion}$ of C will be

(*a*) -393.5 kJ mol^{-1} (*b*) 112.0 kJ mol

(*c*) -678.6 kJ mol^{-1} (*d*) -112.0 kJ mol.

2. The value of ΔS is negative for the process

(*a*) Burning of rocket fuel (*b*) Dissolution of sugar

(*c*) Sublimation of iodine (*d*) Freezing of water.

3. In the relation ; H—TS = G, TS refers to

(*a*) Helmholtz free energy (*b*) random energy

(*c*) organised energy (*d*) Gibb's free energy.

4. The solubility product of AgCl is 1.6×10^{-10} and log K_{sp} is -9.80. The value of $\Delta G°$ for the process,

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

(*a*) -55.9 kJ (*b*) $+55.9$ kJ

(*c*) $+100.8$ kJ (*d*) -100.8 kJ.

5. Certain endothermic reaction $X + Y \longrightarrow W + Z$ is spontaneous in the forward direction. The corresponding signs of ΔG and ΔS should be respectively

(*a*) + ve and – ve (*b*) – ve and + ve

(*c*) + ve and + ve (*d*) – ve and – ve.

6. Combustion of hydrogen in a fuel cell at 300 K is represented as $2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$. If ΔH and ΔG are -241.60 kJ mol^{-1} and -228.40 kJ per mole of H_2O. The value of ΔS for the aforesaid process is

(*a*) 4.4 kJ (*b*) -88 J

(*c*) $+88$ J (*d*) -44 J.

7. What is not zero for elementary substances at their standard state ?

(*a*) S° (*b*) H°

(*c*) G° (*d*) Both H° and S°.

8. All the naturally occuring processes proceed spontaneously in a direction which leads to

(*a*) increase in enthalpy of system

(*b*) decrease in entropy of system

(*c*) increase in entropy of system

(*d*) increase in entropy of universe.

9. What is correct for a reversible adiabatic process ?

(*a*) $\delta W = 0$ (*b*) $\Delta T = 0$

(*c*) $\Delta P = 0$ (*d*) $\delta q = 0$.

10. A hypothetical reaction $\mathbf{X} \longrightarrow \mathbf{2Y}$ proceeds by the following sequence of steps

$$\frac{1}{2}X \longrightarrow Z ; \quad \Delta H = q_1$$
$$Z \longrightarrow 2W ; \quad \Delta H = q_2$$
$$W \longrightarrow \frac{1}{2}Y ; \quad \Delta H = q_3$$

The values of ΔH of reaction is

(*a*) $q_1 + q_2 + q_3$ (*b*) $2q_1 + 2q_2 + 3q_3$

(*c*) $2(q_1 + q_2 + 2q_3)$ (*d*) $2(q_1 + q_2 + q_3)$.

11. In thermodynamics, a quantity whose value simply depends upon the initial and final state of the system is called

(*a*) thermodynamic quantity

(*b*) state function

(*c*) adiabatic quantity

(*d*) path function.

12. Thermodynamic parameter which is a state function and is also used to measure disorder of the system is

(*a*) Entropy (*b*) Fugacity

(*c*) Viscosity (*d*) Periodicity.

13. The values of $\Delta H°_f$ of $C_2H_2(g)$ and $C_6H_6(g)$ are respectively 230 and 85 kJ mol^{-1}. The standard enthalpy change for trimerisation of acetylene to benzene is

(*a*) 205 kJ mol^{-1} of benzene

(*b*) 605 kJ mol^{-1} for benzene

(*c*) -605 kJ mol^{-1} of benzene

(*d*) -205 kJ mol^{-1} for benzene.

14. Enthalpy of combustion of a substance is always

(*a*) > 0
(*b*) ≥ 0
(*c*) ≤ 0
(*d*) < 0.

15. Which one of the following is correct according to Hess's law ?

(*a*) $H = E + PV$
(*b*) $H = G + TS$
(*c*) For a chemical process occurring by two paths $\Delta H_{(\text{Path I})} = \Delta H_{(\text{Path II})}$
(*d*) For a chemical process occurring by two paths $\Delta S_{(\text{Path I})} = \Delta S_{(\text{Path II})}$.

16. All naturally occurring processes proceed spontaneously in a direction which leads to

(*a*) increase in enthalpy of system
(*b*) decrease in entropy of system
(*c*) decrease in free energy of system
(*d*) increase in free energy of system.

17. $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l) + x$ kJ. The value of ΔH_f of water is

(*a*) x kJ mol^{-1}
(*b*) $-x$ kJ mol^{-1}
(*c*) $-x/2$ kJ mol^{-1}
(*d*) $-2x$ kJ mol^{-1}.

18. The heat change for a reaction

$$CO(g) + \frac{1}{2}O_2 \longrightarrow CO_2(g) \text{ refers to}$$

(*a*) enthalpy of formation of carbon dioxide
(*b*) enthalpy of combustion of carbon dioxide
(*c*) enthalpy of vaporisation
(*d*) enthalpy of combustion of carbon monoxide.

19. Absorption of heat occurs when

(*a*) carbon burns in air
(*b*) sulphur dioxide is oxidised to sulphur trioxide
(*c*) ammonium chloride dissolves in water
(*d*) cooking gas is burnt.

20. In reversible adiabatic expansion of ideal gas

(*a*) $w = 0$
(*b*) $\Delta E = 0$
(*c*) $\Delta V = 0$
(*d*) $\Delta S = 0$.

21. If x kJ is the heat produced by the neutralisation of 1 L of 1 N H_2SO_4 solution with 1 L of 1 N NaOH, then the amount of heat liberated by neutralising 1 L of 1 N NaOH with HCl will be

(*a*) $> x$
(*b*) $= x$
(*c*) $< x$
(*d*) unpredictable.

22. "*Enthalpy of reaction*" is the heat change accompanying the conversion of

(*a*) 1 mole of reactants into products
(*b*) 1 gm of reactants into products
(*c*) number of moles of reactants into products as are indicated by the balanced equation of the process
(*d*) 22.4 L of reactants at N.T.P. into products.

23. For an isothermal cyclic process, the net energy change

(*a*) > 0
(*b*) ≥ 0
(*c*) < 0
(*d*) $= 0$.

24. At 298 K, the enthalpy changes of cleavage of successive O—H bonds of water molecule are

$$H_2(g) \longrightarrow H(g) + OH(g)\ ;\ \Delta H = 498 \text{ kJ mol}^{-1}$$
$$OH(g) \longrightarrow H(g) + O(g)\ ;\ \Delta H = 428 \text{ kJ mol}^{-1}$$

From the above data, the value of ΔH_{O-H} bond is

(*a*) 498 kJ mol^{-1}
(*b*) 428 kJ mol^{-1}
(*c*) 463 kJ mol^{-1}
(*d*) 70 kJ mol^{-1}.

25. For a chemical process at constant temperature and pressure, ΔH is equal to

(*a*) $\frac{q}{T}$ (rev.)
(*b*) $\Delta S - T\Delta G$
(*c*) $\Delta E + P\Delta V$
(*d*) $\Delta E - P\Delta V$.

26. Internal energy of a given mass of an ideal gas depends upon

(*a*) Temperature
(*b*) Pressure
(*c*) Volume
(*d*) On all the above factors.

27. A system absorbs 20 kJ of heat and also does 10 kJ of work. The net internal energy of the system

(*a*) increases by 10 kJ
(*b*) decreases by 10 kJ
(*c*) increases by 30 kJ
(*d*) decreases by 30 kJ.

28. The values of ΔH for the process

$$I(g) + e^-(g) \longrightarrow I^-(g) \text{ is}$$

(*a*) > 0
(*b*) < 0
(*c*) ≥ 0
(*d*) ≤ 0.

29. $CuSO_4(s) + 5H_2O(l) \longrightarrow CuSO_4 \cdot 5H_2O(s)$; $\Delta H = -x$ kJ

The value of ΔH represents

(*a*) enthalpy of solution of copper (II) sulphate
(*b*) enthalpy of hydration of copper (II) sulphate
(*c*) enthalpy of hydrolysis of copper (II) sulphate
(*d*) lattice energy of copper (II) sulphate.

30. Enthalpy of neutralisation of acetic acid with KOH will be numerically

(*a*) = 57.1 kJ
(*b*) > 57.1 kJ
(*c*) < 57.1 kJ
(*d*) unpredictable.

31. The value of ΔG for the process $H_2O(s) \longrightarrow H_2O(l)$ at 1 atm and 260 K is

(*a*) < 0 (*b*) $= 0$

(*c*) > 0 (*d*) unpredictable.

32. A system X undergoes following changes

$$\begin{array}{cccc} X \longrightarrow & W \longrightarrow & Z \longrightarrow & X \\ (P_1V_1T_1) & (P_2V_2T_1) & (P_3V_2T_2) & (P_1V_1T_1) \end{array}$$

The overall process may be called

(*a*) Reversible process

(*b*) Cyclic process

(*c*) Cyclic as well as reversible

(*d*) Isochoric process.

33. $N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g) + x$ kJ

$2NO(g) + O_2(g) \longrightarrow 2NO_2(g) + y$ kJ.

The value of ΔH_f of NO(*g*) is

(*a*) $\frac{1}{2}(y - x)$ (*b*) $y - 2x$

(*c*) $x - y$ (*d*) $2(x - y)$.

34. The vaporisation process is always

(*a*) exothermic

(*b*) endothermic

(*c*) can be exothermic or endothermic

(*d*) isoentropic.

35. One mole of H_2SO_4 is completely neutralised with 2 moles of NaOH in dilute solutions. The amount of heat evolved during the process is

(*a*) 57.0 kJ (*b*) > 57.0 kJ

(*c*) < 57.0 kJ (*d*) > 114.0 kJ.

36. The most random state of H_2O system is

(*a*) ice

(*b*) $H_2O(l)$ at 80°C ; 1 atm.

(*c*) steam

(*d*) $H_2O(l)$ at 25°C ; 1 atm.

37. The process ; $CH_3COOH \longrightarrow CH_3COO^- + H^+$, should be

(*a*) exothermic

(*b*) endothermic

(*c*) neither exothermic nor endothermic

(*d*) exothermic or endothermic depending upon temperature.

38. The correct mathematical expression for the first law of thermodynamics as per latest sign conventions is

(*a*) $\Delta H = \Delta E + P\Delta V$ (*b*) $q + w = \Delta E$

(*c*) $\Delta E = q - w$ (*d*) $q \pm w = \Delta E$.

39. Which of the following reaction is exothermic ?

(*a*) $N_2(g) + O_2(g) + 180.5 \text{ kJ} \longrightarrow 2NO(g)$

(*b*) $Zn(s) + O_2(g) - 693.8 \text{ kJ} \longrightarrow ZnO(s)$

(*c*) $HgO(s) \longrightarrow Hg(l) + \frac{1}{2}O_2(g)$; $\Delta H = +180$ kJ

(*d*) $H_2O(g) + C(s) + 131.2 \text{ kJ} \longrightarrow CO(g) + H_2(g)$.

40. Which of the following process should be endothermic ?

(*a*) $C(s) + O_2(g) \longrightarrow CO_2(g)$

(*b*) $A^+(g) + X^-(g) \longrightarrow AX(s)$

(*c*) $O^-(g) + e^- \longrightarrow O^{2-}(g)$

(*d*) $Na^+(g) + e^- \longrightarrow Na(g)$.

41. Heat liberated by burning 2.0 g of carbon in excess of oxygen is *x* kJ. The value of $\Delta H_{comb.}$ of carbon is

(*a*) *x* kJ (*b*) $6x$ kJ mol^{-1}

(*c*) $-x$ kJ mol^{-1} (*d*) $-6x$ kJ mol^{-1}.

42. A combustion reaction is performed in a Bomb-Calorimeter. The value of heat change determined will be equal to

(*a*) ΔE of the process (*b*) ΔH of the process

(*c*) Sum of $\Delta E + \Delta H$ (*d*) the difference $\Delta H - \Delta E$.

43. A substance A(*g*) with molecular mass 40 has $\Delta H^\circ_f = 0$. What is true about it ?

(*a*) A is a molecular solid

(*b*) $A(s) \longrightarrow A(l)$ is an exothermic process

(*c*) A is an element

(*d*) A is a ionic solid.

44. The value of ΔH_{sol} of $BaCl_2(s)$ and $BaCl_2.2H_2O(s)$ are $-a$ kJ and b kJ respectively. The value of $\Delta H_{Hydration}$ of $BaCl_2(s)$ is

(*a*) $b - a$ (*b*) $a + b$

(*c*) $-a - b$ (*d*) $a - b$

45. The enthalpy of formation of the compound is

(*a*) always + ve (*b*) always − ve

(*c*) can be + ve or − ve (*d*) unpredictable.

46. For a gaseous reaction ; $N_2O_4(g) \longrightarrow 2NO_2(g)$

(*a*) ΔH and ΔE are equal (*b*) $\Delta H > \Delta E$

(*c*) $\Delta H < \Delta E$ (*d*) $\Delta H - \Delta E = 0$.

47. According to Gibb's Helmholtz equation

(*a*) $\Delta G = \Delta H$ (*b*) $\Delta G > \Delta H$

(*c*) ΔG can be > or < ΔH (*d*) $\Delta G < \Delta H$.

48. Given that, $H_2O(l) \longrightarrow H_2O(g)$; $\Delta H = +43.7$ kJ

$H_2O(s) \longrightarrow H_2O(l)$; $\Delta H = +6.05$ kJ

The value of $\Delta H_{(\text{sublimation})}$ of ice is

(*a*) 49.75 kJ mol^{-1} (*b*) 37.65 kJ mol^{-1}

(*c*) 43.7 kJ mol^{-1} (*d*) – 43.67 kJ mol^{-1}.

49. Given that, $\frac{1}{2} S_8(s) + 6O_2 \longrightarrow 4SO_3(g)$; $\Delta H = -1590$ kJ the enthalpy of combustion of sulphur is

(*a*) – 1590 kJ mol^{-1} (*b*) – 3180 kJ mol^{-1}

(*c*) + 1590 kJ mol^{-1} (*d*) – 795 kJ mol^{-1}.

50. Which of the following is an extensive property ?

(*a*) Temperature (*b*) Pressure

(*c*) Mass/Volume ratio (*d*) Energy.

51. Which of the following represents the largest amount of energy ?

(*a*) 1 Electron volt (*b*) 1 Erg

(*c*) 1 Calorie (*d*) 1 Joule.

52. Which of the following is correct for an adiabatic process ?

(*a*) $\Delta E = q$ (*b*) $\delta q = 0$

(*c*) $q = +w$ (*d*) $P\Delta V = 0$.

53. ΔS° and ΔH° for combustion of methane are 186 JK^{-1} and – 74.8 kJ mol^{-1} respectively. The value of ΔE° for the process would be

(*a*) unpredictable (*b*) (74.8 – R) JK^{-1}

(*c*) 74.78 kJ (*d*) (596R – 74.8) kJ.

54. For which of the following process ΔS is > 0

(*a*) $MgCO_3(s) \longrightarrow MgO(s) + CO_2(g)$

(*b*) $2I(g) \longrightarrow I_2(g)$

(*c*) $Na^+(g) + Cl^-(g) \longrightarrow NaCl(s)$

(*d*) $H_2O(l) \longrightarrow H_2O(s)$.

55. A system which can exchange energy but not matter with the surrounding is classified as

(*a*) closed system (*b*) microfined system

(*c*) open system (*d*) heterogeneous system.

56. Given the reaction

$CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g)$; $\Delta H = 40$ kJ.

The ΔH is specifically called

(*a*) Heat of formation of CO

(*b*) Heat of combustion

(*c*) Heat of reaction

(*d*) Heat of hydrogenation of C = O bond.

57. If $H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$; $\Delta H = -X$ kJ, then heat liberated for complete neutralisation of 1 gm-molecule of H_2SO_4 in aqueous solution will be

(*a*) – 57.0 kJ (*b*) – 2X kJ

(*c*) – X kJ (*d*) – X/2 kJ.

58. What is correct about heat of combustion ?

(*a*) It is + ve in some cases while – ve in others.

(*b*) It is applicable to gaseous substances only.

(*c*) It is always – ve.

(*d*) It is always + ve.

59. The net energy change in a reversible, cyclic process is

(*a*) 3/2 RT (*b*) zero

(*c*) always > 0 (*d*) always < 0.

60. Which of the following expressions represents Kirchhoff's equation ?

(*a*) $K = Ae^{-Ea/RT}$ (*b*) $E^\circ_{cell} = \frac{2.304\ RT}{nF} \log \frac{c_2}{c_1}$

(*c*) $\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_p$ (*d*) $\Delta H - \Delta E = \Delta nRT$.

61. The mixing of gases is generally accompanied by

(*a*) decrease in entropy

(*b*) decrease in free energy

(*c*) change in heat content

(*d*) increase in free energy.

62. For a reaction, $2C_6H_6(l) + 15O_2(g) \longrightarrow 12CO_2(g) + 6H_2O(l)$ the value of $q_{(P)} - q_{(V)}$ will be (at 25°C)

(*a*) – 7.43 kJ

(*b*) + 3.72 kJ

(*c*) + 7.43 kJ

(*d*) unpredictable as values of ΔH is not given.

63. XY, X_2 and Y_2 are diatomic molecules if ΔH_{X-X}, ΔH_{Y-Y} and ΔH_{X-Y} are in the ratio of 2 : 1 : 2 and enthalpy of formation of XY from X_2 and Y_2 is – 100 kJ mol^{-1}. The value of ΔH_{X-X} in kJ mol^{-1} is

(*a*) 200 (*b*) 400

(*c*) 250 (*d*) 500.

64. One *litre-atmosphere* is approximately equal to

(*a*) 101 J (*b*) 8.314 J

(*c*) 931 J (*d*) 19.2 J.

65. $Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s)$; $\Delta H = -22.4$ kJ. The heat change represented by above equation is called (*a*) heat of formation of $BaSO_4$

(*b*) heat of precipitation

(*c*) heat of association

(*d*) integral heat of formation.

66. One mole of ideal gas expands freely at 310 K from five litre volume to 10 litre volume. Then ΔU and ΔH of the process are respectively.

(*a*) 0 and 5 cal (*b*) 0 and 5×300 cal

(*c*) 0 and 0 (*d*) 5 and 0 cal.

67. The enthalpy of formation steadily changes from -17.89 kcal mol^{-1} to -49.82 kcal mol^{-1} in going from CH_4 to C_2H_6 ...... to C_8H_{18}. The value of $\Delta G°_f$, however, shows the opposite trend -12.12 kcal mol^{-1} to -4.14 kcal mol^{-1}. The correct reason for this is

(*a*) The number of possible isomers increases with the increase in the number of C atoms

(*b*) The number of C—C bonds increases in relation to C—H bonds

(*c*) The formation of C_nH_{2n+2} from nC and $(n + 1)$ H_2 molecules cause considerable decrease in entropy and ΔS becomes more negative with increase in value of n.

(*d*) None of the reason is correct.

68. A gas absorbs 400 J of heat and expands by 2×10^{-3} m^3 against the external pressure of 10^5 N m^{-2}. The change in internal energy of gas is

(*a*) zero (*b*) 197.4 V

(*c*) -600 J (*d*) $+200$ J.

69. Which of the following changes is exothermic ?

(*a*) $NH_4Cl(s) + aq \longrightarrow NH_4Cl\,(aq)$

(*b*) $Br(g) + e^- \longrightarrow Br^-\,(g)$

(*c*) $Br_2(g) \longrightarrow 2Br(g)$

(*d*) $Na(g) \longrightarrow Na^+ + e^-$.

70. Which of the following changes at constant T, P can be associated with positive value of work as per conversions ?

(*a*) $Sn(s) + 2F_2(g) \longrightarrow SnF_4(s)$

(*b*) $C(s) + O_2(g) \longrightarrow CO_2(g)$

(*c*) $PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$

(*d*) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$.

71. For the reaction, $3O_2(g) \rightarrow 2O_3(g)$; the sign of ΔG and ΔS respectively are

(*a*) + ve and − ve (*b*) + ve and + ve

(*c*) − ve and − ve (*d*) − ve and + ve.

72. If values of $\Delta H°_f$ of ICl(g), Cl(g), I(g) are respectively 17.57, 121.34, 106.96 J mol^{-1}. The value of ΔH_{I-Cl} in J mol^{-1} is

(*a*) 17.57 (*b*) 210.73

(*c*) 35.15 (*d*) 106.69.

73. For hypothetical reversible reaction :

$$\tfrac{1}{2}A_2(g) + \tfrac{3}{2}B_2(g) \rightleftharpoons AB_3(g)$$

the values of $\Delta H = -20$ kJ while the values of standard entropies of A_2, B_2, AB_3 are 60, 40, 50 JK^{-1} mol^{-1} respectively. The temperature at which the above reaction attains equilibrium will approximately, be

(*a*) 400 K (*b*) 500 K

(*c*) 250 K (*d*) 200 K.

74. Identify the quantity which is a state function out of the following

(*a*) q (*b*) q/w

(*c*) $q \times w$ (*d*) $q + w$.

75. If $CH_3COOH(aq) + OH^-(aq) \longrightarrow CH_3COO^- + H_2O + q_1$,

$$H^+ + OH^- \longrightarrow H_2O(l) + q_2$$

Then enthalpy change for the reaction,

$$CH_3COOH \longrightarrow CH_3COO^- + H^+ \text{ is}$$

(*a*) $q_1 - q_2$ (*b*) $q_1 + q_2$

(*c*) $q_2 - q_1$ (*d*) q_1/q_2.

76. The enthalpy change for a given reaction at 298 K is $-x$ J mol^{-1}. If the reaction occurs spontaneously at 298 K, the entropy change at that temperature

(*a*) can be negative but numerically larger than x/298

(*b*) can be negative but numerically smaller than x/298

(*c*) cannot be negative

(*d*) cannot be positive.

77. For the precipitation of silver chloride from Ag^+ ions with NaCl solution what is correct ?

(*a*) ΔH is zero for the reaction

(*b*) ΔG is zero for the process

(*c*) ΔG is equal to ΔH

(*d*) ΔG is less than zero for the reaction.

78. In certain chemical reaction ΔH = 150 kJ and ΔS is 100 JK^{-1} at 300 K. The value of ΔG would be

(*a*) zero (*b*) 300 kJ

(*c*) 330 kJ (*d*) 120 kJ.

79. The internal energy change (ΔU) of a process does not depends upon

(*a*) amount of substance undergoing the change

(*b*) temperature

(*c*) path of the process

(*d*) nature of substance undergoing the change.

80. Vibrational energy is

(*a*) partly potential and partly kinetic

(*b*) only potential

(*c*) only kinetic

(*d*) neither kinetic nor potential.

81. Which of the following thermochemical equation will represent the enthalpy of formation of $OH^-(aq)$ ion ?

(*a*) $\frac{1}{2}O_2(g) + \frac{1}{2}H_2(g) + e^- + aq \longrightarrow OH^-(aq)$

(*b*) $H_2O \rightleftharpoons H^+(aq) + OH^-(aq)$

(*c*) $H^+(aq) + O^{2-}(aq) \longrightarrow HO^-(aq)$

(*d*) none of these.

82. Given

$$C + 2S \longrightarrow CS_2 \,;\, \Delta H^\circ = +117 \text{ kJ}$$
$$C + O_2 \longrightarrow CO_2 \,;\, \Delta H^\circ = -393 \text{ kJ}$$
$$S + O_2 \longrightarrow SO_2 \,;\, \Delta H^\circ = -297 \text{ kJ.}$$

The value of $\Delta H_{combustion}$ of carbon disulphide in kJ mol^{-1} is

(*a*) – 1104 (*b*) + 1104

(*c*) + 807 (*d*) – 807.

83. The heat of transition is the heat evolved or absorbed when a substance is converted from

(*a*) solid to liquid

(*b*) solid to vapour

(*c*) one allotrope to another

(*d*) liquid to vapour.

84. Which of the following process involves decrease in the entropy of system ?

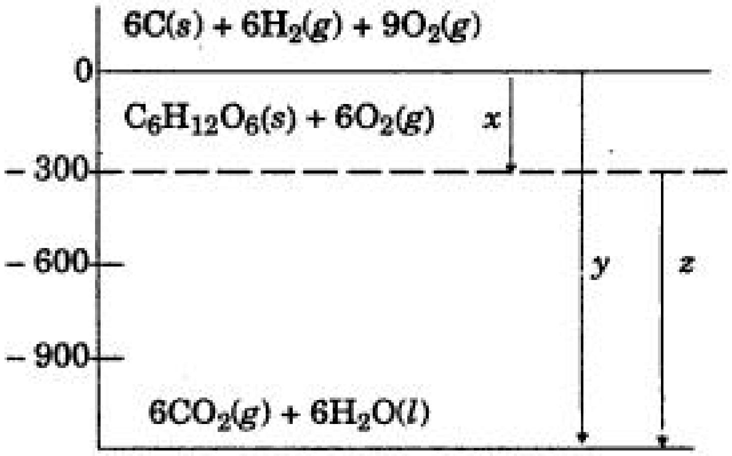
(*a*) $Br_2(l) \longrightarrow Br_2(g)$

(*b*) Diamond to graphite

(*c*) $N_2(g)$ 1 atm $\longrightarrow$ $N_2(g)$ 10 atm

(*d*) hard boiling of egg.

Consider the diagram and answer Q. 85-87.



85. In the above diagram, *z* refers to

(*a*) $6 \times \Delta H^\circ_f$ of CO_2

(*b*) ΔH°_f of $C_6H_{12}O_6$

(*c*) $\Delta H^\circ_{combustion}$ of $C_6H_{12}O_6$

(*d*) [$\Delta H^\circ_{comb.}$ of C + ΔH°_f of H_2O].

86. The heat of formation of glucose is

(*a*) – *x* (*b*) – *y*

(*c*) *x* – *y* (*d*) – *x* + *z*.

87. The quantity Y is equal to

(*a*) sum of $\Delta H_{comb.}$ of C and H_2

(*b*) *x* + *z*

(*c*) *x* – *z*

(*d*) ΔH_f of CO_2 + ΔH_f of H_2O.

88. Which of the following expressions gives the relationship between $\Delta S_{universe}$ and free energy change ?

(*a*) $\Delta S_{universe} = \Delta S_{sys.} + \Delta S_{surr.}$

(*b*) $\Delta S_{universe} = \Delta S_{sys.} + \Delta H_{syst.}$

(*c*) $\Delta S_{universe} = -\Delta G/T + \Delta H$

(*d*) $\Delta S_{universe} = -\Delta G/T$.

89. The standard free energy change for a gaseous reaction at 27°C is X kcal. If equilibrium constant for a reaction is 100 and R is 2 cal K^{-1} mol^{-1}. Then X is

(*a*) – 2.7636 (*b*) – 2.6736

(*c*) + 2.6746 (*d*) + 2.7636.

90. If $\Delta H_{vap.}$ of pure water at 100°C is 40.627 kJ mol^{-1}. The value of $\Delta S_{vap.}$ is

(*a*) 108.91 kJ mol^{-1} (*b*) 108.91 JK^{-1} mol^{-1}

(*c*) 606.27 JK^{-1} mol^{-1} (*d*) 808.27 JK^{-1} mol^{-1}.

91. "*Energy of universe is conserved but entropy of universe always increases during any natural process*". The statement is based on

(*a*) Faradays Laws

(*b*) 3rd law of thermodynamics

(*c*) Ist and 2nd law of thermodynamics

(*d*) Zeroth law of thermodynamics.

92. A human being requires 2700 kcal of energy per day. If $\Delta H_{com.}$ of glucose is – 1350 kcal mol^{-1}. How many gram of glucose a person has to consume every day ?

(*a*) 360 g (*b*) 36.0 g

(*c*) 3.6 kg (*d*) 360 mg.

93. Which of the following expression gives the value of heat capacity of 1 mol of ideal gas at constant pressure ?

(*a*) $\frac{dE}{dT}$ (*b*) $\frac{dS}{dT}$

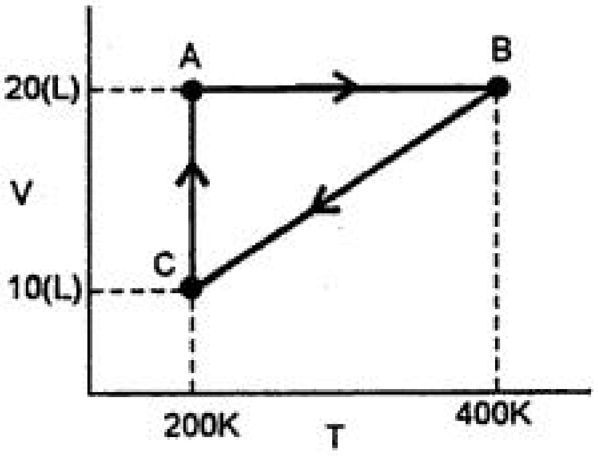
(*c*) $\frac{dH}{dT}$ (*d*) $\frac{dH}{dP}$.

94. Work done in vaporiation of one mol of water at 373 K against the pressure of 1 atmosphere is approximately.

(*a*) – 3100.0 J (*b*) 31.20 J

(*b*) – 20.2 J (*d*) + 20.2 J.

Consider the diagram given below for one mole of ideal gas and answer the following questions 95-99.



95. The process occuring in going from B → C is

(*a*) isothermal (*b*) adiabatic

(*c*) isobaric (*d*) isochoric.

96. The pressures at A and B in atmosphere are respectively

(*a*) 0.821 and 1.642 (*b*) 1.642 and 0.821

(*c*) 1 and 2 (*d*) 0.082 and 0.164.

97. The pressure at C is

(*a*) 3.284 atm (*b*) 1.642 atm

(*c*) 0.0821 atm (*d*) 0.821 atm.

98. The work done in going from C to A is

(*a*) zero (*b*) 8.21 L atm

(*c*) 16.2 L atm (*d*) unpredictable.

99. The process A ⟶ B refers to

(*a*) isoentropic process (*b*) reversible process

(*c*) isochoric process (*d*) isobaric process.

100. The latent heats of fusion in J g^{-1} of five substances A (mol. mass = 18) ; B (mol. mass = 20) ; C (mol. mass = 30) ; D (mol. mass = 60) and E (mol. mass = 30) are respectively 80, 45, 90, 45, 45. Which of following pair has same value of ΔH_{fusion} ?

(*a*) A, C (*b*) B, E

(*c*) D, E (*d*) C, D.

101. Formation of one mole of $H_2(g)$ from two moles of H(*g*) is most exothermic reaction librating 436 kJ of heat. The theoretical decrease in mass during the reaction is $X \times 10^{-2}$ kg. The value of X is approx.

(*a*) 4.8 (*b*) 2.4

(*c*) 1.2 (*d*) 8.8.

102. The molar heat capacity of Al is 27.0 J mol^{-1} K^{-1}. The heat absorbed by the aluminium sheet of 6 kg mass placed in sun which shows increase in its temperature from 25°C to 45°C is

(*a*) 60 kJ (*b*) 120 kJ

(*c*) 240 kJ (*d*) 392.4 kJ.

103. $\Delta H°$ for a reaction

$$F_2 + 2HCl \longrightarrow 2HF + Cl_2$$

is given to be 352.8 kJ. If $\Delta H°_f$ for HF is – 268.3 kJ mol^{-1} the $\Delta H°_f$ of HCl would be

(*a*) – 22 kJ mol^{-1} (*b*) 88.0 kJ mol^{-1}

(*c*) – 91.9 kJ mol^{-1} (*d*) – 183.8 kJ mol^{-1}.

104. Which of the following equation represents the value for ΔH_f of AgI

(*a*) $Ag^+(aq) + I^-(aq) \longrightarrow AgI(s)$

(*b*) $Ag(g) + \frac{1}{2} I_2(g) \longrightarrow AgI(s)$

(*c*) $2Ag(s) + I_2(g) \rightarrow 2AgI(s)$

(*d*) $Ag(s) + \frac{1}{2} I_2(g) \rightarrow AgI(s)$.

105. If $\Delta H°_f$ of HgO is 90.5 kJ mol^{-1}. The amount of Hg that could be theoretically produced by 1000 kJ of heat will be (At. mass Hg = 200.0)

(*a*) 2.20 kg (*b*) 4.40 kg

(*c*) 1.10 kg (*d*) 220.9 g.

QUESTION BANK

Level II

Choose the correct answer from the four alternatives given in each of the following questions :

1. The heat of formation of $Cl^{-1}(aq)$ can be represented by the equation

(*a*) $Cl_2(aq) \longrightarrow 2Cl^-(aq)$

(*b*) $\frac{1}{2}Cl_2(g) + e^- \longrightarrow Cl^-(g)$

(*c*) $\frac{1}{2}Cl_2(g) + e^- + aq \longrightarrow Cl^-(aq)$

(*d*) $HCl(g) + aq \longrightarrow H^+(aq) + Cl^-(aq)$.

2. The $\Delta H_{\text{atomisation}}$ of $H_2(g)$ is 436 kJ mol^{-1} while ΔH_f of $H_2O(g)$ is – 241.81 kJ mol^{-1}. The ratio of the energy yield for the combustion of hydrogen atoms to steam to the yield for combustion of equal mass of hydrogen molecules to steam is

(*a*) 1.80

(*b*) 2.80

(*c*) 0.55

(*d*) unpredictable because $\Delta H_{O=O}$ is not given.

3. For the process $2F(g) \rightarrow F_2(g)$, the sign of ΔH and ΔS respectively are

(*a*) +, – (*b*) +, +

(*c*) –, – (*d*) –, +.

4. The free energy change occuring during the irreversible process is

(*a*) negative

(*b*) positive

(*c*) dependent on whether the process is exothermic or endothermic

(*d*) negative only if the process is exothermic.

5. Given that $\Delta H_{\text{comb.}}$ of cyclopropane as – 4000 kJ mol^{-1}. The amount of cyclopropane that needs to be burnt in oxygen for producing 2×10^5 kJ of heat is

(*a*) 20 kg (*b*) 2.1 kg

(*c*) 21 g (*d*) 210 mg.

6. In certain chemical process both ΔH and ΔS have values greater than zero. Under what conditions, the reaction would not be spontaneous

I. $\Delta H > T\Delta S$ II. $T\Delta S - \Delta H > 0$

III. $\Delta H = T\Delta S$ IV. $\Delta G < 0$.

(*a*) I, II (*b*) I, III

(*c*) III, IV (*d*) only III.

7. Which of the following processes proceed with increase of entropy ?

I. solid changing into liquid

II. expansion of gas

III. dissolution of solid in liquid

IV. polymerisation.

(*a*) Only I (*b*) I, II, III

(*c*) II, III (*d*) III, IV.

8. The heat of reaction depends upon

(*a*) temperature of the reaction

(*b*) physical states of reactants and products

(*c*) both *a* and *b*

(*d*) path of the reaction and temperature.

9. Which statement is not applicable to thermochemical equations ?

I. They represent chemical change as well as heat change

II. They give the idea about mechanism of the process

III. They depict the spontaneity of the process

IV. Exothermic or endothermic nature of reaction.

(*a*) II, IV (*b*) III, IV

(*c*) III, I (*d*) II, III.

10. Which of the following process shows negative values of ΔS ?

I. $H_2O(l) \longrightarrow H_2O(s)$ II. $3O_2(g) \longrightarrow 2O_3(g)$

III. $H_2O(l) \longrightarrow H_2O(g)$ IV. Hard boiling of egg.

(*a*) I, II (*b*) Only III

(*c*) III, IV (*d*) None.

11. In which of the following process entropy increases ?

I. Rusting of iron

II. Vaporisation of Camphor

III. Crystallisation of sugar from syrup

IV. Atomisation of dihydrogen.

(*a*) I, II (*b*) II, III

(*c*) I, IV (*d*) Only IV.

12. The heat evolved during the combustion of 46 g ethanol in a bomb calorimeter was determined to be 670.48 kcal mol^{-1} at 25°C. The value of ΔE of the reaction at the same temperature is (*a*) – 335.24 kcal (*b*) – 669.28 kcal

(*c*) – 670.48 kcal (*d*) – 280.26×10^4 kcal.

13. When a solid melts, there is

(*a*) an increase in entropy

(*b*) an increase in enthalpy

(*c*) a decrease in internal energy

(*d*) Both (*a*) and (*b*) are correct.

14. Which of the following processes have positive value of ΔH ?

I. $I_2(g) \longrightarrow 2I(g)$

II. $I^-(g) + \text{water} \longrightarrow I^-(aq)$

III. $N_2(g) + O_2(g) \longrightarrow 2NO(g)$

IV. $2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O$.

(*a*) I, II (*b*) I, III

(*c*) II, III (*d*) II, IV.

15. The heat of combustion of *yellow P* and *red P* are – 9.91 kJ mol^{-1} and – 8.78 kJ mol^{-1} respectively. The heat of transition of *yellow P* → *red P* is

(*a*) – 18.69 kJ (*b*) + 1.13 kJ

(*c*) + 18.69 kJ (*d*) – 1.13 kJ.

16. For a system in equilibrium, ΔG = 0 under conditions of constant

(*a*) temperature, pressure (*b*) temperature, volume

(*c*) pressure, volume (*d*) energy, volume.

17. In a reversible reaction of the type $A + B \rightleftharpoons AB$, in general,

(*a*) neither of the reaction is exothermic

(*b*) both forward and backward reactions are exothermic

(*c*) forward reaction is exothermic

(*d*) backward reaction is exothermic.

18. Given that

$C(s) + O_2(g) \longrightarrow CO_2(g)$; ΔH = – 395 kJ

$S(s) + O_2(g) \longrightarrow SO_2(g)$; ΔH = – 295 kJ

$CS_2(l) + 3O_2(g) \longrightarrow CO_2(g) + 2SO_2(g)$; ΔH = – 1110 kJ

The heat of formation of CS_2 is

(*a*) 125 kJ mol^{-1} (*b*) 31.25 kJ mol^{-1}

(*c*) 62.5 kJ mol^{-1} (*d*) 250 kJ mol^{-1}.

19. Which of the following equations represents the standard heat of formation ?

(*a*) $C(\text{diamond}) + 2H_2(g) \longrightarrow CH_4(g)$

(*b*) $C(\text{graphite}) + 2H_2(g) \longrightarrow CH_4(g)$

(*c*) $C(\text{diamond}) + 4H(g) \longrightarrow CH_4(g)$

(*d*) $C(\text{graphite}) + 4H(g) \longrightarrow CH_4(g)$.

20. The enthalpy of formation of ammonia at 298 K is given as $\Delta H^\circ_f = -46.11$ kJ per mol of $NH_3(g)$. To which of the following equation does this value apply ?

(*a*) $\frac{1}{2} N_2(g) + \frac{3}{2} H_2(g) \longrightarrow NH_3(g)$

(*b*) $N(g) + 3H(g) \longrightarrow NH_3(g)$

(*c*) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

(*d*) $\frac{1}{2} N_2(g) + \frac{3}{2} H_2(g) \longrightarrow NH_3(l)$.

21. Given that

$C_{12}H_{22}O_{11}(s) + 11O_2(g) \longrightarrow 12CO_2(g) + 11H_2O(l)$; $\Delta H = -5.65 \times 10^3$ kJ. Complete combustion of 1.00 kg of sucrose will produce heat equal to

(*a*) 1.65×10^4 kJ (*b*) 5.25×10^3 kJ

(*c*) 7.38×10^5 kJ (*d*) 3.51×10^5 kJ.

22. For exothermic reactions to be spontaneous

(*a*) Temperature should be high

(*b*) Temperature should be zero °C

(*c*) Temperature should be low

(*d*) Temperature should be above 373 K.

23. Heat of neutralisation of strong acid and strong base is – 57.0 kJ. The amount of heat released when 0.5 mol of HNO_3 solution is added to 0.2 mol of NaOH solution is

(*a*) 11.40 kJ (*b*) 57.0 kJ

(*c*) 28.5 kJ (*d*) 34.9 kJ.

24. For an ideal gas the value of $(\partial E/\partial V)_T$ is

(*a*) zero (*b*) positive

(*c*) negative (*d*) unpredictable.

25. What is true about entropy ?

(*a*) Entropy of universe increases and tends towards maximum value

(*b*) Entropy of universe decreases and tends to be zero

(*c*) Entropy of universe always remain constant

(*d*) increases and decreases with a periodic rate.

26. Given : $C + 2S \longrightarrow CS_2$; ΔH = 117 kJ

$C + O_2 \longrightarrow CO_2$; ΔH = – 393 kJ

$S + O_2 \longrightarrow SO_2$; ΔH = – 297 kJ

The heat of combustion of CS_2 to form CO_2 and SO_2 is

(*a*) – 1104 kJ mol^{-1} (*b*) + 1104 kJ mol^{-1}

(*c*) + 807 kJ mol^{-1} (*d*) – 807 kJ mol^{-1}.

27. The enthalpies of combustion of carbon and carbon monoxide are – 390 kJ mol^{-1} and – 278 kJ mol^{-1} respectively. The enthalpy of formation of carbon monoxide is (*a*) 668 kJ mol^{-1} (*b*) 112 kJ mol^{-1}

(*c*) – 112 kJ mol^{-1} (*d*) – 668 kJ mol^{-1}.

28. Consider the following reaction occuring in a automobile engine

$$2C_8H_{18}(g) + 25O_2(g) \longrightarrow 16CO_2(g) + 18H_2O(g)$$

the signs of ΔH, ΔS and ΔG for above reaction would be

(*a*) +, –, + (*b*) –, +, –

(*c*) –, +, + (*d*) +, +, –.

29. Latent heat of vaporisation of a liquid at 500 K and 1 atm pressure is 10.0 kcal/mol. What will be the change in internal energy (ΔU) of 3 mol of liquid at same temperature ?

(*a*) 13.0 kcal (*b*) – 13.0 kcal

(*c*) 27.0 kcal (*d*) – 27.0 kcal

30. The table given below lists the bond dissociation energy (E_{diss}) for single covalent bonds formed between C and atoms A, B, D, E.

Bond	E_{diss} *(kcal* mol^{-1}*)*
C—A	240
C—B	382
C—D	276
C—E	486

Which of the atoms has smallest size ?

(*a*) D (*b*) E

(*c*) A (*d*) B.

31. Which of the following is true for a reaction,

$H_2O(l) \rightleftharpoons H_2O(g)$ at 100°C, 1 atm pressure ?

(*a*) $\Delta H = \Delta E$ (*b*) $\Delta E = 0$

(*c*) $\Delta H = 0$ (*d*) $\Delta H = T\Delta S$.

32. The enthalpy of formation for $C_2H_4(g)$, $CO_2(g)$ and $H_2O(l)$ at 25°C and 1 atm pressure be 52, – 394 and – 286 kJ mol^{-1} respectively. The enthalpy of combustion of $C_2H_4(g)$ will be

(*a*) + 1412 kJ mol^{-1} (*b*) – 1412 kJ mol^{-1}

(*c*) + 141.2 kJ mol^{-1} (*d*) – 141.2 kJ mol^{-1}.

33. For a reaction to occur spontaneously

(*a*) ($\Delta H - T\Delta S$) must be negative

(*b*) ($\Delta H + T\Delta S$) must be negative

(*c*) ΔH must be negative

(*d*) ΔS must be negative.

34. The heat of formation of the compound in the following reaction is

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g) + 44 \text{ kcal}$$

(*a*) – 44 kcal mol^{-1} (*b*) – 22 kcal mol^{-1}

(*c*) 11 kcal mol^{-1} (*d*) – 88 kcal mol^{-1}.

35. Variation of heat of reaction with temperature is given by relation known as

(*a*) Vant Hoff's isotherm (*b*) Vant Hoff's isochore

(*c*) Kirchhoff's equation (*d*) Born-Lande equation.

36. Enthalpy of reaction ΔH is expressed as

(*a*) $\Delta H = \Sigma H_P - \Sigma H_R$ (*b*) $\Delta H = dH_P + dH_R$

(*c*) $\Delta H = \dfrac{dH_P}{d\,H_R}$ (*d*) $\Delta H = \dfrac{\Sigma\,H_P}{dH_R}$

37. Molar heat capacity is given by

(*a*) $\dfrac{dQ}{dT}$ (*b*) $dQ \times dT$

(*c*) $\Sigma Q \,.\, \dfrac{1}{dt}$ (*d*) none of these.

38. The enthalpy of combustion of C(graphite) and C(diamond) are – 393.5 and – 395.4 kJ mol^{-1} respectively. The enthalpy of conversion of C(graphite) to C(diamond) in kJ mol^{-1} is

(*a*) – 1.9 (*b*) – 788.9

(*c*) 1.9 (*d*) 788.9.

39. Given that

(*i*) $C + O_2 \longrightarrow CO_2\,;\ \Delta H° = -x$ kJ

(*ii*) $2CO + O_2 \longrightarrow 2CO_2\,;\ \Delta H° = -y$ kJ

The enthalpy of formation of carbon monoxide will be

(*a*) $y - 2x$ (*b*) $\dfrac{2x - y}{2}$

(*c*) $\dfrac{y - 2x}{2}$ (*d*) $2x - y$.

40. $S + \frac{3}{2}O_2 \longrightarrow SO_2 + 2x$ kcal

$SO_2 + \frac{1}{2}O_2 \longrightarrow SO_3 + y$ kcal

Find out the heat of formation of SO_2

(*a*) $(y - 2x)$ (*b*) $(2x + y)$

(*c*) $(x + y)$ (*d*) $2x/y$.

41. In a flask, colourless N_2O_4 is in equilibrium with brown coloured NO_2. At equilibrium when the flask is heated at 100°, the brown colour deepens and on cooling it becomes less coloured. The change in enthalpy, ΔH for this system is (*a*) Negative (*b*) Positive

(*c*) Zero (*d*) Unpredictable.

42. Molar heat capacity of water in equilibrium with ice at constant pressure is

(*a*) zero (*b*) ∞

(*c*) 40.45 kJ $K^{-1}mol^{-1}$ (*d*) 75.48 JK^{-1} mol^{-1}.

43. Standard molar enthalpy of formation of CO_2 is equal to

(*a*) zero

(*b*) Standard molar enthalpy of combustion of carbon (graphite)

(*c*) Standard molar enthalpy of combustion of gaseous carbon

(*d*) Sum of molar enthalpies of formation of CO and O_2.

44. Given

$NH_3(g) + 3Cl_2(g) \rightleftharpoons NCl_3(g) + 3HCl(g)$; $-\Delta H_1$

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$; $-\Delta H_2$

$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl\ (g)$; ΔH_3

The heat of formation of $NCl_3(g)$ in the terms of ΔH_1, ΔH_2 and ΔH_3 is

(*a*) $\Delta H_f = -\Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$

(*b*) $\Delta H_f = \Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$

(*c*) $\Delta H_f = \Delta H_1 - \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$

(*d*) None of these.

45. When enthalpy and entropy change for a chemical reaction are -2.5×10^3 cals and 7.4 cals deg^{-1} respectively. Predict that reaction at 298 K is

(*a*) spontaneous (*b*) reversible

(*c*) irreversible (*d*) non-spontaneous.

46. The bond dissociation energies of H_2, Cl_2 and HCl are 104, 58 and 103 kcal respectively. The enthalpy of formation of HCl gas will be

(*a*) – 44 kcal (*b*) – 88 kcal

(*c*) – 22 kcal (*d*) – 11 kcal.

47. One mole of an ideal gas at 300 K is expanded isothermally from an initial volume of 1 litre to 10 litre. The ΔE for this process is ($R \approx 2$ cal. K^{-1} mol^{-1})

(*a*) 163.7 cal (*b*) 1381.1 cal

(*c*) 9 lt atm (*d*) zero.

48. Identify the correct statement regarding entropy

(*a*) At absolute zero of temperature, the entropy of perfectly crystalline substance is + ve

(*b*) At absolute zero of temperature, entropy of perfectly crystalline substance is taken to be zero

(*c*) At 0°C the entropy of a perfectly crystalline substance is taken to be zero.

(*d*) At absolute zero of temperature, the entropy of all crystalline substances is taken to be zero.

49. In an exothermic reaction,

(*a*) Electric energy is converted into mechanical work

(*b*) Heat is converted into electrical energy

(*c*) H(Products) is smaller than H(reactants

(*d*) There is absorption of heat.

50. Enthalpy of which of the following elements at standard state conditions is not zero.

(*a*) S_8 (rhombic) (*b*) $I_2(s)$

(*c*) Na(*s*) (*d*) C(diamond).

51. Which of the following equation represent the heat of formation of $SO_3(g)$?

(*a*) $Fe_2(SO_4)_3 \xrightarrow{\text{heat}} Fe_2O_3 + 3SO_3$; $\Delta H = -x$ kJ

(*b*) $SO_2 + \frac{1}{2}O_2 \longrightarrow SO_3$; $\Delta H = -y$ kJ

(*c*) $S + \frac{3}{2}O_2 \longrightarrow SO_3$; $\Delta H = -z$ kJ

(*d*) All of the above.

52. What is not correct about $\Delta H°_f$?

(*a*) Its value gives the idea of chemical stability of the compound w.r.t. its constituent elements.

(*b*) Its value is always – ve.

(*c*) Its value is always + ve.

(*d*) Its value can be greater or less than zero.

53. Which statement is not correct ?

(*a*) ΔH of the reaction is independent of temperature

(*b*) ΔH of reaction can be > or < zero

(*c*) ΔH of reaction can be > or < ΔE

(*d*) $\Delta H_{neut.}$ is always < 0.

54. For the process, $H_2O(s) \longrightarrow H_2O(l)$ at 1 atm pressure and 270 K, the value of ΔG

(*a*) < 0 (*b*) > 0

(*c*) $= 0$ (*d*) ≤ 0.

55. If a process is carried out under the conditions that ΔT and ΔP are zero, it may be called

(*a*) reversible process

(*b*) isochoric process

(*c*) isobaric process

(*d*) isobaric as well as isothermal.

56. The value of ΔH° for the hypothetical reaction,

$$A_2B(s) \longrightarrow 2A(s) + \frac{1}{2}B_2(g) \text{ is } + 7.3 \text{ kJ}$$

The value of ΔE° for the reaction is

(*a*) > 7.3 kJ (*b*) < 7.3 kJ

(*c*) = 7.3 kJ (*c*) unpredictable.

57. Which of the following is not required to calculate the value of ΔH°_f of $C_2H_2(g)$?

(*a*) ΔH°_f of CO_2 (*b*) ΔH°_f of $H_2O(l)$

(*c*) $\Delta H_{\text{sublimation}}$ of diamond (*d*) $\Delta H^\circ_{\text{comb.}}$ of $C_2H_2(g)$.

58. For which of the following process will ΔH be + ve ?

(*a*) $H_2(g) + I_2(g) \longrightarrow 2HI(g)$ (*b*) $C + O_2 \longrightarrow CO_2$

(*c*) $CO + \frac{1}{2} O_2 \longrightarrow CO_2$ (*d*) $SO_2 + \frac{1}{2} O_2 \longrightarrow SO_3$.

59. Enthalpy of combustion of liquid benzene is – 3264.6 kJ mol^{-1}. The heat produced by burning 3.9 g of benzene is

(*a*) $\frac{3264.6}{78}$ kJ (*b*) $\frac{3264.6}{20}$ kJ

(*c*) $\frac{3264.6}{3.9}$ kJ (*d*) 3264.6 kJ.

60. Which of the following relation is incorrect ?

(*a*) $\Delta S = \Delta H + T\Delta G$ (*b*) $\Delta S = \frac{\Delta H - \Delta G}{T}$

(*c*) $-\Delta G = -W_{\text{non. exp.}}$ (*d*) $W_{PV} = -P\,\Delta V$.

61. For an endothermic spontaneous reaction which two parameters are greater than zero.

(*a*) ΔG, ΔH (*b*) ΔS, ΔG

(*c*) ΔH, ΔS (*d*) ΔG, ΔE.

62. Which of the following can give the value of ΔH ?

(*a*) $\Delta G + T\Delta S$ (*b*) $\Delta E + P\Delta V$

(*c*) both (*a*) and (*b*) (*d*) $\Delta E - \Delta nRT$.

63. An isothermal process proceeds with the absorption of heat *q* but does not involve any change in volume. The value of ΔP, however, is greater than zero. Then *q* represents

(*a*) ΔE (*b*) ΔG

(*c*) $\Delta E + P\Delta V$ (*d*) $\Delta E + V\Delta P$.

64. *a* gram of ethanol was subjected to combustion in bomb calorimeter producing *x* Joules of heat then,

(*a*) $\Delta E_{\text{comb.}} = -\frac{46x}{a}$ J mol^{-1} (*b*) $\Delta E_{\text{comb.}} = -\frac{46a}{x}$ J mol^{-1}

(*c*) $\Delta E_{\text{comb.}} = -x$ J mol^{-1} (*d*) $\Delta H_{\text{comb.}} = -\frac{46a}{x}$ J mol^{-1}.

65. Under certain conditions, the value of ΔG° for a hypothetical reaction, $X + Y \rightleftharpoons Z$ is greater than zero, then

(*a*) The reaction has tendency to proceed towards Z

(*b*) The reaction has attained equilibrium

(*c*) Increase in temperature increases the yield of product Z

(*d*) X and Y predominate in the reaction mixture.

66. For a hypothetical reaction,

$$2A(g) + 3B(g) \longrightarrow A_2B_3(g)$$

the value of $\Delta H^\circ = -x$ kJ. Which of the following expressions can help in calculation of ΔS° ?

(*a*) $S^\circ_{A_2B_3} + 3S^\circ_B - 2S^\circ_A$ (*b*) $-x - T\Delta G$

(*c*) $\frac{-x - \Delta G^\circ}{298}$ (*d*) $\frac{x - \Delta G}{298}$.

67. For which of the following, the standard enthalpy of formation is 0.0 kJ ?

(*a*) $Br_2(g)$ (*b*) $Br_2(l)$

c) $I_2(g)$ (*d*) $Br(g)$.

68. Standard free energy of which of the following is zero

(*a*) $O_3(g)$ (*b*) $I_2(l)$

(*c*) $O_2(g)$ (*d*) both O_2 and O_3.

69. AB, A_2 and B_2 are gaseous diatomic molecules. If $\Delta H_{A-A} : \Delta H_{A-B} : \Delta_{H-B}$ are 2 : 2 : 1 and ΔH°_f of AB from A_2 and B_2 is – 100 kJ mol^{-1}, then ΔH°_f of $A(g)$ is

(*a*) 200 kJ mol^{-1} (*b*) 100 kJ mol^{-1}

(*c*) 50 kJ mol^{-1} (*d*) 300 kJ mol^{-1}.

70. Which of the following chemical processes proceeds towards increase in entropy ?

(*a*) $Ca(s) + \frac{1}{2} O_2 \longrightarrow CaO(s)$

(*b*) $C(g) + O_2(g) \longrightarrow CO_2(g)$

(*c*) $N_2(g) + O_2(g) \longrightarrow 2NO(g)$

(*d*) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$.

71. In which of the following process, the total entropy change of the process is greater than zero

(*a*) Reversible

(*b*) Irreversible

(*c*) Reversible and endothermic

(*d*) Reversible and exothermic.

72. ΔH°_f of $H(g)$ is 217.5 kJ mol^{-1}. The energy required to atomise 4.0 g of gaseous hydrogen is

(*a*) 435 kJ
(*b*) 870 kJ
(*c*) 217.5 kJ
(*d*) unpredictable.

73. Every perfect machine working reversibly between same temperatures of sink and source has the same efficiency irrespective of the nature of the substance used. The above statement constitutes

(*a*) Zeroth law of thermodynamics
(*b*) Hess's law
(*c*) Second law of thermodynamics
(*d*) Lavoisier's law.

74. For the chemical reaction involving precipitation of $Ag^+(aq)$ ion by addition of sodium chloride solution. Which statement is correct ?

(*a*) ΔH of reaction is zero
(*b*) $\Delta G = 0$
(*c*) ΔG is $> \Delta H$
(*d*) ΔG is less than zero.

75. The standard heat of combustion of carbon is – 393 kJ mol^{-1}. This implies that

(*a*) CO_2 is a non-polar compound
(*b*) Standard enthalpy of carbon dioxide is – 393 kJ mol^{-1}
(*c*) CO_2 is less stable as compared to the constituent elements
(*d*) CO_2 is a gas at ordinary temperature.

76. For adiabatic reversible expansion of an ideal gas the expression relating pressure and volume of the gas is

(*a*) $P_1V_1 = P_2V_2$
(*b*) $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$
(*c*) $P_1V_1^\gamma = P_2V_2^\gamma$
(*d*) $P = \frac{1}{V}$.

77. Temperature is a measure of :

(*a*) quantity of heat energy
(*b*) intensity of energy
(*c*) heat capacity
(*d*) None of these.

78. 2.8 L of N_2 gas at 300 K and 20 atm was allowed to expand isothermally against the external pressure of 1 atm. The value of ΔE of the process is

(*a*) 10 J
(*b*) 0
(*c*) – 10 J
(*d*) 4.18 J.

79. The specific heat of $I_2(s)$ and $I_2(g)$ are 0.055 cal g^{-1} and 0.031 cal g^{-1} respectively. If heat of sublimation of iodine is 24 cal g^{-1} at 200°C, the value of heat of sublimation of iodine at 250°C will be

(*a*) 22.8 cal g^{-1}
(*b*) 24 cal g^{-1}
(*c*) 44.0 cal g^{-1}
(*d*) 30 cal g^{-1}.

80. One g-atom each of diamond and graphite are separately burnt to give carbon dioxide. The heat liberated were 393.5 kJ and 395.4 kJ respectively. This means that

(*a*) Graphite has greater affinity for oxygen
(*b*) Diamond has greater affinity for oxygen
(*c*) Graphite is stabler than diamond
(*d*) Diamond is stabler than graphite.

81. The latent heat of vaporisation of a liquid at 500 K and 1 atm pressure is 10.0 kcal mol^{-1}. The internal energy change of 3 mol of liquid at the same temperature and pressure is

(*a*) 30 kcal
(*b*) 27 kcal
(*c*) 33 kcal
(*d*) 13 kcal.

82. For the combustion of gasoline (C_8H_{18}) in an automobile, the signs of ΔH, ΔS and ΔG will be

(*a*) +, –, +
(*b*) –, +, –
(*c*) –, +, +
(*d*) +, +, –.

83. Which of the following pair contain only extensive properties ?

(*a*) Enthalpy, refractive index
(*b*) Volume, temperature
(*c*) Enthalpy, volume
(*d*) Viscosity, volume.

84. The standard free energy formation of $HI(g)$ is + 1.7 kJ mol^{-1}. The value of equilibrium constant for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is antilog of

(*a*) – 114.18
(*b*) 114.18
(*c*) -1.37×10^{-3}
(*d*) 1.37×10^{-3}.

85. The value of ΔS for the process $H_2O(s) \longrightarrow H_2O(l)$ at 1 atm pressure and 260 K is greater than zero. The value of ΔG will be

(*a*) > 0
(*b*) < 0
(*c*) $= 0$
(*d*) lies between – 1 and 0.

86. The physical significance of free energy change can be defined by the relation

(*a*) $-\Delta G = T\Delta S$
(*b*) $\Delta G = -W_{rev.}$
(*c*) $-\Delta G = P\Delta V - W_{rev.}$
(*d*) $\Delta G = \Delta H - T\Delta S$.

87. Given two processes :

$$\tfrac{1}{2}P_4(s) + 3Cl_2(g) \longrightarrow 2PCl_3(l)\ ;\ \Delta H = -635 \text{ kJ}$$

and $PCl_3(l) + Cl_2(g) \longrightarrow PCl_5(s)\ ;\ \Delta H = -137$ kJ

The value of ΔH_f of PCl_5 is

(*a*) 454.5 kJ mol^{-1}
(*b*) – 454.5 kJ
(*c*) – 772 kJ mol
(*d*) – 498 kJ.

88. At 0°C ice and water are in equilibrium. If ΔH for the process $H_2O(s) \longrightarrow H_2O(l)$ is 6.0 kJ mol^{-1}. The value of ΔS for conversion of water to ice in $JK^{-1}\ mol^{-1}$ is

(*a*) 21.97 (*b*) – 21.97

(*c*) 6.0 (*d*) – 6.0.

89. S° for which of the following substance is greater than zero

(*a*) $Br_2(l)$ (*b*) $Br_2(g)$

(*c*) $Br_2(s)$ (*d*) all.

90. $\Delta E^\circ_{comb.}$ of solid naphthalene ($C_{10}H_8$) is – 1228.2 kcal mol^{-1}. The value of $\Delta H^\circ_{Comb.}$ of $C_{10}H_8(s)$ in kcal mol^{-1} would be

(*a*) – 1229.39 (*b*) – 1225.3

(*c*) + 1225.39 (*d*) + 1029.39.

91. 2 moles of an ideal gas are compressed isothermally (100°C) and reversibly from a pressure of 10 atm to 25 atm. The value of $W_{rev.}$ is

(*a*) – 200R log 2/5 (*b*) 746R log 2/5

(*c*) + 200R log 5/2 (*d*) 746R log 5/2.

92. If $\Delta H_{lattice}$ and $\Delta H_{hydration}$ of NaCl are respectively 778 and – 774.3 kJ mol^{-1} and $\Delta S_{dissolution}$ of NaCl at 298 = 43 J mol^{-1}. The value of ΔG° for dissociation of 1 mole of NaCl is

(*a*) – 9.114 kJ (*b*) – 11.14 kJ

(*c*) – 7.114 kJ (*d*) + 9.114 kJ.

93. A gas occupies 2 L at STP. It is provided with 300 J of heat so that its volume becomes 2.5 L at a pressure of 1 atm. The value of ΔE of process is

(*a*) 249.35 J (*b*) 350.65 J

(*c*) 150.35 J (*d*) 400.0 J.

94. The correct relationship between free energy change and equilibrium constant (K) is

(*a*) $\Delta G = RT \log K$ (*b*) $\Delta G^\circ = RT \log K$

(*c*) $\Delta G^\circ = - RT$ in K (*d*) $\Delta G = \frac{2.303 \log K}{T}$.

95. The neutralisation of strong acid-strong base in aqueous solutions can be best represented as

(*a*) $H^+ + OH^- \longrightarrow H_2O$ (*b*) $Na^+ + Cl^- \longrightarrow NaCl$

(*c*) $H_2(g) + \frac{1}{2}O_2 \longrightarrow H_2O(l)$ (*d*) $H^+ + H_2O \rightleftharpoons H_3O^+$.

96. Which of the following represents the thermochemical equation for standard heat of formation of methane

(*a*) $C(g) + 4H(g) \longrightarrow CH_4(g)$

(*b*) $C_{(diamond)} + 4H(g) \longrightarrow CH_4(g)$

(*c*) $C_{(diamond)} + 2H_2(g) \longrightarrow CH_4(g)$

(*d*) $C_{(graphite)} + 2H_2(g) \longrightarrow CH_4(g)$.

97. If standard free energy of formation of $H_2O(g)$, $C_6H_6(l)$ and $CO_2(g)$ are respectively – 228.6, 172.8 and – 394.4 kJ mol^{-1} respectively. The value of ΔG° for reaction given below is

$$C_6H_6(l) + 15/2\ O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(g)$$

(*a*) unpredictable because ΔG°_f of O_2 is not given

(*b*) – 3225 kJ mol^{-1}

(*c*) + 3225 kJ mol^{-1}

(*d*) – 1612.5 kJ mol^{-1}.

98. A mixture of 2 mole of carbon monoxide gas and one mole of dioxygen gas is enclosed in a close vessel and is ignited to convert carbon monoxide into carbon dioxide. If the enthalpy change is ΔH and internal change is ΔE, then for the above process

(*a*) $\Delta H = \Delta E$ (*b*) $\Delta H + \Delta E = 1$

(*c*) $\Delta H - \Delta E > 0$ (*d*) $\Delta H < \Delta E$.

99. A gas expands against the external pressure of 1 atm from 0.5 L to 1 litre after absorbing 100 J of heat. The value of ΔE of the process is approximately

(*a*) 49.35 J (*b*) – 49.35 J

(*c*) 150.65 J (*d*) – 150.65 J.

100. The process : $N(g) + 3e^- \longrightarrow N^{3-}(g)$, should be

(*a*) exothermic

(*b*) endothermic

(*c*) neither exothermic nor endothermic

(*d*) unpredictable.

101. $\Delta H^\circ_{comb.}$ of isobutane [$C_4H_{10}(g)$] is – 2650 kJ mol^{-1}. The amount of heat at constant pressure that can be obtained by burning 5.8 kg of isobutane is approx.

(*a*) 2.65×10^3 kJ (*b*) 265×10^5 J

(*c*) 2.65×10^5 cal (*d*) 2.65×10^4 kJ.

102. When 100 ml of 0.2 M HCl is mixed with 100 ml of 0.2 M NaOH solution, the amount of heat produced will be

(*a*) 1.142 kJ (*b*) 57.1 kJ

(*c*) – 1.142 kJ (*d*) 5.71 kJ.

103. When 10 ml of 0.1 M soln. of HCl is mixed with 10 ml of 0.1 M of KOH solution the rise in temperature was observed to be 4°C. If 100 ml of 0.1 M HCl and 100 ml of 0.1 M KOH is mixed in the same vessel, the rise in temperature would be

(*a*) 40°C (*b*) 4°C

(*c*) 20°C (*d*) unpredictable.

104. $\Delta H^\circ_{\text{vaporisation}}$ of HCl and a weak base MOH was found to be – 51.5 kJ. What is enthalpy of ionisation of MOH ?

(*a*) 6.6 kJ mol^{-1} (*b*) 5.6 kJ mol^{-1}

(*c*) 56 kJ mol^{-1} (*d*) cannot be predicted.

105. The heat produced by the neutralisation of 100 ml of HNO_3 with KOH solution is 1.713 kJ. The molarity of HNO_3 solution will be

(*a*) 0.1 (*b*) 1

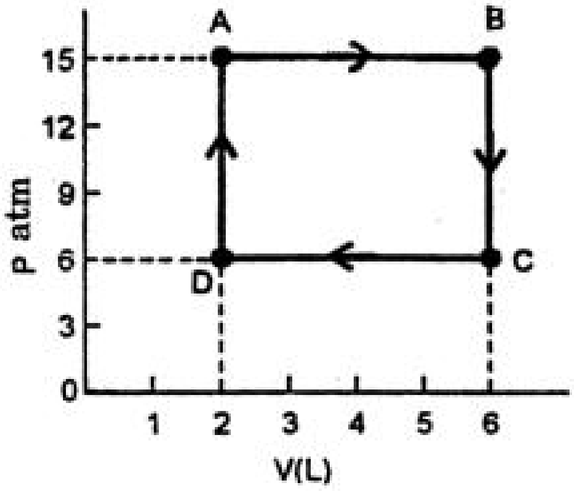
(*c*) 0.3 (*d*) 0.5.

106. What is correct for adiabatic expansion of ideal gas ?

(*a*) PV^γ = constant (*b*) TV^γ = constant

(*c*) P/T = constant (*d*) $PV^{\gamma-1}$ = constant.

107. In the P-V graph of ideal gas given below, the work done in complete cycle ABCD in J is 1 L-atm ≈ 101.3 J



(*a*) 3646.8 J (*b*) – 3646.8 J

(*c*) 5000 J (*d*) – 8670 J.

108. Enthalpy of vaporisation of water is 40800 J mol^{-1} at 1 atm pressure. The mountain where, the pressure is 380 mm of Hg, water will boil at

(*a*) 100°C (*b*) 81.6°C

(*c*) 104°C (*d*) 50°C.

109. The enthalpy of formation of water is – 286 kJ mol^{-1}. The enthalpy of dissociation of water into hydrogen and hydroxyl ions would be

(*a*) + 286 kJ mol^{-1} (*b*) + $\frac{286}{2}$ kJ mol^{-1}

(*c*) + 57 kJ approx. (*d*) + 71.25 kJ mol^{-1}.

110. The enthalpies of atomisation of $CH_4(g)$ and $C_2H_6(g)$ are respectively 400 kJ mol^{-1} and 670 kJ mol^{-1}. The value of $\Delta H_{C—C}$ would be

(*a*) 270 kJ mol^{-1} (*b*) 70 kJ mol^{-1}

(*c*) 200 kJ mol^{-1} (*d*) 240 kJ mol^{-1}.

ANSWERS

QUESTION BANK (Level I)

1. (*a*)	**2.** (*d*)	**3.** (*b*)	**4.** (*b*)	**5.** (*b*)	**6.** (*b*)	**7.** (*a*)	**8.** (*d*)
9. (*d*)	**10.** (*c*)	**11.** (*b*)	**12.** (*a*)	**13.** (*c*)	**14.** (*d*)	**15.** (*c*)	**16.** (*c*)
17. (*c*)	**18.** (*d*)	**19.** (*c*)	**20.** (*d*)	**21.** (*b*)	**22.** (*c*)	**23.** (*d*)	**24.** (*c*)
25. (*a*)	**26.** (*a*)	**27.** (*a*)	**28.** (*b*)	**29.** (*b*)	**30.** (*c*)	**31.** (*c*)	**32.** (*b*)
33. (*a*)	**34.** (*b*)	**35.** (*b*)	**36.** (*c*)	**37.** (*b*)	**38.** (*b*)	**39.** (*b*)	**40.** (*c*)
41. (*d*)	**42.** (*a*)	**43.** (*c*)	**44.** (*c*)	**45.** (*c*)	**46.** (*b*)	**47.** (*c*)	**48.** (*a*)
49. (*b*)	**50.** (*d*)	**51.** (*c*)	**52.** (*b*)	**53.** (*d*)	**54.** (*a*)	**55.** (*a*)	**56.** (*c*)
57. (*b*)	**58.** (*c*)	**59.** (*b*)	**60.** (*c*)	**61.** (*b*)	**62.** (*a*)	**63.** (*b*)	**64.** (*a*)
65. (*b*)	**66.** (*c*)	**67.** (*c*)	**68.** (*d*)	**69.** (*b*)	**70.** (*a*)	**71.** (*c*)	**72.** (*b*)
73. (*b*)	**74.** (*d*)	**75.** (*c*)	**76.** (*b*)	**77.** (*d*)	**78.** (*d*)	**79.** (*c*)	**80.** (*a*)
81. (*a*)	**82.** (*a*)	**83.** (*c*)	**84.** (*d*)	**85.** (*c*)	**86.** (*a*)	**87.** (*b*)	**88.** (*d*)
89. (*b*)	**90.** (*b*)	**91.** (*c*)	**92.** (*a*)	**93.** (*c*)	**94.** (*a*)	**95.** (*c*)	**96.** (*a*)

97. (*b*) **98.** (*b*) **99.** (*c*) **100.** (*d*) **101.** (*a*) **102.** (*b*) **103.** (*c*) **104.** (*d*)
105. (*a*).

QUESTION BANK (Level II)

1. (*c*) **2.** (*b*) **3.** (*c*) **4.** (*a*) **5.** (*b*) **6.** (*b*) **7.** (*b*) **8.** (*c*)
9. (*d*) **10.** (*a*) **11.** (*c*) **12.** (*c*) **13.** (*d*) **14.** (*c*) **15.** (*d*) **16.** (*a*)
17. (*c*) **18.** (*a*) **19.** (*b*) **20.** (*a*) **21.** (*a*) **22.** (*c*) **23.** (*a*) **24.** (*a*)
25. (*a*) **26.** (*a*) **27.** (*c*) **28.** (*b*) **29.** (*c*) **30.** (*b*) **31.** (*d*) **32.** (*b*)
33. (*a*) **34.** (*b*) **35.** (*c*) **36.** (*a*) **37.** (*a*) **38.** (*c*) **39.** (*c*) **40.** (*a*)
41. (*b*) **42.** (*b*) **43.** (*b*) **44.** (*a*) **45.** (*a*) **46.** (*c*) **47.** (*d*) **48.** (*b*)
49. (*c*) **50.** (*d*) **51.** (*c*) **52.** (*d*) **53.** (*a*) **54.** (*b*) **55.** (*d*) **56.** (*b*)
57. (*c*) **58.** (*a*) **59.** (*b*) **60.** (*a*) **61.** (*c*) **62.** (*c*) **63.** (*a*) **64.** (*a*)
65. (*d*) **66.** (*c*) **67.** (*b*) **68.** (*c*) **69.** (*a*) **70.** (*d*) **71.** (*b*) **72.** (*b*)
73. (*c*) **74.** (*d*) **75.** (*b*) **76.** (*c*) **77.** (*b*) **78.** (*b*) **79.** (*a*) **80.** (*c*)
81. (*b*) **82.** (*b*) **83.** (*c*) **84.** (*a*) **85.** (*a*) **86.** (*c*) **87.** (*b*) **88.** (*b*)
89. (*d*) **90.** (*a*) **91.** (*d*) **92.** (*a*) **93.** (*a*) **94.** (*c*) **95.** (*a*) **96.** (*d*)
97. (*b*) **98.** (*a*) **99.** (*a*) **100.** (*b*) **101.** (*c*) **102.** (*a*) **103.** (*b*) **104.** (*b*)
105. (*c*) **106.** (*a*) **107.** (*b*) **108.** (*b*) **109.** (*c*) **110.** (*b*).

HINTS/SOLUTIONS

QUESTION BANK (Level I)

1. (*a*) $\Delta H_{combustion}$ of carbon is same as ΔH_f of CO_2.

2. (*d*) Freezing of water involves decrease in randomness.

3. (*b*) TS refers to the random form of energy, which is **non-available** for conversion into work.

4. (*b*) $\Delta G° = -2.303\ RT \log K$ or $-2.303\ R \log (K_{sp})$

$$= \frac{-2.303 \times 8.314 \times 298(-9.80)}{1000}\ kJ = 55.9\ kJ.$$

5. (*b*) Endothermic process can be spontaneous only if $\Delta G < \mathbf{0}$ and $\Delta S_{Total} > 0$.

6. (*a*) For one mole of $H_2O(g)$;

$$\Delta S = \frac{\Delta G - \Delta H}{T} = \frac{-241.6 - (-228.4)}{300} = -0.044\ kJ$$

For 2 mol of $H_2O(g)$, $\Delta n = 2 \times (-0.044) \times 1000\ J$ **= – 88 J.**

7. (*a*) S is zero only at absolute zero.

8. (*d*) Entropy criterion of spontaneity is $\Delta S_{Total} > 0$.

9. (*d*) In adiabetic process, no heat enters or leaves the system.

10. (*c*) Multiply equation (*i*) by (2), eqn. (*ii*) by 2, eqn. (*iii*) by **4** and add to get the final equation.

11. **(*b*) Factual question based on definition of state function.**

13. **(*a*)** $3C_2H_2 \longrightarrow C_6H_6$;

$$\Delta H_{reaction} = \Delta H_f (C_6H_6) - 3\Delta H_{C_2H_2}$$

$$= 85 - 3(230) = -605\ kJ\ mol^{-1}\ \text{benzene}.$$

15. **(*c*) This is in accordance with Hess's law.**

16. **(*c*) For spontaneity** $\Delta G_{T,\,P} < 0$.

17. **(*c*)** ΔH_f, **refers to formation of 1 mol of** $H_2O(l)$

Heat given out for 2 mol = x **kJ**

$\therefore$ **Heat given out for 1 mol =** $\frac{x}{2}$ **kJ.**

19. **(*c*) Dissolution of** NH_4Cl **is endothermic :**

$$NH_4Cl(s) + aq \longrightarrow NH_4^+(aq) + Cl^-(aq)\ ;\ \Delta H = +\ ve.$$

Other processes, being combustion processes are exothermic.

20. **(*d*) By definition,** $\Delta S = \frac{\delta q}{T}$ **. Since** $\delta q = 0$ **for adiabatic reversible process.**

Hence $\Delta S = 0$.

21. (*b*) $\Delta H_{neut.}$ of strong acid/strong base is same.

24. (*c*) It is average of bond dissociation energies of two O—H bonds.

26. (*a*) E is extensive property, but for a fixed mass of ideal gas, $E \propto T^{1/2}$.

27. (*a*) $\Delta E = q + w = 20 + (-10) = 10$ kJ.

28. (*b*) The addition of electron to a gaseous atom releases energy equal to its electron affinity. Thus $\Delta H < 0$.

30. (*c*) $\Delta H_{neut.}$ of weak acid-strong base is numerically less than 57.1 kJ.

31. (*c*) Because melting of ice below 273 K at 1 atm pressure is non-spontaneous.

32. (*b*) Because the system is returning to its original state after undergoing series of changes.

33. (*a*) ΔH_f of NO(*g*) is represented by

$$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \longrightarrow NO(g)$$

For getting this divide eqn. (*i*) and (*ii*) by 2 and subtract (*ii*) from the (*i*).

34. (*b*) Because heat is always absorbed during evaporation.

35. (*b*) 1 mol of H_2SO_4 gives 2 mol of H^+. Thus, combination of 2 mol of H^+ ions and 2 mol OH^- liberate heat more than 57.1 kJ.

37. (*b*) Ionisation of weak acid requires energy.

40. (*c*) The process in choice (*c*) refers to 2nd electron affinity of oxygen where, energy is required to add electron to a negative ion.

$(O^-(g) + e^- + \text{energy} \rightarrow O^{2-}(g))$.

41. (*d*) 2 g of C produces heat = x kJ

12 g of C produce heat $= \frac{x}{2} \times 12 = 6x$ kJ

Hence $\Delta H_{comb.}$ of C $= -6x$ kJ mol^{-1}.

42. (*a*) In bomb calorimeter, the reaction occurs at constant volume. Hence it gives ΔE of the process.

43. (*c*) ΔH°_f is zero only for elements in their standard state.

44. (*c*) According to Hess's law,

$$\Delta H_{Hyd.} \text{ of } BaCl_2(s) = \Delta H_{soln.}(BaCl_2) - \Delta H_{soln.}(BaCl_2 \cdot 2H_2O).$$

46. (*b*) Δn for the reaction is $2 - 1 = +1$

$\therefore$ $\Delta H = \Delta E + \Delta nRT$. Since Δn is + ve.

Hence, $\Delta H > \Delta E$.

47. (*c*) Gibbs-Helmoholtz equation is $\Delta G = \Delta H - T\Delta S$

Now, ΔS of the process can be + ve or – ve depending upon the reaction. Hence, ΔG can be > or < ΔH.

48. (*a*) $\Delta H_{sublimation} = \Delta H_{fusion} + \Delta H_{vap.}$

49. (*b*) Burning of $\frac{1}{2}$ mol of S_8 produce heat = 1590 kJ

Burning of 1 mol of S_8 produce heat = 2 × 1590 = 3180 kJ

Since reaction is exothermic, the value of ΔH

$$= -3180 \text{ kJ mol}^{-1}.$$

52. (*b*) Adiabatic process does not involve any heat change. Hence $\delta q = 0$.

54. (*a*) In $MgCO_3(s) \longrightarrow MgO(s) + CO_2(g)$, a solid decomposes to give solid and a gas. Hence the process is accompanied by increase in entropy.

55. (*a*) This is as per definition of closed system (see Study Material).

57. (*b*) The process is reverse of neutralisation.

58. (*c*) Combustion process is always exothermic.

59. (*b*) In cyclic process, $\Delta E = 0$.

60. (*c*) The equation in choice (*c*) gives the variation of ΔH with temperature.

61. (*b*) Mixing of gases is spontaneous and proceeds with increase in entropy and decrease in free energy.

62. (*a*) $q_{(P)} = q_{(V)} + n\Delta RT$; Here, $\Delta n = (12 - 15) = -3$

$$q_{(P)} - q_{(V)} = \Delta nRT = -3(8.314 \text{ JK}^{-1} \text{ mol}^{-1})(298 \text{ K})$$
$$= -7.43 \text{ kJ}.$$

63. (*b*) $\frac{1}{2}X_2 + \frac{1}{2}Y_2 \longrightarrow X-Y$; $\Delta H = -100$ kJ

or $\quad -100 \text{ kJ} = \frac{1}{2}\Delta H_{X—X} + \frac{1}{2}\Delta H_{Y—Y} - \Delta H_{X—Y}$

(If $\Delta H_{Y—Y} = a$)

or $\quad -100 \text{ kJ} = \frac{1}{2}2a + \frac{1}{2}a - 2a$ or $a = 200$ kJ

$\therefore \quad \Delta H_{X—X} = 2 \times 200 = 400 \text{ kJ mol}^{-1}$.

64. (*a*) 1 L-atm = 101.325 J.

65. (*b*) This refers to heat of precipitation as per definition.

66. (*c*) For ideal gas expansion, $\Delta U = 0$.

$\Delta H = \Delta U + P\Delta V$. Since expansion is free *i.e.*, $P_{ext.} = 0$.

Hence $\Delta H = 0 + 0 = 0$.

67. (*c*) Answer (*c*) is self-explanation of the question.

68. (*d*) $\quad \Delta E = q + w = 400 + (-2 \times 10^{-2} \times 10^5)$

$$= 400 - 200 = 200 \text{ V}.$$

69. (*b*) The process $Br(g) + e^- \longrightarrow Br^-(g)$ pertains to electron affinity of bromine.

70. (*a*) The process given in choice (*a*) refers to decrease in number of gas moles. Hence, in such a case work will be done on the system *i.e.*, it will be positive.

71. (*c*) The process involves formation of 2 molecules from 3 molecules of reactants. Hence ΔS will have – ve sign as there is decrease in randomness. Then $\Delta G > 0$ because the process is non-spontaneous.

QUESTION BANK (Level II)

2. (*b*) $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O(g)$; $\Delta H_1 = -241.8$ kJ

$H_2 \longrightarrow 2H$; $\Delta H_2 = 436$ kJ

Eqn. 1 – Eqn. 2 gives

$$2H + \frac{1}{2}O_2 \longrightarrow H_2O\,(g)\,;\quad \Delta H_3 = -678 \text{ kJ.}$$

Now, the ratio $\frac{\Delta H_3}{\Delta H_1} = \frac{-678}{-241.8} = 2.80$

3. (*c*) The process $2F(g) \longrightarrow F_2(g)$ involves formation of bond between F atoms. Hence $\Delta H = -$ ve.

As randomness decreases. Therefore, ΔS is also – ve.

4. (*a*) Spontaneous processes are irreversible in nature.

5. (*b*) Cyclopropane has formula C_3H_6

4090 kJ of heat is produced from $C_3H_6 = 42$ g

2×10^5 kJ of heat is produced from

$$C_3H_6 = \frac{42 \times 2 \times 10^5}{4000} \times 10^{-3} \text{ kg} = 2.1 \text{ kg.}$$

15. (*d*) $P(Y) + \frac{5}{2}O_2 \longrightarrow \frac{1}{2}P_2O_5$; $\Delta H = -9.91$;

$P(R) + \frac{5}{2}O_2 \longrightarrow \frac{1}{2}P_2O_5$; $\Delta H = -8.78$

Subtract (*ii*) from (*i*) $P(R) \longrightarrow P(Y)$;

$\Delta H = -9.91 + 8.78$ or $\Delta H(P_{(Y)} \rightarrow P_{(R)}) = -1.13$ kJ.

16. (*a*) Factual question.

17. (*c*) Forward reaction involves combination of two entities, *i.e.*, decrease of randomness, thus, the value ΔH must be negative.

18. (*a*) Multiply equation (*ii*) by 2, then add (*i*) and (*ii*), subtract the 3rd equation from the resultant. Thus

(*i*) + 2(*ii*) – (*iii*).

Therefore $\Delta H = -395 - 2(295) + 1110 = 125 \text{ kJ mol}^{-1}$.

19. (*b*) Conceptual question.

20. (*a*) Formation of ammonia is represented as :

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g)\,;\ \Delta H = -46.11 \text{ kJ.}$$

21. (*a*) 342 g of sugar on combustion produces heat = 5.65×10^3 kJ

1000 g of sugar on combustion will produce heat

$$= \frac{5.65 \times 10^3 \times 1000}{342} = 1.65 \times 10^4 \text{ kJ.}$$

22. (*c*) For exothermic reaction ΔH = – ve.

Therefore for ΔG to be negative, *i.e.*, ΔH – TΔS to be negative, T should be low, because in general sign of ΔS for exothermic reactions is negative.

23. (*a*) Here 0.2 mole of NaOH is limiting reagent

∴ Neutralisation of one mole of NaOH release heat

= 57.0 kJ

Neutralisation of 0.2 mole of NaOH release heat

= 57.0 × 0.2 = 11.4 kJ.

26. (*a*) $CS_2 + 3O_2 \longrightarrow CO_2 + 2SO_2$

Eq. (*ii*) + 2 × Eq. (*iii*) – Eq. (*i*) will give the desired value

$$\Delta H = -393 - 2(297) - 117 = -1104 \text{ kJ.}$$

27. (*c*) $C + O_2 \longrightarrow CO_2$; $\Delta H_1 = -390$ kJ ;

$CO + \frac{1}{2}O_2 \longrightarrow CO_2$; $\Delta H_2 = -278$ kJ

Subtract Eqn. (*ii*) from equation (*i*)

$$\Delta H = -390 - (-278) = -112 \text{ kJ mol}^{-1}.$$

28. (*b*) ΔH = – ve (combustion process) ; ΔS = + ve ($n_P > n_R$)

$$\Delta G = (\Delta H - T\Delta S) = (-) - (+) = -\text{ve.}$$

29. (*c*) Vaporisation of three mol of water vapour is

$3H_2O(l) \longrightarrow 3H_2O(g)$; ∴ $\Delta n = 3 - 0 = 3$

∴ $\Delta U = \Delta H - \Delta nRT = (3 \times 10) - 3(0.002)\,(500) = 27$ k cal.

30. (*b*) Smaller the atom, more effective will be the overlap and larger is the bond dissociation energy.

31. (*d*) For reaction at equilibrium ΔG = 0 ∴ ΔH = TΔS.

32. (*b*) $C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$

$\Delta H = 2(-286) + 2(-394) - (52) = -1412$ kJ.

33. (*a*) Factual problem.

34. (*b*) ΔH_f refers to the formation of 1 mol of HCl

$$= -\frac{44}{2} = -22 \text{ kcal mol}^{-1}.$$

38. (*c*) $\Delta H_{\text{graphite} \rightarrow \text{Diamond}} = \Delta H_{\text{comb.}}$ (graphite)

$- \Delta H_{\text{comb.}}$ (Diamond)

$$= -393.5 + 395.4 = 1.9 \text{ kJ mol}^{-1}.$$

39. (*c*) Carry out the operation, equation (*i*) $- \frac{1}{2} \times$ (eqn. *ii*)

$$\Delta H = -x + \frac{y}{2} \quad \text{or} \quad \frac{y - 2x}{2}.$$

40. (*a*) ΔH_f of SO_2 = Eq. (*i*) – Eq. (*ii*) = $-2x - (-y) = (y - 2x)$.

41. (*b*) $N_2O_4 \rightleftharpoons 2NO_2$

(colourless) (brown)

Since rise in temperature pushes the reaction in the forward direction. Hence, ΔH for forward reaction should be **positive**.

43. (*b*) ΔH_f of CO_2 also represents $\Delta H_{combustion}$ of carbon (graphite).

44. (*a*) Required equation is ;

$$\frac{1}{2} N_2 + \frac{3}{2} Cl_2 \longrightarrow NCl_3 \; ; \Delta H = ?$$

Carry out the operation, Eq. (*i*) $- \frac{1}{2}$ Eq. (*ii*) $- \frac{3}{2}$ Eq. (*iii*)

$$= -\Delta H_1 - \left(-\frac{\Delta H_2}{2}\right) - \frac{3}{2}\Delta H_3$$

$$= -\Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3.$$

45. (*a*) $\Delta G = \Delta H - T\Delta S = -2500 - 298 \times 7.4$

$$= -2500 - 2205 = -4705 \text{ cal}$$

Since ΔG is – ve, the reaction is spontaneous.

46. (*c*) $\Delta H_f = \Sigma$ *B.E. of reactants* $- \Sigma$ *B.E. of products.*

47. (*d*) For isothermal process $dT = 0$. Thus, $\Delta E = 0$.

48. (*b*) It refers to third law of thermodynamics.

49. (*c*) This is as per definition of exothermic reaction.

50. (*d*) $C_{(graphite)}$ has $H° = 0$.

51. (*c*) ΔH_f pertains to formation of one mole of compound from its elements.

53. (*a*) ΔH of reaction varies with temperature.

54. (*b*) Melting of ice is non-spontaneous below 273 K at one atmospheric pressure. Hence, $\Delta G > 0$.

55. (*d*) This is according to definitions.

56. (*b*) Here, $\Delta n = \frac{1}{2} - 0 = 0.5$ *i.e.*, + ve $\quad \therefore \quad \Delta H° > \Delta E°$.

57. (*c*) (*a*), (*b*), (*d*) choices are sufficient for calculating $\Delta H°_f$.

58. (*b*) HI is an endothermic compound. Others refer to combustion process which is exothermic always.

59. (*a*) Burning of 78 g (1 mol) of benzene gives heat

$$= 3264.6 \text{ kJ}$$

Burning of 3.9 g of benzene gives heat

$$= \frac{3264.6}{78} \times 3.9 = \frac{3264.6}{20} \text{ kJ}.$$

60. (*a*) Refer Gibb's Helmholtz equation in study material.

61. (*c*) For endothermic process ΔH = + ve. This process will be spontaneous only if ΔS = + ve.

62. (*c*) Question is based on the relations ; ($\Delta G = \Delta H - T\Delta S$) and ($\Delta H = \Delta E + \Delta nRT$).

63. (*a*) $q_v = \Delta E$.

64. (*a*) $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

Heat produced at constant volume by 46 g of C_2H_5OH

$$= \frac{46x}{a} \text{ J}$$

Hence, $\Delta E_{comb.} = -\frac{46x}{9} \text{ J mol}^{-1}$.

65. (*d*) $\Delta G°$ is < 0 for the backward process. Hence backward process will be spontaneous under the given conditions.

66. (*c*) Apply the relation $\Delta G° = \Delta H° - T\Delta S°$.

67. (*b*) Standard state conditions for bromine refers to $Br_2(l)$.

68. (*c*) Standard state conditions for oxygen refer to $O_2(g)$

Hence $\Delta G°_f$ for O_2 is zero.

69. (*a*) $\frac{1}{2} A_2(g) + \frac{1}{2} B_2(g) \longrightarrow AB(g)$

$$\Delta H = \frac{1}{2} \times \Delta H_{A-A} + \frac{1}{2} \Delta H_{B-B} - \Delta H_{A-B}$$

or $\quad -100 = \frac{1}{2}(2x) + \frac{1}{2}(x) - 2x \quad$ or $\quad x = 200$

$$\therefore \; \Delta H_{A-A} = 2x = 400 \text{ kJ or } \Delta H°_f \text{ of } A(g) = 200 \text{ kJ mol}^{-1}.$$

70. (*d*) In $CaCO_3$, a solid decomposes to form a solid and a gaseous product. Hence randomness increase.

71. (*b*) In irreversible process ; $\Delta S_{syst.} + \Delta S_{surr.} > 0$.

72. (*b*) 2 g of H_2 require energy = 2 × 217.5 kJ

4 g of H_2 require energy = 2 × 2 × 217.5 = 870 kJ.

73. (*c*) It refers to the Carnot theorem.

74. (*d*) Process being spontaneous, the value of $\Delta G < 0$.

75. (*b*) The value of heat of combustion of $C_{(graphite)}$ and ΔH_f of CO_2 is same because both the processes are represented by

$$C_{(graphite)} + O_2(g) \longrightarrow CO_2(g).$$

76. (*c*) For adiabatic expansion of ideal gas the relationship between P and V is that

$P_1V_1^{\gamma} = P_2V_2^{\gamma}$, where γ is Poisson's ratio $\left(\frac{c_p}{c_v}\right)$.

77. (*b*) Factual question.

78. (*b*) $\Delta E = 0$ for isothermal process.

79. (*a*) Apply Kirchoff's equation

$$\Delta H_2 - \Delta H_1 = (T_2 - T_1)\,[C_p' - C_p]$$

$$\Delta H_2 - 24 = 50(0.031 - 0.055)$$

or $\quad \Delta H_2 = 24 - 1.2 = 22.8 \text{ cal g}^{-1}$.

80. (*c*) The data reflects relatively greater stability of graphite from the thermodynamics point of view.

81. (*b*) $3A(l) \longrightarrow 3A(g) \; ; \Delta n = 3 - 0 = 3$

$$\Delta E = \Delta H - \Delta nRT = 3 \times 10 - 3 \times 0.002 \times 500 = 27 \text{ kcal}.$$

82. (*b*) $C_8H_{18}(g) + \frac{25}{2} O_2(g) \longrightarrow 8CO_2(g) + 9H_2O(g)$

Being a combustion process $\Delta H < 0$, ΔS is > 0 because the process proceeds with increase in number of gas moles. Since ΔH = – ve, ΔS = + ve, the ΔG has to be negative.

84. (*a*) $H_2(g) + I_2(g) \rightleftharpoons 2HI$

$\therefore \quad \Delta G^\circ = 2 \times 1.7 - 0 - 0 = 3.4$

$-\Delta G^\circ = 2.303 \times R \times T \log K$

or $\quad K = \text{Antilog}\left[\dfrac{-3.4 \times 1000}{8.314 \times 298}\right] = \text{antilog}\,(-114.18)$.

85. (*a*) Melting of ice at 260 K, 1 atm is non-spontaneous.

86. (*c*) $-\Delta G = P\Delta V - W_{rev}$

or $\quad -\Delta G = -(W_{rev} - P\Delta V) = -W_{non\text{-}PV}$.

87. (*b*) Divide equation 1 by 2 and add it to second equation

$\therefore \quad \Delta H = \dfrac{635}{2} - 137 = (317.5 + 137) = -454.5$ kJ.

88. (*b*) $\Delta S_{fusion} = \dfrac{\Delta H_{fusion}}{M.P.} = \dfrac{6 \times 10^3}{273} = 21.97\ JK^{-1}$.

The value of ΔS for reverse process $= -21.97\ JK^{-1}$.

89. (*d*) Standard entropy of all the substances is greater than zero.

90. (*a*) $C_{10}H_8(s) + 12O_2(g) \longrightarrow 10CO_2(g) + 4H_2O(l)$

Apply $\Delta H = \Delta E + \Delta nRT$ (Here, $\Delta n = 10 - 12 = -2$).

91. (*d*) Apply $W_{rev.} = -2.303\, nRT \log P_1/P_2$.

92. (*a*) $\Delta H_{sol.} = \Delta H_{Lattice} + \Delta H_{Hydr.} = 778 - 774.3$

$= 3.7\ kJ\ mol^{-1}$

$\Delta S_{sol.} = 43\ JK^{-1}\ mol^{-1}$

$\Delta G_{sol.} = \Delta H - T\Delta S = 3.7 \times 10^3 - 298 \times 43$

$= -9114\ J = -9.114\ J$.

93. (*a*) The PV work $= -1 \times 0.5$ L atm

$= -0.5 \times 101.3 = -50.63$ J

$q = +300$ J

$\therefore \quad \Delta E = q + w = 300 - 50.63 = +249.35$ J.

96. (*d*) The formation of methane can be represented by

$C(\text{graphite}) + 2H_2(g) \longrightarrow CH_4(g)$.

97. (*b*) $\Delta G^\circ = 6(-394.4) + 3(-228.6) - 172.8 = -3225$ kJ.

98. (*a*) Since the process is being carried in a closed vessel, $\Delta H = \Delta E$.

100. (*b*) Formation of divalent and trivalent anion is endothermic process. (Refer to successive electron affinity).

101. (*c*) $C_4H_{10} + \frac{13}{2}O_2 \longrightarrow 4CO_2 + 5H_2O$; $\Delta H = -2650$ kJ

Heat produced by burning 1 mol (58 g) of C_4H_{10} = 2650 kJ

Heat produced by burning 5.8 kg of C_4H_{10}

$= \dfrac{2650}{58} \times 5.8 \times 10^3 = 2.65 \times 10^5$ kJ.

102. (*a*) Moles of HCl $= M \times V_{(L)} = 0.2 \times 100 \times 10^{-3} = 0.02$ mol

Heat produced by neutralisation of 1 mol HCl = 57.1 kJ

Heat produced by neutralisation of 0.02 mol HCl = 1.142 kJ.

104. (*b*) $\Delta H_{ionisation}$ of MOH $= \Delta H_{neuter} - (-57.1)$

$= -51.5 + 57.1 = 5.6$ kJ.

105. (*c*) Let the molarity be M

$\therefore$ Moles of $HNO_3 = M \times 100 \times 10^{-3} = 0.1\ M$

Heat produced by 0.1 moles of HNO_3 = 1.713 kJ

Heat produced by 1 mol of $HNO_3 = \dfrac{1.713}{0.1\ M}$ kJ

Now, since HNO_3 and KOH are strong

$\therefore \quad \dfrac{1.713}{0.1\ M} = 57.1 \quad \text{or} \quad M = \dfrac{1.713}{0.1 \times 57.1} = 0.3$.

107. $W_{A \to B} = -P\Delta V = -15 \times 4 = -60$ L-atm

$W_{B \to C} = 0$

$W_{C \to D} = -P\Delta V = -6(-4) = 24$ L-atm

$W_{D \to A} = 0$

$W_{net} = -60 + 24 = -36$ L-atm

$= -36 \times 101.3 = -3646.8$ J.

108. (*b*) $\log \dfrac{P_2}{P_1} = \dfrac{\Delta H_{vap}}{2.303R}\left[\dfrac{1}{T_1} - \dfrac{1}{T_2}\right]$

or $\quad \log \dfrac{380}{760} = \dfrac{40.8 \times 10^3}{2.303\ R}\left[\dfrac{1}{373} - \dfrac{1}{T_2}\right]$

or $\quad \dfrac{1}{373} - \dfrac{1}{T_2} = \dfrac{-0.310 \times 2.303 \times 8.314}{40.8 \times 10^3}$

or $\quad T_2 = 354.6$ K or **81.6°C.**

109. (*c*) The process of dissociation of 1 mol of H_2O into H^+ and OH^- ions refers to reverse of neutralisation. Hence, the value of heat change = + 57.1 kJ.

110. (*b*) $CH_4(g) \longrightarrow C(g) + 4H(g)$;

$\Delta H = 400$ kJ $\therefore \quad \Delta H_{C-H} = 100\ kJ\ mol^{-1}$

$CH_3 - CH_3(g) \rightarrow 2C(g) + 6H(g)$; $\Delta H = 670$ kJ

$670\ kJ = \Delta H_{C-C} + 6\Delta H_{C-H}$

$\therefore \quad \Delta H_{C-C} = 670 - 6 \times 100 = 70\ kJ\ mol^{-1}$.

6 CHEMICAL EQUILIBRIUM

Important Terms, Facts and Formulae

LAW OF CHEMICAL EQUILIBRIUM

$$\boxed{K_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}}$$

The constant K_c is called **equilibrium constant.**

- For gaseous equilibria, equilibrium constant may be expressed in terms of partial pressures of various species

$$K_p = \frac{(p_C)^c\,(p_D)^d}{(p_A)^a\,(p_B)^b}$$

- Relation between K_p and K_c

$$K_p = K_c\,(RT)^{\Delta n}$$
$$K_p = K_c \quad \text{when} \quad \Delta n = 0$$

- **Concentration Quotient,** $Q = \dfrac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$

  At equilibrium $Q = K$.
- If Q is greater than K, net reaction is taking place in backward direction and if Q is less than K, the net reaction is taking place in forward direction.

CHARACTERISTICS OF EQUILIBRIUM CONSTANT

(*i*) *The equilibrium constant has a definite value for every chemical reaction at particular temperature. The value of equilibrium constant is independent of initial concentrations of reacting species.*

(*ii*) *For a reversible reaction, the equilibrium constant for the backward reaction is inverse of the equilibrium constant for the forward reaction.*

(*iii*) *The equilibrium constant is independent of the presence of catalyst.*

(*iv*) The value of K changes if the co-efficients of various species in the equation representing equilibrium are multiplied by some number. For example, equilibrium constant for the equation

$$H_2 + I_2 \rightleftharpoons 2HI \quad ; \quad K_1 = 49$$

is different from the equilibrium constant for the equation

$$\tfrac{1}{2}H_2 + \tfrac{1}{2}I_2 \rightleftharpoons HI \quad ; \quad K_2 = 7$$

The equilibrium constants of the two equations are related to each other as

$$K_2 = (K_1)^{1/2} = (49)^{1/2} = 7$$

In general, if K_1 is the equilibrium constant for a particular equation then equilibrium constant K_2 for some new equation which is obtained by multiplying the first equation by n is given by the following relation :

$$K_2 = (K_1)^n.$$

(*v*) *If a reaction can be expressed as the sum of two other reactions, then the equilibrium constant for the overall reaction is equal to the product of the equilibrium constants for the individual reactions.*

For example,

$$H_2S \rightleftharpoons H^+ + HS^- \quad ; \quad K_1 = 1 \times 10^{-7}$$
$$HS^- \rightleftharpoons H^+ + S^{2-} \quad ; \quad K_2 = 1 \times 10^{-13}$$
$$\overline{H_2S \rightleftharpoons 2H^+ + S^{2-} \quad ; \quad K = K_1 \times K_2 = 10^{-7} \times 10^{-13}}$$

- **Effect of Temperature on the Value of K**

$$\log\frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303\,R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

The relation given above is called **van't Hoff's equation.**

- **Calculation of Degree of dissociation from vapour density data for the equilibria such as** ($PCl_5 \rightleftharpoons PCl_3 + Cl_2$)

$$\boxed{\alpha = \frac{D - d}{d(n-1)}}$$

Here, D is the density in the beginning, d = density at equilibrium, n is the no. of particles formed by dissociation of one molecule.

LE-CHATELIER'S PRINCIPLE

- **Le-Chatelier's Principle** states that : *If a system at equilibrium is subjected to a change of concentration, pressure or temperature, the equilibrium shifts in the direction that tends to undo the effect of the change.*

- ***Effect of Concentration***. Addition of reactants or removal of products shifts the equilibrium in forward direction.
- ***Effect of Temperature***. Increase in temperature shifts the equilibrium in endothermic direction.
- ***Effect of Pressure***. Increase in pressure shifts the gaseous equilibria in the direction where no. of moles of gaseous species is less.
- ***Effect of Catalyst***. Addition of catalyst does not disturb the equilibrium state.
- ***Addition of Inert gas at Constant Volume*** does not disturb the equilibrium state.
- ***Addition of Inert gas at Constant Pressure*** shifts the equilibrium in the direction where no. of moles of gaseous species is more.

SOLUBILITY PRODUCT

- In general, for any sparingly soluble salt A_xB_y, which dissociates to set up the equilibrium

$$A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$$

the solubility product constant may be expressed as :

$$K_{sp} = [A^{y+}]^x [B^{x-}]^y$$

- The expressions of solubility products of some sparingly soluble salts are given below :

$$PbCl_2 \ : \ PbCl_2 \rightleftharpoons Pb^{2+} + 2Cl^- :$$

$$K_{sp} = [Pb^{2+}][Cl^-]^2$$

$$Ca_3(PO_4)_2 \ : Ca_3(PO_4)_2 \rightleftharpoons 3Ca^{2+} + 2PO_4^{3-} :$$

$$K_{sp} = [Ca^{2+}]^3 [PO_4^{3-}]^2$$

- **Calculation of solubility product.** Knowing the solubility of the salt, its solubility product (K_{sp}) can be calculated.

Expressions, correlating K_{sp} and solubility (in mol L^{-1}) of some common types of salts are :

Salt Type	Relation between K_{sp} and S
AB_2	$K_{sp} = (s)(2s)^2 = 4s^3$
A_2B	$K_{sp} = (2s)^2(s) = 4s^3$
AB_3	$K_{sp} = (s)(3s)^3 = 27s^4$
A_3B_2	$K_{sp} = (3s)^3(2s)^2 = 108s^5$
AB	$K_{sp} = (s)(s) = s^2$

- Larger value of K_{sp} indicates the salt is more soluble in water.
- In the solution, the ionic product of a salt cannot exceed its K_{sp}. Thus, K_{sp} is the highest limit of ionic product at a particular temperature.
- Solubility of a sparingly soluble salt decreases if some strong electrolyte having some ion common with the ions of the salt is added. Thus, AgCl is less soluble in NaCl solution as compared with solubility in water.

BRONSTED AND LOWRY CONCEPT OF ACIDS AND BASES

According to this concept :

An acid is a substance that can donate a proton and base is a substance that can accept a proton.

- ***Substances***, such as water, ***which can act as acids as well as bases are called amphoteric substances***. Some more examples of amphoteric species are NH_3, C_2H_5OH, HCO_3^-, HS^- and HSO_4^-.

LEWIS CONCEPT OF ACIDS AND BASES

According to this concept :

An acid is a species that can accept a pair of electrons whereas a base is a species that can donate a pair of electrons.

- Some examples of **Lewis Acids :**

$AlCl_3$, BF_3, Cu^{2+}, Ag^+, Fe^{3+}, H^+, SO_3, CO_2, $SnCl_2$, $SnCl_4$, PF_5, SiF_4, SiO_2.

- Some examples of **Lewis Bases :**

OH^-, Cl^-, Br^-, O^{2-}, CN^-, NH_2^-, CH_3COO^- H_2O, NH_3, R—OH, R—O—R, R – NH_2, R_2NH, R_3N, CO, C_2H_4.

DISSOCIATION CONSTANTS OF ACIDS AND BASES IN WATER

- **Dissociation constant of Acids (Ka)**

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

- $pK_a = -\log K_a$.
- ***Larger the value of K_a or smaller the value of pK_a higher is the concentration of H_3O^+ ions and stronger is the acid.***
- $$\alpha = \sqrt{\frac{K_a}{C}}$$
- $$[H_3O^+] = C\alpha = C\sqrt{\frac{K_a}{C}} = \sqrt{Ka \times C}$$
- In a solution of two weak monobasic acids having dissociation constants K_{a_1} and K_{a_2} and molar con-

centrations C_1 and C_2 respectively, the $[H_3O^+]$ is given by the relation :

$$[H_3O^+] = \sqrt{K_{a_1}C_1 + K_{a_2}C_2}.$$

- The ionisation constant K_b for a weak base B can be represented as follows :

$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

- $pK_b = -\log K_b$
- ***Larger the value of K_b or smaller the value of pK_b, stronger is the base.***
- $$\alpha = \sqrt{\frac{K_b}{C}}$$

$$[OH^-] = \sqrt{K_b \times C}.$$

- **Relation between K_a and K_b**

The dissociation constant K_a of an acid is related to the dissociation constant, K_b of its conjugate base as :

$$\boxed{K_a \times K_b = K_w}$$

- $$\frac{\text{Strength of Acid}_1}{\text{Strength of Acid}_2} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}$$

IONIC PRODUCT OF WATER

- $$\boxed{K_w = [H_3O^+][OH^-]}$$

The values of K_w at 298 K is 1.008×10^{-14} mol^2 L^{-2}.

- **In pure water $[H_3O^+]$ and $[OH^-]$ are equal.**

$$[OH^-] = [H_3O^+] = 1 \times 10^{-7} \text{ mol L}^{-1}$$

- ***With increase in temperature dissociation of water increases, therefore, value of K_w increases with increase in temperature.***
- **In neutral solutions $[H_3O^+] = [OH^-]$**

In acidic solutions $[H_3O^+] > [OH^-]$

In basic solutions $[H_3O^+] < [OH^-]$.

- $-\log K_w = pK_w$. The value of pK_w at 298 K is equal to 14.

pH SCALE

- ***The pH of a solution may be defined as negative logarithm of hydronium ion concentration in moles per litre.***

$$pH = -\log [H_3O^+] \quad = \log \frac{1}{[H_3O^+]}$$

or $$[H_3O^+] = 1 \times 10^{-pH}$$

- ***pOH of solution is defined as the negative logarithm of hydroxyl ion concentration in moles per litre.***

$$pOH = -\log [OH^-]$$

For **pure water** at 298 K, $pH = pOH = 7$

For acidic solutions $pH < 7$ and for basic solutions $pH > 7$.

- At 298 K, the sum of pH and pOH is equal to 14

$$\boxed{pH + pOH = 14}$$

or $$\boxed{pH + pOH = pK_w}$$

BUFFER SOLUTIONS

- **pH of a buffer solution** is given by **Henderson-Hasselbalch** equation.

For acidic buffer : $$\boxed{pH = pK_a + \log \frac{[Salt]}{[Acid]}}$$

For basic buffer : $$\boxed{pOH = pK_b + \log \frac{[Salt]}{[Base]}}$$

HYDROLYSIS OF SALTS

$$\text{Salt} + \text{Water} \rightleftharpoons \text{Acid} + \text{Base}$$

$$K_h = \frac{[Acid][Base]}{[Salt]}$$

where K_h is the hydrolysis constant of the salt.

- ***The fraction of the total salt that is hydrolysed at equilibrium is called degree or extent of hydrolysis.*** It is denoted by '*h*'.

1. **Hydrolysis of Salt of a Weak Acid and a Strong Base**

This type of salts includes salts of sodium and potassium except halides, nitrates and sulphates. For example, Na_3BO_3, Na_2CO_3, KCN, CH_3COONa etc.

This type of salts produce ***alkaline solutions*** on hydrolysis.

$$MX + H_2O \rightleftharpoons \underset{\text{Strong base}}{MOH} + \underset{\text{Weak acid}}{HX}$$

- ***Hydrolysis constant :*** $$\boxed{K_h = \frac{K_w}{K_a}}$$
- ***Degree of hydrolysis :***

$$\boxed{h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_w}{K_a \times C}}}$$

- **Hydronium ion conc. and pH**

$$[H_3O^+] = K_w\sqrt{\frac{K_a}{K_w \times C}}$$

$$= \sqrt{\frac{K_w \times K_a}{C}}$$

$$\boxed{\mathbf{pH = \frac{1}{2}\,(pK_w + pK_a + \log C)}}$$

2. **Hydrolysis of Salt of a Strong Acid and a Weak Base**

This type of salts includes halides, nitrates and sulphates of all metals except that of sodium and potassium. For example, **zinc nitrate, copper sulphate, aluminium sulphate, ferric chloride** etc. This type of salts produce **acidic solutions on hydrolysis.**

$$MX + H_2O \rightleftharpoons \underset{\text{Weak base}}{MOH} + \underset{\text{Strong acid}}{HX}$$

- ***Hydrolysis constant*** : $\boxed{K_h = \frac{K_w}{K_b}}$
- **Degree of Hydrolysis** :

$$\boxed{h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_w}{K_b \times C}}}$$

- **Hydronium ion conc. and pH**

$$[H_3O^+] = \sqrt{\frac{K_w \times C}{K_b}}$$

$$\boxed{\mathbf{pH = \frac{1}{2}\,[pK_w - \log C - pK_b]}}$$

3. **Hydrolysis of Salt of a Weak Acid and a Weak Base**

This type of salts include all salts except halides, nitrates and sulphates of all metals except sodium and potassium. For example, **zinc acetate, aluminium phosphate, calcium carbonate, ammonium phosphate**, etc. This type of salts produce weak acids and weak bases on hydrolysis. Therefore, aqueous solutions of such salts are ***almost neutral*** and have pH nearly equal to 7.

$$MX + H_2O \rightleftharpoons \underset{\text{Weak base}}{MOH} + \underset{\text{Weak acid}}{HX}$$

or $$M^+ + X^- + H_2O \rightleftharpoons MOH + HX$$

- ***Hydrolysis constant*** : $K_h = \frac{K_w}{K_a \times K_b}$
- **Degree of Hydrolysis** : $h = \sqrt{K_h}$.

Thus, ***in case of salts of weak acids and weak bases, the degree of hydrolysis does not depend upon the concentration of the salt.***

$$h = \sqrt{\frac{K_w}{K_a \times K_b}}$$

- **Hydronium ion conc. and pH** :

$$[H_3O^+] = \sqrt{\frac{K_w \times K_a}{K_b}}$$

$$\boxed{\mathbf{pH = \frac{1}{2}\,[pK_w + pK_a - pK_b]}}$$

In case $K_a = K_b$

$$pH = \frac{1}{2}\,(pK_w) = 7$$

In case $K_a > K_b$, the solution would be slightly acidic and the pH would be less than 7. On the other hand if $K_a < K_b$, the solution would be slightly alkaline and the pH would be greater than 7.

4. **Salt of a Strong Acid and a Strong Base**

This type of salts includes halides, nitrates and sulphates of sodium and potassium. For example, NaCl, KCl, KNO_3, Na_2SO_4, etc. ***Salts of this type are not hydrolysed*** and hence their aqueous solutions are ***neutral***.

QUESTION BANK

Level I

Choose the correct answer from the four alternatives given in each of the following questions :

1. A quantity of PCl_5 was heated in a 10 L vessel at 525 K.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

At equilibrium the vessel contains 0.10 mole of PCl_5, 0.20 mole of PCl_3 and 0.20 mole of Cl_2. The equilibrium constant for the reaction is

(*a*) 0.04 (*b*) 0.4

(*c*) 0.02 (*d*) 0.05.

2. For the reaction, $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$, the partial pressures of CO_2 and CO are 2.0 and 4.0 atm respectively at equilibrium. The K_p for the reaction is

(*a*) 2.0 atm (*b*) 0.5 atm

(*c*) 4.0 atm (*d*) 8.0 atm.

3. Consider the two gaseous equilibria involving SO_2 and the corresponding equilibrium constants at 298 K

$$SO_2(g) + \frac{1}{2} O_2(g) \rightleftharpoons SO_3(g) \qquad ...K_1$$

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g) \qquad ...K_2$$

The values of equilibrium constants are related as :

(*a*) $2K_1 = K_2^2$ (*b*) $K_2^2 = \frac{1}{K_1}$

(*c*) $K_1^2 = \frac{1}{K_2}$ (*d*) $K_2 = \frac{2}{K_1^2}$.

4. Which of the following statements is correct about the equilibrium constant ?

(*a*) Its value increases by increase in temperature

(*b*) Its value decreases by decrease in temperature

(*c*) Its value may increase or decrease with increase in temperature

(*d*) Its value is constant at all temperature.

5. Which of the following statements is not correct regarding the equilibrium constant ?

(*a*) Its value does not depend upon the initial conc. of the reactants

(*b*) Its value does not depend upon the initial conc. of the products

(*c*) Its value does not depend upon nature of the reactants

(*d*) Its value does not depend upon presence of catalyst.

6. Which of the following will not change the concentration of ammonia at the equilibrium ?

(*a*) Increase of pressure (*b*) Increase of volume

(*c*) Addition of catalyst (*d*) Decrease of temperature.

7. Pure ammonia is placed in a vessel at a temperature when its dissociation is appreciable. At equilibrium

(*a*) α does not change with pressure

(*b*) concentration of ammonia does not change with pressure

(*c*) concentration of hydrogen is less than that of nitrogen

(*d*) K_p does not change significantly with pressure.

8. In which of the following equilibria will K_c and K_p have the same value ?

(*a*) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

(*b*) $N_2 + 3H_2 \rightleftharpoons 2NH_3$

(*c*) $2CO + O_2 \rightleftharpoons CO_2$

(*d*) $N_2 + O_2 \rightleftharpoons 2NO$.

9. In which of the following gaseous equilibria, the equilibrium will shift to the right if total pressure is increased.

(*a*) $N_2 + 3H_2 \rightleftharpoons 2NH_3$ (*b*) $N_2O_4 \rightleftharpoons 2NO_2$

(*c*) $H_2 + Cl_2 \rightleftharpoons 2HCl$ (*d*) $N_2O_4 \rightleftharpoons 2NO_2$.

10. Which of the following is not favourable for the formation of SO_3 ?

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \; ; \Delta H = -188 \text{ kJ}$$

(*a*) High pressure (*b*) High temperature

(*c*) Decreasing $[SO_3]$ (*d*) Increasing $[SO_2]$.

11. Vapour density of PCl_5 is 104.16 but when heated to 230°C its vapour density is reduced to 62. The degree of dissociation of PCl_5 at this temperature will be

(*a*) 6.8% (*b*) 68%

(*c*) 46% (*d*) 64%.

12. For which of the following gaseous equilibria at constant temperature, doubling the volume would cause a shift of equilibrium to the right ?

(*a*) $2CO + O_2 \rightleftharpoons 2CO_2$ (*b*) $N_2 + 3H_2 \rightleftharpoons 2NH_3$

(*c*) $N_2 + O_2 \rightleftharpoons 2NO$ (*d*) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$.

13. For the gas phase reaction

$$N_2 + O_2 \rightleftharpoons 2NO \,;\, \Delta H = +180 \text{ kJ mol}^{-1}$$

which of the following is true ?

(*a*) The value of K changes with change in pressure

(*b*) The value of K changes with introduction of NO

(*c*) The value of K changes with change in concentration of N_2

(*d*) The value of K changes with change in temperature.

14. The decomposition of N_2O_4 to NO_2 is carried out at 280° in chloroform. When equilibrium is reached, 0.2 mol of N_2O_4 and 2×10^{-3} mol of NO_2 are present in a 2L solution, the equilibrium constant for the reaction $N_2O_4 \rightleftharpoons 2NO_2$ is

(*a*) 1×10^{-2} (*b*) 2×10^{-3}

(*c*) 1×10^{-5} (*d*) 2×10^{-5}.

15. One mole of SO_3 was placed in a two litre vessel at a certain temperature. The following equilibrium was established in the vessel

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$$

At equilibrium, the vessel was found to contain 0.5 mol of SO_3. The value of K would be

(*a*) 0.25 (*b*) 0.125

(*c*) 0.5 (*d*) 1.

16. For an elementary reaction, the specific rate constants for forward and reverse reactions are 0.50 and 5×10^4 respectively. The equilibrium constant for the reaction would be

(*a*) 2.5×10^3 (*b*) 2.5×10^4

(*c*) 1×10^{-5} (*d*) 1×10^5.

17. The value of $\Delta G°$ for a reaction having K = 1 would be

(*a*) – RT (*b*) – 1

(*c*) 0 (*d*) + RT.

18. For the reaction

$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g) \,;\, \Delta H = +41 \text{ kJ}$$

The equilibrium can be shifted in the forward direction by

(*a*) Lowering the temperature

(*b*) Increasing the pressure

(*c*) Increasing [CO]

(*d*) Increasing $[H_2]$.

19. For a reaction, the value of K increases with increase in temperature. The ΔH for the reaction would be

(*a*) + ve (*b*) – ve

(*c*) zero (*d*) cannot be predicted.

20. At 90°C, pure water has $[H_3O^+] = 10^{-6}$ mol L^{-1}. What is the value of K_w at 90°C ?

(*a*) 10^{-6} (*b*) 10^{12}

(*c*) 10^{-14} (*d*) 10^{-12}.

21. pH of an aqueous solution is 5.5. The hydroxyl ion conc. in the solution would be

(*a*) – 5.5 (*b*) – 8.5

(*c*) $10^{-8.5}$ (*d*) $10^{8.5}$.

22. K_{sp} of a substance XY is 10^{-2} $mol^2 L^{-2}$. Molecular mass of the substance is 100. Its solubility would be

(*a*) 100 g L^{-1} (*b*) 1 g L^{-1}

(*c*) 10 g L^{-1} (*d*) 10^{-1} g L^{-1}.

23. 200 mL of $\frac{M}{50}$ HCl are mixed with 100 mL of $\frac{M}{100}$ HCl, the pH of the resulting solution would be

(*a*) 2.22 (*b*) 1.78

(*c*) 2 (*d*) zero.

24. Which one is the strongest Bronsted-Lowry base out of the following ?

(*a*) ClO^- (*b*) ClO_2^-

(*c*) ClO_3^- (*d*) ClO_4^-.

25. pK_a values of three acids A, B and C are 4.5, 3.5 and 6.5 respectively. Which of the following represents the correct order of acid strength ?

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

(*c*) B > A > C (*d*) C > B > A.

26. Which of the following is not a Lewis base ?

(*a*) CH_3^- (*b*) $AlCl_3$

(*c*) R—OH (*d*) RNH_2.

27. Which one of the following is not amphiprotic ?

(*a*) HSO_4^- (*b*) HCO_3^-

(*c*) $H_2PO_4^-$ (*d*) $HCOO^-$.

28. The ionic product of water changes when

(*a*) An acid is added to it

(*b*) A base is added to it

(*c*) Either a base or an acid is added to it

(*d*) Temperature is raised.

29. A 0.20 M solution of methanoic acid has degree of dissociation 0.032. Its dissociation constant is

(*a*) 2.1×10^{-2} (*b*) 9.6×10^{-8}

(*c*) 2.1×10^{-4} (*d*) 1.1×10^{-6}.

30. Which of the following is the strongest base ?

(*a*) H^- (*b*) Cl^-

(*c*) NO_3^- (*d*) CH_3O^-.

31. The conjugate base of HCO_3^- is

(*a*) H_2CO_3 (*b*) CO_2

(*c*) H_2O (*d*) CO_3^{2-}.

32. The conjugate acid of HSO_3^- is

(*a*) SO_3^{2-} (*b*) SO_4^{2-}

(*c*) H_2SO_4 (*d*) H_2SO_3.

33. The pH of 0.1 M acetic acid is

(*a*) 1 (*b*) zero

(*c*) less than 1 (*d*) more than 1.

34. Which of the following aqueous solutions will have highest pH ?

(*a*) Sodium acetate (*b*) Sodium chloride

(*c*) Ammonium phosphate (*d*) Calcium chloride.

35. The pH of 0.005 M aqueous solution of H_2SO_4 is nearly,

(*a*) 0.005 (*b*) 2

(*c*) 1 (*d*) 0.01.

36. When 100 mL of N/10 NaOH are added to 50 mL of N/5 HCl. The pH of the resulting solution would be

(*a*) 7 (*b*) > 7

(*c*) < 7 (*d*) zero

37. Given, $HF + H_2O \xrightarrow{K_a} H_3O^+ + F^-$

$$F^- + H_2O \xrightarrow{K_b} HF + OH^-$$

Which one of the following relations is correct ?

(*a*) $K_a = \frac{1}{K_b}$ (*b*) $K_a \times K_b = K_w$

(*c*) $\frac{K_a}{K_b} = K_w$ (*d*) $\frac{K_b}{K_a} = K_w$.

38. The compound that is not a Lewis acid is

(*a*) BF_3 (*b*) $AlCl_3$

(*c*) NF_3 (*d*) $SnCl_4$.

39. If $K_a = 10^{-5}$ for a weak acid, then pK_b for its conjugate base would be

(*a*) 10^{-10} (*b*) 9

(*c*) 10^{-9} (*d*) 5.

40. A certain weak acid has a dissociation constant 1.0×10^{-4}. The equilibrium constant for its reaction with strong base is

(*a*) 1.0×10^{-4} (*b*) 1.0×10^{-10}

(*c*) 1.0×10^{10} (*d*) 1.0×10^{-14}.

41. In the reaction, $AlCl_3 + Cl^- \longrightarrow AlCl_4^-$, $AlCl_3$ acts as a

(*a*) Salt (*b*) Lewis acid

(*c*) Lewis base (*d*) Bronsted base.

42. The weakest base among the following is

(*a*) H^- (*b*) CH_3^-

(*c*) CH_3O^- (*d*) Cl^-.

43. Which of the following equimolar solutions can act as an acidic buffer ?

(*a*) NH_4Cl and NH_4OH (*b*) HCl and NaCl

(*c*) HCOOH and HCOONa (*d*) HNO_3 and NH_4NO_3.

44. The conjugate acid of NH_2^- is

(*a*) NH_3 (*b*) NH_4^+

(*c*) N_2H_4 (*d*) NH_2OH.

45. Which of the following has the highest pH ?

(*a*) Distilled water

(*b*) 1 M NH_3

(*c*) 1 M NaOH

(*d*) Water saturated with chlorine.

46. The pH of 10^{-8} M HCl is

(*a*) 8 (*b*) 6

(*c*) Between 6 and 7 (*d*) Between 7 and 8.

47. The solubility of $Fe(OH)_3$ is x mol L^{-1}. Its K_{sp} would be

(*a*) $9x^3$ (*b*) $3x^4$

(*c*) $27x^4$ (*d*) $9x^4$.

48. Among the following, the weakest Bronsted base is

(*a*) F^- (*b*) Cl^-

(*c*) Br^- (*d*) I^-.

49. If x is the degree of dissociation of PCl_5

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

at a given temperature and if 2 moles of PCl_5 are taken in a vessel, then at equilibrium the total number of moles of various species would be

66. $Ba(OH)_2$ is a strong base. The pH of its 0.005 M solution would be

(*a*) 11.31
(*b*) 11.7
(*c*) 12
(*d*) None of these.

67. $[OH^-]$ in a solution is 1 mol L^{-1}. The pH of the solution is

(*a*) 1
(*b*) 0
(*c*) 14
(*d*) 10^{-14}.

68. For the reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, the forward reaction at constant temperature is favoured by

(*a*) Introducing an inert gas at constant volume
(*b*) Introducing Cl_2 gas at constant volume
(*c*) Introducing inert gas at constant pressure
(*d*) Decreasing the volume of the container.

69. Which of the following solutions will have pH close to 2.0 ?

(*a*) 50 ml of $\frac{M}{10}$ HCl + 50 ml of $\frac{M}{10}$ NaOH
(*b*) 55 ml of $\frac{M}{10}$ HCl + 45 ml of $\frac{M}{10}$ NaOH
(*c*) 10 ml of $\frac{M}{10}$ HCl + 40 ml of $\frac{M}{10}$ NaOH
(*d*) 75 ml of $\frac{M}{5}$ HCl + 25 ml of $\frac{M}{5}$ NaOH.

70. What is the decreasing order of strength of bases (OH^-, NH_2^-, $H—C \equiv C^-$, $CH_3CH_2^-$)

(*a*) $CH_3CH_2^- > NH_2^- > H—C \equiv C^- > OH^-$
(*b*) $H—C \equiv C^- > CH_3CH_2^- > NH_2^- > OH^-$
(*c*) $H—C = C^- > CH_3CH_2^- > NH_2^- > OH^-$
(*d*) $NH_2^- > H—C \equiv C^- > OH^- > CH_3CH_2^-$.

71. Hydrogen ion concentration of a solution of a weak base of dissociation constant K_b and concentration C is

(*a*) $\frac{K_w}{\sqrt{K_b \times C}}$
(*b*) $K_w \times K_b$
(*c*) $\frac{K_w}{K_b}$
(*d*) $K_w \times \sqrt{K_b \times C}$.

72. When sodium acetate is added to an aqueous solution of acetic acid its pH

(*a*) Increases
(*b*) Decreases
(*c*) Remains constant
(*d*) May increase or decrease.

73. The pH of a mixture of containing 70 ml of 0.1 M HCl and 30 ml of 0.1 M NaOH solution will be

(*a*) 0.7
(*b*) 1.4
(*c*) 0.8
(*d*) 0.5.

74. Which of the following mixtures of solutions can function as a buffer solution ?

(*a*) 50 ml of 0.2 M NH_3 + 50 ml of 0.1 M HCl
(*b*) 50 ml of 0.2 M NH_3 + 50 ml of 0.2 M HCl
(*c*) 50 ml of 0.2 M HCl + 05 ml of 0.2 M NaOH
(*d*) 50 ml of 0.1 CH_3COOH + 50 ml of 0.1 M NaOH.

75. A certain buffer solution contains equal concentrations of X^- and HX. The K_b for X^- is 1×10^{-10}, the pH of the buffer is

(*a*) 10
(*b*) 5
(*c*) 4
(*d*) 7.

76. Which of the following pairs is best suited to prepare a buffer solution having pH 9.0 ?

(*a*) CH_3COOH and CH_3COO^-
(*b*) $H_2CO_3 + HCO_3^-$
(*c*) $H_2PO_4^- + HPO_4^{2-}$
(*d*) $NH_4Cl + NH_4OH$.

77. One litre of a buffer solution containing 0.01 M NH_4Cl and 0.1 M NH_4OH has a pH of about

$(K_{b(NH_4OH)} = 1.0 \times 10^{-5})$

(*a*) 10
(*b*) 4
(*c*) 6
(*d*) 9.

78. For the equilibrium,

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

the total pressure at equilibrium is P and degree of dissociation of PCl_5 is x. Which of the following is the partial pressure of PCl_3 ?

(*a*) $\frac{x}{x-1} \times P$
(*b*) $\frac{x}{1-x} \times P$
(*c*) $\frac{x}{x+1} \times P$
(*d*) $\frac{2x}{1-x} \times P$.

79. When 1 mole of N_2 and 1 mole of H_2 is enclosed in 5 L vessel and the reaction is allowed to attain equilibrium, it is found that at equilibrium there is x mole of N_2. The no. of moles of NH_3 formed would be

(*a*) $2x$
(*b*) $2(1 + x)$
(*c*) $2(1 - x)$
(*d*) $(1 - x)$.

80. For NH_3, $K_b = 1.8 \times 10^{-5}$. K_a for NH_4^+ would be

(*a*) 1.8×10^{5}
(*b*) 5.56×10^{5}
(*c*) 1.8×10^{10}
(*d*) 5.56×10^{-10}.

81. Which of the following can act as a Bronsted acid as well as a Bronsted base ?

(*a*) S^{2-}
(*b*) H_2S
(*c*) HS^-
(*d*) None of these.

82. For the reaction, $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ K_p is equal to

(*a*) K_c
(*b*) K_cRT
(*c*) $K_c(RT)^2$
(*d*) $K_c(RT)^{-1}$.

83. One mole of N_2O_4 is enclosed in a 5 L container. At equilibrium, the container has 0.5 mole of N_2O_4. The equilibrium constant for the decomposition of N_2O_4

$$[N_2O_4(g) \rightleftharpoons 2NO_2(g)] \text{ is}$$

(*a*) 1
(*b*) 2/5
(*c*) 3
(*d*) 1/5.

84. Equal volumes of two solutions, one having pH 6 and the other having pH 4 are mixed. The pH of the resulting solution would be

(*a*) 5.7
(*b*) 4.3
(*c*) 5.0
(*d*) 5.5.

85. 100 ml of 0.1 M CH_3COOH are mixed with 100 ml of 0.1 NaOH, the pH of the resulting solution would be

(*a*) zero
(*b*) 7
(*c*) > 7
(*d*) < 7.

86. 100 ml of 0.2 M HCl are mixed with 100 ml of 0.2 M CH_3COOH, the pH of the resulting solution would be nearly

(*a*) 1
(*b*) 0.7
(*c*) 1.3
(*d*) 1.6.

87. The solubility of AgCl would be maximum in

(*a*) 0.1 M NaCl
(*b*) Water
(*c*) 0.1 M $BaCl_2$
(*d*) 0.1 M KCl.

88. When 100 ml of 0.4 M CH_3COOH are mixed with 100 ml of 0.2 M NaOH, the $[H_3O^+]$ in the solution is approximately : $[K_a(CH_3COOH) = 1.8 \times 10^{-5}]$

(*a*) 1.8×10^{-6}
(*b*) 1.8×10^{-5}
(*c*) 9×10^{-6}
(*d*) 9×10^{-5}.

89. Addition of which of the following solutions will have no effect on the pH of the 100 ml of 0.1 M HCl

(*a*) 100 ml of 0.1 M NaOH
(*b*) 100 ml of H_2O
(*c*) 100 ml of 0.1 M HCl
(*d*) 100 ml of NaCl.

90. Which of the following solutions when added to 1 L of 0.1 M CH_3COOH will decrease the pH of the solution

(*a*) 1 L of H_2O
(*b*) 1 L of 0.1 M CH_3COONa
(*c*) 1 L of 0.1 M HCl
(*d*) 1 L of 0.1 M CH_3COOH.

91. 0.2 M solution of a weak acid HA is 1% ionised at 25°C. K_a for the acid is equal to

(*a*) $\frac{0.002 \times 0.002}{0.198}$
(*b*) $\frac{0.02 \times 0.02}{0.18}$
(*c*) $\frac{0.01 \times 0.01}{0.19}$
(*d*) $\frac{0.19}{0.01 \times 0.01}$.

92. The value of K_w for water at a certain temperature is 4×10^{-12}. The pH of pure water at the given temperature would be

(*a*) 7
(*b*) 2×10^{-6}
(*c*) 5.7
(*d*) 6.3.

93. The $[OH^-]$ in 10^{-10} M solution of NaOH in water would be approximately

(*a*) 10^{-10} M
(*b*) 10^{10} M
(*c*) 10^{-8} M
(*d*) 10^{-7} M.

94. Among the following hydroxides the one which has the lowest value of K_{sp} at ordinary temperature (about 25°C) is

(*a*) $Mg(OH)_2$
(*b*) $Ca(OH)_2$
(*c*) $Ba(OH)_2$
(*d*) $Be(OH)_2$.

95. The following equilibrium is established when hydrogen chloride is dissolved in acetic acid

$$HCl + CH_3COOH \rightleftharpoons Cl^- + CH_3COOH_2^+$$

The set that characterises the conjugate acid-base pairs is

(*a*) (HCl, CH_3COOH) and $(CH_3COOH_2^+, Cl^-)$
(*b*) $(HCl, CH_3COOH_2^+)$ and (CH_3COOH, Cl^-)
(*c*) $(CH_3COOH_2^+, HCl)$ and (Cl^-, CH_3COOH)
(*d*) (HCl, Cl^-) and $(CH_3COOH_2^+, CH_3COOH)$.

96. Which of the following will occur if a 0.1 M solution of a weak acid is diluted to 0.01 M at constant temperature ?

(*a*) $[H^+]$ will decrease to 0.01 M
(*b*) pH will decrease
(*c*) percentage ionisation will increase
(*d*) K_a will increase.

97. The solubility of AgCl is maximum in

(*a*) Pure water (*b*) 0.1 M NH_3

(*c*) 0.1 M NaCl (*d*) 0.1 M $CaCl_2$.

98. Which of the following is true for the saturated solution of sparingly soluble PbI_2 ?

(*a*) $[Pb^{2+}] = [I^-]$ (*b*) $[Pb^{2+}] = \sqrt{K_{sp}}$

(*c*) $[Pb^{2+}] = K_{sp}$ (*d*) $[Pb^{2+}] = 0.5[I^-]$.

99. The solubility of AgI in NaI solution is less than that in pure water because

(*a*) AgI forms complex with NaI

(*b*) of common ion effect

(*c*) solubility product of AgI is less than that of NaI

(*d*) the temperature of the solution decreases.

100. Cu^{2+} and Pb^{2+} ions are both present in aqueous solution. To precipitate one of the ions and leave the other in the solution add

(*a*) $H_2S(aq)$ (*b*) $HNO_3(aq)$

(*c*) $NH_4NO_3(aq)$ (*d*) $H_2SO_4(aq)$.

QUESTION BANK

Level II

Choose the correct answer from the four alternatives given in each of the following questions :

1. For the reaction

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

the value of K_c at 250°C is 26. The value of K_p at this temperature will be

(*a*) 0.61 (*b*) 0.57

(*c*) 0.83 (*d*) 0.46.

2. In a vessel containing SO_3, SO_2 and O_2 at equilibrium some helium gas is introduced so that the total pressure increases while temperature and volume remain constant. According to Le Chatelier's principle, the dissociation of SO_3

(*a*) increases (*b*) decreases

(*c*) remains unaltered (*d*) changes unpredictably.

3. In a reversible reaction, two substances are in equilibrium. If the concentration of each one is doubled, the equilibrium constant will be

(*a*) Reduced to half its original value

(*b*) Reduced to one fourth of its original value

(*c*) Doubled

(*d*) Constant.

4. What is the solubility of $Al(OH)_3$, $K_{sp} = 1 \times 10^{-33}$, in a solution having pH = 4.

(*a*) 10^{-3} M (*b*) 10^{-6} M

(*c*) 10^{-4} M (*d*) 10^{-10} M.

5. The solubility of $Fe(OH)_3$ would be maximum in

(*a*) 0.1 M NaOH (*b*) 0.1 M HCl

(*c*) 0.01 M KOH (*d*) 0.1 M H_2SO_4.

6. Which of the following sulphides has the largest value of K_{sp} ?

(*a*) CuS (*b*) CdS

(*c*) PbS (*d*) ZnS.

7. A certain buffer solution contains X^- and HX. The concentration of X^- is twice the concentration of HX. If K_a for HX is 10^{-6}, the pH of the buffer is

(*a*) 6 (*b*) 4

(*c*) 6.3 (*d*) 5.8.

8. The equilibrium constant for the reaction,

$$N_2(g) + O_2(g) \qquad 2NO(g) \text{ is } 4 \times 10^{-4}$$

at 2000 K. In presence of a catalyst, equilibrium is attained ten times faster. Therefore, the equilibrium constant, in presence of the catalyst, at 2000 K is

(*a*) 40×10^{-4}

(*b*) 4×10^{-4}

(*c*) 4×10^{-3}

(*d*) difficult to compute without more data.

9. The sparingly soluble salt Ag_2CrO_4 is expected to be most soluble in

(*a*) Pure water (*b*) 0.10 M K_2CrO_4

(*c*) 0.10 M $AgNO_3$ (*d*) 0.10 M KNO_3.

10. The pK_a of HCN is 9.30. The pH of a solution prepared by mixing 2.5 moles of KCN and 2.5 moles of HCN in water and making up to total volume to 500 ml is

(*a*) 9.30
(*b*) 7.30
(*c*) 10.30
(*d*) 8.30.

11. The number of moles of H_3O^+ ions in 200 mL of 0.005 M H_2SO_4 is

(*a*) 0.005
(*b*) 0.01
(*c*) 0.002
(*d*) 0.001.

12. The reaction of CH_3COOH with a base will proceed towards right to maximum extent when the base is

(*a*) H_2O
(*b*) Cl^-
(*c*) $HClO_4$
(*d*) NH_3.

13. Which of the following when added to 1.0 L of 0.5 M HCl would result in maximum increase in pH ?

(*a*) 0.5 mol CH_3COOH
(*b*) 1.0 mol NaCl
(*c*) 0.4 mol NaOH
(*d*) 0.6 mol CH_3COONa.

14. According to Le Chatelier's principle adding heat to a solid and liquid in equilibrium will cause the

(*a*) amount of solid to decrease
(*b*) amount of liquid to decrease
(*c*) temperature to rise
(*d*) temperature to fall.

15. Which of the following, when added to a saturated aqueous solution of $CaCO_3$ would increase the molar solubility of $CaCO_3$?

(*a*) Na_2CO_3
(*b*) NH_3
(*c*) $NaHSO_4$
(*d*) more water.

16. If the concentration of CrO_4^{2-} ions in a saturated solution of silver chromate is 2×10^{-4} M, the solubility product of silver chromate would be

(*a*) 32×10^{-12}
(*b*) 8×10^{-12}
(*c*) 16×10^{-12}
(*d*) 8×10^{-8}.

17. The K_{sp} values of $PbCO_3$ and $MgCO_3$ are 1.5×10^{-15} and 1×10^{-15} respectively at 298 K. What would be the concentration of Pb^{2+} ions in a solution that is saturated with respect to $PbCO_3$ and $MgCO_3$?

(*a*) 3×10^{-8} M
(*b*) 5×10^{-8} M
(*c*) 4×10^{-8} M
(*d*) 1.5×10^{-8} M.

18. In the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

the value of the equilibrium constant depends on

(*a*) volume of the reaction vessel
(*b*) total pressure of the system
(*c*) the initial concentration of nitrogen and hydrogen
(*d*) the temperature.

19. One mole of SO_3 was placed in a litre reaction vessel at a certain temperature. The following equilibrium was established

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$$

At equilibrium, 0.6 moles of SO_2 were formed. The equilibrium constant of the reaction will be

(*a*) 0.36
(*b*) 0.45
(*c*) 0.54
(*d*) 0.675.

20. For a system in equilibrium $\Delta G = 0$, under conditions of constant

(*a*) temperature and pressure
(*b*) temperature and volume
(*c*) energy and volume
(*d*) pressure and volume.

21. An equilibrium mixture for the reaction

$$2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$$

had 1 mole of H_2S, 0.2 mole of H_2 and 0.8 mole of S_2 in a 2 litre flask. The value of K_c in mol L^{-1} is

(*a*) 0.004
(*b*) 0.080
(*c*) 0.016
(*d*) 0.160.

22. $\Delta G°_f(HI, g) \simeq +1.7$ kJ what is the equilibrium constant at 25°C for $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$?

(*a*) 24.0
(*b*) 3.9
(*c*) 2.0
(*d*) 0.5.

23. 0.1 M solution of which of the substance will behave basic ?

(*a*) sodium borate
(*b*) ammonium chloride
(*c*) calcium nitrate
(*d*) sodium sulphate.

24. Given that K_a for acetic acid as 1.8×10^{-5} and K_b of NH_4OH as 1.8×10^{-5} at 25°C, predict the nature of aqueous solution of ammonium acetate.

(*a*) Acidic
(*b*) Basic
(*c*) Slightly acidic or basic
(*d*) Neutral.

25. If the solubility of lithium sodium hexafluoroaluminate, $Li_3Na_3(AlF_6)_2$ is 'S' mol L^{-1}, its solubility product is equal to

(*a*) S^8
(*b*) $12 S^3$
(*c*) $18 S^3$
(*d*) $2916 S^8$.

26. Sulphanilic acid is a/an

(*a*) Arrhenius acid
(*b*) Lewis base
(*c*) Neither (*a*) nor (*b*)
(*d*) Both (*a*) and (*b*).

27. 10^{-6} M NaOH is diluted by 100 times. The pH of diluted base is

(*a*) Between 6 and 7 (*b*) Between 10 and 11

(*c*) Between 7 and 8 (*d*) Between 5 and 6.

28. Ostwald's dilution law is applicable to

(*a*) Strong electrolytes only

(*b*) Weak electrolytes only

(*c*) Non-electrolytes

(*d*) Strong as well as weak electrolytes.

29. To a solution containing equimolar mixture of sodium acetate and acetic acid, some more amount of sodium acetate solution is added. The *p*H of mixture solution

(*a*) increases (*b*) decreases

(*c*) remains unchanged (*d*) unpredictable.

30. The best explanation for the solubility of MnS in dil HCl is that

(*a*) solubility product of $MnCl_2$ is less than that of MnS

(*b*) concentration of Mn^{2+} is lowered by the formation of complex ions with chloride ions

(*c*) concentration of sulphide ions is lowered by oxidation to free sulphur

(*d*) concentration of sulphide ions is lowered by the formation of the weak H_2S.

31. The pK_a of HCN is 9.30. The pH of a solution prepared by mixing 2.5 moles of KCN and 2.5 moles of HCN in water and making up to total volume to 500 ml is

(*a*) 9.30 (*b*) 7.30

(*c*) 10.30 (*d*) 8.30.

32. In which of the following reaction doubling the volume of container cause a shift to right ?

(*a*) $2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$

(*b*) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(*c*) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

(*d*) $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$.

33. If H^+ ion conc. of a solution is increased by 10 times, its *p*H will

(*a*) increase by one (*b*) remains unchanged

(*c*) decrease by one (*d*) increase by 10.

34. In what manner will increase of pressure affects the following equilibrium ?

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$

(*a*) Shift in the forward direction

(*b*) Shift in the reverse direction

(*c*) Increase in the yield of hydrogen

(*d*) No effect.

35. Consider the following reaction occurring in an automobile

$$2C_8H_{18}(g) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(g)$$

The sign of ΔH, ΔS and ΔG would be

(*a*) +, –, + (*b*) –, +, –

(*c*) –, +, + (*d*) +, +, –.

36. The concentration of Ag^+ ions in a given saturated solution of AgCl at 25°C is 1.06×10^{-5} mole ion per litre. The solubility product of AgCl is

(*a*) 0.353×10^{-10} (*b*) 0.530×10^{-10}

(*c*) 1.12×10^{-10} (*d*) 2.12×10^{-10}.

37. 1.1 mol of A is mixed with 2.2 mol of B and the mixture is kept in one litre flask till the equilibrium is reached. At equilibrium, 0.2 mol of C is formed. If the equilibrium reaction is $A + 2B \rightleftharpoons 2C + D$, the value of equilibrium constant is

(*a*) 0.002 (*b*) 0.004

(*c*) 0.001 (*d*) 0.003.

38. At a certain temperature $2HI \rightleftharpoons H_2 + I_2$, only 50% HI is dissociated at equilibrium. The equilibrium constant is

(*a*) 0.25 (*b*) 1.0

(*c*) 3.0 (*d*) 0.5.

39. Which two of the following will have nearly equal H^+ concentration ?

(*i*) 100 ml 0.1 M HCl mixed with 50 ml water

(*ii*) 50 ml 0.1 M H_2SO_4 mixed with 50 ml water

(*iii*) 50 ml 0.1 M H_2SO_4 mixed with 100 ml water

(*iv*) 50 ml 0.1 M HCl mixed with 50 ml water.

(*a*) (*i*) and (*iii*) (*b*) (*ii*) and (*iii*)

(*c*) (*i*) and (*ii*) (*d*) (*iii*) and (*iv*).

40. The reaction, $SO_2 + Cl_2 \rightleftharpoons SO_2Cl_2$ is exothermic and reversible. A mixture of $SO_2(g)$, $Cl_2(g)$ and $SO_2Cl_2(l)$ is at equilibrium in a closed container. Now a certain quantity of extra SO_2 is introduced into the container, the volume remaining the same. Which of the following is/are true ?

(*a*) The pressure inside the container will not change

(*b*) The temperature will not change

(*c*) The temperature will increase

(*d*) The temperature will decrease.

41. The standard state Gibb's free energy change for the isomerisation reaction *cis*-2-pentene $\rightleftharpoons$ *trans*-2-pentene, is – 3.67 kJ mol at 400 K. If more *trans*-2-pentene is added to the reaction vessel

(*a*) More *cis*-2-pentene is formed
(*b*) Equilibrium shifts in the forward direction
(*c*) Equilibrium remains unaltered
(*d*) More *trans*-2-pentene is produced.

42. The solubility of $PbCl_2$ is

(*a*) $\sqrt{K_{sp}}$ (*b*) $(K_{sp})^{1/3}$
(*c*) $(K_{sp}/4)^{1/3}$ (*d*) $(8K_{sp})^{1/2}$.

43. Why only As^{+3} gets precipitated as As_2S_3 and not Zn^{+2} as ZnS when H_2S is passed through an acidic solution containing As^{+3} and Zn^{+2} ?

(*a*) Solubility product of As_2S_3 is less than that of ZnS
(*b*) Enough As^{+3} are present in acidic medium
(*c*) Zinc salt does not ionise in acidic medium
(*d*) Solubility product changes in presence of an acid.

44. If α is the fraction of HI dissociated at equilibrium in the reaction, $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$, starting with 2 moles of HI, the total number of moles of reactants and products at equilibrium are

(*a*) $1 + \alpha$ (*b*) $2 + 2\alpha$
(*c*) 2 (*d*) $2 - \alpha$.

45. In a reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$, the yield of NH_3 increases on

(*a*) increasing the temperature
(*b*) increasing pressure
(*c*) increasing temperature as well as pressure
(*d*) decreasing temperature as well as pressure.

46. One mole of $N_2O_4(g)$ at 300 K is kept in a closed vessel at 1 atmosphere pressure. It is heated to 600 K when 20% by mass of $N_2O_4(g)$ decomposes to $NO_2(g)$. The resultant pressure is

(*a*) 1.2 atm (*b*) 2.4 atm
(*c*) 2.0 atm (*d*) 1.0 atm.

47. In a mixture of weak acid and its salt, the ratio of concentration of acid to salt is increased by 10 fold. The pH of the solution

(*a*) decreases by one (*b*) decreases by one-tenth
(*c*) increase by one (*d*) increase by ten fold.

48. In a reaction $A + 2B \rightleftharpoons 2C$, if 2.0 moles of A, 3.0 moles of B and 2.0 moles of C are placed in a flask of 2L capacity and equilibrium concentration of C is 0.5 mol L^{-1}. The value of equilibrium constant K_c of the reaction is

(*a*) 0.073 (*b*) 0.147
(*c*) 0.05 (*d*) 0.026

49. In the reaction $I_2 + I^- \rightarrow I_3^-$, the Lewis base is

(*a*) I_2 (*b*) I^-
(*c*) I_3^- (*d*) None of these.

50. The conc. of NH_4^+ ions in a solution which is 0.02 M NH_3 and 0.01 M KOH would be

$$(K_{b(NH_3)} = 1.8 \times 10^{-5})$$

(*a*) 3.6×10^{-5} (*b*) 1.8×10^{-5}
(*c*) 9.0×10^{-6} (*d*) 4.5×10^{-5}.

51. A physician wishes to prepare a buffer solution at *p*H = 3.58 that efficiently resists a change in *p*H yet contains only small conc. of the buffering agents. Which one of the following weak acid together with its sodium salt would be best to use ?

(*a*) *m*-chloro benzoic acid ($pK_a = 3.98$)
(*b*) *p*-chlorocinnamic acid ($pK_a = 4.41$)
(*c*) 2, 5-dihydroxy benzoic acid ($pK_a = 2.97$)
(*d*) Acetoacetic acid ($pK_a = 3.58$).

52. The solubility product of CuS, Ag_2S and HgS are 10^{-31}, 10^{-44} and 10^{-54} respectively.

The solubility of these sulphides are in the order

(*a*) $Ag_2S > CuS > HgS$ (*b*) $AgS > HgS > CuS$
(*c*) $HgS > Ag_2S > CuS$ (*d*) $CuS > Ag_2S > HgS$.

53. A white salt is readily soluble in water and gives a colourless solution with a *p*H of about 9. The salt would be

(*a*) NH_4NO_3 (*b*) CH_3COONa
(*c*) CH_3COONH_4 (*d*) $CaCO_3$.

54. Why are strong acids generally used as standard solutions in acid-base titrations ?

(*a*) The *p*H at the equivalent point will always be 7
(*b*) They can be used to titrate both strong and weak bases
(*c*) Strong acids form more stable solutions than weak acids
(*d*) The salts of strong acid do not hydrolyse.

55. For preparing a buffer solution of pH 6 by mixing sodium acetate and acetic acid, the ratio of the connectration of salt and acid should be ($K_a = 10^{-5}$)

(*a*) 1 : 10 (*b*) 10 : 1
(*c*) 100 : 1 (*d*) 1 : 100.

56. 4.5 moles each of hydrogen and iodine are heated in a sealed ten litre vessel. At equilibrium 3 moles of HI were found. The equilibrium constant for

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \text{ is}$$

(*a*) 1 (*b*) 10

(*c*) 5 (*d*) 0.33.

57. The pH of a solution is increased from 3 to 6 ; its H^+ ion concentration will be

(*a*) reduced to half (*b*) doubled

(*c*) reduced by 1000 times (*d*) increased by 1000 times

58. In the reaction $A + B \rightarrow C + D$, if we start with equal concentration of A and B, at equilibrium we find that the moles of C is two times of A. What is the equilibrium constant of the reaction ?

(*a*) 4 (*b*) 2

(*c*) $\frac{1}{4}$ (*d*) $\frac{1}{2}$.

59. K_p/K_c for the reaction

$$CO(g) + \frac{1}{2}O_2(g) \rightleftharpoons CO_2(g) \text{ is}$$

(*a*) 1 (*b*) RT

(*c*) $\frac{1}{\sqrt{RT}}$ (*d*) $(RT)^{1/2}$.

60. K_1 and K_2 are the respective equilibrium constants for the two reactions

(*i*) $Xe_2F_6(g) + H_2O(g) \rightleftharpoons XeOF_4(g) + 2HF(g)$

(*ii*) $XeO_4(g) + XeF_6(g) \rightleftharpoons XeOF_4(g) + XeO_3F_2(g)$

The equilibrium constant of the reaction

$XeO_4(g) + 2HF(g) \rightleftharpoons XeO_3F_2(g) + H_2O(g)$ will be

(*a*) $K_1/(K_2)^2$ (*b*) $K_1 - K_2$

(c) K_1/K_2 (*d*) K_2/K_1.

61. For the reaction,

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g),$$

at a given temperature the equilibrium amount of $CO_2(g)$ can be increased by

(*a*) Adding a suitable catalyst

(*b*) Adding an inert gas

(*c*) Decreasing the volume of container

(*d*) Increasing the amount of $CO(g)$.

62. Which of the following statements is correct ?

(*a*) The pH of 1×10^{-8} M solution of HCl is 8

(*b*) The conjugate base of $H_2PO_4^-$ is HPO_4^{2-}

(*c*) Autoprotolysis constant of water decreases with temperature

(*d*) When a solution of a weak monoprotic acid is titrated against a strong base, at half neutralization point

$$pH = \left(\frac{1}{2}\right)pK_a.$$

63. The pH of 0.1 M solution of the following salts increases in the order

(*a*) $NaCl < NH_4Cl < NaCN < HCl$

(*b*) $HCl < NH_4Cl < NaCl < NaCN$

(*c*) $NaCN < NH_4Cl < NaCl < HCl$

(*d*) $HCl < NaCl < NaCN < NH_4Cl$.

64. For the chemical reaction $3X(g) + Y(g) \rightleftharpoons X_3Y(g)$ the amount of X_3Y at equilibrium is affected by

(*a*) temperature and pressure

(*b*) temperature only

(*c*) pressure only

(*d*) temperature, pressure and catalyst.

65. A buffer solution cannot be prepared from a mixture of

(*a*) sodium acetate and acetic acid in water

(*b*) sodium acetate and hydrochloric acid in water

(*c*) ammonia and ammonium chloride in water

(*d*) ammonia and sodium hydroxide in water.

66. The concentration of $[H^+]$ and concentration of $[OH^-]$ of a 0.1 M aqueous solution of 2% ionised weak acid is [ionic product of water $= 1 \times 10^{-14}$]

(*a*) 0.02×10^{-3} M and 5×10^{-11} M

(*b*) 1×10^{-3} M and 3×10^{-11} M

(*c*) 2×10^{-3} M and 5×10^{-12} M

(*d*) 3×10^{-2} M and 4×10^{-13} M.

67. For the reversible reaction,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \text{ at } 500°C,$$

the value of K_p is 1.44×10^{-5} when partial pressure is measured in atmospheres. The corresponding value of K_c, with concentration in mole litre^{-1} is

(*a*) $1.44 \times 10^{-5}/(0.082 \times 500)^{-2}$

(*b*) $1.44 \times 10^{-5}/(8.314 \times 773)^{-2}$

(*c*) $1.44 \times 10^{-5}/(0.082 \times 773)^{2}$

(*d*) $1.44 \times 10^{-5}/(0.082 \times 773)^{-2}$.

68. When two reactants, A and B are mixed to give products C and D, the reaction quotient, Q, at the initial stages of the reaction

(*a*) is zero (*b*) decreases with time

(*c*) is independent of time (*d*) increases with time.

69. For an equilibrium ; $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ the total pressure at equilibrium is P and degree of dissociation of N_2O_4 is x.

Which one of the following is the partial pressure of NO_2 ?

(*a*) $\frac{2x}{(1+x)}$ P

(*b*) $2 \times$ P

(*c*) $\frac{2}{(1-x)}$ P

(*d*) $\frac{2}{3} \times$ P.

70. If the gas mixture for the following reaction,

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$, is compressed, then

(*a*) Products are favoured

(*b*) Reactants are favoured

(*c*) No change

(*d*) Products become equal to reactants.

71. For a gaseous reaction,

$pA + qB \rightleftharpoons qC + pD$,

which of the following relationships is true ?

(*a*) $K_p = K_c$

(*b*) $K_p = K_c(RT)^{p+q}$

(*c*) $K_p = K_c(RT)^{p-q}$

(*d*) $K_p = K_c = (RT)^{1/p+q}$.

72. For the reaction,

$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(l)$; $\Delta H = +$ ve

which of the following factors will not change the $[NH_3]$ at equilibrium ?

(*a*) Increase of pressure

(*b*) Increase of volume

(*c*) Addition of catalyst

(*d*) Decrease of temperature.

73. One mole of SO_3 was placed in a litre vessel at a certain temperature. When equilibrium was established in the reaction,

$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$

the vessel was found to contain 0.4 moles of SO_3. The value of equilibrium constant is

(*a*) 0.13

(*b*) 0.36

(*c*) 0.68

(*d*) 0.45.

74. Which of the following statements is incorrect about the equilibrium state ?

(*a*) It is dynamic in nature

(*b*) There is no change in properties with time

(*c*) It readjusts with the change in conditions

(*d*) It can be attained from the side of reactants only.

75. Which of the following salts has maximum solubility ?

(*a*) CaF_2 ; $K_{sp} = 1.7 \times 10^{-10}$

(*b*) $BaSO_4$; $K_{sp} = 1.5 \times 10^{-9}$

(*c*) $PbSO_4$; $K_{sp} = 1.3 \times 10^{-8}$

(*d*) AgCl ; $K_{sp} = 1.7 \times 10^{-10}$.

76. Which has the highest degree of ionization ?

(*a*) 1 M NH_3

(*b*) 0.001 M NH_3

(*c*) 0.1 M NH_3

(*d*) 0.0001 M NH_3.

77. Which of the following salts will yield basic solution on dissolution in water ?

(*a*) A salt of weak acid and a weak base

(*b*) A salt of strong acid and a strong base

(*c*) A salt of weak acid and a strong base

(*d*) A salt of strong acid and a weak base.

78. Molar concentration of water is

(*a*) 555 mol L^{-1}

(*b*) 5.55 mol L^{-1}

(*c*) 55.5 mol L^{-1}

(*d*) 0.555 mol L^{-1}.

79. The compound whose water solution has the highest pH is

(*a*) KNO_3

(*b*) NH_4Cl

(*c*) $(NH_4)_2CO_3$

(*d*) Na_2CO_3.

80. When 100 ml of 0.1 M solution of acetic acid is mixed with 100 ml of 0.1 M solution of NaOH, the resulting solution will have pH

(*a*) Zero

(*b*) 7

(*c*) More than 7

(*d*) Less than 7.

81. Which buffer solution out of the following will have pH > 7 ?

(*a*) $CH_3COOH + CH_3COONa$

(*b*) $HCOOH + HCOOK$

(*c*) CH_3COONH_4

(*d*) $NH_4OH + NH_4Cl$.

82. The initial pressure of $COCl_2$ is 1000 torr. The total pressure of the system becomes 1500 torr, when the equilibrium $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$ is attained at constant temperature. The value of K_p of a reaction is

(*a*) 1500

(*b*) 1000

(*c*) 2500

(*d*) 500.

83. For the equilibrium,

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

the total pressure at equilibrium is P and degree of dissociation of PCl_5 is x. Which of the following is the partial pressure of PCl_3 ?

(*a*) $\frac{x}{x-1} \times P$
(*b*) $\frac{x}{1-x} \times P$
(*c*) $\frac{x}{x+1} \times P$
(*d*) $\frac{2x}{1-x} \times P$.

84. When 1 mole of N_2 and 1 mole of H_2 is enclosed in 5 L vessel and the reaction is allowed to attain equilibrium, it is found that at equilibrium there is x mole of H_2. The number of moles of NH_3 formed would be

(*a*) $\frac{2x}{3}$
(*b*) $2(1+x)/3$
(*c*) $\frac{2(1-x)}{3}$
(*d*) $\frac{(1-x)}{2}$.

85. One mole of N_2O_4 is enclosed in a 10 L container. At equilibrium, the container has 0.5 mole of N_2O_4. The equilibrium constant for the decomposition of

$$N_2O_4\ [N_2O_4(g) \rightleftharpoons 2NO_2(g)] \text{ is}$$

(*a*) 1
(*b*) 2/5
(*c*) 3
(*d*) 1/5.

86. Degree of hydrolysis of a salt of strong acid and a weak base is equal to

(*a*) $\frac{K_h}{C}$
(*b*) $\sqrt{\frac{K_h}{C}}$
(*c*) $\sqrt{K_h}$
(*d*) K_h.

87. Addition of which of the following solutions will have no effect on the pH of the 50 ml of 0.1 M NaOH ?

(*a*) 100 ml of 0.1 M NaOH
(*b*) 100 ml of H_2O
(*c*) 100 ml of 0.1 M HCl
(*d*) 100 ml of NaCl.

88. At 25°C, the dissociation constants of CH_3COOH and NH_4OH in aqueous solution are almost the same. The pH of a solution of 0.01 N CH_3COOH is 4.0 at 25°C. The pH of 0.01 N NH_4OH solution at the same temperature would be

(*a*) 3.0
(*b*) 4.0
(*c*) 10.0
(*d*) 10.5.

89. A solution is saturated with respect to AgSCN as well as AgBr. The conc. of Ag^+ in the solution would be (K_{sp} for AgSCN = 1.2×10^{-12} and for AgBr = 5×10^{-13})

(*a*) 1.3×10^{-5}
(*b*) 1.3×10^{-12}
(*c*) 1.3×10^{-6}
(*d*) 1.3×10^{-8}.

90. The dissociation constants of two weak acids are K_1 and K_2. The relative strength of the two acids is given by

(*a*) K_1/K_2
(*b*) $(K_1/K_2)^{1/2}$
(*c*) $(K_1/K_2)^{3/2}$
(*d*) $K_1 - K_2$.

91. If solubility of $Ca_3(PO_4)_2$ is x mole/litre, its solubility product would be

(*a*) $4x^3$
(*b*) x^2
(*c*) $27x^4$
(*d*) $108x^5$.

92. For which of the following reactions, the degree of dissociation (α) and equilibrium constant (K_p) are related as $K_p = 4\alpha^2 p/(1-\alpha^2)$

(*a*) $N_2O_4(g) \rightleftharpoons 2NO_2$
(*b*) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
(*c*) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
(*d*) $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$.

93. For the reaction,

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

the value of K_c at 250° is 26. The value of K_p at this temperature will be

(*a*) 0.61
(*b*) 0.57
(*c*) 0.83
(*d*) 0.46.

94. Among the following hydroxides, the one which has the lowest value of K_{sp} at ordinary temperature (about 25°C) is

(*a*) $Mg(OH)_2$
(*b*) $Ca(OH)_2$
(*c*) $Ba(OH)_2$
(*d*) $Be(OH)_2$.

95. The aqueous solution of aluminium chloride is acidic due to

(*a*) Cation hydrolysis
(*b*) Anion hydrolysis
(*c*) Hydrolysis of both anion and cation
(*d*) Dissociation.

96. If K_p for a reaction,

$$A(g) + 2B(g) \rightleftharpoons 3C(g) + D(g)$$

is 0.05 atm at 1000 K. Its K_c in terms of R will be

(*a*) 20000 R
(*b*) 0.02 R
(*c*) 5×10^{-5} R
(*d*) $\frac{5 \times 10^{-5}}{R}$.

97. If C is the number of moles of a monoprotic acid present in one litre of solution and α is the degree of dissociation for weak acid, the dissociation constant of acid is given by the expression

(*a*) $C^2\alpha^2/1-\alpha$
(*b*) $C\alpha^2/(1-\alpha)^2$
(*c*) $\frac{C\alpha}{1-\alpha}$
(*d*) $\frac{C\alpha^2}{1-\alpha}$.

98. One litre of water contains 10^{-7} moles of H^+ ions. Degree of ionisation of water is

(*a*) $1.8 \times 10^{-7}\%$ (*b*) $0.8 \times 10^{-9}\%$

(*c*) $3.6 \times 10^{-9}\%$ (*d*) $3.6 \times 10^{-7}\%$.

99. When 4 gm of NaOH is dissolved in 10 litre of solution, the pH is

(*a*) 6 (*b*) 12

(*c*) 18 (*d*) 24.

100. An acid solution of pH 6 is diluted thousand times. The pH of solution becomes approximately.

(*a*) 6.96 (*b*) 6

(*c*) 4 (*d*) 9.

ANSWERS

QUESTION BANK (Level I)

1. (*a*) **2.** (*d*) **3.** (*c*) **4.** (*c*) **5.** (*c*) **6.** (*c*) **7.** (*d*) **8.** (*d*)
9. (*a*) **10.** (*b*) **11.** (*b*) **12.** (*d*) **13.** (*d*) **14.** (*c*) **15.** (*b*) **16.** (*c*)
17. (*c*) **18.** (*d*) **19.** (*a*) **20.** (*d*) **21.** (*c*) **22.** (*c*) **23.** (*b*) **24.** (*a*)
25. (*c*) **26.** (*b*) **27.** (*d*) **28.** (*d*) **29.** (*c*) **30.** (*a*) **31.** (*d*) **32.** (*d*)
33. (*d*) **34.** (*a*) **35.** (*b*) **36.** (*a*) **37.** (*b*) **38.** (*c*) **39.** (*b*) **40.** (*c*)
41. (*b*) **42.** (*d*) **43.** (*c*) **44.** (*a*) **45.** (*c*) **46.** (*c*) **47.** (*c*) **48.** (*d*)
49. (*d*) **50.** (*b*) **51.** (*b*) **52.** (*b*) **53.** (*d*) **54.** (*b*) **55.** (*c*) **56.** (*d*)
57. (*a*) **58.** (*c*) **59.** (*b*) **60.** (*c*) **61.** (*c*) **62.** (*a*) **63.** (*b*) **64.** (*d*)
65. (*c*) **66.** (*c*) **67.** (*c*) **68.** (*c*) **69.** (*b*) **70.** (*a*) **71.** (*a*) **72.** (*a*)
73. (*b*) **74.** (*a*) **75.** (*c*) **76.** (*d*) **77.** (*a*) **78.** (*c*) **79.** (*c*) **80.** (*d*)
81. (*c*) **82.** (*b*) **83.** (*b*) **84.** (*b*) **85.** (*c*) **86.** (*a*) **87.** (*b*) **88.** (*b*)
89. (*c*) **90.** (*c*) **91.** (*a*) **92.** (*c*) **93.** (*d*) **94.** (*d*) **95.** (*d*) **96.** (*c*)
97. (*b*) **98.** (*d*) **99.** (*b*) **100.** (*d*).

QUESTION BANK (Level II)

1. (*a*) **2.** (*c*) **3.** (*d*) **4.** (*a*) **5.** (*d*) **6.** (*d*) **7.** (*c*) **8.** (*b*)
9. (*d*) **10.** (*a*) **11.** (*c*) **12.** (*d*) **13.** (*d*) **14.** (*a*) **15.** (*c*) **16.** (*a*)
17. (*a*) **18.** (*d*) **19.** (*d*) **20.** (*a*) **21.** (*c*) **22.** (*b*) **23.** (*a*) **24.** (*d*)
25. (*d*) **26.** (*d*) **27.** (*c*) **28.** (*b*) **29.** (*a*) **30.** (*d*) **31.** (*a*) **32.** (*c*)
33. (*c*) **34.** (*b*) **35.** (*b*) **36.** (*c*) **37.** (*c*) **38.** (*a*) **39.** (*a*) **40.** (*c*)
41. (*a*) **42.** (*c*) **43.** (*a*) **44.** (*c*) **45.** (*b*) **46.** (*a*) **47.** (*a*) **48.** (*c*)
49. (*b*) **50.** (*a*) **51.** (*d*) **52.** (*a*) **53.** (*b*) **54.** (*b*) **55.** (*b*) **56.** (*a*)
57. (*c*) **58.** (*a*) **59.** (*c*) **60.** (*d*) **61.** (*d*) **62.** (*b*) **63.** (*b*) **64.** (*a*)
65. (*d*) **66.** (*c*) **67.** (*d*) **68.** (*d*) **69.** (*a*) **70.** (*b*) **71.** (*a*) **72.** (*c*)
73. (*c*) **74.** (*d*) **75.** (*a*) **76.** (*d*) **77.** (*c*) **78.** (*c*) **79.** (*d*) **80.** (*c*)
81. (*d*) **82.** (*d*) **83.** (*c*) **84.** (*c*) **85.** (*d*) **86.** (*b*) **87.** (*a*) **88.** (*c*)
89. (*c*) **90.** (*b*) **91.** (*d*) **92.** (*a*) **93.** (*a*) **94.** (*d*) **95.** (*a*) **96.** (*d*)
97. (*d*) **98.** (*a*) **99.** (*b*) **100.** (*a*).

HINTS/SOLUTIONS

QUESTION BANK (Level I)

1. (*a*) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

Equilibrium conc. $\left(\frac{0.1}{10}\right) \quad \left(\frac{0.2}{10}\right) \quad \left(\frac{0.2}{10}\right)$

$$K = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{(0.02)(0.02)}{0.01} = \mathbf{0.04}.$$

2. (*d*) $K_p = \frac{(p_{CO})^2}{p_{CO_2}} = \frac{(4.0)^2}{2.0} = 8$ atm.

3. (*c*) $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g) \qquad ...K_1$

$$SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g) \qquad ...\frac{1}{K_1}$$

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g) \qquad ...\frac{1}{K_1^2}$$

$$\therefore \quad K_2 = \frac{1}{K_1^2} \qquad \text{or} \qquad K_1^2 = \frac{1}{K_2}.$$

4. (*c*) For exothermic reactions the value of K decreases with increase in temperature while for endothermic reactions the value of K increases with increase in temperature.

5. (*c*) The value of K is characteristic of the reaction at a particular temperature.

6. (*c*) Catalyst does not disturb the equilibrium state.

7. (*d*) K_p is constant at the particular temperature.

8. (*d*) $K_p = K_c\,(RT)^{\Delta n}$. Here $\Delta n = 0$.

9. (*a*) Here, number of moles of products is less than the number of moles of reactants.

10. (*b*) Here the reaction is exothermic and hence increase in temperature would shift the equilibrium in backward direction.

11. (*b*) $\alpha = \frac{D - d}{d(n-1)} = \frac{104.16 - 62}{62(2-1)} = 0.68$ or 68%.

12. (*d*) Doubling the volume would reduce the pressure and shift the equilibrium in that direction where number of moles is more so that effective decrease in pressure is undone to some extent.

13. (*d*) K depends upon temperature.

15. (*b*) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$

At start			
No. of moles	1	0	0
At eq.			
No. of moles	0.5	0.5	0.25
Conc.	0.5/2	0.5/2	0.25/2

$$K = \frac{[SO_2]^2\,[O_2]}{[SO_3]^2} = \frac{(0.5/2)^2\,(0.25/2)}{(0.5/2)^2} = 0.125.$$

16. (*c*) $K = \frac{k_f}{k_b} = \frac{0.5}{5 \times 10^4} = 1 \times 10^{-5}$.

17. (*c*) $\Delta G° = -RT \ln K = -2.303\,RT \log K$

When $K = 1$, $\log K = 0$.

18. (*d*) Le-chatelier's principle.

19. (*a*) For endothermic reactions, the value of K increases with increase in temperature.

20. (*d*) $K_w = [H_3O^+]^2 = (10^{-6})^2 = 10^{-12}$.

21. (*c*) pH = 5.5, pOH = 14 – 5.5 = 8.5

$[OH^-] = 10^{-pOH} = 10^{-8.5}$.

22. (*c*) $K_{sp} = S^2$, $S = \sqrt{K_{sp}} = \sqrt{10^{-2}} = 10^{-1}$ mol L^{-1}

$= 10^{-1} \times 100$ g $L^{-1} = 10$ g L^{-1}.

23. (*b*) Total volume = 300 mL

m moles of HCl $= 200 \times \frac{1}{50} + 100 \times \frac{1}{100} = 5$

$$[HCl] = \frac{5}{300} = 1.66 \times 10^{-2} = [H_3O^+]$$

$$pH = -\log(1.66 \times 10^{-2}) = 1.78.$$

24. (*a*) It is the conjugate base of weakest acid HClO. Acid strength of oxy-acids of chlorine is in the order

$HClO < HClO_2 < HClO_3 < HClO_4$.

25. (*c*) Acid having least pK_a value is the strongest acid.

26. (*b*) $AlCl_3$ is electron deficient. It cannot donate a pair of elec-trons.

27. (*d*) $HCOO^-$ cannot donate a proton. It can only accept a proton.

28. (*d*) K_w increases with increase in temperature.

29. (*c*) $\alpha = \sqrt{K_a/C}$ or $K_a = C\alpha^2$.

30. (*a*) H^- is the conjugate base of H_2 which is the weakest acid among H_2, HCl, HNO_3 and CH_3OH.

31. (*d*) $\underset{\text{Acid}}{HCO_3^-} \xrightarrow{-H^+} \underset{\text{Conjugate base}}{CO_3^{2-}}$

32. (*d*) $$\underset{\text{Base}}{\mathrm{HSO_3^-}} \xrightarrow{+\mathrm{H}^+} \underset{\text{Conjugate acid}}{\mathrm{H_2SO_3}}$$

33. (*d*) Acetic acid is not completely dissociated. Therefore, $[\mathrm{H_3O^+}] < [\mathrm{CH_3COOH}] < 0.1$ M.

34. (*a*) It is a salt of strong base and weak acid. On hydrolysis it would give basic solution.

35. (*b*) $[\mathrm{H_3O^+}] = 2[\mathrm{H_2SO_4}] = 0.005 \times 2 = 0.01$

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = -\log(0.1) = 2.$$

36. (*a*) Milli equivalents of HCl $= 100 \times \frac{1}{10} = 10$

Milli equivalents of NaOH $= 50 \times \frac{1}{5} = 10$

Resulting solution would be neutral and hence have a pH of 7.

37. (*b*) For a pair of conjugate acid and base, $\mathrm{K}_a \times \mathrm{K}_b = \mathrm{K}_w$.

38. (*c*) $\mathrm{NF_3}$ has a lone pair on nitrogen and hence is Lewis base.

39. (*b*) $\mathrm{K}_a = 10^{-5}, p\mathrm{K}_a = -\log \mathrm{K}_a = -\log 10^{-5} = 5$

$$p\mathrm{K}_a + p\mathrm{K}_b = 14$$
$$p\mathrm{K}_b = 14 - 5 = \mathbf{9}.$$

40. (*c*) $\mathrm{HA + OH^- \longrightarrow H_2O + A^-}$

$$\mathrm{K} = \frac{[\mathrm{A^-}]}{[\mathrm{HA}][\mathrm{OH^-}]}, \mathrm{K}_a = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]}, \mathrm{K}_w = [\mathrm{H_3O^+}][\mathrm{OH^-}]$$

$$\mathrm{K} = \frac{\mathrm{K}_a}{\mathrm{K}_w} = \frac{1 \times 10^{-4}}{1 \times 10^{-14}} = \mathbf{1 \times 10^{10}}.$$

41. (*b*) Here $\mathrm{AlCl_3}$ accepts a lone pair from $\mathrm{Cl^-}$ for sharing, and hence acts as a Lewis acid.

42. (*d*) $\mathrm{Cl^-}$ is the conjugate base of a strong acid (HCl). Among the given choices $\mathrm{Cl^-}$ is the conjugate base of the strongest acid. Acid strength is in the order $\mathrm{HCl > CH_3OH > CH_4 > H_2}$.

43. (*c*) It is a mixture of weak acid and its salt with strong base.

44. (*a*) $\mathrm{NH_2^- + H^+ \longrightarrow NH_3}$.

45. (*c*) It is a strong base.

46. (*c*) $$[\mathrm{H_3O^+}] = \underset{\text{From water}}{10^{-7}} + \underset{\text{From HCl}}{10^{-8}} = 1.1 \times 10^{-7}$$

47. (*c*) $$\mathrm{Fe(OH)_3} \rightleftharpoons \underset{x}{\mathrm{Fe^{3+}}} + \underset{3x}{\mathrm{3OH^-}}$$

$$\mathrm{K}_{sp} = [\mathrm{Fe^{3+}}][\mathrm{OH^-}]^3 = (x)(3x)^3 = 27x^4.$$

48. (*d*) $\mathrm{I^-}$ is conjugate base of the strongest acid HI.

49. (*d*) $$\mathrm{PCl_5} \rightleftharpoons \mathrm{PCl_3 + Cl_2}$$

$$2(1-x) \rightleftharpoons 2x \quad 2x$$

Total $= 2 - 2x + 2x + 2x = 2 + 2x = 2(1 + x)$.

50. (*b*) $\frac{1}{\mathrm{K}} = \frac{1}{0.025} = 40.$

51. (*b*) $\mathrm{K}_{sp} = [\mathrm{Ca^{2+}}][\mathrm{F^-}]^2 = x \,.\, y^2$

When $[\mathrm{Ca^{2+}}] = 4x$

$$\mathrm{K}_{sp} = [4x][\mathrm{F^-}]^2 = xy^2$$

$$[\mathrm{F^-}]^2 = \frac{y^2}{4} \quad \text{or} \quad [\mathrm{F^-}] = \frac{y}{2}.$$

52. (*b*) $[\mathrm{Ca^{2+}}] = \frac{10^{-2}}{2}$ M ; $[\mathrm{F^-}] = \frac{10^{-3}}{2}$ M

$$\text{I.P.} = [\mathrm{Ca^{2+}}][\mathrm{F^-}]^2 = \left(\frac{10^{-2}}{2}\right)\left(\frac{10^{-3}}{2}\right)^2 = \frac{10^{-8}}{8}$$

I.P. $> \mathrm{K}_{sp}$.

53. (*d*) $\mathrm{K}_{sp} = 4s^3 = 4 \times 10^{-12}$, $s = 10^{-4}$ mol $\mathrm{L^{-1}}$.

54. (*b*) $[\mathrm{H_3O^+}] = 10^{-4}$ M, $[\mathrm{OH^-}] = \frac{\mathrm{K}_w}{[\mathrm{H_3O^+}]} = \frac{10^{-14}}{10^{-4}} = 10^{-10}$ M.

55. (*c*) $\mathrm{K}_w = [\mathrm{H_3O^+}][\mathrm{OH^-}] = (\mathrm{mol\ L^{-1}})(\mathrm{mol\ L^{-1}})$.

56. (*d*) $\mathrm{K}_{sp} = [\mathrm{Fe^{3+}}][\mathrm{OH^-}]^3 = x \,.\, y^3$

When $[\mathrm{OH^-}]$ is reduced to $y/3$

$$\mathrm{K}_{sp} = [\mathrm{Fe^{3+}}]\,(y/3)^3 = xy^3$$

$$[\mathrm{Fe^{3+}}] = xy^3 \,.\left(\frac{27}{y^3}\right) = 27x.$$

57. (*a*) Largest value of K. Greater the value of K greater is the extent of reaction.

58. (*c*) $$\underset{(1-0.6)}{\mathrm{A}} + \underset{(1-0.6)}{\mathrm{B}} \rightleftharpoons \underset{0.6}{\mathrm{C}} + \underset{0.6}{\mathrm{D}}$$

$$\mathrm{K} = \frac{(0.6)(0.6)}{(0.4)(0.4)} = 2.25.$$

59. (*b*) For equimolar solutions of weak acid and its salt

$$\mathrm{pH} = \mathrm{pK}_a.$$

60. (*c*) $\mathrm{pH} = \mathrm{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$

$$5 = 6 + \log\frac{[\text{Salt}]}{[\text{Acid}]} \Rightarrow \log\frac{[\text{Salt}]}{[\text{Acid}]} = -1$$

$$\frac{[\text{Salt}]}{[\text{Acid}]} = 10^{-1} \quad \text{or} \quad \frac{1}{10} \Rightarrow \frac{[\text{Acid}}{\text{Salt}]} = 10.$$

61. (*c*) Introduction of inert gas at constant volume does not disturb the partial pressures of various reactants and products and hence does not disturb the equilibrium.

62. (*a*) Introduction of inert gas at constant pressures reduces the individual pressures of various reactants and products and hence shifts the equilibrium in the direction where there is more number of moles (in accordance with Le-Chatelier's principle).

63. (*b*) $\mathrm{pH} = \mathrm{pK}_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$

$[\text{Salt}] = 0.1\ \text{M}, [\text{Acid}] = 0.2\ \text{M}.$

64. (*d*) K_w is always 10^{-14} at 298 K.

65. (*c*) $K_p = K_c\,(RT)^{\Delta n}$.

66. (*c*) $[OH^-] = 0.005 \times 2 = 0.01$

$$pOH = -\log 10^{-2} = 2$$
$$pH = 14 - 2 = 12.$$

67. (*c*) $[H_3O^+] = \dfrac{K_w}{[OH^-]} = \dfrac{10^{-14}}{1}$

$$pH = 14.$$

68. (*c*) See Hint 62.

69. (*b*) m mols of HCl $= 55 \times \frac{1}{5} = 5.5$

m mols of NaOH $= 45 \times \frac{1}{10} = 4.5$

m mols of HCl left unreacted $= 5.5 - 4.5 = 1$

$$[HCl] = \frac{1.0}{100}\ \text{M} = [H_3O^+]$$

$$[H_3O^+] = 0.01\ \text{M},\ pH = 2.$$

70. (*a*) Acidic strength of H_2O, NH_3, C_2H_2 and C_2H_6 is in the order

$$H_2O > C_2H_2 > NH_3 > C_2H_6$$

Basic strength of their conjugate bases would be in the order

$$OH^- < HC\equiv C^- < NH_2^- < C_2H_5^-.$$

71. (*a*) $[OH^-] = \sqrt{K_b \times C}$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{K_w}{\sqrt{K_b \times C}}.$$

72. (*a*) $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$

Addition of CH_3COONa suppresses the degree of dissociation of CH_3COOH due to common ion effect, reduces $[H_3O^+]$ and hence increases pH.

73. (*b*) m mols of HCl $= 0.1 \times 70 = 7$

m mols of NaOH $= 0.1 \times 30 = 3$

m mols of HCl left unreacted $= 7 - 3 = 4$

Volume of solution = 100 ml

Molarity of HCl $= \frac{4}{100} = 4 \times 10^{-2}$ m

$$[H_3O^+] = 4 \times 10^{-2} \quad \text{or} \quad pH = -\log 4 \times 10^{-2} = 1.4.$$

74. (*a*) It will behave as a mixture of NH_4^+ and NH_3 because some of the NH_3 would react with HCl to form NH_4^+.

75. (*c*) K_a for HA $= \dfrac{K_w}{K_b} = \dfrac{1 \times 10^{-14}}{1 \times 10^{-10}} = 10^{-4}$

$$pH = pK_a + \log\frac{[\text{Salt}]}{[\text{Acid}]} = pK_a = 4.$$

76. (*d*) It is a basic buffer. Others are acidic buffers and hence would have pH less than 7.

77. (*a*) $pH = 14 - \left[pK_b + \log\dfrac{[\text{Salt}]}{[\text{Base}]}\right]$

$$= 14 - \left[5 + \log\frac{0.01}{0.1}\right] = 14 - [5 - 1] = 10.$$

78. (*c*) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

$$1 - x \qquad x \qquad x$$

Total no. of moles $= 1 - x + x + x = 1 + x$

$$p_{PCl_3} = \frac{\text{Moles of } PCl_3}{\text{Total no. of moles}} \times \text{Total pressure}$$

$$= \frac{x}{1+x} \times P.$$

79. (*c*) $N_2 + 3H_2 \rightleftharpoons 2NH_3$

Initial no. of moles 1 1 0

At equilibrium moles of N_2 left $= x$

Moles of N_2 reacted $= 1 - x$

Moles of NH_3 formed $= 2(1 - x)$.

80. (*d*) $K_a \times K_b = K_w$

$$K_a = \frac{K_w}{K_b} = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10}.$$

81. (*c*) $HS^- \longrightarrow H^+ + S^{2-}$ ...As Acid

$HS^- + H^+ \longrightarrow H_2S$ ...As Base

82. (*b*) $\Delta n = 1$

$$K_p = K_c\,(RT)^{\Delta n} = K_c\,RT.$$

83. (*b*) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

Eq. conc. $\frac{0.5}{5} = 0.1 \qquad \frac{2 \times 0.5}{5} = \frac{1}{5} = 0.2$

$$K = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.2)^2}{(0.1)} = 0.4.$$

84. (*b*) $[H_3O^+] = \dfrac{10^{-6} + 10^{-4}}{2} = 5.05 \times 10^{-5}$

$$pH = -\log(5.05 \times 10^{-5}) = 4.3.$$

85. (*c*) Sodium acetate formed on hydrolysis would yield basic solution and hence pH > 7.

86. (*a*) [HCl] after mixing $= \frac{0.2}{2} = 0.1$ M

$[H_3O^+]$ would be mainly due to HCl

$$[H_3O^+] = [HCl] = 0.1\ \text{M}$$

$$pH = -\log[H_3O^+] = -\log(0.1) = 1.$$

87. (*b*) Cl^- ions suppress the solubility of AgCl. Hence, solubility is maximum in water.

88. (*b*) It would result in a buffer containing equimolar quantities of CH_3COOH and CH_3COONa and hence,

$$pH = pK_a \quad \text{or} \quad [H_3O^+] = K_a.$$

89. (*c*) Addition of 0.1 M HCl to 0.1 M HCl will not result in any change in conc. of HCl or H_3O^+ ions.

90. (*c*) Addition of 0.1 M HCl (a strong acid) will increase the conc. of H_3O^+ ions and hence decrease the pH.

91. (*a*) $\quad HA + H_2O \rightleftharpoons H_3O^+ + A^-$

$$[HA] = 0.2 - \frac{0.2 \times 1}{100} = 0.198\ M$$

$$[A^-] = 0.002\ M$$

$$[H_3O^+] = 0.002\ M$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{0.002 \times 0.002}{0.198}.$$

92. (*c*) $K_w = [H_3O^+]^2$, for pure water

$$[H_3O^+] = \sqrt{K_w} = \sqrt{4 \times 10^{-12}} = 2 \times 10^{-6}$$

$$pH = -\log [H_3O^+] = -\log [2 \times 10^{-6}] = \mathbf{5.7}.$$

93. (*d*) $[OH^-] = \underset{\text{(From NaOH)}}{10^{-10}\ M} + \underset{\text{(From water)}}{10^{-7}\ M} = 10^{-7}\ M.$

94. (*d*) $Be(OH)_2$ being least soluble has lowest value of K_{sp}.

96. (*c*) Percent ionization increases with decrease in concentration (Ostwald's dilution law).

97. (*b*) $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \quad ...(i)$

$$Ag^+ + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ \quad ...(ii)$$

Due to removal of Ag^+ ions through reaction (*ii*), equilibrium (*i*) shifts in the forward direction.

98. (*d*) $\quad PbI_2 \rightleftharpoons Pb^{2+} + 2I^-$

$$[I^-] = 2\,[Pb^{2+}] \quad \text{or} \quad [Pb^{2+}] = 0.5[I^-].$$

100. (*d*) Addition of H_2SO_4 precipitates Pb^{2+} as $PbSO_4$.

QUESTION BANK (Level II)

1. (*a*) $K_p = K_c\,(RT)^{\Delta n} = 26(0.082 \times 523)^{-1} = 0.61\ atm^{-1}$.

2. (*c*) Introduction of inert gas at constant volume does not disturb the partial pressures of various reactants and products and hence does not disturb the equilibrium.

3. (*d*) The equilirbium constant does not depend upon the initial concentration of reactants and products.

4. (*a*) $[H_3O^+] = 10^{-4}\ M$, $[OH^-] = 10^{-10}\ M$

$$K_{sp} = [Al^{3+}]\,[OH^-]^3$$

$$[Al^{3+}] = \frac{1 \times 10^{-33}}{(10^{-10})^3} = 10^{-3}\ M.$$

5. (*d*) $Fe(OH)_3(s) \qquad Fe^{3+}(aq) + 3OH^-(aq)$

Higher conc. of H_3O^+, means low conc. of OH^-.

This would shift the equilibrium in forward direction, resulting in greater solubility.

6. (*d*) Sulphides of group-IV metal ions are more soluble and hence have greater values of K_{sp}.

7. (*c*) $pH = pK_a + \log \dfrac{[Salt]}{[Acid]}$

$$= -\log (10^{-6}) + \log \frac{2}{1} = 6 + 0.3 = \mathbf{6.3}.$$

8. (*b*) Catalyst does not affect the value of K.

10. (*a*) For solutions containing equimolar concentrations of weak acid and its salt, pH is equal to pK_a.

$$pH = pK_a + \log \frac{[Salt]}{[Acid]} = pK_a.$$

11. (*c*) No. of moles of $H_3O^+ = 2 \times 0.005 \times \dfrac{200}{1000} = 0.002$.

12. (*d*) NH_3 is the strongest base among the given bases.

13. (*d*) CH_3COO^- ions would remove almost all $[H_3O^+]$ ions to form nearly unionised CH_3COOH.

14. (*a*) Solid $\rightleftharpoons$ Liquid ; $\Delta H = +ve$

Adding heat shifts the equilibrium in forward (endothermic) direction.

15. (*c*) $CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq) \quad ...(i)$

$$CO_3^{2-} + 2HSO_4^- \rightarrow 2SO_4^{2-} + CO_2 + H_2O \quad ...(ii)$$

Consumption of CO_3^{2-} ions in reaction (*ii*) shifts the equilibrium (*i*) in the forward direction.

16. (*a*) $K_{sp} = [Ag^+]^2\,[CrO_4^{2-}]$

$$[Ag^+] = 2[CrO_4^{2-}] = 2 \times 2 \times 10^{-4}\ M$$

$$K_{sp} = (4 \times 10^{-4})^2\,(2 \times 10^{-4}) = \mathbf{32 \times 10^{-12}}.$$

17. (*a*) $1.5 \times 10^{-15} = [Pb^{2+}]\,[CO_3^{2-}]$

$$1 \times 10^{-15} = [Mg^{2+}][CO_3^{2-}]$$

By applying electroneutrality $[CO_3^{2-}] = [Pb^{2+}] + [Mg^{2+}]$

$$[CO_3^{2-}] = \frac{1.5 \times 10^{-15}}{[CO_3^{2-}]} + \frac{1 \times 10^{-15}}{[CO_3^{2-}]}$$

$$[CO_3^{2-}]^2 = 2.5 \times 10^{-15} \quad \text{or} \quad [CO_3^{2-}] = 5 \times 10^{-8}$$

$$[Pb^{2+}] = \frac{1.5 \times 10^{-15}}{5 \times 10^{-8}} = 3 \times 10^{-8}\ M.$$

18. (*d*) The value of K depends on temperature only (For a particular reaction).

19. (*d*)

$$\begin{array}{llll} & 2SO_3(g) \rightleftharpoons & 2SO_2(g) \; + & O_2(g) \\ \text{Initial conc.} & 1\ \text{mol L}^{-1} & 0 & 0 \\ \text{At equilibrium (conc.)} & 0.4\ \text{mol L}^{-1} & 0.6\ \text{mol L}^{-1} & 0.3\ \text{mol L}^{-1} \end{array}$$

$$K = \frac{[SO_2]^2\,[O_2]}{[SO_3]^2} = \frac{(0.6)^2\,(0.3)}{(0.4)^2} = 0.675.$$

20. (*a*) $\Delta G = 0$ at constant temperature and pressure.

21. (*c*)

$$\begin{array}{llll} & 2H_2S(g) \rightleftharpoons & 2H_2(g) + & S_2(g) \\ \text{Equilibrium conc. (mol L}^{-1}) & \frac{1}{2} & \frac{0.2}{2} & \frac{0.8}{2} \end{array}$$

$$K = \frac{[H_2]^2\,[S_2]}{[H_2S]^2} = \frac{(0.1)^2\,(0.4)}{(0.5)^2} = 0.016.$$

22. (*b*) $\Delta G^\circ = -2\,\Delta G^\circ_{f(HI)} = -2 \times 1.7 = -3.4$ kJ

$\Delta G^\circ = -2.303\ RT \log K$

$\log K = +0.5959$ or $K = \mathbf{3.9}$.

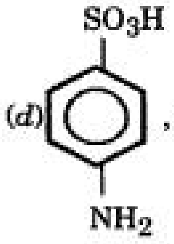
23. (*a*) Sodium borate is a salt of strong base and weak acid.

24. (*d*) Since K_a and K_b are equal solution would be neutral.

$$pH = \frac{1}{2}\,[pK_w + pK_a - pK_b].$$

25. (*d*) $Li_3Na_3(AlF_6)_2(s) \rightleftharpoons \underset{3s}{3Li^{3+}} + \underset{3s}{3Na^+} + \underset{2s}{2AlF_6^{3-}}$

$$K_{sp} = [Li^+]^3\,[Na^+]^3\,[AlF_6^{3-}]^2$$
$$= (3s)^3\,(3s)^3\,(2s)^2 = 2916s^8.$$



26. (*d*) , Arrhenius acid due to —SO_3H and Lewis base due to —NH_2 group.

29. (*a*) $pH = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$

Increasing the conc. of salt would increase the pH.

30. (*d*) $H_2S \rightleftharpoons S^{2-} + 2H^+$

On addition of dil. HCl, $[H^+]$ increases and shifts the above equilibrium in backward direction and hence $[S^{2-}]$ decreases.

31. (*a*) $pH = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$

when [Salt] = [Acid], $pH = pK_a$

32. (*c*) Doubling the volume would result in less moles per litre. In order to undo the effect according to Le-Chatelier's principle, the equilibrium shifts in the direction where number of moles is more.

33. (*c*) $pH = -\log [H_3O^+] = -\log x$

when conc. is increased 10 times

$$pH = -\log 10x = -[\log 10 + \log x]$$
$$= -\log x - 1.$$

34. (*b*) Increase in pressure shifts the equilibrium in the direction where number of moles of gaseous species is less.

35. (*b*) It is an exothermic reaction $\Delta H = -$ ve

It is a spontaneous reaction $\Delta G = -$ ve

No. of moles of gaseous species is increasing $\Delta S = -$ ve.

36. (*c*) $K_{sp} = [Ag^+][Cl^-] = [Ag^+]^2 = (1.06 \times 10^{-10})^2$.

37. (*c*)

$$\begin{array}{lllll} & A \; + & 2B \rightleftharpoons & 2C \; + & D \\ \text{Initial conc. (mol L}^{-1}) & 1.1 & 2.2 & 0 & 0 \\ \text{At equilibrium} & 1.0 & 2.0 & 0.2 & 0.1 \end{array}$$

$$K = \frac{[C]^2\,[D]}{[A][B]^2} = \frac{(0.2)^2\,(0.1)}{(1)(2)^2} = 0.001.$$

38. (*a*)

$$\begin{array}{llll} 2HI \rightleftharpoons & H_2 + & I_2 & \\ 2 & 0 & 0 & \text{...Initial conc. (Suppose)} \\ 1 & 0.5 & 0.5 & \text{...Equilibrium conc.} \end{array}$$

$$K = \frac{[H_2][I_2]}{[HI]^2} = \frac{0.5 \times 0.5}{1} = 0.25.$$

40. (*c*) Temperature would increase due to shift of equilibrium in the forward direction.

41. (*a*) Addition of product at equilibrium shifts the reaction in backward direction.

42. (*c*) $PbCl_2 \rightleftharpoons \underset{x}{Pb^{2+}} + \underset{2x}{2Cl^-}$

$$K_{sp} = [Pb^{2+}]\,[Cl^-]^2 = (x)\,(2x)^2 = 4x^3$$
$$x = (K_{sp}/4)^{1/3}.$$

43. (*a*) Sulphide having lower value of K_{sp} is precipitated first.

44. (*c*)

$$\begin{array}{llll} 2HI \rightleftharpoons & H_2(g) \; + & I_2(g) & \\ 2 - 2\alpha & \alpha & \alpha & \textit{...Moles at equilibrium} \end{array}$$

Total no. of moles $= 2 - 2\alpha + \alpha + \alpha = 2$.

45. (*b*) Apply Le-Chatelier's principle.

46. (*a*)

$$\begin{array}{lll} N_2O_4(g) \rightleftharpoons & 2NO_2(g) & \\ (1 - 0.2) & 0.4 & \textit{...Moles at equilibrium} \end{array}$$

Total no. of moles = 0.8 + 0.4 = 1.2.

47. (*a*) $pH = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} = pK_a - \log \frac{[\text{Acid}]}{[\text{Salt}]}$

$\log 10 = 1$.

48. (*c*)

$$\begin{array}{llll} A \; + & 2B \rightleftharpoons & 2C & \\ 2.0 & 3.0 & 2.0 & \text{Initial moles} \end{array}$$

$(2.0 + 0.75)$ $(3.0 + 1.5)$ 0.5 Equilibrium moles

$2.75/2$ $4.5/2$ $0.5/2$ Equilibrium conc.

$$K = \frac{(0.5/2)^2}{(4.5/2)^2\,(2.75/2)}.$$

50. (*a*) $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$[NH_4^+] = \frac{K_b \times [NH_3]}{[OH^-]} = \frac{1.8 \times 10^{-5} \times 0.02}{0.01} = 3.6 \times 10^{-5}.$$

51. (*d*) pK_a is same as pH in this case.

52. (*a*) In case of CuS and HgS, $K_{sp} = S^2$ whereas in case of Ag_2S, $K_{sp} = 4S^3$.

53. (*b*) CH_3COONa is a salt of strong base and weak acid. Its aqueous solution would be basic due to hydrolysis.

55. (*b*) $pH = pK_a + \log\frac{[Salt]}{[Acid]}$

$$pH - pK_a = \log\frac{[Salt]}{[Acid]}$$

$$6 - 5 = \log\frac{[Salt]}{[Acid]}.$$

56. (*a*) $H_2 \quad + \quad I_2 \longrightarrow 2HI$

$(4.5 - 1.5)$ $(4.5 - 1.5)$ 3 At equilibrium (moles)

$$K = \frac{[HI]^2}{[H_2][I_2]} = \frac{(3)^2}{(3)(3)} = 1.$$

57. (*c*) pH increases by 3 units, H^+ ion concentration decreases by 10^3 times

58. (*a*) $A + B \rightleftharpoons C + D$

3 3 0 0 Initial moles (suppose)

1 1 2 2 At equilibrium

$$K = \frac{[C][D]}{[A][B]} = \frac{(2)(2)}{1 \times 1} = 4.$$

59. (*c*) $K_p = K_c\,(RT)^{\Delta n}$

$$\frac{K_p}{K_c} = (RT)^{-1/2} = \frac{1}{\sqrt{RT}}.$$

60. (*d*) Subtracting equation (*i*) from (*ii*), we get the required equation.

$\therefore$ $K = K_2/K_1$.

61. (*d*) Apply Le-Chatelier's principle.

62. (*b*) $H_2PO_4^- \xrightarrow{-H^+} HPO_4^{2-}$

Acid Conjugate base

63. (*b*) Conceptual question.

64. (*a*) Apply Le-Chatelier's principle.

66. (*c*) $[H^+][OH^-] = K_w = 1 \times 10^{-14}$.

67. (*d*) $K_p = K_c(RT)^{\Delta n}$

$$K_c = \frac{K_p}{(RT)^{-2}} = \frac{1.44 \times 10^{-5}}{(0.082 \times 773)^{-2}}.$$

68. (*d*) Q increases with time and finally becomes equal to K at equilibrium.

69. (*a*) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

$1 - x$ $2x$

Total no. of moles at equilibrium $= 1 - x + 2x = 1 + x$

$$P_{NO_2} = \frac{2x}{1+x} \times P.$$

70. (*b*) High pressures favours backward reaction. (Le-Chatelier's Principle).

71. (*a*) No. of moles of reactants = No. of moles of products

$$K_p = K_c\,(RT)^{\Delta n} = K_c \qquad (\because\ \Delta n = 0)$$

72. (*c*) A catalyst does not disturb the equilibrium state.

73. (*c*) $2SO_3 \rightleftharpoons 2SO_2 + O_2$

$1 - 0.6 = 0.4$ 0.6 0.3

$$K = \frac{[SO_2]^2\,[O_2]}{[SO_3]^2} = \frac{(0.6)^2\,(0.3)}{(0.4)^2} = 0.68.$$

75. (*a*) $K_{sp} = 4s^3 = 1.7 \times 10^{-10}$, $s = 5.5 \times 10^{-4}$

For others $K_{sp} = s^2$.

76. (*d*) Degree of dissociation increases with decrease in concentration.

78. (*c*) 1 L = 1000 mL = 1000 g

moles of H_2O in 1000 g $= \frac{1000}{18} = 55.5$

$$[H_2O] = 55.5 \text{ mol L}^{-1}.$$

79. (*d*) It is a salt of strong base and weak acid and would give basic solution on hydrolysis.

80. (*c*) Acetic acid would be neutralised with NaOH to form sod. acetate. This salt on hydrolysis would yield basic solution and hence pH > 7.

81. (*d*) It is a basic buffer.

82. (*d*) $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$

$(1000 - p)$ p p ...At equilibrium.

Total pressure at equilibrium

$$= (1000 - p) + p + p = 1000 + p = 1500$$

$\therefore$ $p = 500$ torr.

$$K_p = \frac{p_{CO} \times p_{Cl_2}}{p_{COCl_2}} = \frac{500 \times 500}{500}.$$

83. (*c*) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

$(1 - x)$ (x) (x)

Total no. of moles $= 1 - x + x + x = 1 + x$

$$P_{PCl_3} = \frac{\text{moles of } PCl_3}{\text{Total no. of moles}} \times \text{Total pressure}$$

$$= \frac{x}{1+x} \times P.$$

84. (*c*) $N_2 + 3H_2 \rightleftharpoons 2NH_3$

Initial no. of moles 1 1 0

At equilibrium moles of N_2 left $= x$

Moles of N_2 reacted $= 1 - x$

Moles of NH_3 formed $= 2(1 - x)$.

85. (*d*) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

Eq. conc. $\frac{0.5}{5} = 0.1$ $\frac{2 \times 0.5}{5} = \frac{1}{5} = 0.2$

$$K = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.2)^2}{(0.1)} = 0.4.$$

87. (*a*) Addition of 0.1 M HCl to 0.1 M HCl will not result in any change in conc. of HCl or H_3O^+ ions.

88. (*c*) If pH for CH_3COOH is 4.0, the pOH for NH_4OH having equivalent concentration would also be 4.

$$pH + pOH = 14$$

$$pH = 14 - pOH = 14 - 4 = 10.$$

89. (*c*) $[SCN^-] = \frac{1.2 \times 10^{-12}}{[Ag^+]}$

$$[Br^-] = \frac{5 \times 10^{-13}}{[Ag^+]}$$

By applying electroneutrality

$$[Ag^+] = [SCN^-] + [Br^-] = \frac{1.2 \times 10^{-12}}{[Ag^+]} + \frac{5 \times 10^{-13}}{[Ag^+]}$$

$$[Ag^+]^2 = 17 \times 10^{-13} \quad \text{or} \quad [Ag^+] = \mathbf{1.3 \times 10^{-6}}.$$

90. (*b*) $\alpha \propto \sqrt{\frac{K}{C}}$.

91. (*d*) $Ca_3(PO_4)_2 \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$

$3x$ $2x$

$$K_{sp} = [Ca^{2+}]^3 [PO_4^{3-}]^2 = (3x)^3 (2x)^2 = 108x^5.$$

92. (*a*) Since *p* is in the numerator it indicates the no. of moles of products is more and hence choice (*a*) is correct

$$N_2O_4 \rightleftharpoons 2NO_2$$

At equilibrium $1 - \alpha$ 2α

Total no. of moles $= 1 + \alpha$

$$p_{N_2O_4} = \left(\frac{1-\alpha}{1+\alpha}\right)p \qquad p_{NO_2} = \left(\frac{2\alpha}{1+\alpha}\right)p$$

$$K_p \frac{p^2_{NO_2}}{p_{N_2O_4}} = \left(\frac{2\alpha}{(1+\alpha)}p\right)^2 \left(\frac{(1+\alpha)}{(1-\alpha)p}\right) = \frac{4\alpha^2}{1-\alpha^2}p.$$

93. (*a*) $K_p = K_c (RT)^{\Delta n}$

$$K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{26}{(0.082 \times 523)} = 0.61.$$

94. (*d*) Solubility of hydroxides of alkaline earth metals increases on moving down the group. K_{sp} is proportional to solubility.

95. (*a*) $Al^{3+} + 3H_2O \longrightarrow \underset{\text{Weak base}}{Al(OH)_3} + 3H^+$

96. (*d*) $K_p = K_c(RT)^{\Delta n}$

$$K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{0.05}{(R \times 1000)} = \frac{5 \times 10^{-5}}{R}.$$

97. (*d*) $HA + H_2O \rightleftharpoons H_3O^+ + A^-$

$C(1-\alpha)$ $C\alpha$ $C\alpha$

$$K_a = \frac{C\alpha \, . \, C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}.$$

98. (*a*) $H_2O \rightleftharpoons H^+ + OH^-$

55.55 moles 10^{-7} moles

$$\alpha = \frac{10^{-7}}{55.55} \times 100 = 1.8 \times 10^{-7}$$

(Note. 1 L of water contains 55.55 moles of H_2O)

99. (*b*) $[NaOH] = \frac{4/40}{10} = 10^{-2}$ M

$[OH^-] = [NaOH] = 10^{-2}$ M

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{10^{-2}} = 10^{-12} \text{ M}$$

pH = 12.

100. (*a*) [Acid] after dilution $= 10^{-9}$ M

$[H_3O^+]$ in acidic solution would approach 10^{-7} M. It cannot become less than 10^{-7} M because H_3O^+ ions are also formed by dissociation of H_2O.

7 REDOX REACTIONS AND ELECTROCHEMISTRY

Important Terms, Facts and Formulae

OXIDATION AND REDUCTION IN TERMS OF OXIDATION NUMBER

- **Oxidation.** Chemical process involving **increase** in oxidation number.
- **Reduction.** Chemical process involving decrease in oxidation number.
- **Oxidising agent.** Substance which undergoes decrease in oxidation number of one or more of its element.
- **Reducing agent.** Substance which undergoes increase in oxidation number of one or more of its elements.

BALANCING OF CHEMICAL REDOX EQUATIONS

The equations are balanced by two methods

(*i*) **Ion electron method**

(*ii*) **Oxidation number method.**

During balancing of equations the number of electrons lost during oxidation and those gained during reduction must be equal.

ELECTROCHEMISTRY

SOME COMMON TERMS

1. **Ohm's Law.** The potential difference across the conductor is directly proportional to the current flowing through it.
2. **Resistance (R).** It is obstruction to the flow of current.

   If T is the current in ***amperes,*** and **V** is the potential difference across the conductor in ***volts,*** then

   $$R = V/I \quad \text{or} \quad I = V/R$$

   R is expressed in **ohms** or Ω.
3. **Resistivity** (ρ). It is the resistance offered by one centimeter cube of the conductor. Its units are ***ohm-cm*** or Ω ***cm.*** For a conductor of length l cm and area of cross-section a cm^2.

   $$R = \rho\left(\frac{l}{a}\right).$$
4. **Conductance (C).** Conductance is a measure of the ease with which current flows through the conductor. It is the *reciprocal of resistance.* Its units are, Ω^{-1} or ***ohm***$^{-1}$ or ***mho*** or *S* (*Siemens*)

   $$C = \frac{1}{R} = \frac{1}{\rho} \times \frac{a}{l}.$$
5. **Specific conductance or conductivity** (κ). It is reciprocal of specific resistance or resistivity.

or It is the conductance of one centimeter cube of the conductor. Its units are **ohm^{-1} cm^{-1}** or **Ω^{-1} cm^{-1}** or **S cm^{-1}**.

- For a conductor of length l cm and area of cross-section a cm^3.

$$\kappa = \frac{1}{\rho} = \frac{1}{R}\left(\frac{l}{a}\right) \quad \text{or} \quad C\left(\frac{l}{a}\right).$$

The quantity $\frac{l}{a}$ is called **cell constant.**

The units of cell constant are **cm^{-1}**.

MOLAR CONDUCTIVITY

It is defined as the conductance of the solution containing one gram-mole of the electrolyte such that the entire solution is placed between two electrodes one centimeter apart.

- Molar conductivity is related to conductivity (κ) by the relation

  $$\Lambda_m = \frac{\kappa \times 1000}{M}$$

  where, M is the molarity of the solution.
- Units of Λ_m are **ohm^{-1} cm^2 mol^{-1}** or **Ω^{-1} cm^2 mol^{-1}** or **S-cm^2 mol^{-1}** .
- The values of Λ_m and Λ_{eq} for **strong electrolytes** are **high,** however these values increase slightly on increasing the dilution because on dilution the ions move apart and interionic attraction decrease.
- The behaviour of strong electrolytes is mathematically given by **Onsagar equation** :

$\Lambda_m = \Lambda_m^\infty - b\sqrt{c}$, b being constant which depends on temperature and nature of solvent.

As c approaches zero ; Λ_m approaches Λ_m^∞, *i.e.*, molar conductivity at infinite dilution.

The values of equivalent or molar conductivity at infinitely dilute solution are called limiting equivalent or molar conductivity and are represented by Λ_{eq}^∞ or Λ_m^∞.

- The values of Λ_m^∞ for strong electrolytes can be determined graphically by extrapolating the plot of Λ_m *vs.* $\sqrt{c}$. Whereas the same for weak electrolyte cannot be determined graphically.

KOHLRAUSCH'S LAW

It states that at infinite dilution, when the dissociation of electrolyte is complete, each ion makes a definite contribution towards the molar conductivity of electrolyte, irrespective of the nature of the other ion with which it is associated.

- The molar conductivity of an electrolyte at infinite dilution can be expressed as the sum of the contributions from its individual ions. It λ_+^∞ and λ_-^∞ represent the ionic conductivities at infinite dilution. Then

$$\Lambda_m^\infty = \gamma_+ \lambda_+^\infty + \gamma_- \lambda_-^\infty$$

where γ_+ and γ_- represent the number of + ve and – ve ions furnished by each formula unit of the electrolyte.

- Kohlrausch law can help to calculate :

(*i*) *degree of ionisation of weak electrolyte* (α)

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\infty}$$

(*ii*) *the value of* Λ_m^∞ *for weak electrolytes and*

(*iii*) *ionic mobilities.*

ELECTROCHEMICAL CELL

It is the device in which the decrease of free energy during the indirect redox reaction is made to appear as electrical energy.

TYPES OF ELECTRODES

The various types of electrodes which are frequently used in the electrochemical cells are described as follows :

1. **Metal-Metal ion electrode.** It includes a metal strip dipped in the solution of its own cations. Some examples are Zn/Zn^{2+}, Cu/Cu^{2+}, Ag/Ag^{+}, etc.
2. **Amalgam electrode.** It is similar to metal-metal ion type electrode, but here, metal is replaced by its amalgam with Hg. This is done to improve the activity of metal. $Zn - Hg/Zn^{2+}$ is a common example.
3. **Gas electrode.** It involves the inert metal foil like Pt immersed in the solution capable of furnishing ions of gas. $Pt, H_2/H^+$ and $Pt, Cl_2/Cl^-$ are common examples of gas electrodes.
4. **Metal-Metal insoluble Salt-Salt anion.** This type of electrode include metal in contact with its sparingly soluble salt and aqueous solution of some salt containing same anion. Some examples are :
   $Hg - Hg_2Cl_2(s) - KCl\,(aq)$ **Calomel electrode,**
   $Pb - PbSO_4(s) - K_2SO_4\,(aq)$ and
   $Ag - AgCl(s) - KCl\,(aq)$.
5. **Redox electrode.** These electrodes include a platinum wire dipped in a solution of mixture of the two salts of the same metal but with different oxidation states. The common example is $Pt, Fe^{2+}/Fe^{3+}$.
6. **Standard Hydrogen Electrode (SHE).**

- *The standard electrode potential of* SHE *is taken to be zero.*
- *The* SHE *can act as* **cathode** ($2H^+ + 2e^- \longrightarrow H_2$) *as well as* **anode** ($H_2 \longrightarrow 2H^+ + 2e^-$) *electrode.*
- Pt. foil is used in SHE because it is very good absorber of H_2 gas.
- The pH of acid solution in SHE is zero.

CONCEPT OF ELECTRODE POTENTIAL

The tendency of an electrode in a half cell to lose or to gain electrons when it is in equilibrium with the solution of its ions is called **half cell electrode potential (E).**

- The reduction potential of the electrode at standard state conditions (*1 molar conc. of the ions, 298 K and 1 atm. pressure*) is called **standard reduction potential** (E°).
- E° is an ***intensive property*** like temperature or molar volume. This means that E° is same for half cell reaction whether it is represented as

$$2X^+ + 2e^- \longrightarrow X_2 \quad \text{or} \quad X^+ + e^- \longrightarrow \frac{1}{2}X_2.$$

- E° values are not thermodynamic functions and may not be added directly. However, they can be calculated from free energy which is extensive property.

For example,

$Fe^{3+} + e^- \longrightarrow Fe^{2+}$; $E_1° = 0.77$ V ; $\Delta G_1° = -1(0.77)$ F

$Fe^{2+} + 2e^- \longrightarrow Fe$; $E_2° = -0.44$V ; $\Delta G_2° = -2(-0.44)$ F

Add $Fe^{3+} + 3e^- \longrightarrow Fe$; $E° \neq E_1° + E_2°$;

But $\Delta G^\circ = \Delta G_2^\circ - \Delta G_1^\circ = 0.11\ F$

$$\therefore \quad E^\circ = \frac{\Delta G^\circ}{nF} = \frac{0.11F}{-3F} = \mathbf{-0.04\ V}.$$

EMF OF THE CELL OR CELL VOLTAGE

It is the potential difference between the two terminals of the cell when no current is drawn from it.

- It is measured with the help of potentiometer or vacuum tube voltmeter.
- Mathematically, it may be expressed as :

$$E_{cell} \text{ or EMF} = [E_{red}\ (cathode) - E_{red}\ (anode)]$$

or $$= [E_{red}\ (cathode) + E_{oxi}\ (anode)]$$

Similarly,

$$E^\circ_{cell} \text{ or EMF}^\circ = [E^\circ_{red}\ (cathode) - E^\circ_{red}\ (anode)]$$

- For cell reaction to occur the E_{cell} should be positive. This can happen only if $\mathbf{E_{red}}$ *(cathode)* > $\mathbf{E_{red}}$ *(anode)*.

NERNST EQUATION

This equation gives the relationship between electrode potential and concentration of ions in the solution – 1.

- For a single electrode involving the reduction process, $M^{n+} + ne^- \longrightarrow M$, the Nernst equation is

$$E = E^\circ + \frac{2.303\ RT}{nF} \log \frac{[M^{n+}]}{[M]}$$

or $$E = E^\circ + \frac{2.303 \times 8.314 \times 298}{n \times 96500} \log \frac{[M^{n+}]}{[M]}$$

or $$\mathbf{E = E^\circ + \frac{0.059}{n} \log \frac{[M^{n+}]}{[M]}}.$$

- In using the above equation, the following facts should be kept in mind
  - (i) *concentration or activity of solids is taken to be UNITY.*
  - (ii) concentration or activity of gases is expressed in terms of their partial pressures.
  - (iii) *n, the number of electrons transferred should be calculated from the balanced net cell reaction.*
- Relationship between free energy change and cell potential can be written as

$$\Delta G = -\mathbf{nF\ E_{cell}}$$

For standard state conditions

$$\Delta G^\circ = -\mathbf{nF\ E^\circ_{cell}}.$$

- Equilibrium constant of net cell reaction is related to the standard EMF as

$$\mathbf{E^\circ_{cell} = \frac{0.059}{n} \log K}.$$

CONCENTRATION CELLS

These are the galvanic cells in which the electrodes are made of same material but they have different concentration of electrolytes. The difference in concentration of the electrolytes gives rise to the potential difference across the two electrodes. It may be noted that the electrode in which the concentration of electrolyte ***is less***, acts a ***– ve terminal*** and constitutes the ***anodic half cell***. On the other hand, the electrode in which the concentration of electrolyte is ***more***, acts as **+ *ve terminal*** and constitutes **cathodic half cell.** Some examples are :

(i) $Cu(s)/Cu^{2+}\ (0.01\ M) \parallel Cu^{2+}\ (0.1\ M)/Cu$

(ii) $Pt, H_2/H^+\ (0.01\ M) \parallel H^+\ (0.02\ M)/H_2, Pt$.

- **EMF of concentration cell.** The cell voltage or EMF of concentration cell ; $M/M^+\ (C_1) \parallel M^+\ (C_2)/M$ can be directly calculated by Nernst equation

$$E_{cell} = E^\circ_{cell} + \frac{0.059}{n} \log \frac{C_2}{C_1}$$

Since electrodes are same, therefore, E°_{cell} is zero

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

- *For concentration cell to work $C_2 > C_1$ so that E_{cell} is positive.*

ELECTROLYSIS

It is a process of decomposition of electrolyte by the passage of electricity through its molten or dissolved state.

- **Competing reactions at the electrodes.** For more than one competing reactions at the electrodes the product is generally decided on the basis of electrode potentials.

QUANTITATIVE ASPECT OF ELECTROLYSIS

Consider the electrode reaction ; $M^{n+} + ne^- \longrightarrow M$, the number of electrons required for depositing 1 mole of element M = n mols.

Charge on one mole of electrons = 1 F

(F being Faraday constant = 96500 C)

Charge on n mole of electrons = $nF = n \times 96500$ C.

Thus, for depositing 1 mole of element M, the quantity of electricity (Q) equal to **n × 96500 Coulombs** has to be passed through the electrolyte. The amount of product formed at the electrode, thus, depends on the quantity of electricity passing through the electrolyte. The quantity of electricity (**Q**) is also related to current strength C (*expressed in amperes*) and the time ***t*** **(expressed in seconds)** as

$$\mathbf{Q = C \times t\ coulomb}$$

Hence, by knowing the electrode reaction, and quantity of electricity passing through the electrolyte, the amount of product can be calculated.

- **Current Efficiency.** This is the term used to express the effective current or efficiency of the electrolytic cell. It is described *as the ratio of the mass of the product actually formed to the mass of the product expected from the theoretical considerations.* Thus,

  Current efficiency

  $$= \frac{\textit{Mass of the substance actually produced}}{\textit{Mass of substance expected}}.$$

- **Faraday's First Law of Electrolysis.** This law states that ***the mass of the substance produced at the electrode (anode or cathode) in the electrolytic cell is directly proportional to the quantity of electricity passed.*** The law can be mathematically put as

  $m \propto Q$ Q is the quantity of electricity
  $\propto It$ I is current in amperes
  $m = ZIt$ t is time in seconds
  Z is the constant of proportionality called *electrochemical equivalent.* (E.C.E.)

  If I = 1 ampere, t = 1 sec, then

  $$m = Z$$

  Thus, electrochemical equivalent may be defined as the *mass of the substance produced by passing 1 ampere of current through the electrolyte for one second.*

- Passage of 96500 C of electricity through electrolyte causes the deposition of one *g*-equivalent of the product.

- E.C.E. of substance = GEM/96500.

- **Faraday's Second Law of Electrolysis.** This law states ***that when same quantity of electricity is passed through two or more electrolytes connected in series, then the masses of the substances produced at the electrodes are directly proportional to their equivalent masses or electro-chemical equivalents.*** For example, if same quantity of electricity produces the product A and B at the respective electrodes of the electrolytic cells connected in series, then

  $$\frac{\textit{Mass of A}}{\textit{Mass of B}} = \frac{\textit{Equivalent mass of A}}{\textit{Equivalent mass of B}} = \frac{\textit{ECE of A}}{\textit{ECE of B}}.$$

SOME MISCELLANEOUS IMPORTANT POINTS

1. **Liquid Junction Potential (LJP).** It is the potential difference set up across the junction of two solutions of electrolytes when they are in direct contact with each other.

- It arises as a result of accumulation of charges at the junction due to difference in the speeds of ions of two solutions.
- In case of electrochemical cell, the LJP causes decrease in the cell potential.
- In order to avoid LJP in the electrochemical cell, the electrolyte used in salt bridge should be such that ions furnished by it should have almost same speeds.

2. **Ionic Mobility.** It is the distance travelled by the ion per second under the potential gradiant of 1 volt per cm.

- It is units are $cm^{-1} s^{-1} V^{-1}$.

3. **Transport Number.** It is the fraction of the total current carried by each ion of the electrolyte.

- Larger the ionic mobility, greater will be the transport number of the ion.
- If u_+ and u_- are ionic mobilities of the ions of the electrolyte, then

  $$t_+ = \frac{u_+}{u_+ + u_-} \text{ and } t_- = \frac{u_-}{u_+ + u_-}.$$

- The sum of the transport numbers of cation and anion of the electrolyte is unity.

QUESTION BANK

Level I

***Choose the** correct answer from the four alternatives given in each of the following questions :*

OXIDATION-REDUCTION

1. Which of the following process always involve the decrease in oxidation number ?

(*a*) Hydrolysis (*b*) Decomposition
(*c*) Reduction (*d*) Oxidation.

2. During reaction of copper with aqueous solution of silver nitrate

(*a*) Silver atoms are reduced
(*b*) Cu^{2+} ions are oxidised
(*c*) Silver ions are reduced
(*d*) NO_3^- ions are reduced.

3. In which of the following compound, oxidation number of Cl is + 3 ?

(*a*) ICl (*b*) ClO_3^-
(*c*) ClF_3 (*d*) $HClO_4$.

4. Burning of lime to give calcium oxide is

(*a*) oxidation process (*b*) redox process
(*c*) disproportionation (*d*) decomposition.

5. The oxidation number of I in HIO_4 is

(*a*) + 7 (*b*) + 6
(*c*) + 3 (*d*) + 14.

6. The oxidation state of phosphorus is + 3 in

(*a*) Orthophosphoric acid (*b*) Phosphorus acid
(*c*) Metaphosphoric acid (*d*) Pyrophosphoric acid.

7. In which of the compound, iron has lowest oxidation state

(*a*) $K_4[Fe(CN)_6]$ (*b*) $FeCl_3$
(*c*) $Fe(CO)_5$ (*d*) $FeCl_2$.

8. In which of the following reaction, oxidation number of N does not change

(*a*) $2NO_2 + H_2O \longrightarrow HNO_3 + HNO_2$
(*b*) $N_2 + O_2 \longrightarrow 2NO$
(*c*) $2NO_2 \longrightarrow N_2O_4$
(*d*) $NH_4NO_2 \longrightarrow N_2 + 2H_2O$.

9. In which of the following compound, valency of carbon is 4 but its oxidation number is zero

(*a*) methane (*b*) carbon dioxide
(*c*) carbon monoxide (*d*) Formaldehyde.

10. In ferrous ammonium sulphate, the oxidation number of iron is

(*a*) + 3 (*b*) + 2
(*c*) + 1 (*d*) 0.

11. In which of the following compound, oxidation number of iron is not 3 ?

(*a*) Fe_3O_4 (*b*) Fe_2O_3
(*c*) $FeCl_3$ (*d*) $FePO_4$.

12. The oxidation number of Mn in MnC_2O_4 is

(*a*) + 3 (*b*) + 8/3
(*c*) + 1 (*d*) + 2.

13. In which chrominum compound, the oxidation number of Cr is not + 6 ?

(*a*) $PbCrO_4$ (*b*) $K_2Cr_2O_7$
(*c*) Cr_2O_3 (*d*) $NH_4Cr_2O_7$.

14. Which of the following process represents the gain of 8 electrons per molecule ?

(*a*) conversion of $HNO_3 \longrightarrow NO_2$
(*b*) conversion of $HNO_3 \longrightarrow NH_3$
(*c*) conversion of $NH_3 \longrightarrow NH_4^+$
(*d*) conversion of $N_2O_5 \longrightarrow NO$.

15. Which of the following process represents disproportionation ?

(*a*) $Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$
(*b*) $3I_2 + 6OH^- \longrightarrow IO_3^- + 5I^- + 3H_2O$
(*c*) $Cl_2 + I_2 \longrightarrow 2ICl$
(*d*) $Zn + 2HCl \longrightarrow ZnCl_2 + H_2$.

16. Oxidation number of carbon in diamond is

(*a*) − 4 (*b*) + 4

(*c*) 0 (*d*) + 2.

17. Which of the following redox reaction is feasible ?

(*a*) $Zn(s) + 2Ag^+(aq) \longrightarrow Zn^{2+}(aq) + 2Ag(s)$

(*b*) $Zn^{2+}(aq) + 2Ag(s) \longrightarrow 2Ag^+(aq) + Zn(s)$

(*c*) $Zn(s) + 2Ag(s) \longrightarrow 2Ag^+(aq) + Zn^{2+}(aq)$

(*d*) $Zn^{2+}(aq) + Ag^+(aq) \longrightarrow Ag(s) + Zn(s)$.

18. The species undergoing reduction in the following reaction is

$$Cr + 2H_2O + OCl^- \longrightarrow Cr^{3+} + 3Cl^- + 6OH^-$$

(*a*) Cr (*b*) H_2O

(*c*) ClO^- (*d*) Cl^-.

19. In the following equation :

$ClO_3^- + 6H^+ + X \longrightarrow Cl^- + 3H_2O$, X is

(*a*) O (*b*) $6e^-$

(*c*) O_2 (*d*) $5e^-$.

20. The oxidation state of phosphorus in barium hypophosphite $[Ba(H_2PO_2)_2]$ is

(*a*) + 3 (*b*) + 2

(*c*) + 1 (*d*) − 1.

21. The correct oxidation number of phosphorus in magnesium pyrophosphate $[Mg_2P_2O_7]$ is

(*a*) + 2 (*b*) + 3

(*c*) − 3 (*d*) + 5.

22. In the reaction ;

$3Cl_2 + 6OH^- \longrightarrow 5Cl^- + ClO_3^- + 3H_2O$, chlorine is

(*a*) reduced

(*b*) oxidised

(*c*) oxidised as well as reduced

(*d*) neither oxidised nor reduced.

23. In the reaction ; $I_2 + 5O_3 + H_2O \longrightarrow 2HIO_3 + 5O_2$, the substance undergoing reduction is

(*a*) Iodine (*b*) Ozone

(*c*) Water (*d*) I_2 as well as H_2O.

24. Conversion of $C_{12}H_{22}O_{11}$ (sugar) $\longrightarrow CO_2$ involves

(*a*) oxidation of sugar

(*b*) reduction of sugar

(*c*) oxidation of oxygen

(*d*) both oxidation of sugar and reduction of oxygen.

25. $2MnO_4^- + 6H^+ + 5SO_3^{2-} \longrightarrow 5SO_4^{2-} + 3H_2O + X$. In the above equation X stands for

(*a*) Mn^{2+} (*b*) $2Mn^{2+}$

(*c*) MnO_4^{2-} (*d*) MnO_2.

26. In the equation ;

$Cr_2O_7^{2-} + Fe^{2+} + H^+ \longrightarrow Cr^{3+} + Fe^{3+} + H_2O$

the coefficients of Fe^{2+} and H^+ are respectively

(*a*) 6, 7 (*b*) 6, 14

(*c*) 5, 7 (*d*) 5, 14.

27. $KMnO_4$ oxidises $C_2O_4^{2-}$ to CO_2 and each **two** molecules of $KMnO_4$ gain $5e^-$ during the process. The number of moles of $KMnO_4$ required to oxidise 126 g of oxalic acid ($H_2C_2O_4 . 2H_2O$) is

(*a*) 0.2 (*b*) 0.4

(*c*) 0.6 (*d*) 1.0.

28. The number of moles of $KMnO_4$ required to oxidise one mole of ferrous oxalate in acidic medium is

(*a*) 0.6 (*b*) 0.4

(*c*) 0.2 (*d*) 1.67.

29. The oxidation states of most electronegative element in each of the species BaO_2 and Na_2SO_4 are respectively

(*a*) + 2, − 2 (*b*) + 1, − 2

(*c*) − 1, − 2 (*d*) − 2, − 2.

30. Which of the following reaction is not a redox reaction ?

(*a*) $SO_2 + 2H_2S \longrightarrow 2H_2O + S$

(*b*) $Na + O_2 \longrightarrow Na_2O_2$

(*c*) $Na_2O + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O$

(*d*) $4KClO_3 \longrightarrow 3KClO_4 + KCl$.

31. What is correct about $Fe_4[Fe(CN)_6]_3$?

(*a*) All the iron atoms have same oxidation number

(*b*) O.N. of iron atoms outside the square brackets is + 3

(*c*) O.N. of iron atoms outside square brackets is + 2

(*d*) O.N. of iron atoms inside square brackets is + 3.

32. Oxidation number of sulphur in H_2SO_5 is

(*a*) + 2 (*b*) + 4

(*c*) + 8 (*d*) + 6.

33. A compound of xenon and fluorine is found to have 53.3% Xe. What is the oxidation number of Xe in this compound? (At. mass F = 19)

(*a*) 0 (*b*) + 4
(*c*) – 4 (*d*) + 6.

34. The oxidation number of Pt in $[Pt(C_2H_4)Cl_3]^{-1}$ is

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

35. In which of the following compound Cl exhibits more than one oxidation states ?

(*a*) $CaOCl_2$ (*b*) $CaCl_2$
(*c*) Cl_2O_7 (*d*) ICl_3.

ELECTROCHEMISTRY

36. A direct current deposits 54 g of silver (At. mass = 108) during the electrolytic reaction. The same amount of electricity would deposit aluminium (At. mass = 27) from aluminium chloride solution equal to

(*a*) 4. 5 g (*b*) 5.4 g
(*c*) 54 g (*d*) 27 g.

37. How much copper can be deposited by 2.5 Faraday of electricity ?

(*a*) 2 moles (*b*) 2.5 moles
(*c*) 1.25 moles (*d*) 0.125 moles.

38. In order to get 9 gm of aluminium (At. mass = 27) during the electrolysis experiment, how many Faraday of electricity has to be passed ?

(*a*) 3 Faraday (*b*) 2 Faraday
(*c*) 1 Faraday (*d*) 1.5 Faraday.

39. The conduction of electricity through the electrolyte solution is due to

(*a*) movement of molecules of electrolyte
(*b*) movement of ions of electrolyte
(*c*) movement of separate atoms
(*d*) movement of particles of the solvent.

40. The charge required for the reduction of 0.4 mol of $K_2Cr_2O_7$ to Cr^{3+} ions is

(*a*) 0.6 Faraday (*b*) 2.4 × 96500 C
(*c*) 6 × 96500 C (*d*) 12.4 × 96500 F.

41. During the electrolysis of water 4 mol of electrons were transferred from anode to cathode. The total volume of the gases produced at STP will be approximately

(*a*) 67.2 L (*b*) 22.4 L
(*c*) 44.8 L (*d*) 89.4 L.

42. A certain quantity of current *i* amp was passed through three electrolytic cells P, Q, R connected in series and containing aqueous solutions of silver nitrate, mercuric nitrate and mercurous nitrate respectively. It resulted in the deposition of 0.216 g of Ag. The masses of Hg deposited in cell Q and R are respectively (At. mass Ag = 108 ; Hg = 200.6)

(*a*) 0.4012 g, 0.9024 g (*b*) 0.4012 g, 0.2006 g
(*c*) 0.2006 g, 0.4012 g (*d*) 0.1003 g, 0.2006 g.

43. Two electrolytic cell contain 0.1 M ferrous sulphate and 0.2 M ferric chloride respectively are subjected to electrolysis, the ratio of iron deposited in the two cells is

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

44. A bulb draws a current of 4.0 ampere, the charge in coulombs used by the bulb in 30 seconds is

(*a*) 60 C (*b*) 120 C
(*c*) 15 C (*d*) 7.5 C.

45. The time taken by the galvanic cell which operates almost ideally under reversible conditions at a current of 10^{-16} A to deliver 1 mol of electrons is

(*a*) unpredictable (*b*) 19.30×10^{20} s
(*c*) 4.825×10^{20} s (*d*) 9.65×10^{20} s.

46. Certain quantity of current is passed through 2 voltameters connected in series and containing $XSO_4(aq)$ and $Y_2SO_4(aq)$ respectively. If the atomic masses of X and Y are in the ratio of 2 : 1, the ratio of the masses of Y librated to that of X is

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

47. A current of 3 A was passed through the solution of $AuCl_4^-$ ions using gold electrodes and it caused deposition of 1.234 g of Au. The time for which the current was passed is ..... (At. mass of gold is 197)

(*a*) = 604 sec (*b*) 1208 sec
(*c*) 302 sec (*d*) 1812 sec.

48. The resistance of 0.0025 M solution of K_2SO_4 is 326 ohm. The specific conductance of the solution is

(*a*) 4.997×10^{-4} (*b*) 5.997×10^{-7}
(*c*) 6.997×10^{-4} (*d*) unpredictable.

49. The conductivity of four electrolytes P, Q, R, S in $ohm^{-1}\ cm^{-1}$ are as follows P (5×10^{-5}) ; Q(1×10^{-10}) ; R(7×10^{-8}) ; S(9.2×10^{-3}). The one which offers highest resistance to the passage of electric current is

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

50. When same quantity of electricity is passed through two electolytic cells, the ratio of the masses of the products obtained at the cathode is the same as the ratio of their

(*a*) densities
(*b*) atomic masses
(*c*) equivalent masses
(*d*) atomic numbers.

51. The single unit for the combinations *volt-ampere* and *volt / ampere* are respectively

(*a*) ohm, coulomb
(*b*) watt, coulomb
(*c*) watt, ohm
(*d*) coulomb, watt.

52. The combination *Joule / ampere²-sec* represents

(*a*) watt
(*b*) coulomb
(*c*) volt
(*d*) ohm.

53. The standard reduction potential (E°), 0.34 V for copper pertains to the reaction

(*a*) $\frac{1}{2}\,Cu \longrightarrow \frac{1}{2}\,Cu^{2+} + e^-$
(*b*) $Cu \longrightarrow Cu^+ + e$
(*c*) $Cu^{2+} + 2e^- \longrightarrow Cu$
(*d*) $2Cu^+ \longrightarrow Cu^{2+} + Cu$

54. Which of the following is a cathodic reaction ?

(*a*) $Fe^{2+} \longrightarrow Fe^{3+}$
(*b*) $4OH^- \longrightarrow 2H_2O + O_2$
(*c*) $2H_2O \longrightarrow 2OH^- + H_2$
(*d*) $2SO_4^{2-} \longrightarrow S_2O_8^{2-}$.

55. The standard electrode potential of four elements X, Y, Z, W are – 3.05, – 1.66, – 0.40 and 0.76 volts respectively. The highest chemical activity will be shown by

(*a*) X
(*b*) Y
(*c*) Z
(*d*) W.

56. The hydrogen electrode can exhibit electrode potential > 0 if

(*a*) H_2 is bubbled through the solution at 2 atm. pressure
(*b*) concentration of H^+ ion in solution is increased
(*c*) concentration of H^+ ions in solution is decreased
(*d*) concentration of H^+ ions is decreased and simultaneously pressure of H_2 gas is increased.

57. A certain half cell reaction $X + e^- \longrightarrow X^-$ has a very large value of negative reduction potential. This implies that

(*a*) X can be readily reduced
(*b*) X can be readily oxidised
(*c*) X^- can be readily reduced
(*d*) X^- can be readily oxidised.

58. For a reaction, $Mg^{2+} + 2e^- \longrightarrow Mg$; $E° = -\,2.37$ V which of the following statement is true ?

(*a*) E depends upon temperature
(*b*) E changes when Mg plate is made bigger in size
(*c*) E becomes double if equation is multiplied by 2
(*d*) Mg^{2+} can be reduced to Mg by H_2 gas.

59. In SHE, the pH of the acid solution should be

(*a*) 7
(*b*) 14
(*c*) 0
(*d*) 4.

60. The standard electrode potentials $E°_{I_2/I^-}$, $E°_{Br^-/Br_2}$ and $E°_{Fe/Fe^{2+}}$ are respectively + 0.54 V, – 1.09 V and 0.44 V on the basis of above data which of the following process is non-spontaneous

(*a*) $Br_2 + 2I^- \rightarrow 2Br^- + I_2$
(*b*) $Fe + Br_2 \rightarrow Fe^{2+} + 2Br^-$
(*c*) $Fe + I_2 \rightarrow Fe^{2+} + 2I^-$
(*d*) $I_2 + 2Br^- \rightarrow 2I^- + Br_2$.

61. The values of $E°_{Zn/Zn^{2+}} = 0.76$ V and that of $E°_{Fe^{2+}/Fe} = -\,0.41$ V. The $E°_{cell}$ of the cell with net cell reaction

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

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

62. If standard reduction potentials of Ni^{2+}/Ni and Au^{3+}/Au couples are – 0.25 V and 1.50 V respectively, then the EMF of the cell

$$Ni/Ni^{2+}\,(0.01M)\,||\,Au^{3+}\,(0.1\ M)Au \text{ will be}$$

(*a*) > EMF°
(*b*) = EMF°
(*c*) < EMF°
(*d*) unpredictable.

63. The reaction $M + 2H^+ \longrightarrow M^{2+} + H_2$, most suitably applies to the combination

(*a*) Cu and HCl
(*b*) Ag and HCl
(*c*) Cu and HNO_3
(*d*) Mg and HCl.

64. From the E° values for the half cells

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

Which two combination would give cell with largest cell potential ?

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

65. If the standard reduction potential, E° for four divalent elements X, Y, Z, W are – 1.46 V, – 0.36 V, 0.15 V and – 1.24 V respectively, then

(*a*) X will replace Z^{+2} from aqueous solution

(*b*) Y will replace Z^{+2} from aqueous solution

(*c*) W will replace Z^{+2} from aqueous solution

(*d*) All the above statements are correct.

66. The emf of the cell, $Zn \mid Zn^{2+} \parallel Ag^{+} \mid Ag$ is independent of

(*a*) the volumes of Zn^{2+} and Ag^{+} solution

(*b*) the molarity of Cu^{2+} ions in solution

(*c*) the molarity of Ag^{+} ions in solution

(*d*) temperature.

67. The two aqueous solutions ; A($AgNO_3$) and B(LiCl) were electrolysed using Pt. electrodes. The pH of the resulting solutions will

(*a*) increase in A and decrease in B

(*b*) decrease in both

(*c*) increase in both

(*d*) decrease in A and increase in B.

68. Standard cell voltage for the cell

$$Pb/Pb^{2+} \parallel Sn^{2+}/Sn$$

is – 0.01 V. If the cell is to exhibit $E_{cell} = 0$, the value of $[Sn^{2+}]/[Pb^{2+}]$ should be antilog of

(*a*) + 0.3 (*b*) 0.5

(*c*) 1.5 (*d*) – 0.5.

69. The potential at which a solution containing 1 M $CuSO_4$, 1 M $NiSO_4$ and 2M H_2SO_4 be electrolysed so as to deposite only copper and no nickel so that 1×10^{-9} M Cu^{2+} is left is

(*a*) 0.04 V (*b*) 0.4 V

(*c*) 0.07 V (*d*) 0.007 V.

70. In the diagram given below the value of X is

$$\begin{tikzcd} Cu^{2+} \arrow[r, "+0.15\ V"] \arrow[rr, bend right, "E^\circ = X\ volt"'] & Cu^{+} \arrow[r, "+0.50\ V"] & Cu \end{tikzcd}$$

(*a*) 0.325 V (*b*) 0.65 V

(*c*) – 0.35 V (*d*) – 0.65 V.

71. A cell is constituted as follows

$$Pt, H_2\ (1\ atm) \mid HA_1 \mid HA_2 \mid H_2\ (1\ atm), Pt$$

The pH of two acids solutions HA_1 and HA_2 are 3 and 5 respectively. The emf of the cell is

(*a*) 0.059 V (*b*) 0.0295 V

(*c*) 0.118 V (*d*) – 0.118 V.

72. Two hydrogen electrodes are constituted using buffer solutions of CH_3COONa and CH_3COOH in the ratio of *x* : *y* and *y* : *x* respectively and have electrode potentials E_1 and E_2 volts, at 25°C. The pK_a value of acetic acid is

(*a*) $\frac{E_1 + E_2}{0.118}$ (*b*) $\frac{E_2 - E_1}{0.118}$

(*c*) $-\frac{E_2 + E_1}{0.118}$ (*d*) $\frac{E_1 + E_2}{0.059}$.

73. The emf of the cell Zn/Zn^{2+} (1 M) $\parallel$ X^{2+} (1 M) / X is found to be 1.1 V. If E°_{red} of Zn^{2+} / Zn is – 0.76, then E°_{oxi} of X is

(*a*) unpredictable (*b*) 0.34 V

(*c*) – 0.34 V (*d*) 1.86 V.

74. An electrochemical cell stops working after sometime because

(*a*) electrode potentials of both the electrodes become equal

(*b*) electrode potential of both the electrodes becomes zero

(*c*) anode electrode is completely eaten up

(*d*) solutions in the two half cell become neutral.

75. Zn rod is placed in 100 mL of 1 M $CuSO_4$ solution so that molarity of Cu^{2+} change to 0.7 M. The molarity of SO_4^{2-} ions at this stage will be

(*a*) 0.8 M (*b*) 1 M

(*c*) 0.7 M (*d*) 1.8 M.

76. An electrochemical cell has two half cell reactions as,

$$A^{2+} + 2e^- \longrightarrow A \,;\, E^\circ = 0.34\ V$$

$$X \longrightarrow X^{2+} + 2e^- \,;\, E^\circ = +\ 2.37\ V$$

The cell voltage will be

(*a*) 2.71 V (*b*) 2.03 V

(*c*) – 2.71 V (*d*) – 2.03 V.

77. From the following facts :

(*i*) $2X^- + Y_2 \longrightarrow 2Y^- + X_2$

(*ii*) $2W^- + Y_2 \longrightarrow$ No reaction

(*iii*) $2Z^- + X_2 \longrightarrow 2X^- + Z_2$, which of the following is true ?

(*a*) $E_{W_2/W^-} > E_{Y_2/Y^-} > E_{X_2/X^-} > E_{Z_2/Z^-}$

(*b*) $E_{W_2/W^-} > E_{Y_2/Y^-} > E_{Z_2/Z^-} > E_{X_2/X^-}$

(c) $E_{W_2/W^-} > E_{Z_2/Z^-} > E_{Y_2/Y^-} > E_{X_2/X^-}$

(d) $E_{W_2/W^-} > E_{X_2/X^-} > E_{Y_2/Y^-} > E_{Z_2/Z^-}$.

78. The standard EMF of the cell reaction ;

$$\frac{1}{2}\,Cu(s) + \frac{1}{2}\,Cl_2(g) \longrightarrow \frac{1}{2}\,Cu^{2+} + Cl^-$$

is 1.02 V. The value of $\Delta G°$ will be

(a) unpredictable (b) – 98.43 kJ

(c) – 196.86 kJ (d) – 98.43 J.

79. The depolarizer used in dry cell batteries is

(a) NH_4Cl (b) Manganese dioxide

(c) Potassium hydroxide (d) Sodium triphosphide.

80. In lead storage battery, the anode reaction is

(a) $Pb^{2+} + 2e^- \longrightarrow Pb$

(b) $Pb + H_2SO_4 \longrightarrow PbSO_4 + 2H^+ + 2e^-$

(c) $PbO + H_2SO_4 \longrightarrow PbSO_4 + H_2O$

(d) None of these.

81. The molar ionic conductance at infinite dilution of Ag^+ is 61.92×10^{-4} S mol^{-1} m^2 at 25°C. The ionic mobility of Ag^+ will be

(a) 6.4×10^{-8} (b) 6.192

(c) 6.192×10^{-4} (d) 3.2×10^{-4}.

82. Sodium metal cannot be produced by the electrolysis of an aqueous solution of sodium chloride because

(a) Sodium reacts with water

(b) Sodium reacts Cl^- ions in the solution

(c) Solution ions are more stable than sodium atom

(d) Reduction of water is preferred to reduction of Na^+ ions.

83. On electrolysis of 10^{-6} M HCl solution

(a) Cl_2 gas is produced at the cathode

(b) Cl_2 is produced at the anode

(c) O_2 gas is produced at the cathode

(d) H_2 is produced at the cathode.

84. The electrolysis of aqueous solution of $CuBr_2$ using platinum electrode would lead to the evolving of

(a) O_2 gas at anode

(b) Br_2 gas at anode and O_2 gas at cathode

(c) Copper(s) at cathode

(d) H_2 gas at cathode.

85. For the cell reaction to be spontaneous

(a) $E°_{cell} > 0$ (b) $E°_{cell} < 0$

(c) $\Delta G > 0$ (d) $\Delta G = 0$.

QUESTION BANK

Level II

Choose the correct answer from the four alternatives given in each of the following questions :

1. The conductivity of strong electrolyte

(a) increases on dilution slightly

(b) does not change on dilution

(c) decreases on dilution

(d) depends on density of electrolyte itself.

2. The amount of electricity that can deposit 108 g of silver from silver nitrate solution is

(a) 1 amp. (b) 1 coulomb

(c) 1 Faraday (d) 2 amp.

3. Which statement about $Na_2S_4O_6$ is correct ?

(a) O.N of all atoms is 2.5

(b) Two S atoms have O.N. + 2 while other two have O.N + 3

(c) Three S atoms have ON. + 3 while the fourth S atoms has O.N. + 4

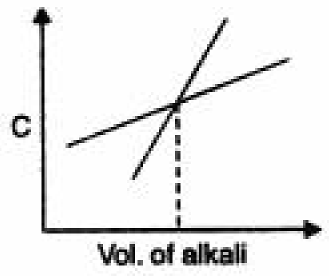
(d) Two S atoms have O.N. + 5 while, the other two S atoms have O.N = 0.

4. The brown ring complex is formulated as $[Fe(H_2O)_5NO]SO_4$. The oxidation state of iron is

(a) + 1 (b) + 2

(c) + 3 (d) 0.

5. The plot of conductance *vs* volume of alkali represents as titration between



(*a*) HCl and NaOH (*b*) HCl and NH_4OH

(*c*) CH_3COOH and KOH (*d*) H_2SO_4 and KOH.

6. When electricity is passed to aqueous solution of aluminium chloride, 13.5 g of Al are deposited. The number of Faradays of electricity passed must be

(*a*) 2.0 (*b*) 1.5

(*c*) 1.0 (*d*) 0.5.

7. The resistance of 1 N solution of acetic acid is 250 ohms when measured in a cell of cell constant 1.5 cm^{-1}. The equivalent conductance of 1 N acetic acid in ohm^{-1} cm^2 $equiv^{-1}$ is

(*a*) 4.6 (*b*) 9.2

(*c*) 18.4 (*d*) 0.023.

8. The mass of copper that will be deposited at cathode in electrolysis of 0.2 M solution of copper sulphate when a quantity of electricity equal to that required to liberate 2.24 L of H_2 from 0.1 M aqueous H_2SO_4 is passed (At. mass of Cu = 63.5) will be

(*a*) 1.59 g (*b*) 3.18 g

(*c*) 6.35 g (*d*) 12.70 g.

9. Electrode potentials ($E°_{red}$) of 4 elements A, B, C, D are − 1.36, − 0.32, 0, − 1.26 V respectively. The decreasing reactivity order of these elements is

(*a*) A, D, B and C (*b*) C, B, D and A

(*c*) B, D, C and A (*d*) C, A, D and B.

10. In a solution of $CuSO_4$ how much time will be required to precipitate 2 g copper by 0.5 ampere current ?

(*a*) 12157.48 sec (*b*) 102 sec

(*c*) 510 sec (*d*) 642 sec.

11. 2.5 Faradays of electricity is passed through solution of $CuSO_4$. The number of gram equivalents of copper deposited on the cathode would be

(*a*) 1 (*b*) 2

(*c*) 2.5 (*d*) 1.25.

12. An electrolytic cell contains a solution of Ag_2SO_4 and has Pt electrodes. A current is passed till 1.6 g of O_2 has been liberated at anode. The amount of silver deposited at cathode will be

(*a*) 107.88 g (*b*) 1.6 g

(*c*) 0.8 g (*d*) 21.60 g.

13. The equivalent conductance of NaCl, HCl and C_2H_5COONa at infinite dilution are 126.45, 426.16 and 91 ohm^{-1} cm^2. The *eq*. conductance of C_2H_5COOH is

(*a*) 201.28 ohm^{-1} cm^2 (*b*) 390.71 ohm cm^2

(*c*) 698.28 ohm cm^2 (*d*) 540.48 ohm cm^2.

14. At STP 1.12 litre of H_2 is obtained on flowing a current for 965 seconds in a solution. The value of current is

(*a*) 10 amp (*b*) 1.0 amp

(*c*) 1.5 amp (*d*) 2.0 amp.

15. How long will it take to remove half of silver from 200 cm^3 of 0.1 M $AgNO_3$ solution with a current of 0.1 amp. ?

(*a*) 40.2 min. (*b*) 80.4 min.

(*c*) 160.8 min. (*d*) 120 min.

16. How many cm^3 of O_2 at S.T.P. will be liberated from acidified water by 193 C of electricity ?

(*a*) 11.2 cm^3 (*b*) 22.4 cm^3

(*c*) 44.8 cm^3 (*d*) 33.6 cm^3.

17. In the electrolysis of aqueous solution of copper (II) chloride the mass of cathode electrode is increased by 3.2 g by a certain quantity of current. If anode is a copper strip, then, at the anode

(*a*) 0.112 L of Cl_2 at S.T.P. is liberated

(*b*) 0.56 L of O_2 at S.T.P. is liberated.

(*c*) 3.2 g of O_2 is produced

(*d*) 0.05 mol of copper will dissolve.

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

(*a*) The spoon gets coated with aluminium

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

(*c*) No reaction occurs

(*d*) The solution starts turning blue.

19. The number of moles of electrons required for causing reduction of 0.2 moles of nitrobenzene ($C_6H_5NO_2$) to amino benzene ($C_6H_5NH_2$) is

(*a*) 1.2 mole (*b*) 0.6 mole

(*c*) 0.3 mole (*d*) 0.4 mole.

20. The oxidation of ammonia occurs by some oxidising agent to the stage of NO. If the oxidant gains $2e^-$ per molecule. How many molecules of oxidant are used to affect the oxidation of 0.5 mol of ammonia. (N_A being Avogadro number)

(*a*) 1.25 N_A (*b*) 2.50 N_A

(*c*) 5 N_A (*d*) unpredictable.

21. Certain quantity of current librated 0.504 g of hydrogen in 2 hr. The number of grams of copper that can be librated by same current under similar conditions will be approximately

(*a*) 12.7 g
(*b*) 16.0 g
(*c*) 31.8 g
(*d*) 63.5 g.

22. Cadmium amalgam is prepared using a mercury cathode. The electricity required to prepare 10% Cd-Hg amalgam on a cathode of 3 g of Hg is

(*a*) 9650 C
(*b*) 568.6 C
(*c*) 484 C
(*d*) 600 C

23. In a H_2—O_2 fuel cell, 6.72 L of hydrogen at NTP reacts in 15 minutes, the average current produced in amperes is

(*a*) 64.3 amp
(*b*) 643.3 amp
(*c*) 6.43 amp
(*d*) 0.643 amp.

24. A current of 9.65 ampere is passed through the aqueous solution of NaCl using suitable electrodes for 1000 s. The amount of NaOH formed during electrolysis is

(*a*) 2.0 g
(*b*) 4.0 g
(*c*) 6.0 g
(*d*) 8.0 g.

25. The net charge on one gram-ion of N^{3-} has been calculated by a student as $Y \times 10^6$ C. The value of Y is

(*a*) 2.88
(*b*) 8.2
(*c*) 6
(*d*) 3.49.

26. The passage of 25 milliampere of current through molten $CaCl_2$ for 60 seconds will cause the deposition of X calcium atoms on cathode. The value of X is

(*a*) 6.02×10^{19}
(*b*) 2×10^{18}
(*c*) 3×10^{18}
(*d*) 4.68×10^{18}.

27. 0.5 Faraday of electricity was passed to deposit all the copper present in 500 ml of $CuSO_4$ solution. The molarity of the solution is

(*a*) 0.5 M
(*b*) 0.25 M
(*c*) 1.5 M
(*d*) 1.25 M.

28. A current of 2 amp passing for five hours through the molten tin salt deposits 22.2 g of tin. The oxidation state of tin in the salt is

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

29. The time required to remove electrolytically one fourth of Ag from 0.2 litre of 0.1 M $AgNO_3$ solution by a current of 0.1 amp. is approx.

(*a*) 320 min.
(*b*) 160 min.
(*c*) 80 min
(*d*) 100 min.

30. In the electrolysis of copper chloride solution using copper electrodes, the mass of cathode increases by 3.25 g. In the anode,

(*a*) 0.05 mol of Cu will go into solution as Cu^{2+} ions
(*b*) 560 ml of O_2 at S.T.P. will be librated
(*c*) 112 ml of Cl_2 will librate
(*d*) 3.2 mol of copper metal will dissolve.

31. The oxidation number of Br in $KBrO_4$ is

(*a*) – 1
(*b*) + 3
(*c*) + 1
(*d*) + 7.

32. The oxidising agent in the following reaction

$$KI + I_2 \rightleftharpoons KI_3 \text{ is}$$

(*a*) KI
(*b*) I_2
(*c*) both KI and I_2
(*d*) neither KI nor I_2.

33. In the reaction,

$$(NH_4)_2Cr_2O_7 \longrightarrow N_2 + 4H_2O + Cr_2O_3,$$

the number of electrons lost by each N atom is

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

34. $SnCl_2$ gives a silky white precipitate of $SnCl_4$ with $HgCl_2$. In this reaction $HgCl_2$ is

(*a*) reduced
(*b*) oxidised
(*c*) converted into a chloro complex of Hg
(*d*) converted into Hg.

35. In the following half reaction,

$$C_2O_4^{2-} \longrightarrow 2CO_2 + x\,e^-$$

the value of *x* is

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

36. The number of electrons to be added to reactant side in the following half reaction is

$$NO_3^- + 6H_2O \longrightarrow NH_3 + 9OH^-$$

(*a*) 2
(*b*) 4
(*c*) 3
(*d*) 8.

37. In the reaction,

$$5H_2O_2 + 2ClO_2 + 2OH^- \longrightarrow 2Cl^- + 5O_2 + 6H_2O,$$

the substance oxidised is

(*a*) H_2O_2
(*b*) ClO_2
(*c*) OH^-
(*d*) unpredictable.

38. One mole of N_2H_4 loses 10 moles of electrons to form a new compound Y. Assuming that all nitrogen appears in the new compound, the oxidation state of nitrogen in the new compound will be *(a)* + 3 *(b)* + 5

(c) − 1 *(d)* − 3.

39. A current of 2 ampere is passed for 5 hrs through the molten metal salt and it causes deposition of 22.2 g of metal (At. mass 177). The oxidation state of the metal in the salt is

(a) + 2 *(b)* + 3

(c) + 4 *(d)* + 5.

40. The conductivity of the saturated solution of some bi-bivalent salt XY is 3.06×10^{-6} ohm^{-1} cm^{-1} and its equivalent conductivity is 1.53 ohm^{-1} cm^2 $equi^{-1}$. The value of K_{sp} of XY is

(a) 4×10^{-6} *(b)* 2.5×10^{-9}

(c) 2.5×10^{-13} *(d)* 1×10^{-6}.

41. The conductivity of 0.25 M solution of uni-univalent weak electrolyte XY is 0.0125 Ω^{-1} cm^{-1}. The value of Λ_m^∞ of XY is 500 Ω^{-1} cm^2 mol^{-1}. The value of Ostwald dilution constant of AB is

(a) 2.5×10^{-3} *(b)* 2.5

(c) 2.5×10^{-1} *(d)* 0.00025.

42. For which of the following electrolytic solution $\wedge_m$ and $\wedge_{eq}$ are equal

(a) $BaCl_2$ *(b)* KCl

(c) $Al_2(SO_4)_3$ *(d)* $CaCl_2$.

43. The relationship between the resistance of certain electrolytic solution 'R', its molarity M, its molar conductivity Λ_m and cell constant k_{cell} is

(a) $\Lambda_m = \dfrac{R\,k_{cell}}{M}$ *(b)* $\Lambda_m = \dfrac{k_{cell} \times 10^3}{RM}$

(c) $\Lambda_m = RM\,k_{cell}$ *(d)* $\Lambda_m = \dfrac{M\,k_{cell} \times 10^{-3}}{R}$.

44. Which of the following statement is wrong ?

(a) The ionic conductivity of Na^+ is different at infinite dilution for NaCl and NaBr solution

(b) $\Lambda^\infty_{(BaCl_2)} = \lambda^\infty_{(Ba^{2+})} + 2\,\lambda^\infty_{Cl^-}$

(c) The value of Λ_m^∞ for weak electrolyte can be determined by using Kohlrausch's law

(d) The electrodes of same metal can be used to constitute galvanic cell.

45. A galvanic cell is set up by zinc bar weighing 100 g and 1.0 L of 0.1 M solution of copper (II) sulphate. For how long the cell will deliver a steady current of 2 ampere

(a) 0.286 hr *(b)* 23 hr

(c) 2.68 hr *(d)* unpredictable.

46. $xI_2 + ySO_2 + zH_2O \longrightarrow aSO_4^{2-} + bI^- + cH^+$. The values of *z, b, c* are respectively

(a) 1, 1, 2 *(b)* 2, 2, 4

(c) 1, 2, 4 *(d)* 2, 4, 2.

47. Reaction that takes place at graphite anode in dry cell is

(a) $Zn^{2+} + 2e^- \rightarrow Zn(s)$ *(b)* $Zn(s) \rightarrow Zn^{2+} + 2e^-$

(c) $Mn^{2+} + 2e^- \rightarrow Mn(s)$ *(d)* $Mn(s) \rightarrow Mn^+ + e^- + 1.5$ V.

48. The standard reduction potentials of Cu^{2+}/Cu and Cu^{2+}/Cu^+ are 0.337 and 0.153 respectively. The standard electrode potential of Cu^+/Cu half cell will be approximately,

(a) 0.184 V *(b)* 0.827 V

(c) 0.521 V *(d)* 0.490 V.

49. $E°_{cell}$ of $Zn/Zn^{2+} \parallel Cu^{2+}/Cu$ is 1.10 V at 25°C. The equilibrium constant for the reaction

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

(a) 10^{-28} *(b)* 10^{+37}

(c) 10^{-18} *(d)* 10^{17}.

50. Electrode potential data are given below :

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

$Al^{3+}\,(aq) + 3e^- \longrightarrow Al(s)\,;\quad E° = -\,1.66$ V

$Br_2\,(aq) + 2e^- \longrightarrow 2Br^-\,(aq)\,;\quad E° = +\,1.08$ V.

Based on the data, the reducing power of Fe^{2+}, Al and Br^- will increase in the order

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

(c) $Al < Br^- < Fe^{2+}$ *(d)* $Al < Fe^{2+} < Br^-$.

51. For the cell reaction,

$$Cu^{2+}\,[C_1(aq)] + Zn(s) \longrightarrow Zn^{2+}\,[C_2(aq)] + Cu(s)$$

of an electrochemical cell, the change in free energy, ΔG at a given temperature is a function of

(a) *ln* (C_1) *(b)* *ln* (C_2/C_1)

(c) ln $(C_1 + C_2)$ *(d)* *ln* (C_2).

52. Mark the false statement among the following :

(a) A salt bridge is used to eliminate liquid junction potential

(b) ΔG and EMF (E) are related as $\Delta G = -\,nFE$

(*c*) Nernst equation for single electrode potential is

$$E = E^\circ - \frac{RT}{nF} \log a_{M^{n+}}$$

(*d*) The efficiency of H_2—O_2 fuel cell is 70%.

53. A gas X at one atm. pressure is bubbled through the solution containing mixture of 1 M Y^- and 1 M Z^- at 25°C. If reduction potential of $X < Y < Z$, then

(*a*) Y will oxidise X and not Z

(*b*) Y will oxidise Z and not X

(*c*) Y will oxidise Z and X

(*d*) Y will reduce both Y and Z.

54. Thermodynamic efficiency of cell is given by

(*a*) $\Delta H / \Delta G$ (*b*) $\frac{nFE}{\Delta G}$

(*c*) $\frac{-nEF}{\Delta H}$ (*d*) nFE°.

55. $E^\circ_{Ni^{2+}/Ni} = -0.25$ V ; $E^\circ_{Au^{3+}/Au} = 1.50$ V. The value of E°_{cell} for the cell Ni | Ni^{2+} (1 M) ‖ Au^{3+} (1 M) | Au is

(*a*) 1.25 V (*b*) – 1.75 V

(*c*) 1.75 V (*d*) 4.0 V.

56. The electrode potential of hydrogen electrode at pH 10 is

(*a*) 0.51 V (*b*) 0.00 V

(*c*) – 0.59 V (*d*) 0.059 V.

57. Red hot carbon removes oxygen from XO and YO but not from ZO. Y also removes oxygen from XO. The above information is sufficient to provide the order of activity among the metals X, Y, Z as

(*a*) $X > Y > Z$ (*b*) $Z > Y > X$

(*c*) $Y > X > Z$ (*d*) $Z > X > Y$.

58. A cell is constituted by coupling the two electrodes Sn/Sn^{2+} and Ag/Ag^+, if $E^\circ_{Sn^{2+}/Sn}$, $E^\circ_{Ag^+/Ag}$ and E°_{cell} are – 0.14 V, 0.80 V and 0.94 V respectively. The correct representation of cell is

(*a*) Sn/Sn^{2+} (1 M) ‖ Ag^+ (0.1 M)/Ag

(*b*) Ag/Ag^+ (1 M) ‖ Sn^{2+} (1 M)/Sn

(*c*) Sn/Sn^{2+} (1 M) ‖ Ag^+ (1 M)/Ag

(*d*) Sn/Sn^{2+} (0.1 M) ‖ Ag^+ (1 M)/Ag.

59. The measured electrode potential for the reaction $Pb^{2+} + 2e^- \longrightarrow Pb(s)$ does not change if

(*a*) concentration of Pb^{2+} ions is increased in the solution

(*b*) size of lead strip is increased

(*c*) temperature of the system is raised

(*d*) volume of solution is doubled by adding water.

60. Given that $E^\circ_{Al^{3+}/Al} = -1.67$ V ; $E^\circ_{Mg^{2+}/Mg} = -2.34$ V ; $E^\circ_{Cu^{2+}/Cu} = 0.34$ V and $E^\circ_{I_2/I^-} = +0.53$ V, predict as to which one is the best reducing agent ?

(*a*) Al (*b*) I_2

(*c*) Mg (*d*) Cu.

61. If the solution of copper sulphate in which copper rod is immersed is diluted 10 times. The electrode potential will

(*a*) increase by 0.030 V (*b*) decrease by 0.030 V

(*c*) increase by 0.059 V (*d*) decrease by 0.059 V.

62. Given four half cell reactions

(*i*) $A + e^- \longrightarrow A^-$; $E^\circ = -0.24$ V

(*ii*) $C^- + 2e^- \longrightarrow C^{3-}$; $E^\circ = -1.25$ V

(*iii*) $B^- + e^- \longrightarrow B^{2-}$; $E^\circ = 1.25$ V

(*iv*) $D + 2e^- \longrightarrow D^{2-}$; $E^\circ = 0.68$ V

Which combination would give a cell with largest cell voltage ?

(*a*) A and B (*b*) B and C

(*c*) C and D (*d*) D and A.

63. In which of the following cell, the value of $E_{cell} > 0$ but $E^\circ_{cell} = 0$.

(*a*) Cu/Cu^{2+} (1 M) ‖ Ag^+ (1 M)/Ag

(*b*) Pt, H_2/H^+ (0.25 M) ‖ H^+ (0.025 M)/H_2, Pt

(*c*) Ag/Ag^+ (0.01 M) ‖ Ag^+ (0.1 M)/Ag

(*d*) Both in (*b*) and (*c*).

64. Zinc is generally coated over iron to prevent its corrosion because

(*a*) zinc is cheaper metal

(*b*) zinc gives a good luster to iron

(*c*) $E^\circ_{Zn^{2+}/Zn} > E^\circ_{Fe^{2+}/Fe}$

(*d*) $E^\circ_{Zn/Zn^{2+}} > E^\circ_{Fe/Fe^{2+}}$.

65. When a solution of sodium hydroxide is added to acetic acid solution, the conductivity of the resulting solution

(*a*) increases (*b*) remains unchanged

(*c*) decreases (*d*) becomes zero.

66. Given E° values for some reactions as

$$I_2 + 2e^- \longrightarrow 2I^- ; E^\circ = 0.54 \text{ V}$$

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O ; E^\circ = 1.52 \text{ V}$$

$$Fe^{3+} + e^- \longrightarrow Fe^{2+} ; E^\circ = 0.77$$
$$Sn^{4+} + 2e^- \longrightarrow Sn^{2+} ; E^\circ = +0.1 \text{ V}$$

The strongest reductant and oxidant respectively are

(*a*) Sn^{2+}, MnO_4^- (*b*) MnO_4^-, Sn^{4+}

(*c*) I_2, Fe^{3+} (*d*) I_2, Sn^{2+}.

67. The chemical reaction

$$2X + nH_2SO_4 \longrightarrow X_2(SO_4)_n + nH_2$$

can take place only if

(*a*) $\Delta H < 0$ (*b*) $n > 2$

(*c*) $E^\circ X/X^{n+} > 0$ (*d*) $E^\circ X^{n+}/X > 0$.

68. The standard electrode potential of OX^-/X^- and X^-/X_2 respectively are 0.94 V and – 1.36 V. The E° value for OX^-/X_2 will be

(*a*) – 0.42 V (*b*) + 0.42 V

(*c*) 0.21 V (*d*) – 1.04 V.

69. The standard emf of Daniel cell is 1.10 Volts. The maximum electrical work obtained from the cell is

(*a*) 212.3 kJ (*b*) 175.4 kJ

(*c*) 106.15 kJ (*d*) 53.07 kJ.

70. A compound contains X, Y, Z atoms. The oxidation states of X, Y and Z are + 2, + 2, – 2 respectively. The probable formula of the compound is

(*a*) XYZ_2 (*b*) $(XZ_3)_2Y_2$

(*c*) $X_3(Y_4Z)_2$ (*d*) $X_3(YZ_4)_2$.

71. The cell Pt, H_2 (1 atm) / H^+ (pH = *x*) ‖ calomel electrode has emf of 0.67 V at 25°C. If reduction potential of calomel electrode is 0.28 V, the value of *x* will be

(*a*) 6.6 (*b*) 3.3

(*c*) 13.2 (*d*) 1.1.

72. In an electrolytic cell 1 L of 0.1 M aqueous solution of MnO_4^{2-} is converted to MnO_4^- at the cathode which statment is incorrect ?

(*a*) The above process occurs at the anode

(*b*) Oxidation number of Mn changes from + 6 to + 7

(*c*) Oxidation number of Mn changes from + 7 to + 6

(*d*) The entire process requires the passage of 9650 C of electricity.

73. Which relation is/are correct ?

(*a*) Conductivity = Specific conductivity × Cell constant

(*b*) Cell constant = Conductivity/Conductance

(*c*) Equivalent conductivity = Conductivity × Cell constant

(*d*) Molar conductivity = Conductivity × Cell constant.

74. The equilibrium constant for a feasible cell reaction is

(*a*) < 1 (*b*) 0

(*c*) = 0 (*d*) > 1.

75. ΔG° for cell reaction,

$$AgCl(s) + \frac{1}{2} H_2(g) \longrightarrow Ag(s) + H^+ + Cl^- \text{ is } -21.52 \text{ kJ}$$

$$\Delta G^\circ \text{ for } 2AgCl(s) + H_2(g) \longrightarrow 2Ag(s) + 2H^+ + 2Cl^- \text{ is}$$

(*a*) – 21.52 kJ (*b*) – 43.04 kJ

(*c*) 43.04 kJ (*d*) – 10.76 kJ.

ANSWERS

QUESTION BANK (Level I)

1. (*c*) **2.** (*c*) **3.** (*c*) **4.** (*d*) **5.** (*a*) **6.** (*b*) **7.** (*c*) **8.** (*c*)
9. (*d*) **10.** (*b*) **11.** (*a*) **12.** (*d*) **13.** (*c*) **14.** (*b*) **15.** (*b*) **16.** (*c*)
17. (*a*) **18.** (*c*) **19.** (*b*) **20.** (*c*) **21.** (*d*) **22.** (*c*) **23.** (*b*) **24.** (*a*)
25. (*b*) **26.** (*b*) **27.** (*b*) **28.** (*a*) **29.** (*c*) **30.** (*c*) **31.** (*b*) **32.** (*d*)
33. (*d*) **34.** (*b*) **35.** (*a*) **36.** (*a*) **37.** (*c*) **38.** (*c*) **39.** (*b*) **40.** (*b*)
41. (*a*) **42.** (*c*) **43.** (*d*) **44.** (*b*) **45.** (*d*) **46.** (*a*) **47.** (*a*) **48.** (*d*)
49. (*d*) **50.** (*c*) **51.** (*c*) **52.** (*d*) **53.** (*c*) **54.** (*c*) **55.** (*a*) **56.** (*b*)
57. (*d*) **58.** (*a*) **59.** (*c*) **60.** (*d*) **61.** (*d*) **62.** (*a*) **63.** (*d*) **64.** (*a*)
65. (*d*) **66.** (*a*) **67.** (*d*) **68.** (*a*) **69.** (*c*) **70.** (*a*) **71.** (*c*) **72.** (*c*)
73. (*c*) **74.** (*a*) **75.** (*b*) **76.** (*a*) **77.** (*a*) **78.** (*b*) **79.** (*b*) **80.** (*b*)
81. (*a*) **82.** (*d*) **83.** (*d*) **84.** (*c*) **85.** (*a*).

QUESTION BANK (Level II)

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

HINTS/SOLUTIONS

QUESTION BANK (Level I)

1. (*c*) Oxidation number always decreases during reduction.

2. (*c*) $\overset{0}{Cu} + 2\overset{+}{Ag}NO_3 \longrightarrow \overset{+2}{Cu}(NO_3)_2 + 2\overset{0}{Ag}$.

3. (*c*) $ClF_3 ; x + 3(-1) = 0 \quad \therefore \quad x = +3$

4. (*d*) $CaCO_3 \longrightarrow CaO + CO_2$

None of the element change oxidation number. Hence it is not a redox reaction.

5. (*a*) HIO_4, O.N. of I = + 7.

6. (*b*)

(*a*) in H_3PO_4, O.N. of P = + 5

(*b*) in H_3PO_3, O.N. of P = + 3

(*c*) in HPO_3, O.N. of P = + 5

(*d*) in $H_4P_2O_7$, O.N. of P = + 5.

7. (*c*) In $Fe(CO)_5$, O.N. of Fe is zero.

8. (*c*) Oxidation state of N on both the compounds is + 2.

9. (*d*) Valency of C is always 4, in $H-\underset{\underset{H}{|}}{C}=O$ the O.N. = 0.

10. (*b*) Ferrous ammonium sulphate is

$FeSO_4(NH_4)_2SO_4 ; x + (-2) + 2(+1) + (-2) = 0$ or $x = +2$.

11. (*a*) $Fe_3O_4 ; 3x + 4(-2) = 0$ or $x = 8/3$.

12. (*d*) $Mn(C_2O_4) ; x + (-2) = 0$ or $x = +2$.

13. (*c*) $Cr_2O_3 ; 2x + 3(-2)$ or $x = +3$.

14. (*b*) $\overset{+5}{HNO_3} \longrightarrow \overset{-3}{NH_3}$ involves addition of 8 electrons per HNO_3 molecule.

15. (*b*) Disproportionation is a process in which same element undergoes decrease as well as increase of O.N. Iodine changes its O.N. from zero to + 5 in IO_3^- and from zero to − 1 in I^-.

16. (*c*) Diamond is a network of carbon atoms.

17. (*a*) The $E°_{red}$ of Ag > $E°_{red}$ of Zn and hence Ag^+ reduces to Ag.

18. (*c*) $\overset{0}{Cr} + 2H_2O + \overset{-2+2}{(OCl)^-} \longrightarrow Cr^{3+} + 3Cl^- + 3OH^-$

OCl^- gets reduced because O.N. of Cl decreases from + 1 to − 1.

19. (*b*) $\overset{+5}{(ClO_3)^-} + 6H^+ + 6e^- \longrightarrow Cl^- + 3H_2O$.

20. (*c*) $Ba(H_2PO_2)_2 ; +2 + 2(2 + x - 4) = 0 ; x = \frac{2}{2} = +1$.

21. (*d*) $Mg_2P_2O_7 ; 4 + 2x + 7(-2) = 0$ or $x = +5$.

22. (*c*) $3\overset{0}{Cl_2} + 6OH^- \longrightarrow 5Cl^- + \overset{+5}{(ClO_3)^-} + 3H_2O$

Reduction

Oxidation

23. (*b*) $\overset{0}{I_2} + 5\overset{0}{O_3} + H_2O \longrightarrow 2H\overset{+5}{I}\overset{-2}{O_3} + 5\overset{0}{O_2}$

O_3 is getting reduced to O^{2-} state.

24. (*a*) $\overset{0}{C}_{12}H_{22}O_{11} \longrightarrow \overset{+4}{C}O_2$

Thus, sugar molecule is getting oxidised to CO_2.

25. (*b*) The equation is,

$2MnO_4^- + 5SO_3^{2-} + 6H^+ \longrightarrow 5SO_4^{2-} + 3H_2O + 2Mn^{2+}$.

26. (*b*) The balanced equation is,

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

27. (*b*) The balanced equation is :

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

Now, 5 moles of oxalic acid ($H_2C_2O_4 . 2H_2O$) require $KMnO_4 = 2$ mol

126 g *i.e.*, $\frac{126}{126}$ mol of oxalic acid require $MnO_4 = \frac{2}{5}$ = 0.4 mol.

28. (*a*) The balanced equation is :

$$3MnO_4^- + 5FeC_2O_4 + 24H^+ \longrightarrow 5Fe^{3+} + 3Mn^{2+} + 10CO_2 + 12H_2O$$

Now, 5 mol of ferrous oxalate require $KMnO_4 = 3$ mol

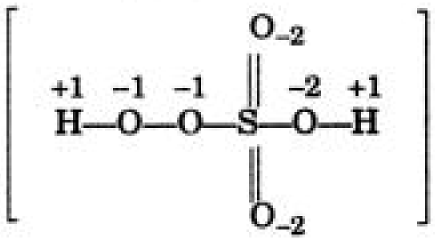
1 mol of ferrous oxalate require $KMnO_4 = 3/5$ mol = 0.6 mol.

29. (*c*) In each, the electronegative element is oxygen. In BaO_2 (barium peroxide) the O.N. of O is – 1 while in $BaSO_4$, it is – 2.

30. (*c*) The given reaction does not involve any change in oxidation number.

31. (*b*) $\overset{3+}{Fe}_4[\overset{2+}{Fe}(CN)_6]$.

32. (*d*) Two O atoms in H_2SO_5 are peroxide and have O.N. = – 1 while the other 3 oxygen atoms have O.N. = – 2. The structure of H_2SO_5 is



$$\left[\overset{+1}{H}-\overset{-1}{O}-\overset{-1}{O}-\underset{\underset{O_{-2}}{\|}}{\overset{\overset{O_{-2}}{\|}}{S}}-\overset{-2}{O}-\overset{+1}{H}\right]$$

Hence O.N. of S is + 6.

33. (*d*) On calculating E.F. from % age we get XeF_6

∴ Oxidation number of Xe = +6.

34. (*b*) $[Pt(C_2H_4)Cl_3]^-$; $x + 0 + 3(-1) = -1$ or $x = +2$.

35. (*a*) $CaOCl_2$ contains Ca^{2+}, OCl^- and Cl^-. Cl has O.N. = – 1 in Cl^- while its O.N. in OCl^- part is + 1.

36. (*a*)

$$\underset{1 \text{ mol}}{Ag^+ + e^-} \longrightarrow \underset{108 \text{ g}}{Ag}$$

54 g of Ag is deposited by electricity = $\frac{96500}{2}$ C

$$Al^{3+} + 3e^- \longrightarrow \underset{27 \text{ g}}{Al}$$

Now, 3 × 96500 C deposit Al = 27 g

$\frac{96500}{2}$ C deposit Al = $\frac{27 \times 96500}{2 \times 3 \times 96500}$ g = 4.5 g.

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

2.0 Faradays can deposit copper = 1 mol

2.5 Faradays can deposit copper = $\frac{2.5}{2}$ = 1.25 mol.

38. (*c*) $Al^{3+} + \underset{3 \text{ mol}}{3e^-} \longrightarrow \underset{27 \text{ g}}{Al}$

In order to deposit 27 g of Al, electricity required = 3 F

In order to deposit 9 g of Al, electricity required

$$= \frac{3F}{27} \times 9 = 1 \text{ F}.$$

39. (*b*) Choice itself is the answer.

40. (*b*) $K_2\overset{+6}{Cr}O_7 \xrightarrow{+\,6e} 2Cr^{3+}$

Reduction of 1 mol of $K_2Cr_2O_7$ needs charge = 6 × 96500 C

Reduction of 0.4 mol of $K_2Cr_2O_7$ needs charge

$$= 0.4 \times 6 \times 96500 \text{ C} = 2.4 \times 96500 \text{ C}.$$

41. (*a*) $\underset{1 \text{ mol}}{\overset{+1\;-2}{H_2O}} \longrightarrow \underset{22.4 \text{ L}}{\overset{0}{H_2}} + \underset{11.2 \text{ L}}{\frac{1}{2}\overset{0}{O_2}}$

Decomposition of 1 mol of water requires 2 mol of electron

∴ 4 mol of electrons produce 2 × 22.4 L = 48.8 L of H_2 and 2 × 11.2 L = 22.4 L of oxygen.

Total volume produced at STP = 44.8 + 22.4 = 67.2 L.

42. (*c*) According to Faraday's second law, comparing P, Q cells.

$$\frac{W_{Ag}}{W_{Hg}} = \frac{E_{Ag}}{E_{Hg}} \text{ or } \frac{0.216}{W_{Hg}} = \frac{108}{200.6/2}$$

$$\text{or} \quad W_{Hg} = \frac{0.216 \times 200.6}{108 \times 2} = 0.2006 \text{ g}$$

In P, R cells, $\frac{0.216}{W_{Hg}} = \frac{108}{200.6}$

$$\text{or} \quad W_{Hg} = \frac{0.216 \times 200.6}{108} = 0.4012 \text{ g}.$$

43. (*d*) The reactions in two cells are $Fe^{2+} + 2e^- \longrightarrow Fe$ and $Fe^{3+} + 3e^- \longrightarrow Fe$.

The ratio of iron produced should be $\frac{1}{2} : \frac{1}{3}$ or **3 : 2**.

44. (*b*) Charge in coulombs = 4 × 30 = 120 C.

45. (*d*) 1 mol of electrons = 96500 C or 96500 C = $1 \times 10^{-16} \times t$ or $t = 96500 \times 10^{16}$ s = 9.65×10^{20} s.

46. (*a*) $X^{2+} + 2e^- \longrightarrow X$; $Y^+ + e^- \longrightarrow Y$

2 mol e^- produce X = 1 mol = 1 × M g

2 mol e^- produce Y = 2 mol = 2 × M/2 = M g.

Hence, ratio of the masses of Y : X is M : M or **1 : 1**.

47. (*a*) $Au^{3+} + 3e^- \longrightarrow Au$

197 g of Au is obtained by charge = 3 × 96500 C

1.234 g of Au is obtained by charge $= \frac{3 \times 96500 \times 1.234}{197}$

Now, $3 \times t = \frac{3 \times 96500 \times 1.234}{197}$

or $\quad t = \frac{96500 \times 1.234}{197} = 604$ sec.

48. (*d*) Cell constant is not given.

49. (*d*) Resistance $\propto \frac{1}{\text{conductivity}}$.

50. (*c*) The statement refers to Faraday's second law of electrolysis.

52. (*d*) $\text{J/amp}^2\text{-sec} = \frac{\text{J}}{\text{amp.sec}} \times \frac{1}{\text{amp}} = \frac{\text{J}}{\text{C}} \times \frac{1}{\text{amp}} = \frac{\text{volt}}{\text{amp}} = \textbf{ohm.}$

53. (*c*) Reduction Means gaining of electrons.

54. (*c*) Cathodic reaction involves reduction.

55. (*a*) X has least reduction potential and hence maximum tendency to oxidise.

56. (*b*) Reaction in hydrogen electrode is

$$2H^+ + 2e^- \longrightarrow H_2$$

$$E = E^\circ + \frac{0.059}{2} \log \frac{[H^+]^2}{[H_2]}$$

E can be greater than E° if conc. of H^+ ions is increased.

57. (*d*) Large negative reduction potential means large positive oxidation potential for $X^- \longrightarrow X + e^-$. Hence X^- can be readily oxidised.

58. (*a*) E is related to temperature as

$$E = E^\circ + \frac{RT}{2F} \ln \frac{[Mg^{2+}]}{[Mg]}.$$

59. (*c*) H^+ conc. should be 1 M. ∴ pH should be zero.

60. (*d*) The reaction $I_2 + 2Br^- \longrightarrow 2I^- + Br_2$ is non-spontaneous because reduction potential of Br_2/Br^- is larger than that of I_2/I^-.

61. (*d*) $E^\circ_{cell} = E^\circ_{red}$ (cathode) + $E^\circ_{oxi.}$ (anode)

$= -0.41 + 0.76 = \mathbf{0.35\ V.}$

62. (*a*) $\text{EMF} = \text{EMF}^\circ + \frac{0.059}{6} \log \frac{[Au^{3+}]^2}{[Ni^{2+}]^3}$

$= \text{EMF}^\circ + \frac{0.059}{6} \log \frac{(0.1)^2}{(0.01)^3} = \text{EMF}^\circ + \frac{0.059}{6} \log 10^4$

$= \text{EMF}^\circ + \frac{0.059}{6} \times 4$. Hence EMF > EMF°.

63. (*d*) Mg^{2+}/Mg couple has reduction potential less than Hydrogen- electrode. Hence Mg can reduce H^+ ions to H_2.

64. (*a*) The highest cell voltage would be obtained from the electrode with highest oxidation potential and highest reduction potential because $E_{cell} = E_{oxi.} + E_{red.}$

65. (*d*) $E^\circ_{red.}$ of *x*, *y*, *w* are less than *y*. Hence all of them can reduce y^{2+} ions.

66. (*a*) Choice itself is the answer.

67. (*d*) $AgNO_3 + H_2O \longrightarrow Ag + H^+ + NO_3^- + \frac{1}{2} O_2$

∴ **pH gradually decreases due to increase in H^+ conc.**

$$LiCl + H_2O \xrightarrow{\text{Electricity}} Li^+ + OH^- + \frac{1}{2} Cl_2 + \frac{1}{2} H_2$$

∴ **pH gradually increases due to increase in OH^- ion conc.**

68. (*a*) Apply Nernst equation, to the reaction

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

or $\quad E^\circ + \frac{0.059}{2} \log \frac{[Sn^{2+}]}{[Pb^{2+}]}$ or $\log \frac{[Sn^{2+}]}{[Pb^{2+}]} = \frac{0.01 \times 2}{0.059} = 0.3$

or $\quad \frac{[Sn^{2+}]}{[Pb^{2+}]} = \text{antilog}\ (0.3).$

69. (*c*) $Cu^{2+} + 2e^- \longrightarrow Cu$; $E^\circ = 0.34$ V

$$E = 0.34 + \frac{0.059}{2} \log [Cu^{2+}]$$

or $\quad E = 0.34 - (0.0296)(9) = 0.34 - 0.266 = 0.07$ V.

70. (*a*) $\quad Cu^{2+} + e \longrightarrow Cu^+$; $E_1^\circ = 0.15$ V

∴ $\Delta G^\circ_1 = -1 \times 0.15 \times F = -0.15$ F

$Cu^+ + e^- \longrightarrow Cu$; $E^\circ_2 = 0.5$ V

∴ $\Delta G^\circ_2 = -1 \times 0.50 \times F = -0.5$ F

$Cu^{2+} + 2e^- \longrightarrow Cu$; $E^\circ_3 = ?$

∴ $\Delta G^\circ_3 = -2 \times E^\circ_3 \times F = -2E^\circ_3$ F

Also, $\Delta G^\circ_3 = \Delta G^\circ_1 + \Delta G^\circ_2 = -0.15\ F - 0.5\ F = -0.65$ F

Now $-2E^\circ_3 F = -0.65$ F or $E^\circ_3 = \frac{0.65}{2} = 0.325$ V.

71. (*c*) $pH_1 = 3$ ∴ $[H^+]_1 = 1 \times 10^{-3}$ M ;

$pH_2 = 5$ ∴ $[H^+]_2 = 1 \times 10^{-5}$

Now, $E_{cell} = \frac{0.059}{1} \log \frac{[1 \times 10^{-3}]}{[1 \times 10^{-5}]} = 0.059 \times 2 = 0.118$ V.

72 (*c*) $E_1 = 0.059 \log [H^+]$ or $\frac{-E_1}{0.059} = pH_1$.

Similarly, $\frac{-E_2}{0.059} = pH_2$

Also, $pH_1 = pK_a + \log \frac{x}{y}$ and $pH_2 = pK_a + \log \frac{y}{x}$

$$pH_2 - pH_1 = \log \frac{y}{x} - \log \frac{x}{y} = \log \frac{y}{x} + \log \frac{y}{x} = 2 \log \frac{y}{x}$$

or $$\frac{-E_2}{0.059} - \left(\frac{-E_1}{0.059} \right) = 2 \log \frac{y}{x} \quad \text{or} \quad \log \frac{y}{x} = \frac{E_1 - E_2}{0.118}$$

Now, $$-\frac{E_2}{0.059} = pK_a + \log \frac{y}{x} \quad \text{or} \quad pK_a = \frac{-E_2}{0.059} - \log \frac{y}{x}$$

$$= \frac{-E_2}{0.059} - \frac{E_1 - E_2}{0.118} = -\left[\frac{E_2 + E_1}{0.118} \right].$$

73. (*c*) $E°_{red}$ of copper = 1.1 – 0.76 = 0.34 V.

∴ $E°_{oxi.} = -0.34$ V.

74. (*a*) Flow of electrons stops when E° values of two electrodes become same and potential difference become zero.

75. (*b*) Molarity of SO_4^{2-} ions remains the same as they do not participate in reaction ($Zn + Cu^{2+} \longrightarrow Cu + Zn^{2+}$).

76. (*a*) $E_{cell} = 0.34 + 2.37 = 2.71$ V.

77. (*a*) From equation (*i*), $E_{Y_2/Y^-} > E_{X_2/X^-}$;

From (*ii*), $E_{W_2/W^-} > E_{Y_2/Y^-}$

From eqn. (*iii*), $E_{X_2/X^-} > E_{Z_2/Z^-}$. This accounts for the sequence (*a*).

78. (*b*) $\Delta G° = -nFE° = -1 \times 96500 \times 1.02 = -98430$ J

or – 98.43 kJ.

79-80. See summary of the chapter.

81. (*a*) Ionic molality

$$= \frac{\lambda_0^\infty}{F} = \frac{61.92 \times 10^{-4}\ Sm^2\ mol^{-1}}{96500\ C\ mol^{-1}} = 6.4 \times 10^{-8}.$$

82. (*d*) Factual (Answer is given in the choice indicated).

83. (*d*) Choice itself is the answer.

84. (*c*) $CuBr_2 \longrightarrow Cu^{2+} + 2Br^-$

Anode : $2Br^- \longrightarrow Br_2 + 2e^-$

Cathode : $Cu^{2+} + 2e^- \longrightarrow Cu$.

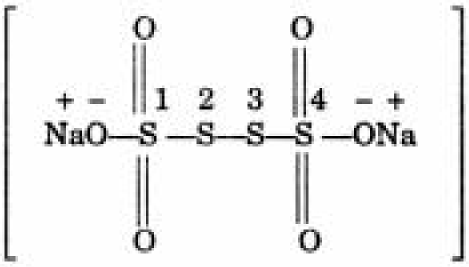
85. (*a*) $E°_{cell}$ should be + ve or ΔG should be < 0.

QUESTION BANK (Level II)

1. (*a*) Dilution increases the distance between ions.

2. (*c*) $Ag^+ + e^- \longrightarrow Ag$. ∴ The electricity required = 1 Faraday.

3. (*d*) The structure of $Na_2S_4O_6$ is :



It is evident, that O.N. of two S atoms, *i.e.*, S_2 and S_3 is 0. The O.N. of two S atoms, *i.e.*, S_1 and S_4 is + 5 each.

4. (*b*) $[Fe(H_2O)_5NO]\ SO_4$

$x + 5(0) + 0 - 2 = 0$ or $x = +2$

5. (*c*) When weak acid is titrated against strong alkali, initially the conductance is low due to poor dissociation of acetic acid. On adding NaOH, highly ionised CH_3COONa is formed and conductance increases.

After neutralisation, addition of NaOH causes sharp increase in conductance.

6. (*b*) $Al^{+3} + 3e^- \longrightarrow Al$.

For depositing 27 g of Al, electricity required = 3F

For depositing 13.5 g of Al, electricity required = 1.5 F.

7. (*a*) Conductivity (κ) = $\frac{1}{R} \times$ cell constant

$$= \frac{1}{250} \times 1.15$$

$$\Lambda_{eq.} = \frac{1.15 \times 1000}{250 \times 0.1} = 4.6\ ohm^{-1}\ cm^2\ eq^{-1}.$$

8. (*c*) $\frac{W_{Cu}}{W_{H_2}} = \frac{E_{Cu}}{E_H}$ or $W_{Cu} = \frac{W_{H_2} \times 31.75}{1}$

$$= \frac{224 \times 2 \times 31.75}{22.4 \times 1} = 6.35\ g.$$

9. (*a*) Lower the reduction potential, more easily, the metal is oxidised and more is its reactivity.

10. (*a*) 63.5 g of copper is deposited by electricity

= 2 × 96500 C

2 g of copper will be deposited by electricity

$$= \frac{2 \times 96500 \times 2}{63.5} = 6078.4\ C$$

Now, time $= \frac{Q}{I} = \frac{6078.4}{0.5} = 12157.48$ sec.

11. (*c*) 1 Faraday deposits one equilvalent

$\therefore$ 2.5 Faradays deposit 2.5 equivalent.

12. (*d*) 2 Equivalent of Ag will deposit for every 1 eq. of O_2 liberated

$\therefore$ Mass of Ag deposited $= \frac{1.6}{16} \times 2 \times 208 = 21.6$ g.

13. (*b*) $\Lambda_{eq}^{\infty} = \Lambda_{C_2H_5COONa}^{\infty} + \Lambda_{HCl}^{\infty} - \Lambda_{Na}^{\infty}$

$= 91 + 426.16 - 126.45$

$= 390.71 \text{ ohm cm}^2 \text{ eq}^{-1}$.

14. (*a*) 1.12 L at N.T.P. $= \frac{1.12}{22.4}$ mol $= 0.05$ mol

1 mol of H_2 is obtained by passing electricity

$= 2 \times 96500$ C

0.05 mol of H_2 is obtained by electricity

$= 2 \times 96500 \times 0.05$

Now if I is current strength,

$I \times 965 = 2 \times 96500 \times 0.05$ or $I = 10$ amp.

15. (*c*) Total $Ag^+ = 200 \times 0.1 \times 10^{-3}$ mol $= 0.02$ mol

$\frac{1}{2}$ of total Ag^+ ions $= \frac{1}{2} \times 0.02 = 0.01$ mol

1 mol of deposition require electricity = 96500 C

0.01 mol of deposition requires electricity = 965 C

Now if *t* sec is the time

$\therefore\ 965 = 0.1 \times t$ or $t = \frac{965}{0.1}$ sec $= \frac{965}{0.1} \times \frac{1}{60}$ min

$= 160.8$ min.

16. (*a*) O_2 is liberated by anodic oxidation of water

$$2H_2O \longrightarrow 4H^+ + O_2 + 4e^-$$

Liberation of 1 mol (22.4 L) require electricity

$= 4 \times 96500$ C

$\therefore$ 193 C of electricity will librate O_2

$= \frac{22.4}{4 \times 96500} \times 193$ L

$= 0.01119$ L or $= 11.2 \text{ cm}^3$.

17. (*d*) Anodic reaction involves $Cu \longrightarrow Cu^{2+} + 2e^-$

Cathodic reaction involves $Cu^{2+} + 2e^- \longrightarrow Cu$

Thus, amount of copper dissolved and that deposited would be same *i.e.*,

$3.2 \text{ g} = \frac{3.2}{63.5}$ mol $= 0.05$ mol.

18. (*c*) Copper cannot displance Al^{+3} ions from the solution.

19. (*a*) In conversion of $C_6H_5NO_2 \longrightarrow C_6H_5NH_2$, no. of electrons per mole of substance involved = 6 mol.

$\therefore$ 0.2 mol will require $= 0.2 \times 6 = 1.2$ mol

20. (*a*) In conversion of NH_3 to NO, number of electrons involved = 5 mol per mol of NH_3. Thus, for 0.5 mole of NH_3, the molecules of oxidant required $= 1.25\ N_A$.

21. (*b*) Let copper produced = *x* g.

According to Faraday's second law

$$\frac{x}{0.504} = \frac{31.75}{1}$$

or $x = 0.504 \times 31.75 = 16.002$ g.

22. (*b*) Cd required for 3 g of Hg $= \frac{10 \times 3}{90} = 0.33$ g

$$Cd^{2+} + 2e^- \longrightarrow Cd$$

Electricity required for depositing 0.33 g of cadmium

$= \frac{2 \times 96500 \times 0.33}{112} = 568.6$ C.

23. (*a*) The anodic reaction in H_2—O_2 fuel cell is

$$H_2 + 2OH^- \longrightarrow 2H_2O + 2e^-$$

Burning of 1 mole of H_2 produces electricity

$= 2 \times 96500$ C

Burning of 0.3 mol $\left(\frac{6.72}{22.4}\right)$ of H_2 gives electricity

$= 0.3 \times 2 \times 96500$ C

Current in amperes $= \frac{0.3 \times 2 \times 96500}{15 \times 60}$

$= 64.3$ amp.

24. (*b*) The libration of each H^+ ion can result in 1 NaOH being formed.

$\therefore$ Moles of electrons $= \frac{9.65 \times 1000}{96500} = 0.1$

Moles of H^+ liberated = 0.1

$\therefore$ Moles of NaOH formed = 0.1

Mass of NaOH formed $= 0.1 \times 40 = 4.0$ g.

25. (*a*) 1 gm-ion of N^{3-} have $3 \times 6.02 \times 10^{23}$ electronic charges amounting to

$3 \times 6.02 \times 10^{23} \times 1.6 \times 10^{-19}\ C = 2.88 \times 10^6$ C.

26. (*d*) Q = 0.025 (amp) × 60 (s) = 1.5 C

2×96500 C deposit Ca atoms $= 6.02 \times 10^{23}$

1.5 C deposit Ca atoms $= \frac{6.02 \times 10^{23} \times 1.5}{2 \times 96500}$

$= 4.68 \times 10^{18}$.

27. (*a*) 0.5 F of electricity will deposit Cu $= \frac{0.5}{2}$ mol = 0.25 mol

Molarity of solution $= \frac{0.25 \times 1000}{500} = 0.5$ M.

28. (*c*) Oxidation state $= \frac{119 \times 5 \times 60 \times 60 \times 2}{96500 \times 22.2} = +2.0$.

29. (*c*) Total Ag^+ ions $= 0.2 \times 0.1 = 0.02$ mol

One fourth of $Ag^+ = \frac{0.02}{4} = 5 \times 10^{-3}$ mol

Quantity of electricity required for deposition of

5×10^{-3} mol of $Ag^+ = 96500 \times 5 \times 10^{-3}$ C

Now, $96500 \times 5 \times 10^{3} = 0.1 \times t$ or $t = 4825$ sec or 80.4 min.

30. (*a*) Moles of Cu deposited $= \frac{3.25}{63} = 0.05$

31. (*d*) $KBrO_4$; $x + (+1) + 4(-2) = 0$ or $x = +7$.

32. (*b*) $\overset{+1}{K}\ \overset{-1}{I} + \overset{0}{I_2} \rightleftharpoons \overset{+1}{K}\ \overset{-1/3}{I_3}$. Hence, I_2 is oxidising agent.

33. (*b*) $\overset{-3}{(NH_4)_2}\ \overset{+6}{Cr_2O_7} \longrightarrow \overset{0}{N_2} + 4H_2O + \overset{+1}{Cr_2O_3}$

Each N atom loses 3 **electrons.**

34. (*a*) $(\overset{+2}{SnCl_2} + \overset{+2}{2HgCl_2} \longrightarrow \overset{+4}{SnCl_4} + \overset{+3}{Hg_2Cl_2}$

Thus, $HgCl_2$ is reduced to Hg_2Cl_2.

35. (*d*) $\overset{+2}{(C_2O_4)^{2-}} \longrightarrow \overset{+4}{2CO_2} + 4e^-$.

36. (*d*) $\overset{+5}{(NO_3)^-} + 6H_2O + 8e^- \longrightarrow \overset{-3}{NH_3} + 9OH^-$.

37. (*a*) $5\overset{-1}{H_2O_2} + 2\overset{+4}{ClO_2} + 2\overset{-}{OH} \longrightarrow 2\overset{-}{Cl} + 5\overset{0}{O_2} + 6H_2O$.

In ClO_2, chlorine atom decreases its oxidation number from + 4 to – 1. Hence ClO_2 is reduced and H_2O_2 is oxidised.

38. (*b*) O.N. of N in N_2H_4 is – 2. Since 1 mol of N_2H_4 contains 2 mol of N atom, therefore each mole of N atom lose 5 mol of electrons. Hence O.N. of N in the new compound will be + 5.

39. (*b*) No. of coulombs passed $= 2 \times 5 \times 60 \times 60$ C

If the oxidation state is n +, then deposition of 177 g of metal, the electricity required is

$$= n \times 96500 \text{ C}$$

∴ The electricity required for 22.2 g of metal

$$= \frac{n \times 96500 \times 22.2}{177}$$

Now $\frac{n \times 96500 \times 22.2}{177} = 2 \times 5 \times 60 \times 60$ or $n = 2.94 = +3$.

40. (*d*) $\Lambda_{eq} = \frac{K \times 1000}{N}$

or $N = \frac{K \times 1000}{\Lambda_{eq}} = \frac{3.06 \times 10^{-6} \times 10^{3}}{1.53}$

$$= 2 \times 10^{-3} \text{ N.}$$

∴ Molarity of XY $= 2 \times 10^{-3} \times \frac{1}{2} = 1 \times 10^{-3}$

$$K_{sp} = [X^{2+}]\,[Y^{2-}] = (1 \times 10^{-3})\,(1 \times 10^{-3}) = 1 \times 10^{-6}.$$

41. (*a*) Λ_m at 0.25 M concentration $= \frac{0.0125 \times 10^3}{0.25} = 50$

$$\alpha = \frac{50}{500} = 0.1$$

$K_{(dil.)} = C\alpha^2 = 0.25 \times (0.1)^2 = 2.5 \times 10^{-3}$.

42. (*b*) Λ_{eq} and Λ_m are equal for uni-univalent electrolytes.

Na^+ makes same contribution irrespective of anion to which it is attached.

43. (*b*) $\Lambda_m = \frac{\kappa \times 10^3}{M} = \frac{1}{R} \times \text{Cell constant} \times 10^3 \times \frac{1}{M}$

$$= \frac{k_{cell} \times 10^3}{RM}.$$

44. (*a*) First statement goes against Kohlrausch's law.

N$\overset{+}{a}$ makes same contribution irrespective of anion to which to is attached.

45. (*c*)

$$\begin{array}{ccccc} Cu^{+2} & + & Zn & \xrightarrow{2e^-} & Cu + Zn^{2+} \\ (0.1 \text{ mol}) & & 100/65 & & \\ & & = (1.54) & & \end{array}$$

Thus, Cu^{2+} ions are limiting reagent

Now 0.1 mole of Cu^{+2} transfers electrons = 0.2 mol

or Amount of electricity $= 0.2 \times 96500$ C.

Now $0.2 \times 96500 = 2 \times t$ or $t = 9650$ C = **2.68 hr.**

46. (*b*) $I_2 + SO_2 + 2H_2O \longrightarrow SO_4^{2-} + 2I^- + 4H^+$

47. (*b*) Oxidation reaction occurs at anode.

48. (*c*) See solution to Q. 70 in Question bank level I.

49. (*b*) Apply, $E^\circ_{cell} = \frac{0.059}{n} \log K$.

50. (*a*) Lesser is the value of red. potential more is the reducing character.

51. (*b*) It is based on Nernst equation.

52. (c) Nernst equation should be $E = E^\circ + \frac{RT}{nF} \ln aM^{n+}$.

53. (*a*) Choice itself is an answer.

54. (*c*) See summary of the chapter.

55. (*c*) $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$$= 1.50\text{V} - (-0.25 \text{ V}) = +1.75 \text{ V}.$$

56. (*c*) For the reaction, $2H^+ + 2e^- \longrightarrow H_2$

$$E = E^\circ + \frac{0.059}{n} \log (H^+)^2$$

$$= 0 + \frac{0.059}{2} \log (10^{-10})^2 = -0.59 \text{ V}.$$

57. (*b*) Choice is the answer itself. Reactivity depends on the tendency to displace the other.

58. (*c*) Since reduction potential of Ag^+/Ag is greater than Sn. Hence silver electrode must act as cathode.

59. (*b*) E° value will not depend upon the size of the strip as concentration of solids is taken to be unity.

60. (*c*) The best reducing agent is one whose E°_{red} is lowest. Thus Mg is the correct choice.

61. (*b*) If solution is diluted to 10 times, molar conc. of Cu^{2+} is reduced to one tenth of its original value.

Nernst equation for $Cu^{2+} + 2e^- \longrightarrow Cu$ is

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

by decreasing the conc. of Cu^{2+} by 1/10, E value will decrease by $\frac{0.059}{2}$ *i.e.*, approx. by 0.03 V.

62. (*b*) B and C combination will give cell voltage = 2.50 V which is maximum out of the given sets.

63. (*c*) For concentrations cells $E^\circ_{cell} = 0$.

64. (*d*) Zinc will undergo oxidation in preference to iron.

65. (*a*) CH_3COOH is a weak acid. Addition of NaOH to

CH_3COOH causes formation of CH_3COONa which is strong electrolyte. Hence conductivity will increase.

66. (*a*) Larger the value of E°_{red} larger is tendency for reduction and consequently stronger will be the oxidant. Similarly, smaller the value of E°_{red} larger the tendency for oxidation and consequently stronger will be the reductant.

67. (*c*) In the given reaction X is getting oxidised to X^{n+}. Hence for this reaction to occur, the oxidation potential of X should be greater than hydrogen electrode (*i.e.*, 0).

68. (*a*) Add the two values of electrode potential to get the desired value.

69. (*a*) Electrical work = nFE°

For Daniel cell $n = 2$

$\therefore$ Work = $2 \times 95600 \times 1.10$

$= 212.3 \times 10^3$ J = 212.3 kJ.

70. (*a*) In XYZ_2 the sum of O.N. of all the atoms is zero.

71. (*a*) $E_{cal.} - E_{H_2} = 0.67$ or $E_{H_2} = -0.67 + 0.28 = -0.39$ V

Now $-0.39 = 0 + \frac{0.059}{1} \log H^+$

or $-\log H^+ = \frac{0.39}{0.059} = 6.6.$

72. (*b*) $MnO_4^{2-} \xrightarrow{-e^-} MnO_4^-$

It is an oxidation process and occurs at anode.

The O.N. of Mn increases from + 6 to + 7.

73. (*b*) Factual based on relationship.

74. (*d*) Choice itself is an answer.

75. (*b*) ΔG° of required reaction $= 2 \times (-21.52) = -43.04$ kJ.

8 RATES OF CHEMICAL REACTIONS AND CHEMICAL KINETICS

Important Terms, Facts and Formulae

RATE OF A REACTION

- **Chemical Kinetics** is the branch of chemistry that deals with study of reaction rates and their mechanisms.
- **Rate of a reaction** is expressed in terms of rate of decrease of conc. of one of the reactants or rate of increase of conc. of one of the products. For example, for the reaction

$$CO_2 + NO \longrightarrow CO + NO_2$$

$$\text{Rate} = -\frac{d[CO_2]}{dt} = -\frac{d[NO]}{dt} = +\frac{d[CO]}{dt} = +\frac{d[NO_2]}{dt}$$

For the reaction, $N_2 + 3H_2 \rightarrow 2NH_3$

$$\text{Rate} = -\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = +\frac{1}{2}\frac{d[NH_3]}{dt}.$$

- **Units of rate of reaction** are mol $L^{-1}\,s^{-1}$ or mol $L^{-1}\,min^{-1}$. In case of gaseous reactions rate may have units of atm. s^{-1} or atm min^{-1}.
- **Law of Mass Action.** This law was proposed by Guldberg and Waage.

For a general hypothetical reaction,

$$aA + bB \longrightarrow cC$$

according to law of mass action,

$$\text{rate} = k\,[A]^a\,[B]^b.$$

RATE EQUATION AND ORDER OF THE REACTION

1. **Rate equation.** It is the expression which represents the dependence of rate of the reaction on concentrations of the reactants as experimentally determined. For example, for the reaction

$$aA + bB \longrightarrow cC + dD$$

the rate of equation may be written as

$$\text{rate} = k[A]^m\,[B]^n$$

Here m and n are experimentally determined powers and k is the rate constant.

2. **Rate constant.** It is defined as the rate of the reaction when concentrations of all the reactants are unity *i.e.*, 1 mole/litre.
3. **Order of the reaction.** The sum of the powers to which various concentration terms are raised in the rate law expression is called order of the reaction.
   - It is an experimentally determined parameter
   - It can be zero or fractional
   - Common values of order are 1, 2 and 3.

RATE CONSTANT

- The value of rate constant depends on the chemical nature of the reactants.
- The value of rate constant changes with temperature.
- The value of rate constant changes in the presence of catalyst.
- k has different units for reactions of different orders. The dimensions of k for various reactions are given below :

For first order : s^{-1}

For second order : $L\,mol^{-1}\,s^{-1}$

For third order : $L^2\,mol^{-2}\,s^{-1}$

For zero order : $mol\,L^{-1}\,s^{-1}$

In general : $(mol\,L^{-1})^{1-n}\,s^{-1}$

where n is the order of the reaction.

- **Temperature coefficient.** The ratio of rate constants of a reaction at two temperatures differing by 10° is called temperature coefficient.

$$\text{Temperature coefficient} = \frac{k_{T+10}}{k_T} = 2 \text{ or } 3.$$

- A higher value of k indicates that the reactions occurs at higher rate.

FIRST ORDER REACTIONS

- Rate equation for first order reaction is rate = k[A]

or $$\boxed{k = \frac{2.303}{t}\log\frac{[A]_0}{[A]}}$$

or $$k = \frac{2.303}{t}\log\frac{a}{(a-x)}$$

Here $[A]_0 = a$ = Initial concentration of reactants

$[A] = (a - x)$ = Concentration of reactants at time t

x = concentration reactants decreased in time t.

- A graph of log [A] versus t is a straight line with slope $= -\dfrac{k}{2.303}$.
- Half-life, $t_{1/2} = \dfrac{0.693}{k}$

  Half-life period of a first order reaction is independent of initial concentration of reactants.
- $t_{3/4} = 2\,t_{1/2}$

  $t_{7/8} = 3\,t_{1/2}$

  $t_{15/16} = 4\,t_{1/2}$.
- Concentration after n half-lives, $[A] = \left(\dfrac{1}{2}\right)^n [A]_0$.

ZERO ORDER REACTIONS

- Rate equation for zero order reaction is

  $$\text{rate} = k[A]^0 = k$$

  or $[A_0] - [A] = kt$.
- A zero order reaction proceeds at a constant rate, which is equal to rate constant of the reaction.
- A graph of rate *vs* time for a zero order reaction is a straight line with zero slope.
- A graph of [A] versus t is a straight line with slope equal to $-k$.
- Half-life period of a zero order reaction is directly proportional to the initial conc. of the reactants.
- **Units of k** for zero order reaction are same as that of rate of reaction, *i.e.*, $\mathbf{mol\,L^{-1}\,s^{-1}}$.
- Some examples of zero order reactions are :

  (*i*) $H_2 + Cl_2 \xrightarrow{\text{UV light}} 2HCl$

  (*ii*) $2NH_3 \xrightarrow[\text{or Molybdenum}]{\text{Tungsten}} N_2 + 3H_2$

  (*iii*) $2HI \xrightarrow[\Delta]{\text{Gold}} H_2 + I_2$

MOLECULARITY

(*i*) The number of reacting species involved simultaneously in collision resulting in the formation of products is called **molecularity.**

(*ii*) Molecularity can have value 1, 2 or 3. Molecularity can never be zero, fractional or more than three.

(*iii*) Molecularity of a reaction cannot be greater than 3 because simultaneous collision between more than three particles is rare on the basis of probability considerations.

(*iv*) Molecularity of a simple reaction can be obtained from the balanced chemical equation. It is equal to the sum of the particles on the reactant side.

COLLISION THEORY

- For a reaction to take place, the reactant molecules must collide with one another.
- For the collision to be effective, the colliding molecules must possess certain minimum amount of energy, called **threshold energy** and should have **proper orientation.**
- Rate $= f \times p \times Z$

  f = fraction of collisions having energy equal to or greater than threshold energy

  p = fraction of collisions with proper orientation

  Z = collision frequency.

ACTIVATION ENERGY (E_{act})

- ***The minimum extra energy over and above the average potential energy of the reactants which must be supplied to the reactants to enable them to cross over the energy barrier between reactants and products is called activation energy.***
- The reactions with smaller activation energy are fast whereas reactions with high activation energy are slow.
- Activation energy depends on the chemical nature of reactants.
- Activation energy = Threshold energy – Average energy of reactants.
- Activation energy does not change with temperature.
- Activation energy is always positive.
- For endothermic reactions the minimum value of E_{act} is equal to ΔE of the reaction and for exothermic reaction the minimum value of $E_{act} = 0$.
- The state of the reactants corresponding to energy maxima (threshold energy) is called **transition state** or **activated complex.**

EFFECT OF TEMPERATURE

(*i*) Rate of a reaction increases with increase in temperature. In case of most of the reactions the rate of reaction doubles for every 10° rise in temperature.

(*ii*) Increase in rate of reaction with increase in temperature is mainly due to increase in the fraction of molecules having energy equal to or greater than threshold energy.

(*iii*) Temperature coefficient $= \dfrac{k_{T+10}}{k_T} \approx 2$ or 3.

(*iv*) The value of temperature coefficient is more at lower temperatures.

(*v*) The value of temperature coefficient is more for the reactions having higher activation energy.

ARRHENIUS RATE EQUATION

- **Arrhenius rate equation,**

$$k = Ae^{-Ea/RT}$$

or
$$\ln k = \ln A - \frac{E_a}{RT}$$

or
$$\log k = \log A - \frac{E_a}{2.303RT}.$$

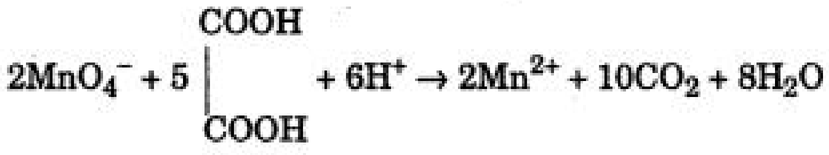
- A plot of log k *versus* $\frac{1}{T}$ is a straight line with slope equal to $\frac{-E_a}{2.303R}$.
- A plot of ln k *versus* $\frac{1}{T}$ is a straight line with slope equal to $-\frac{Ea}{R}$.
- Activation energy (E_a) of a reaction can be calculated from the knowledge of rate constants of the reaction at two different temperatures T_1 and T_2.

$$\boxed{\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]}$$

- Units of A (known as frequency factor) in the Arrhenius equation are same as the units of k for the reaction. Units of A depend on the order of the reaction.

EFFECT OF CATALYST

1. ***Presence of catalyst does not change the position of equilibrium.***
2. ***Catalysts are highly specific in nature.***
3. ***Catalyst do not change ΔH or ΔE*** because they do not disturb the energy levels of reactants and products.
4. **Negative Catalysis.** A substance that can slow down or retard a reaction is called a **negative catalyst.**
5. **Autocatalysis or Self-catalysis.** In this type of catalysis, one of the products acts as a catalyst for the reaction. For example, in the reaction of acidified potassium permanganate with oxalic acid, the product Mn^{2+} catalyses the reaction.



$$2MnO_4^- + 5\begin{array}{l}COOH\\ |\\ COOH\end{array} + 6H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

QUESTION BANK

Level I

Choose the correct answer from the four alternatives given in each of the following questions :

1. The rate of reaction, $2N_2O_5 \longrightarrow 4NO_2 + O_2$, can be expressed in terms of NO_2 as

(*a*) $+\frac{\Delta[NO_2]}{\Delta t}$
(*b*) $-\frac{\Delta[NO_2]}{\Delta t}$
(*c*) $\frac{1}{4}\frac{\Delta[NO_2]}{\Delta t}$
(*d*) $-\frac{1}{4}\frac{\Delta[NO_2]}{\Delta t}$.

2. Which of the following is true for the reaction

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

(*a*) $\frac{d[N_2]}{dt} = 3\frac{d[H_2]}{dt}$
(*b*) $-\frac{d[N_2]}{dt} = +\frac{1}{3}\frac{d[H_2]}{dt}$
(*c*) $-\frac{2}{3}\frac{d[H_2]}{dt} = +\frac{d[NH_3]}{dt}$
(*d*) $-3\frac{d[H_2]}{dt} = 2\frac{d[NH_3]}{dt}$.

3. The units of rate of reaction are

(*a*) mol L^{-1}
(*b*) L mol^{-1} s^{-1}
(*c*) mol L s^{-1}
(*d*) mol L^{-1} s^{-1}.

4. For the reaction, A + B ⟶ C + D, the rate of the reaction may be expressed as $r = -\frac{d[A]}{dt}$. The negative sign in the above expression indicates that

(*a*) rate of the reaction is negative
(*b*) conc. of A is decreasing with time
(*c*) conc. of A is increasing with time
(*d*) none of these.

5. Which of the following reactions is the fastest ?

(*a*) Rusting of iron
(*b*) Burning of sulphur
(*c*) Transition of monoclinic sulphur to rhombic sulphur
(*d*) Precipitation of barium sulphate by mixing solutions of sodium sulphate and barium chloride.

6. The minimum amount of energy that the reacting molecules must possess at the time of collisions in order to produce effective collision is called

(*a*) Activation energy
(*b*) Threshold energy
(*c*) Internal energy
(*d*) Free energy.

7. A reaction has rate law expression as

$$\text{rate} = k\,[A]^{3/2}\,[B]^{-1/2}$$

The order of the reaction is

(*a*) 1
(*b*) 2
(*c*) 3/2
(*d*) – 1/2.

8. For a chemical reaction A ⟶ B, it is found that the rate of reaction doubles when the concentration of A is increased four times. The order of the reaction is

(*a*) 4
(*b*) 2
(*c*) 1
(*d*) 1/2.

9. The unit of rate constant for a third order reaction is

(*a*) mol L^{-1} s^{-1}
(*b*) L mol^{-1} s^{-1}
(*c*) mol^2 L^{-2} s^{-1}
(*d*) L^2 mol^{-2} s^{-1}.

10. The dimensions of rate constant for a first order reaction involve

(*a*) Time and concentration
(*b*) Time only
(*c*) Concentration only
(*d*) Neither time nor concentration.

11. Which of the following simple reactions is a trimolecular reaction ?

(*a*) $N_2 + O_2 \longrightarrow 2NO$
(*b*) $H_2 + I_2 \longrightarrow 2HI$
(*c*) $2NO + O_2 \longrightarrow 2NO_2$
(*d*) $NH_4NO_2 \longrightarrow N_2 + 2H_2O$.

12. For a hypothetical reaction, 2A + B ⟶ Products, the rate constant, *k* is equal to 5.6×10^{-6} L mol^{-1} s^{-1}. The order of the reaction is

(*a*) One
(*b*) Two
(*c*) Three
(*d*) Fractional.

13. One litre of 2M acetic acid is mixed with one litre of 3M ethyl alcohol to form ester.

$$CH_3COOH + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + H_2O$$

The decrease in the initial rate if each solution is diluted by an equal volume of water would be

(*a*) 4 times
(*b*) 2 times
(*c*) 0.5 times
(*d*) 0.25 times.

14. The rate constant of a reaction depends on

(*a*) conc. of reactants
(*b*) conc. of products
(*c*) time
(*d*) temperature.

15. An exothermic reaction, X ⟶ Y, has an activation energy 30 kJ mol^{-1}. If energy change (ΔE) during the

$$O_3 \rightleftharpoons O_2 + O \qquad ...fast$$
$$O_3 + O \longrightarrow 2O_2 \qquad ...slow$$

The rate law expression for the reaction would be

(*a*) $r = k[O_3]^2 [O_2]^{-1}$
(*b*) $r = k[O_3]^2 [O_2]$
(*c*) $r = k[O_3] [O_2]$
(*d*) $r = k[O_3]^2$.

31. For the reaction, $2A + B \longrightarrow C + D$, the rate of reaction increases eight times when concentrations of both A and B are doubled. The rate of reaction increases four times when inital concentration of only B is doubled. The rate expression for the reaction is

(*a*) $r = k[A]^2 [B]$
(*b*) $r = k[A] [B]^2$
(*c*) $r = k[A] [B]$
(*d*) $r = k[A]^2 [B]^2$.

32. Consider a gaseous reaction having rate expression as rate = $k[A] [B]^2$. If volume of the vessel is suddenly reduced to half the initial volume, the rate of the reaction would become ...... times the original rate.

(*a*) 3
(*b*) 2
(*c*) 1/2
(*d*) 8.

33. For an elementary reaction, $2A + B \longrightarrow C + D$, the molecularity is

(*a*) 2
(*b*) 3
(*c*) 1
(*d*) cannot be predicted.

34. For producing the effective collisions, the colliding molecules must possess

(*a*) a certain minimum amount of energy
(*b*) energy equal to or greater than threshold energy
(*c*) proper geometry
(*d*) threshold energy and proper orientation.

35. The following mechanism has been proposed for a reaction :

$$A + B \longrightarrow C + D \qquad (Slow)$$
$$A + C \longrightarrow E \qquad (Fast)$$
$$\overline{2A + B \longrightarrow D + E}$$

The rate law expression for the reaction is

(*a*) $r = k[A]^2 [B]$
(*b*) $r = k[A][B]$
(*c*) $r = k[A]^2$
(*d*) $r = k[A][C]$.

36. For a chemical reaction under a given set of experimental conditions, with increase in conc. of reactants, the rate of reaction generally

(*a*) decreases
(*b*) remains unaltered
(*c*) increases
(*d*) first decreases and then increases.

37. For the reaction between reactants A and B the experimental rate law :

$$\frac{-d[A]}{dt} = k[A] \text{ enables us to state}$$

(*a*) molecularity
(*b*) stoichiometry
(*c*) order
(*d*) energy of activation.

38. The catalyst remains unchanged at the end of the reaction as regards

(*a*) quantity
(*b*) chemical composition
(*c*) quality and chemical composition
(*d*) quantity and chemical composition.

39. On increasing the temperature of a slow reaction by 10°

(*a*) threshold energy increases
(*b*) activation energy decreases
(*c*) number of collisions gets doubled
(*d*) value of rate constant increases.

40. An endothermic reaction, $A \longrightarrow B$, has an activation energy as x kJ mol^{-1} of A. If energy change of the reaction is y kJ, the activation energy of reverse reaction is

(*a*) $-x$
(*b*) $x - y$
(*c*) $x + y$
(*d*) $y - x$.

41. The value of activation energy is primarily determined by

(*a*) temperature
(*b*) collision frequency
(*c*) concentration of reactants
(*d*) chemical nature of reactants and products.

42. Which of the following statements is not correct ?

(*a*) Molecularity of a reaction cannot be fractional.
(*b*) Molecularity of a reaction cannot be more than three.
(*c*) Molecularity of a reaction can be obtained from balanced chemical equation.
(*d*) Molecularity of a reaction may or may not be equal to the order of the reaction.

43. The rate constant for a first order reaction is $1 \times 10^{-2}\ s^{-1}$. The concentration of the reactants would be reduced from 1 mole to 0.25 mole in

(*a*) 10^2 sec
(*b*) 69.3 sec
(*c*) 0.5×10^2 sec
(*d*) 138.6 sec.

44. Which of the following relations in correct ?

(*a*) $k = \text{A}\,e^{\text{E}_a/\text{RT}}$ (*b*) $\ln k - \ln \text{A} = \frac{\text{E}_a}{\text{RT}}$

(*c*) $\ln \text{A} - \ln k = \frac{\text{E}_a}{\text{RT}}$ (*d*) $\ln \text{A} - \ln k = -\frac{\text{E}_a}{\text{RT}}$

45. For a first order reaction, $t_{0.75}$ is 1386 seconds. Therefore, the specific rate constant is

(*a*) $10^{-1}\ \text{s}^{-1}$ (*b*) $10^{-3}\ \text{s}^{-1}$

(*c*) $10^{-2}\ \text{s}^{-1}$ (*d*) $10^{-4}\ \text{s}^{-1}$.

46. For a zero order reaction, $\text{A} \longrightarrow \text{B}$, $t_{1/2}$ is proportional to

(*a*) [A] (*b*) $[\text{A}]^{1/2}$

(*c*) $[\text{A}]^0$ (*d*) $[\text{A}]^2$.

47. $t_{1/2}$ of first order reactions is given by $\frac{0.693}{k}$, $t_{3/4}$ would be equal to

(*a*) $\frac{0.693}{k}$ (*b*) $\frac{0.346}{k}$

(*c*) $\frac{1.386}{k}$ (*d*) $\frac{0.924}{k}$.

48. Ratio $t_{7/8}/t_{1/2}$ for a first order reaction would be equal to

(*a*) 7 (*b*) 2

(*c*) 8 (*d*) 3.

49. For which of the following reactions k_{310}/k_{300} would be maximum

(*a*) $\text{A} + \text{B} \longrightarrow \text{C}$; $\text{E}_a = 50$ kJ

(*b*) $\text{X} + \text{Y} \longrightarrow \text{Z}$; $\text{E}_a = 40$ kJ

(*c*) $\text{P} + \text{Q} \longrightarrow \text{R}$; $\text{E}_a = 60$ kJ

(*d*) $\text{E} + \text{F} \longrightarrow \text{G}$; $\text{E}_a = 100$ kJ.

50. For a first order reaction $\text{A} \longrightarrow \text{B}$, $t_{1/2}$ is proportional is

(*a*) $[\text{A}]^{1/2}$ (*b*) [A]

(*c*) $[\text{A}]^0$ (*d*) $[\text{A}]^2$.

51. For the reaction, $2\text{A} \longrightarrow \text{B} + \text{C}$, a plot of log [A] *vs.* time is found to be a straight line. The order of the reaction must be

(*a*) One (*b*) Zero

(*c*) Two (*d*) Three.

52. For a third order reaction, $3\text{X} \longrightarrow \text{Y} + \text{Z}$, the initial rate is 5×10^{-2} mol $\text{L}^{-1}\ \text{s}^{-1}$ when the conc. of X is 0.1 mol L^{-1}. The value of rate constant for the reaction is

(*a*) $5 \times 10^{-2}\ \text{L}^2\ \text{mol}^{-2}\ \text{s}^{-1}$ (*b*) $5 \times 10^{-3}\ \text{L}^2\ \text{mol}^{-2}\ \text{s}^{-1}$

(*c*) $5 \times 10^{-4}\ \text{L}^2\ \text{mol}^{-2}\ \text{s}^{-1}$ (*d*) $50\ \text{L}^2\ \text{mol}^{-2}\ \text{s}^{-1}$.

53. For the decomposition of HI at 600 K

$$2\text{HI} \longrightarrow \text{H}_2 + \text{I}_2$$

the following data were obtained :

[HI] (*mol.L*$^{-1}$)	*Rate of decomposition of HI* (*mol. L*$^{-1}$ *s*$^{-1}$)
0.10	2.75×10^{-8}
0.20	11.00×10^{-8}
0.30	24.75×10^{-8}

The order of the reaction is

(*a*) 1 (*b*) 2

(*c*) 0 (*d*) 1.5.

54. For a zero order reaction, $\text{A} \longrightarrow \text{B}$, a graph of rate *vs* time has slope equal to

(*a*) *k* (*b*) – *k*

(*c*) zero (*d*) – 2.303*k*.

55. The rate of a first order reaction, $\text{X} \longrightarrow$ Products, is 7.5×10^{-4} mol $\text{L}^{-1}\ \text{s}^{-1}$ when concentration of X is 0.5 mol L^{-1}. The rate constant of the reaction is

(*a*) $3.75 \times 10^{-4}\ \text{s}^{-1}$ (*b*) $2.5 \times 10^{-5}\ \text{s}^{-1}$

(*c*) $1.5 \times 10^{-3}\ \text{s}^{-1}$ (*d*) $8.0 \times 10^{-4}\ \text{s}^{-1}$.

56. For an endothermic reaction, where ΔH represents the enthalpy of the reaction in kJ/mole, the minimum value for the energy of activation will be

(*a*) less than ΔH (*b*) zero

(*c*) more than ΔH (*d*) equal to ΔH.

57. In the titration between oxalic acid and acidified potassium permanganate, the manganous salt formed catalyses the reaction. The manganous salt is

(*a*) a promoter (*b*) a positive catalyst

(*c*) an autocatalyst (*d*) none of the above.

58. In a first order reaction, 75% of the reactants disappeared in 1.386 hr. What is the rate constant ?

(*a*) $3.6 \times 10^{-3}\ \text{s}^{-1}$ (*b*) $2.7 \times 10^{-4}\ \text{s}^{-1}$

(*c*) $72 \times 10^{-3}\ \text{s}^{-1}$ (*d*) $1.8 \times 10^{-3}\ \text{s}^{-1}$.

59. The rate constant for a reaction, $2\text{A} \longrightarrow \text{B} + \text{C}$, is 1.0×10^{-2} mol $\text{L}^{-1}\ \text{s}^{-1}$. The rate of the reaction when concentration of A is 2.0 mol L^{-1} would be

(*a*) 1.0×10^{-2} mol $\text{L}^{-1}\ \text{s}^{-1}$

(*b*) 2.0×10^{-2} mol $\text{L}^{-1}\ \text{s}^{-1}$

(c) 4.0×10^{-2} mol L^{-1} s^{-1}

(d) 8.0×10^{-2} mol L^{-1} s^{-1}.

60. The reaction, $2A + B \longrightarrow$ Products, follows the mechanism

$$2A \rightleftharpoons A_2$$
$$A_2 + B \longrightarrow \text{Products} \quad (\textit{Slow})$$

The order of the reaction is

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

61. For which of the following reactions, the per cent increase in the rate of the reaction is maximum when concentration of the reactants is doubled ?

(a) Zero order reaction	(b) First order reaction
(c) Second order reaction	(d) Third order reaction.

62. For a reversible reaction, the activation energies for the forward and the backward reactions are 60 kJ and 20 kJ respectively. If energy of reactants is 20 kJ the energy of products would be

(a) 40 kJ	(b) 20 kJ
(c) 80 kJ	(d) 60 kJ.

63. For the reaction,

$$2A + B + C \longrightarrow \text{Products}$$

the rate law equation is

$$r = k[A]\,[B]^{-1/2}\,[C]^0$$

The rate of the reaction increases with increase in the concentration of

(a) A only	(b) B only
(c) C only	(d) A or B.

64. Which of the following statements is not correct for the reaction

$$4A + B \longrightarrow 2C + 2D$$

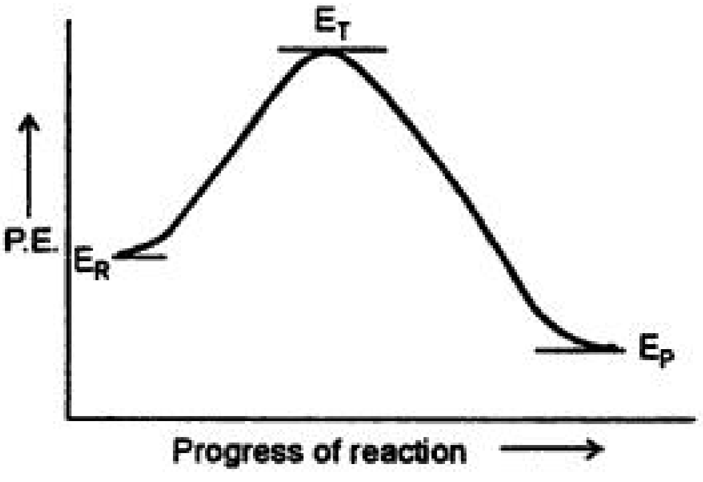
(a) The rate of disappearance of B is one-fourth of the rate of disappearance of A.

(b) The rate of appearance of C is one-half the rate of disappearance of B.

(c) The rate of formation of D is one-half the rate of disappearance of A.

(d) The rates of formation of C and D are equal.

65. In the accompanied diagram, indicating E_R, E_T and E_P as the energies of reactants, activated complex and products respectively which of the following is correct ?



(a) Forward reaction is slow.

(b) Backward reaction is slow.

(c) Reaction is exothermic.

(d) Reaction is endothermic.

66. The activation energy for the forward reaction

$$A + B \longrightarrow C + D - 20 \text{ kJ}$$

is 30 kJ. The activation energy for the reverse reaction is

(a) 48 kJ	(b) 50 kJ
(c) 10 kJ	(d) – 10 kJ.

67. The following mechanism is proposed for a reaction,

$$2A + B \longrightarrow D + E$$
$$A + B \rightleftharpoons C \quad (\textit{Fast})$$
$$A + C \longrightarrow E + D \quad (\textit{Slow})$$

The order of the reaction is

(a) 1	(b) 2
(c) 3	(d) 1.5.

68. In several experiments on the kinetics of the reaction $A + B \longrightarrow$ products, the rate is doubled on doubling the initial concentration of B keeping that of A fixed. On doubling the initial concentration of both A and B, the rate increased by a factor of 8. The rate equation is

(a) $r = k[A]^2[B]$	(b) $r = k[A][B]$
(c) $r = k[A][B]^2$	(d) $r = k[A]^2\,[B]^2$.

69. On increasing the temperature, the rate of reaction increases mainly because

(a) the activation energy of the reaction increases

(b) a large fraction of the molecules attain energy equal to or greater than the threshold energy

(c) concentration of the reacting molecules increases

(d) collision frequency increases.

70. The rate constant for a hypothetical reaction,

$3A \longrightarrow B + C$, is 1.0×10^{-3} mol L^{-1} s^{-1}.

The order of the reaction is

(*a*) one (*b*) two

(*c*) three (*d*) zero.

71. A graph of ln *k* *vs.* 1/T has a slope equal to

(*a*) $\frac{E_a}{2.303\ R}$ (*b*) $\frac{2.303\ E_a}{R}$

(*c*) $+\frac{E_a}{R}$ (*d*) $-\frac{E_a}{R}$.

72. For a single step reaction $A_2 + B_2 \longrightarrow 2AB$, the rate equation is

(*a*) $r = k\ [AB]^2$ (*b*) $r = k\ [A_2]^2\ [B_2]^2$

(*c*) $r = k\ [A_2][B_2]$ (*d*) $r = \frac{[A_2][B_2]}{[AB]^2}$.

73. The rates of a certain reaction $\left(-\frac{dx}{dt}\right)$ at different times are as follows :

Time(s)	*Rate (mol L^{-1} s^{-1})*
10 s	3.20×10^{-2}
100 s	3.20×10^{-2}
400 s	3.21×10^{-2}

The order of the above reaction is

(*a*) 1 (*b*) 2

(*c*) 3 (*d*) 0.

74. 75% of a first order reaction was completed in 32 minutes. The half-life of the reaction is

(*a*) 24 min (*b*) 16 min

(*c*) 32 min (*d*) 8 min.

75. For a first order reaction involving gaseous species, the rate of the reaction changes with change in

(*a*) concentration (*b*) pressure

(*c*) temperature (*d*) all of these.

76. Phosphorus undergoes slow combustion and glows in dark. This process is called

(*a*) phosphorescence (*b*) flourescence

(*c*) photosensitization (*d*) chemiluminscence.

77. The reaction $A + 2B \longrightarrow 2C$ has the rate law :

rate = k[A][B].

Which of the following is an appropriate rate determining step ?

(*a*) $A + 2B \longrightarrow C$ (*b*) $A + C \longrightarrow D$

(*c*) $A + B \longrightarrow E$ (*d*) $2A \longrightarrow C + D$.

78. For a reaction, $A \longrightarrow B$, it has been observed that the rate of reaction doubles when the concentration of A is increased eight times. The order of the reaction is

(*a*) 2 (*b*) 8

(*c*) 1/4 (*d*) 1/3.

79. The rate of reaction, $2A + B \longrightarrow$ Products, is given by the equation rate = $k[A]^2$ [B]. If B is present in excess, the order of the reaction would be

(*a*) 3 (*b*) 1

(*c*) 2 (*d*) 0.

80. For a process, $A + B \longrightarrow$ Products, the rate of the reaction is second order with respect to A and zero order with respect to B. When 1.0 mole each of A and B are taken in a one litre vessel, the initial rate is 1×10^{-2} mol L^{-1} s^{-1}. The rate of the reaction when 50% of the reactants have been converted to products would be

(*a*) 1×10^{-2} mol L^{-1} s^{-1} (*b*) 2.5×10^{-3} mol L^{-1} s^{-1}

(*c*) 5.0×10^{-2} mol L^{-1} s^{-1} (*d*) 0.5×10^{-2} mol^{-1} s^{-1}.

QUESTION BANK

Level II

Choose the correct answer from the four alternatives given in each of the following questions :

1. For the reaction, $N_2 + 3H_2 \longrightarrow 2NH_3$, the rate of disappearance of H_2 is 0.01 mol L^{-1} min^{-1}. The rate of appearance of NH_3 would be

(*a*) 0.01 mol L^{-1} min^{-1} (*b*) 0.02 mol L^{-1} min^{-1}

(*c*) 0.007 mol L^{-1} min^{-1} (*d*) 0.002 mol L^{-1} min^{-1}

2. The reaction, $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$ is first order with respect to N_2O_5. Which of the following graphs would yield a straight line ?

(a) $p_{N_2O_5}$ vs time

(b) $(p_{N_2O_5})^{-1}$ vs time

(c) log $(p_{N_2O_5})$ vs time with positive slope

(d) log $(p_{N_2O_5})$ vs time with negative slope.

3. A catalyst is a substance which

(a) Increases the equilibrium concentration of the product

(b) Changes the equilibrium constant of the reaction

(c) Shortens the time to reach equilibrium

(d) Supplies energy to the reaction.

4. A gaseous reaction,

$$2A(g) + B(g) \longrightarrow 2C(g),$$

shows a decrease in pressure from 120 mm to 100 mm in 10 minutes. The rate of appearance of C is

(a) 2 mm/min	(b) 4 mm/min
(c) 10 mm/min	(d) 12 mm/min.

5. For the reaction, $2SO_2 + O_2 \rightleftharpoons 2SO_3$,

the rate of disappearance of O_2 is 2.0×10^{-4} mol $L^{-1}\,s^{-1}$. The rate of appearance of SO_3 is

(a) 2.0×10^{-4} mol $L^{-1}s^{-1}$	(b) 4.0×10^{-4} mol $L^{-1}s^{-1}$
(c) 1.0×10^{-4} mol $L^{-1}s^{-1}$	(d) 6.0×10^{-4} mol $L^{-1}s^{-1}$.

6. Formation of HI from its elements H_2 and I_2 is an exothermic process. The activation energy for the dissociation of HI into H_2 and I_2 is ...... that of formation of HI.

(a) less than	(b) more than
(c) same as	(d) may be less or more than.

7. Consider the zero order reaction A ⟶ B.

Starting with 4 moles of A in a one litre container, after half an hour only one mole of A is left unreacted. The value of k for the reaction is

(a) 0.4 mol L^{-1} min^{-1}	(b) 0.1 mol L^{-1} min^{-1}
(c) 1 mol L^{-1} min^{-1}	(d) 0.3 mol L^{-1} min^{-1}

8. A hypothetical reaction, $A_2 + B_2 \longrightarrow 2AB$ follows the mechanism as given below :

$$A_2 \rightleftharpoons A + A$$
$$A + B_2 \longrightarrow AB + B \qquad (Slow)$$
$$A + B \longrightarrow AB$$
$$\overline{\underline{A_2 + B_2 \longrightarrow 2AB}}$$

The order of the overall reaction is

(a) 0	(b) 1
(c) $1\frac{1}{2}$	(d) 2.

9. The dimensions of rate constant in a zero order reaction are

(a) L mol sec^{-1}	(b) mol L^{-1} sec^{-1}
(c) dimensionless	(d) sec^{-1}.

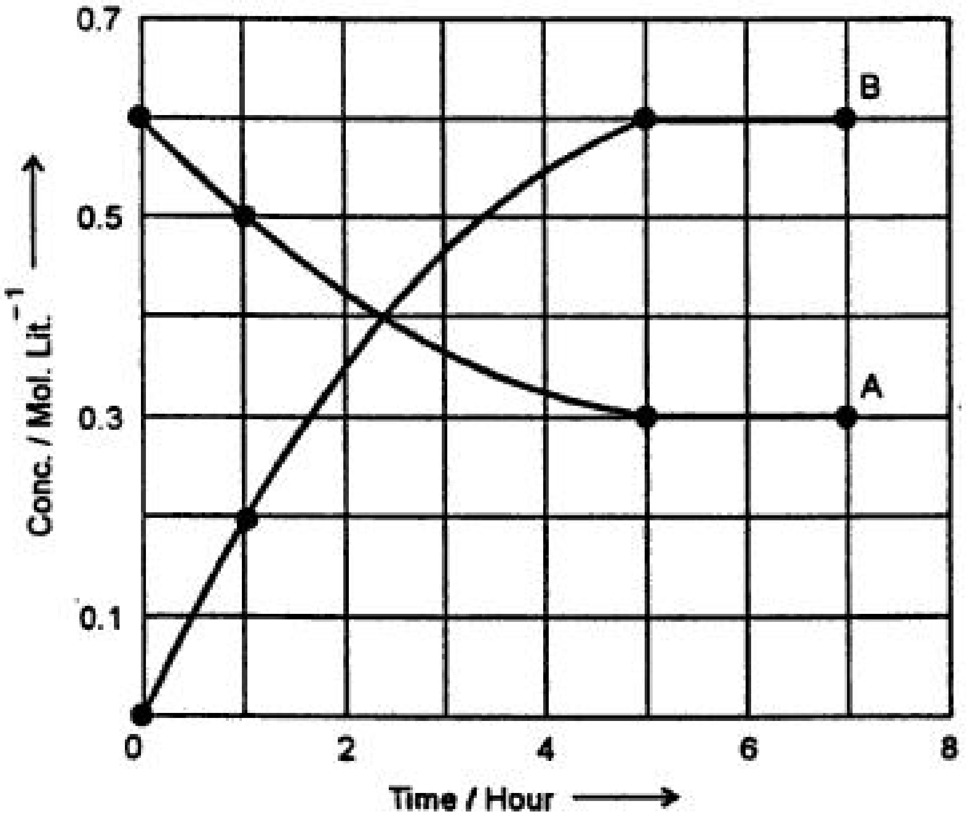
10. For the reaction A + B ⟶ Products, it is found that the order of A is 1 and the order of B is 1/2. When the concentrations of both A and B are increased four times, the rate will increase by a factor

(a) 6	(b) 8
(c) 4	(d) 16

11. For a reaction A ⟶ B, it was found that the rate of reaction doubles when the concentration of A is increased by eight times. The order of reaction is

(a) 2	(b) 8
(c) 1/2	(d) 1/3.

12. The progress of the reaction A $\rightleftharpoons$ nB, with time is represented by the graph given below :



The value of n is

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

13. For a process A + B ⟶ products, the rate is first order with respect to A and first order with respect to B. When 1.0 mole each of A and B are taken in a one litre vessel, the initial rate is 1×10^{-2} mol $L^{-1}\,s^{-1}$. The rate of the reaction when 90% of the reactants have been converted into products would be

(*a*) 1×10^{-2} mol L^{-1} s^{-1} (*b*) 1×10^{-4} mol L^{-1} s^{-1}

(*c*) 1×10^{-3} mol L^{-1} s^{-1} (*d*) 1×10^{-5} mol L^{-1} s^{-1}.

14. While studying the decomposition of gaseous N_2O_5 it is observed that a plot of logarithm of its partial pressure *versus* time is linear. What is the order of the reaction ?

(*a*) 1 (*b*) 1/2

(*c*) 2 (*d*) 0.

15. The half-life of a first order reaction $A \longrightarrow B + C$, is 10 minutes. The concentration of A would be reduced to 10% of the original concentration in

(*a*) 10 minutes (*b*) 90 minutes

(*c*) 33 minutes (*d*) 70 minutes.

16. Consider a reaction $2A \longrightarrow B + C$. If the initial concentration of A was reduced from 10 mol L^{-1} to 8 mol L^{-1} in 2 hours and then was reduced from 8 mol L^{-1} to 4 mol L^{-1} in 4 hours. The reaction is of

(*a*) First order (*b*) Second order

(*c*) Third order (*d*) Zero order.

17. Consider a reaction $A \longrightarrow B + C$. If the initial concentration of A was reduced from 2 M to 1 M in 1 hour and then from 1 M to 0.25 M in 2 hours, the order of the reaction is

(*a*) 1 (*b*) 0

(*c*) 2 (*d*) 3.

18. In which case the per cent increase in the rate will be maximum, when temperature is increased from

(*a*) 270 K to 280 K

(*b*) 280 K to 290 K

(*c*) 290 K to 300 K

(*d*) In all the three cases the increase will be same.

19. In which case the per cent increase in the rate will be maximum, when temperature is increased from 298 to 308 K. In case of the reaction having activation energy is

(*a*) 40 kJ (*b*) 50 kJ

(*c*) 60 kJ (*d*) 20 kJ.

20. The $t_{1/2}$ for the decomposition of CH_3CHO at constant temperature and at initial pressures of 364 mm and 170 mm of Hg were 410 s and 880 s respectively. The order of the reaction is

(*a*) 1 (*b*) 0.5

(*c*) 1.5 (*d*) 2.

21. At a given temperature the energy of activation of two reactions are same if

(*a*) the specific rate constants for the two reactions are equal

(*b*) ΔH for the two reactions is same but not zero

(*c*) ΔH for the two reactions are zero

(*d*) the temperature coefficients of the two reactions are equal.

22. At 100°C, the gaseous reaction $A \longrightarrow 2B + C$ is found to be of first order. Starting with pure A, if at the end of 10 min, the total pressure of the system is 176 mm and after a long time it is 270 mm, the partial pressure of A at the end of 10 min is

(*a*) 94 mm (*b*) 43 mm

(*c*) 47 mm (*d*) 176 mm.

23. Plotting a graph of log $t_{1/2}$ against log $[A]_0$ of a reactant for a first order reaction, the slope will be

(*a*) – 1 (*b*) – 2

(*c*) 0 (*d*) + 1.

24. For a first order reaction, $2A \longrightarrow B + C$, a graph of log [A] *vs* time has a slope equal to

(*a*) $\frac{k}{2.303}$ (*b*) $-\frac{k}{2.303}$

(*c*) $\frac{2.303}{k}$ (*d*) $-\frac{2.303}{k}$.

25. For a reaction $E_a = 0$ and $k = 3.2 \times 10^4\ s^{-1}$ at 300 K. The value of k at 310 K would be

(*a*) $6.4 \times 10^4\ s^{-1}$ (*b*) $3.2 \times 10^4\ s^{-1}$

(*c*) $3.2 \times 10^8\ s^{-1}$ (*d*) $3.2 \times 10^5\ s^{-1}$

26. Ratio $t_{3/4}/t_{1/2}$ for a first order reaction would be equal to

(*a*) 4 (*b*) 3

(*c*) 2 (*d*) None of these.

27. Consider the reaction,

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

If the rate of increase in concentration of ammonia is x mol L^{-1} s^{-1}, the rate of decrease of concentration of hydrogen would be

(*a*) x mol L^{-1} s^{-1} (*b*) $2x$ mol L^{-1} s^{-1}

(*c*) $3x$ mol L^{-1} s^{-1} (*d*) $1.5x$ mol L^{-1} s^{-1}.

28. The reaction

$$2NO + Br_2 \longrightarrow 2NOBr$$

follows the mechanism given below

I. $NO + Br_2 \rightleftharpoons NOBr_2$ ...*Fast*

II. $NOBr_2 + NO \longrightarrow 2NOBr_2$ ...*Slow*

The overall order of this reaction is

(*a*) 2 (*b*) 1

(*c*) 3 (*d*) None of these.

29. For a first order reaction, $A \longrightarrow B$, $t_{1/2} = 1$ hr, what fraction of the initial conc. of A reacts in 4 hrs ?

(*a*) 15/16 (*b*) 1/16

(*c*) 7/8 (*d*) 1/8.

30. Which of the following is not a correct form of Arrhenius equation ?

(*a*) $k = Ae^{-Ea/RT}$ (*b*) $\ln k = \ln A - \frac{Ea}{RT}$

(*c*) $k = Ae^{RT/Ea}$ (*d*) $\log k = \log A - \frac{Ea}{2.303RT}$.

31. For a first order reaction, $X \longrightarrow Y$, $t_{1/3} = 1$ hr. What fraction of the initial conc. of X reacts in the second hour from the start of the reaction ?

(*a*) 1/9 (*b*) 2/9

(*c*) 1/27 (*d*) 4/27.

32. The activation energy of a reaction is found to be 25 kJ at 300 K. When the temperature of reaction is increased to 310 K the rate constant

(*a*) doubles

(*b*) becomes less than double

(*c*) becomes more than double

(*d*) becomes zero.

33. For a particular reaction it is observed that its $t_{0.5}$ becomes one-half when the initial concentration is halved. The order of reaction w.r.t. the reactant is

(*a*) 1 (*b*) 0

(*c*) 1/2 (*d*) 2.0.

34. A graph of $\ln k$ *vs* $\left(\frac{1}{T}\right)$ has slope equal to

(*a*) $-\frac{E}{2.303R}$ (*b*) $+\frac{E_a}{R}$

(*c*) $-\frac{E_a}{2.303R}$ (*d*) $-\frac{E_a}{R}$.

35. If [A], n and $t_{1/2}$ represent the initial concentration of reactants, order of the reaction and half-life of the reaction respectively, then these three parameters are related as

(*a*) $t_{1/2} \propto [A]^n$ (*b*) $t_{1/2} \propto [A]^{n-1}$

(*c*) $t_{1/2} \propto \frac{1}{[A]^n}$ (*d*) $t_{1/2} \propto \frac{1}{[A]^{n-1}}$.

36. For a particular reaction, the rate expression is given as $r = k[A]\,[B]^{0.5}$. If the volume of vessel is reduced to one-fourth of the initial volume, the rate of reaction would

(*a*) decrease 1/4 times (*b*) increase by 8 times

(*c*) decrease 1/8 times (*d*) remains unaffected.

37. For the reaction, $A \longrightarrow B$, it has been found that the order of the reaction is zero with respect to A. Which of the following expressions correctly describes the reaction ?

(*a*) $k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$ (*b*) $[A]_0 - [A] = kt$

(*c*) $t_{1/2} = \frac{0.693}{k}$ (*d*) $t_{1/2} \propto \frac{1}{[A]_0}$.

38. On which of the following factors, the rate constant does not depend ?

(*a*) Temperature (*b*) Concentration

(*c*) Presence of catalyst (*d*) Nature of reactants.

39. The rate of a second order reaction $2A \longrightarrow$ Products is 8×10^{-4} mol L^{-1} s^{-1} when conc. of A is 2 mol L^{-1}. The rate constant of the reaction is

(*a*) 4×10^{-4} L mol^{-1} s^{-1} (*b*) 8×10^{-4} L mol^{-1} s^{-1}

(*c*) 1×10^{-4} L mol^{-1} s^{-1} (*d*) 2×10^{-4} L mol^{-1} s^{-1}.

40. In the reaction,

$$4NH_3(g) + 5O_2(g) \longrightarrow NO(g) + 6H_2O(l),$$

when 1.0 mole of ammonia and 1.0 mole of O_2 are made to react to completion

(*a*) 1.0 mole of NO will be produced

(*b*) All oxygen would be consumed

(*c*) All the ammonia would be consumed

(*d*) 1.0 mole water is produced.

41. The activation energy of a chemical reaction can be determined by

(*a*) Evaluating rate constants at two differnet emperatures

(*b*) Changing concentrations of reactants

(*c*) Evaluating rate constant at standard temperature

(*d*) Evaluating velocities of reaction at two different temperature.

42. The rate constant for the reaction,

$$2N_2O_5 \longrightarrow 4NO_2 + O_2, \text{ is } 3.0 \times 10^{-5} \text{ sec}^{-1}.$$

If the rate is 2.40×10^{-5} mol $litre^{-1}$ sec^{-1}, then the concentration of N_2O_5 (in mol $litre^{-1}$) is

(*a*) 1.4 (*b*) 1.2

(*c*) 0.04 (*d*) 0.8.

43. For a reaction, $X \longrightarrow Y$, the activation energies for the forward and the backward reactions are 30.0 kJ/mole and 50.0 kJ/mole respectively. The value of ΔE for the reaction would be

(*a*) 80.0 kJ
(*b*) 30.0 kJ
(*c*) – 20.0 kJ
(*d*) 20.0 kJ.

44. Which of the following changes in the presence of the catalyst ?

(*a*) Energy of reactants
(*b*) Energy of products
(*c*) Equilibrium constant
(*d*) Activation energy.

45. Which of the following reactions is expected to be a complex reaction ?

(*a*) $H_2 + I_2 \longrightarrow 2HI$
(*b*) $4HCl + O_2 \longrightarrow H_2O + 2Cl_2$
(*c*) $2NO + O_2 \longrightarrow 2NO_2$
(*d*) $NH_4NO_2 \longrightarrow N_2 + 2H_2O$.

46. Which of the following is not the possible value of molecularity ?

(*a*) 2
(*b*) 1
(*c*) – 1/2
(*d*) 3.

47. Which of the following is not the possible value for order of a reaction ?

(*a*) 0
(*b*) 1
(*c*) $2\frac{1}{2}$
(*d*) 4.

48. For a zero order reaction, $A \longrightarrow$ Products, the rate constant is 10^{-2} mol L^{-1} s^{-1}. Starting with 10 mole of A in 1 L vessel, how many moles of A would be left unreacted after 10 minutes ?

(*a*) 5 moles
(*b*) 6 moles
(*c*) 4 moles
(*d*) 10 moles.

49. The rate of a reaction increases three times when concentration of the reactants is increased 9 times. The order of the reaction is

(*a*) 3
(*b*) 2
(*c*) 1/2
(*d*) none of these.

50. What are the dimensions of the rate constant for a third order reaction ?

(*a*) mol L^{-1} s^{-2}
(*b*) L^2 mol^{-2} s^{-2}
(*c*) mol L^{-1} s^{-1}
(*d*) L^2 mol^{-2} s^{-1}.

51. For which of the following reactions, the rate of the reaction does not change with the progress of the reaction ?

(*a*) First order reaction
(*b*) Second order reaction
(*c*) Third order reaction
(*d*) None of these.

52. For which of the following reactions, the rate of the reaction decreases sharply with the progress of the reaction ?

(*a*) First order reaction
(*b*) Second order reaction
(*c*) Third order reaction
(*d*) Zero order reaction.

53. For the reaction, $4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$, the rate of disappearance of NH_3 is 0.02 mol L^{-1} min^{-1}. The rate of appearance of H_2O would be ...... mol L^{-1} min^{-1}.

(*a*) 0.02
(*b*) 0.03
(*c*) 0.013
(*d*) 0.06.

54. Which of the following reactions is the fastest ?

(*a*) $H_2(g) + I_2(g) \longrightarrow 2HI(g)$
(*b*) $CH_4(g) + I_2(g) \longrightarrow CH_3I(g) + HI(g)$
(*c*) $N_2(g) + O_2(g) \longrightarrow 2NO(g)$
(*d*) $AgNO_3(aq) + KI(aq) \longrightarrow AgI(s) + KNO_3(aq)$.

55. A reaction has rate law expression as

$$\text{rate} = k[A]^{3/2}\,[B]^{-1/2}$$

If concentrations of both A and B are increased four times, the rate of the reaction

(*a*) remains same
(*b*) increases four times
(*c*) decreases four times
(*d*) increases 16 times.

56. The hydrolysis of acetic anhydride

$$(CH_3CO)_2O + H_2O \longrightarrow 2CH_3COOH$$

is an example of

(*a*) Pseudo first order reaction
(*b*) Pseudo second order reaction
(*c*) Zero order reaction
(*d*) Third order reaction.

57. Chemical reactions of the type

$$X \xrightarrow{k_1} Y \xrightarrow{k_2} Z$$

are called

(*a*) Consecutive reactions
(*b*) Parallel reactions
(*c*) Reversible reactions
(*d*) Chain reactions.

58. If k is the rate constant and K is the equilibrium constant, then for a reaction, with increase in temperature

(*a*) both k and K increase
(*b*) both k and K decrease
(*c*) k increases K decreases
(*d*) k increases K may increase or decrease.

59. For a reaction, $2A + 3B \longrightarrow 2C + D$, the rate of reaction becomes double when conc. of A is doubled and becomes four times when conc. of both A and B are increased four times. The rate law for the reaction may be written as

(*a*) $r = k[A][B]$ (*b*) $r = k[A][B]^0$.

(*c*) $r = k[A]^2[B]^3$ (*d*) $r = k[A][B]^2$.

60. Which of the following relations is correct ?

(*a*) $A = k\,e^{-E_a/RT}$ (*b*) $A = k\,e^{E_a/RT}$

(*c*) $k = A\,e^{-RT/E_a}$ (*d*) $k = A\,e^{E_a/RT}$.

61. For a first order reaction having the initial conc. *a* mol L^{-1} and the rate constant *k*, the half-life period is equal to

(*a*) $\frac{0.693}{k\,.\,a}$ (*b*) $\frac{\ln 2}{k}$

(*c*) $\frac{\log 2}{k}$ (*d*) $\frac{\log 2}{k\sqrt{a}}$.

62. For a first order reaction, half-life of the reaction is independent of

(*a*) Temperature (*b*) Catalyst

(*c*) Conc. of reactants (*d*) None of these.

63. Arrhenius equation may be written as

(*a*) $\frac{d\ln k}{dT} = \frac{E_a}{RT}$ (*b*) $\frac{d\ln k}{dT} = -\frac{E_a}{RT^2}$

(*c*) $\frac{d\ln k}{dT} = -\frac{E_a}{RT}$ (*d*) $\frac{d\ln k}{dT} = \frac{E_a}{RT^2}$.

64. Consider a system containing NO_2 and SO_2 in which NO_2 is consumed in the following two parallel reactions

$$2NO_2 \overset{k_1}{\rightleftharpoons} N_2O_4$$

$$NO_2 + SO_2 \overset{k_2}{\rightleftharpoons} NO + SO_3$$

The rate of disappearance of NO_2 will be equal to

(*a*) $k_1[NO_2]^2 + k_2[NO_2]$

(*b*) $k_1[NO_2]^2 + k_2[NO_2][SO_2]$

(*c*) $2k_1[NO_2]^2$

(*d*) $2k_1[NO_2]^2 + k_2[NO_2][SO_2]$.

65. The half-time of a zero order reaction, $A \longrightarrow B + C$, is proportional to

(*a*) $[A]^0$ (*b*) $[A]^2$

(*c*) $[A]$ (*d*) $1/[A]$.

66. The temperature coefficient of a reaction is

(*a*) the rate constant at a particular temperature

(*b*) the ratio of the rate constants at any two different temperatures

(*c*) the ratio of the rates of a reaction at two temperatures differing by 10°C

(*d*) the ratio of the rate constants at two temperatures differing by 10°C.

67. If [A] is the concentration of A at any time *t* and $[A]_0$ is its initial concentration, then for a zero order reaction, A → products, the rate equation may be written as

(*a*) $[A]_0 - [A] = k$ (*b*) $[A] - [A]_0 = k$

(*c*) $[A]_0 - [A] = kt$ (*d*) $[A]_0 = k\,[A]$.

68. The equation for the rate constant is

$$k = A\,e^{-E_a/RT}$$

The value of *k* decreases with

(*a*) Increase in T (*b*) Decrease in E_a

(*c*) Decrease in T (*d*) None of these.

69. One litre of 2 M acetic acid is mixed with one litre of 2 M ethyl alcohol to form ester

$$CH_3COOH + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + H_2O$$

The decrease in the initial rate, if each solution is diluted by an equal volume of water would be

(*a*) 2 times (*b*) 4 times

(*c*) 1/2 times (*d*) 1/4 times.

70. For a reaction, $A \longrightarrow B$, *k* is 1×10^{-2} L mol^{-1} s^{-1}. If conc. of A is 2.0 mol L^{-1}, the rate of the reaction would be

(*a*) 1.0×10^{-2} mol L^{-1} s^{-1} (*b*) 2.0×10^{-2} mol L^{-1} s^{-1}

(*c*) 4.0×10^{-2} mol L^{-1} s^{-1} (*d*) 0.5×10^{-2} mol L^{-1} s^{-1}.

71. If the rate law for a reaction is rate = $k[A][B]^2$, the units of *k* would be

(*a*) mol L^{-1} s^{-1} (*b*) mol s^{-1}

(*c*) L^2 mol^{-2} s^{-1} (*d*) mol^2 L^{-2} s^{-1}.

72. For a chemical reaction, $2A + 2B \longrightarrow C + D$, the order of reaction is one with respect to A and one with respect to B. The initial rate of the reaction is 4×10^{-2} mol L^{-1} s^{-1}. When 50% of the reactants are converted into products, the rate of the reaction would become

(*a*) 2×10^{-2} mol L^{-1} s^{-1} (*b*) 1×10^{-2} mol L^{-1} s^{-1}

(*c*) 4×10^{-2} mol L^{-1} s^{-1} (*d*) 2×10^{-1} mol L^{-1} s^{-1}.

73. The half-life of a first order reaction $X \longrightarrow Y$, is 100 minutes. The concentration of X would be reduced to 10% of the original concentration in

(*a*) 100 minutes
(*b*) 332 minutes
(*c*) 900 minutes
(*d*) 700 minutes.

74. Consider a reaction $A \longrightarrow B + C$. If the initial concentration of A was reduced from 4 M to 2 M in 1 hour and from 2 M to 1 M is 0.5 hour, the order of the reaction is

(*a*) One
(*b*) Zero
(*c*) Two
(*d*) Three.

75. For a reaction, $aA \longrightarrow bB$, the rate law is, rate $= k[A]^{1/2}$. If the conc. of A is doubled, the rate of reaction would become

(*a*) twice
(*b*) half
(*c*) four times
(*d*) none of these is correct.

76. For a zero order reaction $t_{1/2} = 4$ hours when the initial conc. of the reactants is 4 mol L^{-1}, $t_{3/4}$ for the reaction would be

(*a*) 4 hours
(*b*) 6 hours
(*c*) 8 hours
(*d*) 12 hours.

77. A first order reaction is 50% complete in 100 minutes. The time required for 100% completion would be

(*a*) 100 minutes
(*b*) 200 minutes
(*c*) 50 minutes
(*d*) Infinite.

78. For a second order reaction $3A \longrightarrow$ Products, the initial rate is 1×10^{-2} mol L^{-1} s^{-1} when [A] is 0.1 mol L^{-1}. The value of rate constant for the reaction is

(*a*) 1.0×10^{-2} L mol^{-1} s^{-1}
(*b*) 1×10^{-3} L mol^{-1} s^{-1}
(*c*) 1.0 L mol^{-1} s^{-1}
(*d*) 1×10^{-5} L mol^{-1} s^{-1}.

79. For the reaction, $2A \longrightarrow B + C$, a plot of [A] vs. time is found to be a straight line. The order of this reaction is

(*a*) One
(*b*) Two
(*c*) Zero
(*d*) Impossible to predict.

80. The rate equation for the reaction $2X + Y \longrightarrow C + D$ is found to be, rate $= k[X][Y]$. Which of the following statements about the reaction is true ?

(*a*) $t_{1/2}$ is constant

(*b*) the unit of k is s^{-1}

(*c*) the value of k depends upon the initial concentrations of X and Y

(*d*) none of these is true.

81. For a first order reaction, $A \longrightarrow B$, $t_{1/2} = 1$ hr. What fraction of the initial conc. of A reacts in the second hour from the start of the reaction ?

(*a*) 1/2
(*b*) 1/4
(*c*) 3/4
(*d*) 1/8.

82. At 100°C, the gaseous reaction $A \longrightarrow 2B + C$ is found to be of first order. Starting with pure A, if at the end of 10 min. the total pressure of the system is 140 mm and after a long time it is 300 mm, the partial pressure of A at the end of 10 min is

(*a*) 70 mm
(*b*) 160 mm
(*c*) 60 mm
(*d*) 80 mm.

83. The reaction

$$2NO + Br_2 \longrightarrow 2NOBr$$

follows the mechanism given below

I. $NO + Br_2 \rightleftharpoons NOBr_2$ ......*Fast*
II. $NOBr_2 + NO \longrightarrow 2NOBr$ ......*Slow*

If concentrations of both NO and Br_2 are increased two times, the rate of reaction would become

(*a*) 4 times
(*b*) 2 times
(*c*) 8 times
(*d*) 6 times.

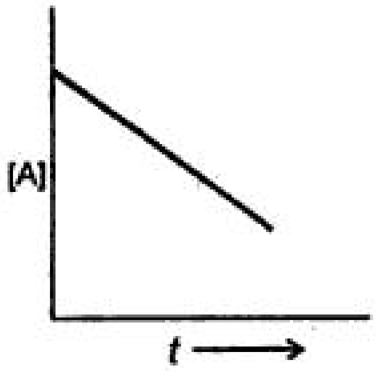
84. Consider the reaction,

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

If the rate of decrease in the concentration of hydrogen is x mol L^{-1} s^{-1}, the rate of increase in the concentration of ammonia would be

(*a*) x mol L^{-1} s^{-1}
(*b*) $2x$ mol L^{-1} s^{-1}
(*c*) $\frac{2}{3}x$ mol L^{-1} s^{-1}
(*d*) $\frac{3}{2}x$ mol L^{-1} s^{-1}.

85. For a particular gaseous reaction a graph was plotted as shown below. It shows that the reaction of A is



(*a*) zero order w.r.t. A

(*b*) 1st order w.r.t. A

(*c*) second order w.r.t. A

(*d*) a non-integer order w.r.t. A.

ANSWERS

QUESTION BANK (Level I)

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

QUESTION BANK (Level II)

1. (*c*) **2.** (*d*) **3.** (*c*) **4.** (*b*) **5.** (*b*) **6.** (*b*) **7.** (*b*) **8.** (*c*)
9. (*b*) **10.** (*b*) **11.** (*d*) **12.** (*b*) **13.** (*b*) **14.** (*a*) **15.** (*c*) **16.** (*d*)
17. (*a*) **18.** (*a*) **19.** (*c*) **20.** (*d*) **21.** (*d*) **22.** (*c*) **23.** (*c*) **24.** (*b*)
25. (*b*) **26.** (*c*) **27.** (*d*) **28.** (*c*) **29.** (*a*) **30.** (*c*) **31.** (*b*) **32.** (*b*)
33. (*b*) **34.** (*d*) **35.** (*d*) **36.** (*b*) **37.** (*b*) **38.** (*b*) **39.** (*d*) **40.** (*b*)
41. (*a*) **42.** (*d*) **43.** (*c*) **44.** (*d*) **45.** (*b*) **46.** (*c*) **47.** (*d*) **48.** (*c*)
49. (*c*) **50.** (*d*) **51.** (*d*) **52.** (*c*) **53.** (*b*) **54.** (*d*) **55.** (*b*) **56.** (*a*)
57. (*a*) **58.** (*d*) **59.** (*b*) **60.** (*b*) **61.** (*b*) **62.** (*c*) **63.** (*d*) **64.** (*d*)
65. (*c*) **66.** (*d*) **67.** (*c*) **68.** (*c*) **69.** (*d*) **70.** (*c*) **71.** (*c*) **72.** (*b*)
73. (*d*) **74.** (*b*) **75.** (*d*) **76.** (*d*) **77.** (*d*) **78.** (*c*) **79.** (*c*) **80.** (*d*)
81. (*b*) **82.** (*d*) **83.** (*c*) **84.** (*c*) **85.** (*a*).

HINTS/SOLUTIONS

QUESTION BANK (Level I)

5. (*d*) It is an ionic reaction.

7. (*a*) Order = 3/2 + (− 1/2) = 1.

8. (*d*)

$$r_1 = k(a)^n$$

$$r_2 = k(4a)^n$$

$$\frac{r_2}{r_1} = (4)^n = 2 \qquad \therefore \quad n = \frac{1}{2}.$$

10. (*b*) k for first order reaction has dimensions s^{-1} or min^{-1} etc.

11. (*c*) All these reactions are simple reactions.

12. (*b*) By observing the dimensions of k we come to know it is second order reaction.

13. (*d*) rate = $k[CH_3COOH][C_2H_5OH]$

When each conc. is reduced to half, the rate of reaction would become $\frac{1}{4}$ times.

15. (*c*)

$$\Delta E = E_{a(f)} - E_{a(b)}$$

$$-20 = 30 - E_{a(b)}$$

$$E_{a(b)} = 50 \text{ kJ}.$$

17. (*a*) $\Delta E = E_{a(f)} - E_{a(b)} = 50 - 30 = 20$ kJ.

18. (*b*) The rate of the reaction becomes is independent of the reactant which is present in excess.

19. (*c*) Factual question.

20. (*a*) Water is present in excess. Therefore, the rate of reaction is independent of conc. of H_2O.

21. (*d*) Rate constant of all reactions is independent of conc. of reactants.

25. (*d*) Molecularity cannot be zero, fractional or more than three.

26. (*d*) Order, generally, cannot be more than three.

27. (*c*) Greater the order of the reaction, more is the per cent increase in the rate of the reaction for a given increase in conc.

30. (*a*)

$$K = \frac{[O_2][O]}{[O_3]},\ [O] = K\frac{[O_3]}{[O_2]} \quad ...(i)$$

$$\text{rate} = k[O_3][O] \quad ...(ii)$$

From (*i*) and (*ii*) rate $= k[O_3]\ .\ K\dfrac{[O_3]}{[O_2]} = K'\dfrac{[O_3]^2}{[O_2]}$.

32. (*d*) By reducing the volume to half, the concentrations of both the reactants become double.

35. (*b*) Rate law depends upon the slowest step.

$\therefore \quad r = k[A][B]$.

37. (*c*) Rate law tells us about the order of the reaction.

40. (*b*)

$$\Delta E = E_{a(f)} - E_{a(b)}$$

$$y = x - E_{a(b)}$$

$$E_{a(b)} = x - y.$$

42. (*c*) Molecularity of a reaction cannot be obtained from balanced equation for complex reactions.

43. (*d*) $t_{1/2} = \dfrac{0.693}{k} = \dfrac{0.693}{1 \times 10^{-2}} = 69.3$ s

1 mole would be reduced to 0.25 mole in two half lives, *i.e.*, $69.3 \times 2 =$ **138.6 s.**

44. (*c*) $k = Ae^{-E_a/RT}$

$\ln k = \ln A - \dfrac{E_a}{RT}$ or $\ln A - \ln k = \dfrac{E_a}{RT}$.

45. (*b*)

$$t_{0.75} = 1386 \text{ s} = 2 \times t_{0.5}$$

$$t_{0.5} = \frac{1386}{2} = 693 \text{ s}$$

$$k = \frac{0.693}{693 \text{ s}} = 1 \times 10^{-3}\ s^{-1}.$$

46. (*a*) $t_{1/2} \propto \dfrac{1}{[A]^{n-1}}$, where n is order of the reaction.

For zero order reaction,

$$t_{1/2} \propto \frac{1}{[A]^{-1}} \propto [A].$$

47. (*c*) $t_{3/4} = 2\,(t_{1/2}) = \dfrac{2 \times 0.693}{k} = \dfrac{1.386}{k}$.

48. (*d*) $t_{7/8} = 3t_{1/2}$

49. (*d*) Increase in rate of reaction is maximum for the reaction having the maximum activation energy.

50. (*c*) For first order reaction $t_{1/2}$ is independent of the initial concentration of the reactants.

51. (*a*) Plot of log [A] *vs.* time is a straight line for first order reactions.

52. (*d*) $\quad \text{rate} = k\,[X]^3$

$$k = \frac{\text{rate}}{[X]^3} = \frac{5 \times 10^{-2}}{(0.1)^3} = 50\ L^2\ mol^{-2}\ s^{-1}.$$

53. (*b*) As the rate of the reaction is increasing four times when conc. of HI is doubled, the order of the reaction is 2.

54. (*c*) For a zero order reaction rate does not change with time.

55. (*c*) $\quad \text{Rate} = k[X]$

$$k = \frac{\text{Rate}}{[X]} = \frac{7.5 \times 10^{-4}}{0.5} = 1.5 \times 10^{-3}\ s^{-1}.$$

59. (*a*) By observing the dimensions of k, we come to know that the given reaction is a zero order reaction. For a zero order reaction,

$$\text{Rate} = \text{Rate constant} = 1.0 \times 10^{-2}\ mol\ L^{-1}\ s^{-1}.$$

60. (*c*)

$$r = k[A_2][B] \quad ...(i)$$

$$K = \frac{[A_2]}{[A]^2}$$

$$\therefore \quad [A_2] = K[A]^2 \quad ...(ii)$$

From (*i*) and (*ii*)

$$r = k\,K[A]^2\,[B] = k'\,[A]^2\,[B].$$

61. (*d*) Greater the order of the reaction, greater is the increase in the rate of the reaction for a given increase in the concentration.

62. (*d*) $\quad \Delta E = E_{a(f)} - E_{a(b)} = 60 - 20 = 40$ kJ

$$\Rightarrow \quad \Delta E = E_P - E_R$$

$$40 = E_P - 20; \qquad E_P = 60 \text{ kJ}.$$

64. (*b*) The rate of appearance of C is twice the rate of appearance of B.

65. (*c*) Since E_P is less than E_R, the reaction must be exothermic.

66. (*c*)

$$\Delta E = +\,20 \text{ kJ}$$

$$\Delta E = E_{act\,(f)} - E_{act\,(b)}$$

$$20 = 30 - E_{act\,(b)}$$

$$E_{act\,(b)} = 30 - 20 = 10 \text{ kJ}.$$

67. (*c*)

$$r = k[A][C] \quad ...(i)$$

From first step, $K = \dfrac{[C]}{[A]\,[B]}$

or

$$[C] = K[A].[B] \quad ...(ii)$$

From (*i*) and (*ii*)

$$r = k[\mathrm{A}]^2\,[\mathrm{B}]$$

$$\text{Order} = 2 + 1 = \mathbf{3}.$$

70. (*d*) By observing the dimensions of k, we come to know it is a zero order reaction.

71. (*d*) $k = \mathrm{A}\,e^{-\mathrm{E}_a/\mathrm{RT}}$

$$\ln k = \ln \mathrm{A} - \left(\frac{\mathrm{E}_a}{\mathrm{R}}\right)\frac{1}{\mathrm{T}}$$

$$\ln k = \left(-\frac{\mathrm{E}_a}{\mathrm{K}}\right)\frac{1}{\mathrm{T}} + \ln \mathrm{A}$$

$$y = mx + c.$$

73. (*d*) As the reaction proceeds at constant speed with the progress, it must be a zero order reaction.

77. (*c*) By observing the rate equation we come to know that the rate determining step involves 1 molecule of A and 1 molecule of B.

79. (*c*) The rate of the reaction becomes independent of the conc. of the reactant that is present in excess. So, the reaction behaves as a second order reaction.

80. (*b*) $k = 1 \times 10^{-2}\ \mathrm{L\ mol^{-1}\ s^{-1}}$

$$\text{rate} = k\,[\mathrm{A}]^2\,[\mathrm{B}]^0$$

When 50% of the reactants are converted into products

$$\text{rate} = 1 \times 10^{-2}\,(0.5)^2 = \mathbf{2.5 \times 10^{-3}\ mol\ L^{-1}\ s^{-1}}.$$

QUESTION BANK (Level II)

1. (*c*) $-\dfrac{1}{3}\dfrac{d[\mathrm{H_2}]}{dt} = \dfrac{1}{2}\dfrac{d[\mathrm{NH_3}]}{dt}$

$$\frac{d[\mathrm{NH_3}]}{dt} = -\frac{2}{3}\frac{d[\mathrm{H_2}]}{dt} = \frac{2}{3}(0.01) = 0.007\ \ \mathrm{mol\ L^{-1}\ s^{-1}}.$$

2. (*d*) $r = k(p\mathrm{N_2O_5})$ $\quad\because$ conc. of $\mathrm{N_2O_5} \propto p\mathrm{N_2O_5}$

$$\frac{-d[p\mathrm{N_2O_5}]}{dt} = k\,p\mathrm{N_2O_5}$$

$$\frac{d[p\mathrm{N_2O_5}]}{p\mathrm{N_2O_5}} = -\,k\,dt \qquad \text{...(1)}$$

Integrating (1), we get

$$\log\,(p\mathrm{N_2O_5}) = (-\,k)t + \mathrm{C}$$

This is an equation of straight line with slope equal to $-\,k$

4. (*b*) Suppose $2p$ is the pressure of C after 10 min.

Fall in pressure of A = $2p$

Fall in pressure of B = p

Total fall in pressure = $(2p + p) - 2p = p$ = 20 mm

Pressure of C = $2p$ = 40 mm

Rate of appearance of C = $\dfrac{40}{10}$ = **4 mm/min.**

7. (*b*) Fall in conc. $= 4 - 1 = 3\ \mathrm{mol\ L^{-1}}$

Time interval = 30 min

For a zero order reaction,

Rate constant = Rate of reaction

$$= \frac{3\ \mathrm{mol\ L^{-1}}}{30\ \mathrm{min}} = 0.1\ \mathrm{mol\ L^{-1}\ min^{-1}}.$$

8. (*c*) From the slow step, the rate law may be written as :

$$r = k[\mathrm{A}][\mathrm{B_2}] \qquad \text{...}(i)$$

From first step we can write, $\mathrm{K} = \dfrac{[\mathrm{A}]^2}{[\mathrm{A_2}]}$

$$[\mathrm{A}]^2 = \mathrm{K}[\mathrm{A_2}]$$

$$[\mathrm{A}] = \mathrm{K}^{1/2}\,[\mathrm{A_2}]^{1/2} \qquad \text{...}(ii)$$

Substituting the value of [A] from equation (*ii*) in equation (*i*)

$$r = k\,.\,\mathrm{K}^{1/2}\,[\mathrm{A}]^{1/2}\,[\mathrm{B_2}]$$

$$= k'\,[\mathrm{A_2}]^{1/2}\,[\mathrm{B_2}]$$

$\therefore$ The order of the reaction is $1\frac{1}{2}$.

10. (*b*) $r_1 = k(a)(b)^{1/2}$

When conc. of both the reactants is increased four times

$$r_2 = k(4a)(4b)^{1/2} = 8k(a(b))^{1/2} = 8r_1.$$

12. (*b*) At equilibrium, the concentration of A falls from 0.6 mol $\mathrm{L^{-1}}$ to 0.3 mol $\mathrm{L^{-1}}$ and the concentration of B rises from zero to 0.6 mol $\mathrm{L^{-1}}$. Thus, 0.3 mol $\mathrm{L^{-1}}$ of A on decomposition give 0.6 mol $\mathrm{L^{-1}}$ of B. Therefore, **n = 2.**

13. (*b*) $k = 1 \times 10^{-2}\ \mathrm{mol\ L^{-1}\ s^{-1}}$

When 90% reaction is complete, [A] = 0.1 mol $\mathrm{L^{-1}}$ and [B] = 0.1 mol $\mathrm{L^{-1}}$.

$$\text{Rate} = k\,[\mathrm{A}][\mathrm{B}] = 1 \times 10^{-2}\,(0.1)\,(0.1)$$

$$= \mathbf{1 \times 10^{-4}\ mol\ L^{-1}\ s^{-1}}.$$

14. (*a*) Here, partial pressure is to proportional to concentration.

15. (*c*) $k = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{10}\ \mathrm{min^{-1}}$

$$t = \frac{2.303}{k}\log\frac{100}{10} = \frac{2.303}{0.0693}\log 10 = \mathbf{33\ min.}$$

16. (*d*) In first two hours the conc. falls by 2 mol $\mathrm{L^{-1}}$. In the next four hours the conc. falls by 4 mol $\mathrm{L^{-1}}$. Thus, the reaction is proceeding at constant speed that is independent of the initial conc. of the reactant. Thus, the order of the reaction is zero.

17. (*a*) In first case conc. is reduced to half in 1 hour. In second case the conc. is reduced to one-fourth in two hours (*i.e.*, 2 half lives). This indicates that the half-life in the present reaction is independent of the initial conc. of the reactants. This is true for first order reactions.

18. (*a*) The per cent increase in the rate for a given rise in temperature is more at lower temperature because at low temperature a large fraction of molecules does not have energy sufficient to cross over the barrier.

19. (*c*) For a given increase in temperature, the per cent increase in the rate of reaction is more in case of reaction having higher activation energy.

20. (*d*) Suppose order of the reaction is n

$$t_{1/2} \propto [\mathrm{CH_3CHO}]^{1-n}$$

$$\frac{410}{880} = \left(\frac{364}{170}\right)^{1-n}$$

$$\log\frac{410}{880} = (1-n)\log\left(\frac{364}{170}\right)$$

$$n = 2.$$

21. (*d*) $\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$

For E_a to be same k_2/k_1 should be equal.

22. (*c*) After long time whole of A would change into B and C. On decomposition one mole of A changes into three moles of B and C. Therefore,

Initial pressure of A $= \frac{270}{3} = 90$ mm.

Suppose after 10 minutes pressure of A falls by x mm. In that case pressure of B and C would be $2x$ and x mm respectively.

Total pressure $= (90 - x) + 2x + x = (90 + 2x)$ mm

$$90 + 2x = 176 \text{ mm}$$

$$2x = (176 - 90) \text{ mm}$$

$$x = 43 \text{ mm}$$

Pressure of A after 10 minutes

$= (90 - x)$ mm $= (90 - 43) =$ **47 mm.**

23. (*c*) For first order reaction $t_{1/2}$ is independent of initial concentration of the reactants. Hence, slope of a graph log $t_{1/2}$ *vs.* log $[A]_0$ would be zero.

24. (*b*) $t = \frac{2.303}{k} = \log\frac{[A]_0}{[A]}$

$$\frac{kt}{2.303} = \log[A]_0 - \log[A]$$

$$\log[A] = -\left(\frac{k}{2.303}\right)t + \log[A]_0$$

$$y = mx + c$$

$$\text{slope, } m = -\left(\frac{k}{2.303}\right).$$

25. (*b*) $t_{3/4} = 2\,t_{1/2} = \frac{0.693 \times 2}{k}.$

26. (*c*) $t_{3/4} = 2\,t_{1/2}.$

27. (*d*) $+\frac{d[\mathrm{NH_3}]}{dt} = x \text{ mol L}^{-1}\text{ s}^{-1}$

$$\frac{1}{2}\frac{d[\mathrm{NH_3}]}{dt} = -\frac{1}{3}\frac{d[\mathrm{H_2}]}{dt}$$

$$-\frac{d[\mathrm{H_2}]}{dt} = \frac{3}{2}\frac{d[\mathrm{NH_3}]}{dt} = \frac{3}{2}x \text{ mol L}^{-1}\text{ s}^{-1}.$$

28. (*c*) From I, $K = \frac{[\mathrm{NOBr_2}]}{[\mathrm{NO}][\mathrm{Br_2}]}$, $[\mathrm{NOBr_2}] = K[\mathrm{NO}]\,[\mathrm{Br_2}]$

From II,

$$\text{rate} = k\,[\mathrm{NOBr_2}]\,[\mathrm{NO}]$$

$$= k\,.\,K\,[\mathrm{NO}]\,[\mathrm{Br_2}]\,[\mathrm{NO}]$$

$$= k'\,[\mathrm{NO}]^2\,[\mathrm{Br_2}]$$

Overall order of the reaction is (2 + 1) = 3.

29. (*a*) 4 hrs. = 4 half lives

$$1 \xrightarrow{t_{1/2}} \frac{1}{2} \xrightarrow{t_{1/2}} \frac{1}{4} \xrightarrow{t_{1/2}} \frac{1}{8} \xrightarrow{t_{1/2}} \frac{1}{16}$$

Fraction left after 4 half lives $= \frac{1}{16}$ or $\left(\frac{1}{2}\right)^4$

Fraction reacted in 4 half lives $= 1 - \frac{1}{16} = \frac{15}{16}.$

31. (*b*) In the first hour fraction reacted $= \frac{1}{3}$

After the first hour fraction left $= \frac{2}{3}$

In the second hour one-third of $\frac{2}{3}$ reacts.

33. (*b*) For zero order reaction, $t_{1/2} \propto [A].$

34. (*d*) $k = A\,e^{-E_a/RT}$

$$\ln k = \ln A - \left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right).$$

36. (*b*) By reducing the volume to one-fourth, the concentrations of both A and B would become 4 times.

37. (*b*) $-\frac{d[A]}{dt} = k\,[A]_0, \quad -d\,[A] = kdt$

Integrating from $t = 0$ to $t = t$

$$[A]_0 - [A] = kt.$$

38. (*b*) Rate constant is independent of the conc. of the reactants.

39. (*d*) Rate $= k_1[A]^2$

$$k = \frac{\text{Rate}}{[\text{A}]^2} = \frac{8 \times 10^{-4}}{(2)^2} = 2 \times 10^{-4}\ \text{L mol}^{-1}\ \text{s}^{-1}.$$

43. (*c*) $\Delta E = E_{a(f)} - E_{a(b)} = 30 - 50 = -20$ kJ.

45. (*b*) Because its apparent molarity is more than three.

48. (*c*) From the dimensions of rate constant it is clear that the reaction is a zero order reaction. It would proceed at constant rate of 10^{-2} mol $\text{L}^{-1}\ \text{s}^{-1}$. In 10 minutes (600 seconds) the amount of A reacted would be

$$= 10^{-2} \times 600\ \text{mol L}^{-1} = 6\ \text{mol L}^{-1}$$

No. of moles of A left unreacted = 10 – 6 = 4 moles.

52. (*c*) Higher the order of the reaction, sharper is the decrease in the rate of the reaction with progress of the reaction (due to fall in conc.).

53. (*b*) $-\frac{1}{4}\frac{d[\text{NH}_3]}{dt} = \frac{1}{6}\frac{d[\text{H}_2\text{O}]}{dt}$

$$\frac{d[\text{H}_2\text{O}]}{dt} = -\frac{6}{4}\frac{d[\text{NH}_3]}{dt} = \frac{6}{4} \times 0.02$$

$$= 0.03\ \text{mol L}^{-1}\ \text{min}^{-1}.$$

54. (*d*) This is an ionic reaction.

55. (*b*) $r_1 = k(a)^{3/2}\,(b)^{-1/2}$

$$r_2 = k(4a)^{3/2}\,(4b)^{-1/2}$$

$$\frac{r_2}{r_1} = (4)^{3/2}\,(4)^{-1/2} = 4.$$

56. (*a*) Here, water is present in excess, so its conc. does not affect the rate of the reaction as the reaction progresses.

58. (*d*) *k* (rate constant) increases with increase in temperature whereas K (equilibrium constant) increases for endothermic reactions and decreases for exothermic reactions.

59. (*b*) $r_1 = k(a)^n\,(b)^m$ ...(*i*)

$r_2 = k(2a)^n\,(b)^m$ ...(*ii*)

$r_3 = k(4a)^n\,(4b)^m$ ...(*iii*)

From (*i*) and (*ii*)

$$\frac{r_2}{r_1} = 2 = \frac{(2a)^n}{(a)^n} = (2)^n \quad \text{or} \quad \boldsymbol{n = 1}$$

From (*ii*) and (*iii*)

$$\frac{r_3}{r_1} = 4 = (4)^n\,(4)^m$$

But $n = 1$

$$4 = (4)\,(4)^m \quad \text{or} \quad m = 0.$$

60. (*b*) $k = \text{A}e^{-\text{E}_a/\text{RT}}$ or $\text{A} = k\,e^{\text{E}_a/\text{RT}}$.

61. (*b*) For a first order reaction $t_{1/2}$ is independent of initial conc.

67. (*c*) $-\frac{d[\text{A}]}{dt} = k[\text{A}]^0$

$$-d[\text{A}] = k\,dt$$

Integrating from $[\text{A}]_0$ to [A] and $t = 0$ to $t = t$

$$[\text{A}]_0 - [\text{A}] = kt.$$

69. (*d*) Conc. of both the reactants after dilution would be reduced to one-half of the initial conc.

70. (*c*) By observing the dimensions of *k*, we come to know that the given reaction is of second order.

$$\therefore \quad r = k[\text{A}]^2 = 1 \times 10^{-2} \times (2)^2$$

$$= \mathbf{4 \times 10^{-2}\ mol\ L^{-1}\ s^{-1}}.$$

71. (*c*) For third order reaction *k* has units $\text{L}^2\ \text{mol}^{-2}\ \text{s}^{-1}$.

72. (*b*) Rate = *k*[A][B]

When concentrations of both A and B become half, the rate of reaction would become one-fourth of the initial rate.

73. (*d*) $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{100} = 6.93 \times 10^{-3}\ \text{min}^{-1}$

$$t = \frac{2.303}{k}\log\frac{[\text{A}]_0}{[\text{A}]} = \frac{2.303}{6.93 \times 10^{-3}}\log\frac{100}{10}$$

= 332 min.

74. (*b*) Starting with 4 mol L^{-1}, the conc. was reduced to half in 1 hour whereas starting with 2 mol L^{-1} the conc. was reduced to half in 0.5 hour. Thus, $t_{1/2}$ here is directly proportional to the initial conc. of the reactants. Hence, order of the reaction is zero.

75. (*d*) Rate would increase $(2)^{1/2}$ or $\sqrt{2}$ times.

78. (*c*) Rate = *k* $[\text{A}]^2$

$$k = \frac{\text{Rate}}{[\text{A}]^2} = \frac{1 \times 10^{-2}}{(0.1)^2} = \mathbf{1.0\ L\ mol^{-1}\ s^{-1}}.$$

79. (*c*) A zero order reaction takes place at constant rate and hence conc. of A decreases with time at constant rate.

81. (*b*) $1 \xrightarrow[\text{1 hr}]{t_{1/2}} \frac{1}{2} \xrightarrow[\text{1 hr}]{t_{1/2}} \frac{1}{4}$

In the second hour the fraction of initial conc. that reacts is $\left(\frac{1}{2} - \frac{1}{4}\right) = \frac{1}{4}$.

85. (*a*) rate = *k*[A]

The rate *vs.* [A] graph would have slope equal to *k*.

9 SURFACES AND CATALYSIS

Important Terms, Facts and Formulae

ADSORPTION

- The phenomenon of existence of a substance in higher concentration at the surface of some other substance than in the adjoining bulk phases is known as **adsorption.**
- **Absorption.** In absorption molecules of one substance are uniformly distributed in the bulk of the other.
- Simultaneous occurrence of adsorption and absorption is referred to as **sorption.**
- **Types of Adsorption.** Adsorption is of two types : (*i*) **Physisorption** (*ii*) **Chemisorption.**
- For adsorption **ΔH, ΔS and** ΔG all are negative.

ADSORPTION OF GASES ON SOLIDS

- Easily liquefiable gases such as NH_3, HCl, CO_2, SO_2, CH_4 etc. are adsorbed to greater extent than the permanent gases such as H_2, O_2, N_2, etc.
- Metals such as Pt, Pd and Ni are good adsorbents for permanent gases whereas activated charcoal is good adsorbent for easily liquefiable gases.
- Extent of adsorption increases with increase in pressure of the gas above the adsorbent.
- **Adsorption isotherm.** A graph between extent of adsorption (x/m) and the pressure (p) of the gas at constant temperature is called adsorption isotherm.
- **Freundlich Adsorption Isotherm**

  Mathematically, the freundlich isotherm is given by the expression

  $$\boxed{\log\left(\frac{x}{m}\right) = \log k + \frac{1}{n}\log p}$$

  A graph of $\log\left(\frac{x}{m}\right)$ *versus* $\log p$ has slope equal to $\frac{1}{n}$.

- **Adsorption Isobars.** A graph between extent of adsorption $\left(\frac{x}{m}\right)$ and temperature at constant pressure is known as adsorption isobar.

ADSORPTION IN SOLUTIONS

- The extent of adsorption is related to the concentration of adsorbate in the solution by the relation

$$\frac{x}{m} = kC^{1/n}$$

$$\log\frac{x}{m} = \log k + \frac{1}{n}\log C$$

APPLICATIONS OF ADSORPTION

Some of its applications are given below :

- Activated charcoal is used in *gas masks* to remove poisonous gases such as CH_4, CO, etc.
- Animal charcoal is used as *decolorizer* in the manufacture of sugar.
- Silica is used for removing moisture and *controlling humidity.*
- *Chromatographic purification* of compounds is based upon phenomenon of adsorption.
- In *volumetric analysis* adsorption indicators such as fluorescence are used.
- The ion exchange resins used *for removing hard- ness for water* are also based upon adsorption.

COLLOIDAL STATE

- When size of solute particles is in the range 1—100 nm, the solute is said to be in **colloidal state.**
- In **crystalloids,** size of solute particles is less than 1 nm.
- In **suspensions** size of particles is greater than 100 nm.
- A colloidal solution is **heterogeneous** and consists of at least two phases : the **disperse phase** and **dispersion medium.**

CLASSIFICATION OF COLLOIDAL SOLUTIONS

1. **Classification Based on Physical states of Disperse Phase and Dispersion Medium**

   Depending upon physical state of disperse phase (solid, liquid or gas) and dispersion medium (solid, liquid or gas) there are eight types of colloidal solutions.

2. **Classification Based on Interaction Between Disperse Phase and Dispersion Medium**

   Lyophilic Sol. In this type of sol there is great affinity between disperse phase and dispersion medium.

   Lyophobic Sol. In this type of sol there is little affinity between disperse phase and dispersion medium.

3. **Classification based on Nature of Colloidal Particles**

(*i*) **Multimolecular colloids.** *Colloidal particles are aggregates of atoms or small molecules with molecular size less than 1 nm.*

(*ii*) **Macromolecular colloids.** *Colloidal particles are themselves large molecules having colloidal dimensions.*

(*iii*) **Associated colloids.** These are formed by the aggregation of particles in solution. The aggregated particles are called **micelles.** The formation of micelles takes place above certain minimum concentration called **Critical Micellization Concentration (CMC).**

PREPARATION OF COLLOIDAL SOLUTIONS

A. CHEMICAL METHODS

- **Double Decomposition :**

$$As_2O_3 + 3H_2S \longrightarrow \underset{\substack{\text{Arsenious}\\\text{sulphide sol.}}}{\mathbf{As_2S_3}} + 3H_2O$$

$$AgNO_3 + NaCl \longrightarrow \underset{\substack{\text{Silver chloride}\\\text{sol.}}}{\mathbf{AgCl}} + NaNO_3$$

- **Oxidation :**

$$SO_2 + H_2S \longrightarrow \mathbf{3S} + 2H_2O$$

$$Br_2 + H_2S \longrightarrow 2HBr + \underset{\text{Sulphur sol}}{\mathbf{S}}$$

- **Reduction :**

$$2AuCl_3 + 3SnCl_2 \longrightarrow \underset{\text{Gold sol.}}{\mathbf{2Au}} + 3SnCl_4$$

- **Hydrolysis :**

$$FeCl_3 + 3H_2O \longrightarrow \underset{\substack{\text{Ferric}\\\text{hydroxide sol.}}}{\mathbf{Fe(OH)_3}} + 3HCl$$

B. PHYSICAL METHODS

- **Exchange of solvent.** Phosphorus and sulphur sol can be prepared by this method.
- **Mechanical Dispersion**
- **Bredig's Arc Method.** Metallic sols such as that of platinum, gold and silver can be prepared by this method.
- **Peptisation.** It is *the process of converting a precipitate into colloidal solution by shaking it with dispersion medium in the presence of small amount of electrolyte.*
- Peptisation can also be achieved by adding organic solvents. For example, colloidal solution of cellulose nitrate is obtained by adding ethyl alcohol to it. The colloidal solution is known as **colloidion.**

PROPERTIES OF COLLOIDAL SOLUTIONS

- Colloidal solutions are **heterogeneous** in nature.
- Colloidal solutions pass through ordinary filter paper.
- They possess low values of colligative properties due to their large average molecular mass.
- They exhibit **Tyndal Effect** due to scattering of light.
- Colloidal particles possess zig-zag motion, known as **Brownian movement,** due to impacts of molecules of the dispersion medium against them.
- Colloidal particles settle down very slowly under the influence of gravity.
- **Electrophoresis.** Colloidal particles move either towards cathode or towards anode under the influence of applied electric field.

STABILITY OF COLLOIDS

- Lyophilic colloids are stabilized due to their extensive solvation and also due to charge on their particles.
- Lyophobic colloids are stabilized due to charge on the colloidal particles which prevents them from uniting.
- **Positively Charged Sols.** $Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$, basic dyes such as methylene blue.
- **Negatively Charged Sols.** As_2S_3, CdS, metallic sols such as Pt, Gold and Ag, Blood, Starch, Clay and Acidic dyes such as congo red.

COAGULATION OF COLLOIDS

- **Coagulation or Flocculation** *is the precipitation of a colloid through induced aggregation of its particles.*
- **Coagulation Value.** The minimum concentration of the electrolyte in millimoles per litre of the solution, required to cause coagulation of a particular sol is called **coagulation value or flocculation value** of the electrolyte for the sol.
- An electrolyte having greater coagulation value has smaller coagulating power.
- **Hardy Schulze Rules**

  (*i*) *The ions carrying charge opposite to that of sol particles are effective in causing the coagulation of the sol.*

(*ii*) *Coagulating power of an electrolyte is directly proportional to the valency of the active ions, i.e., ions causing coagulation.*

GOLD NUMBER

- *The number of milligrams of the protective colloid which just prevent the coagulation of 10 ml of standard red gold sol when 1 mol of 10% solution of sodium chloride is added to it.*
- Smaller the gold number of the protective colloid greater is its protecting power.

GELS

- A colloidal system having solid as dispersion medium and liquid as disperse phase is known as **gel.** Gels have jelly like appearance.
- **Synerisis.** When gels are allowed to stand for long time, they give out small quantity of trapped liquid which accumulates on its surface. This phenomenon is known as **synerisis** or **weeping of gel.**
- **Thixotropy.** Some gels are semi-solid when at rest but change to liquid to sol on agitation. This reversible sol-gel transformation is known as **thixotropy.**
- **Elastic and Non-elastic gels.** Elastic gels are those gels which change to solid mass after loosing water completely and can be regenerated by addition of water.

EMULSIONS

- **Emulsions** are colloidal solutions in which disperse phase as well as dispersion medium are liquids.
- **Types of Emulsions**
  (*i*) *Oil in water.* For example, milk, vanishing cream.
  (*ii*) *Water in oil.* For example, cold cream, cod liver oil.
- Emulsions can be stabilized by adding emulsifying agents such as soap, detergents, proteins, gum, gelatin, etc.
- **Demulsification.** The decomposition of an emulsion into its constituent liquids is called demulsification.

SOME MISCELLANEOUS IMPORTANT POINTS

- **Cottrell smoke precipitator** works on the principle of neutralization of charge on colloidal particles.
- **Formation of delta** is due to coagulation of colloidal dust particles present in river water by action of salts present in sea water.
- **Blue colour of the sky** is due to scattering of blue light by the colloidal dust or ice particles present in the atmosphere.
- Lyophilic sols have less surface tension and higher viscosity than pure dispersion medium.
- Lyophobic sols have nearly same surface tension and viscosity as that of pure dispersion medium.
- **Isoelectric point.** The pH at which a hydrophilic colloid has the lowest charge is known as its isoelectric point. The colloid has minimum stability at isoelectric point.
- Styptic action of alum and $FeCl_3$ solutions for stopping bleeding is due to the coagulation of blood by these electrolytes.
- **Heterogeneous catalysis** can be explained on the basis of phenomenon of adsorption.
- The pore size in zeolites is generally in the range of 260-740 pm.
- Zeolite catalyst, ZSM-5 is used to convert alcohols into hydrocarbons.

QUESTION BANK

Level I

Choose the correct answer from the four alternatives given in each of the following questions :

1. In adsorption of methane on charcoal, charcoal is

(*a*) Adsorbate (*b*) Adsorbent

(*c*) Absorbate (*d*) Absorbent.

2. Size of colloidal particles ranges between

(*a*) 1 nm to 100 nm (*b*) 1 nm to 1000 nm

(*c*) 10 nm to 1000 nm (*d*) 100 nm to 1000 nm.

3. Which of the following is a homogeneous system ?

(*a*) Muddy water (*b*) Vanishing cream

(*c*) Cod liver oil (*d*) Sugar solution.

4. Tyndall effect in colloidal solution is due to

(*a*) Scattering of light

(*b*) Reflection of light

(*c*) Absorption of light

(*d*) Presence of electrically charged particles.

5. Butter is a colloid containing

(*a*) Fat dispersed in water (*b*) Fat dispersed in oil

(*c*) Water dispersed in fat (*d*) None of these.

6. Which of the following will have the least coagulating power for arsenious sulphide sol ?

(*a*) Na^+ (*b*) Mg^{2+}

(*c*) Al^{3+} (*d*) Ca^{2+}.

7. Which of the following is not true for physisorption ?

(*a*) It is reversible

(*b*) It occurs in the form of multimolecular layers

(*c*) It needs activation energy

(*d*) It increases with increase in pressure.

8. Colloidal particles in soap sol carry

(*a*) Negative charge

(*b*) Positive charge

(*c*) No charge

(*d*) Either positive or negative charge.

9. Which of the following is not used for purification of colloidal solutions ?

(*a*) Dialysis (*b*) Ultra-centrifugation

(*c*) Filteration (*d*) Electrodialysis.

10. A colloidal solution of a solid as dispersed phase and liquid as dispersion medium is known as

(*a*) Gel (*b*) Sol

(*c*) Solid foam (*d*) Emulsion.

11. Which of the following electrolytes will have maximum flocculation value for $Fe(OH)_3$ sol ?

(*a*) NaCl (*b*) Na_2S

(*c*) $(NH_4)_3PO_4$ (*d*) K_2SO_4.

12. Protecting power of a lyophilic sol is expressed in terms of

(*a*) Coagulation value (*b*) Gold number

(*c*) Both of the above (*d*) None of these.

13. Hydrophillic sols are stable due to

(*a*) Small size of the particle

(*b*) Large size of the particle

(*c*) Charge on the particle

(*d*) Attractive interaction between colloidal particles and the dispersion medium.

14. For the process of adsorption, ΔH is

(*a*) Positive (*b*) Negative

(*c*) Zero (*d*) May be positive or negative.

15. Bredig's arc method for the preparation of metallic sols involves

(*a*) Dispersion

(*b*) Condensation

(*c*) Dispersion as well as condensation

(*d*) Neither dispersion nor condensation.

16. Gold number is minimum for

(*a*) Starch (*b*) Gelatin

(*c*) Gum arabic (*d*) Albumin.

17. Fog is an example of

(*a*) Foam (*b*) Aerosol

(*c*) Gel (*d*) Emulsion.

18. Lyophilic sols have ...... between disperse phase and dispersion.

(*a*) strong attractive interaction

(*b*) little attractive interaction

(*c*) repulsive interaction

(*d*) None of these.

19. In which of the following respects the lyophilic sols do not differ from lyophobic sols ?

(*a*) Stability

(*b*) Reversibility

(*c*) Particle size

(*d*) Behaviour towards dispersion medium.

20. When a river enters the sea, a delta is formed. Formation of delta is due to

(*a*) Peptization
(*b*) Coagulation
(*c*) Emulsification
(*d*) Dialysis.

21. The lyophilic colloid among the following is

(*a*) Blood
(*b*) Gold sol
(*c*) $Fe(OH)_3$ sol
(*d*) Starch.

22. During electrophoresis of a colloidal solution, colloidal particles move towards

(*a*) Anode

(*b*) Cathode

(*c*) Both cathode as well as anode

(*d*) Either cathode or anode.

23. Gelatin is mostly used in making ice-cream in order to

(*a*) prevent forming the colloidal sol

(*b*) enrich the fragrance

(*c*) prevent crystallisation and stabilise the mix

(*d*) modify the taste.

24. Which of the following will have the highest coagulating power for As_2S_3 colloid ?

(*a*) PO_4^{3-}
(*b*) SO_4^{2-}
(*c*) Al^{3+}
(*d*) Na^+.

25. Which of the following metallic sols cannot be prepared by Bredig's arc method ?

(*a*) Gold
(*b*) Silver
(*c*) Platinum
(*d*) Sodium.

26. A graph of extent of adsorption *versus* pressure at constant temperature is called

(*a*) Adsorption isobar
(*b*) Adsorption isotherm
(*c*) Adsorption isostere
(*d*) None of these.

27. Activated charcoal is good adsorbent for

(*a*) O_2
(*b*) N_2
(*c*) H_2
(*d*) CH_4.

28. For physisorption, heat of adsorption is generally in the range

(*a*) 20-40 kJ
(*b*) 40-60 kJ
(*c*) 100-150 kJ
(*d*) 300-400 kJ.

29. Which of the following statements is not true for lyophilic sols ?

(*a*) It is stable

(*b*) It can be prepared in high concentration

(*c*) Its colloidal particles are highly solvated

(*d*) It is irreversible.

30. For adsorption of a gas on a solid adsorbent which of the following is positive ?

(*a*) ΔH
(*b*) ΔS
(*c*) Both of the above
(*d*) None of these.

31. Brownian movement is a ...... property of colloidal solutions.

(*a*) Optical
(*b*) Mechanical
(*c*) Colligative
(*d*) Electrical.

32. Which of the following statements is true for chemisorption ?

(*a*) It is reversible in nature

(*b*) It is not specific in nature

(*c*) It exists in the form of monomolecular layer

(*d*) It occurs at low temperature.

33. Which of the following is an example of associated colloid ?

(*a*) Polyethylene sol
(*b*) Rubber sol
(*c*) PVC sol
(*d*) Soap sol.

34. A colloidal solution may be coagulated by

(*a*) Adding electrolyte

(*b*) Heating

(*c*) Adding oppositely charged sol

(*d*) All of the above.

35. Which of the following statements is not true for physisorption ?

(*a*) Extent of adsorption increases with increase in temperature

(*b*) Heat of adsorption is generally between 20-40 kJ/mole

(*c*) It is not specific

(*d*) It undergoes desorption easily.

36. Which of the following is true for a Gel ?

(*a*) Solid as disperse phase

(*b*) Liquid as dispersion medium

(*c*) Both of the above

(*d*) None of these.

37. The average molecular mass of colloidal particles can be determined by study of

(*a*) Elevation in boiling point

(*b*) Osmotic pressure

(*c*) Tyndall effect

(*d*) Lowering of vapour pressure.

38. Which of the following is most favourable for van der Waal's adsorption ?

(*a*) High pressure and high temperature

(*b*) Low pressure and low temperature

(*c*) Low pressure and high temperature

(*d*) High pressure and low temperature.

39. Palladium is a good adsorbent for

(*a*) CO_2 (*b*) SO_2

(*c*) CO (*d*) H_2.

40. Surface tension of a lyophilic sol is generally ...... to/than that of the medium.

(*a*) equal (*b*) less

(*c*) more (*d*) twice.

41. Migration of colloidal particles under the effect of an electric field is known as

(*a*) Electro-osmosis (*b*) Electro-phoresis

(*c*) Electro-dialysis (*d*) Dialysis.

42. Which adsorption does not take place at very low temperature ?

(*a*) Physisorption (*b*) Chemisorption

(*c*) Both of the above (*d*) None of these.

43. The colour of standard gold sol is

(*a*) blue (*b*) red

(*c*) purple (*d*) green.

44. The emulsifying agent in milk is

(*a*) Casein (*b*) Lactic acid

(*c*) Lactose (*d*) Citric acid.

45. Which one of the following is not a property of hydrophilic sols ?

(*a*) High concentration of dispersed phase can be easily attained

(*b*) These are irrerersible in nature

(*c*) Viscosity and surface tension are about the same as for water

(*d*) The charge of the particle depends on the pH value of the medium ; it may be positive, negative or even zero.

46. In the preparation of AgI sol, excess of KI solution is added to $AgNO_3$ solution. The charge on the colloidal particles would be

(*a*) Positive (*b*) Negative

(*c*) No charge (*d*) Unpredictable.

47. Gold number gives

(*a*) The amount of gold present in the colloid

(*b*) The amount of gold required to break the colloid

(*c*) The amount of gold required to protect the colloid

(*d*) None of these.

48. Difference between colloids and crystalloids is of

(*a*) Charge (*b*) Particle size

(*c*) Shape of the particle (*d*) Solubility.

49. Which one of the following will have the highest coagulating power for $Fe(OH)_3$ sol ?

(*a*) PO_4^{3-} (*b*) SO_4^{2-}

(*c*) Al^{3+} (*d*) Na^+.

50. The Brownian motion is due to

(*a*) Temperature fluctuation within the liquid phase

(*b*) Attraction and repulsion between charges on the colloidal particles

(*c*) Impact of molecules of the dispersion medium on the colloidal particles

(*d*) Convective currents.

51. Silver iodide is used for producing artificial rain because AgI

(*a*) is easy to spray at high altitudes

(*b*) is insoluble in water

(*c*) is a cheap chemical

(*d*) has crystal structure similar to ice.

52. When a colloidal solution is observed under an ultramicroscope, we can see

(*a*) Light scattered by colloidal particles

(*b*) Size of the particle

(*c*) Shape of the particle

(*d*) Relative size.

53. A negatively charged suspension of clay in water will need for precipitation the minimum amount of

(*a*) Aluminium chloride (*b*) Potassium sulphate

(*c*) Sodium hydroxide (*d*) Hydrochloric acid.

54. Which one of the following substances gives a positively charged sol ?

(*a*) Gold (*b*) A metal sulphide

(*c*) Ferric hydroxide (*d*) An acidic dye.

55. Flocculation value is expressed in terms of

(*a*) millimoles of electrolyte per litre of solution

(*b*) moles of electrolyte per litre of solution

(*c*) grams of electrolyte per litre of solution

(*d*) millimoles of electrolyte per millilitre of solution.

56. On adding one ml solution of 10% NaCl to 10 ml gold sol in the presence of 0.25 gm of starch, the coagulation is just prevented. Starch has the gold number

(*a*) 0.025 (*b*) 0.25

(*c*) 2.5 (*d*) 250.

57. An arsenious sulphide sol carries a negative charge. The maximum precipitating power for this sol is possessed by

(*a*) K_2SO_4 (*b*) $CaCl_2$

(*c*) Na_3PO_4 (*d*) $Al_2(SO_4)_3$.

58. Which of the following colloidal solutions do not contain negatively charged colloidal particles ?

(*a*) $Fe(OH)_3$ sol (*b*) As_2S_3 sol

(*c*) Blood (*d*) Gold sol.

59. Which of the following are macromolecular colloids ?

(*a*) Soap sol (*b*) Starch sol

(*c*) Sulphide sol (*d*) Gold sol.

60. Colloidal solutions can be purified by

(*a*) Filteration (*b*) Dialysis

(*c*) Electrophoresis (*d*) Peptisation

61. Which of the following are examples of aerosols ?

(*a*) Whipped cream (*b*) Tooth paste

(*c*) Fog (*d*) Soap lather.

62. Lyophilic sols among the following are

(*a*) Ferric hydroxide sol. (*b*) Blood

(*c*) Starch (*d*) Sulphur.

63. Which of the following statements are true ?

(*a*) Soap solution contains ionic micelles as the colloidal particles

(*b*) A water in oil emulsion easily spreads over surface of water

(*c*) Chemisorption is non-specific

(*d*) Chemisorption occurs in the form of multimolecular layers.

64. Which of the following statements are true for physisorption ?

(*a*) Extent of adsorption increases with increase in pressure.

(*b*) It needs activation energy.

(*c*) It is an endothermic process.

(*d*) It occurs at high temperature.

65. Which of the following will not cause the precipitation of a lyophobic colloidal solution ?

(*a*) adding lyophilic colloid

(*b*) heating

(*c*) adding electrolyte

(*d*) adding oppositely charged colloid.

66. For adsorption of a gas on solid adsorbent

(*a*) ΔH is positive (*b*) ΔS is positive

(*c*) ΔG is negative (*d*) ΔE is positive.

67. Which of the following is a hydrophobic sols ?

(*a*) Protein sol (*b*) Starch sol

(*c*) Gum sol (*d*) $Fe(OH)_3$ sol.

68. Which of the following is a hydrophilic colloidal sol ?

(*a*) Barium sulphate sol

(*b*) Arsenious sulphide sol

(*c*) Gum sol

(*d*) Silver iodide sol.

69. The colloidal sols are not purified by

(*a*) peptisation (*b*) Electro dialysis

(*c*) dialysis (*d*) Ultra centrifugation.

70. Point out the false statement

(*a*) Colloidal sols are homogeneous

(*b*) Colloids carry + ve or – ve charge

(*c*) Colloids show Tyndall effect

(*d*) The size range of colloidal particles is 10 – 1000 Å.

71. Which of the following is hydrophobic sol ?

(*a*) Starch solution (*b*) Gum solution

(*c*) Protein solution (*d*) Arsenious sulphide solution.

72. Which of the following electrolytes is least effective in causing flocculation of ferric hydroxide sol ?

(*a*) $K_3[Fe(CN)_6]$ (*b*) K_2CrO_4

(*c*) KBr (*d*) K_2SO_4.

73. Which one of the following is not a colloid ?

(*a*) Milk (*b*) Blood

(*c*) Ice-cream (*d*) Urea solution.

74. Smoke is an example of

(*a*) Gas dispersed in liquid
(*b*) Gas dispersed in solid
(*c*) Solid dispersed in gas
(*d*) Solid dispersed in solid.

75. Surface tension of lyophilic sols is

(*a*) Lower than water
(*b*) More than water
(*c*) Equal to water
(*d*) None of these.

76. According to Langmuir adsorption isotherm, the amount of gas adsorbed at very high pressures

(*a*) reaches a constant limiting value
(*b*) goes on increasing with pressure
(*c*) goes in decreasing with pressure
(*d*) increases first and decreases later with pressure.

77. A colloidal system in which gas bubbles are dispersed in liquid is known as

(*a*) Foam
(*b*) Sol
(*c*) Aerosol
(*d*) Emulsion.

78. The colour of the colloidal particles of gold obtained by different methods differ because of

(*a*) variable valency of gold
(*b*) different concentration of gold particles
(*c*) different type of impurities
(*d*) different diameters of colloidal particles.

79. Which of the following is most effective in coagulating a ferric hydroxide sol ?

(*a*) KCl
(*b*) KNO_3
(*c*) K_2SO_4
(*d*) $K_3[Fe(CN)_6]$.

80. Which of the following statements is not correct ?

(*a*) Physical adsorption is due to van der Waal's forces
(*b*) Chemical adsorption decreases at high temperature and low pressure
(*c*) Physical adsorption is reversible
(*d*) Adsorption energy for a phyical adsorption is generally greater than that of chemical adsorption.

QUESTION BANK

Level II

Choose the correct answer from the four alternatives given in each of the following questions :

1. In adsorption of acetic acid on charcoal, the acetic acid is

(*a*) Absorbent
(*b*) Adsorbent
(*c*) Absorbate
(*d*) Adsorbate.

2. The size of the colloidal particles ranges between

(*a*) 10^{-2} to 10^{-3} cm
(*b*) 10^{-3} to 10^{-5} cm
(*c*) 10^{-5} to 10^{-7} cm
(*d*) 10^{-7} to 10^{-9} cm.

3. When beam of light is passed through a colloidal solution ?

(*a*) It passes through as such
(*b*) It is reflected
(*c*) It is scattered
(*d*) It is completely absorbed.

4. The coagulating power of an electrolyte for arsenius sulphide sol decreases in the order

(*a*) Na^+, Al^{3+}, Ba^{2+}
(*b*) $PO_4^{3-}, SO_4^{2-}, Cl^-$
(*c*) Al^{3+}, Ba^{2+}, Na^+
(*d*) $Cl^-, SO_4^{2-}, PO_4^{3-}$.

5. Colloidal solutions are classified on the basis of

(*a*) Molecular size
(*b*) Size of colloidal particles
(*c*) Organic or inorganic
(*d*) Surface tension.

6. The best coagulant for the precipitation of $Fe(OH)_3$ is

(*a*) Na_3PO_4
(*b*) $NaNO_3$
(*c*) Na_2SO_4
(*d*) NaCl.

7. Colloidal solutions are purified by all except

(*a*) Crystallisation
(*b*) Ultra filteration
(*c*) Ultra centrifugation
(*d*) Dialysis.

8. The colloidal solution of a solid as dispersed phase and a gas as the dispersion medium is known as

(*a*) Sol
(*b*) Gel
(*c*) Aerosol
(*d*) Solid foam.

9. Gel is a system of

(*a*) Solid disperse phase—liquid dispersion medium
(*b*) Solid disperse phase—solid dispersion medium
(*c*) Liquid disperse phase—solid dispersion medium
(*d*) Liquid disperse phase—liquid dispersion medium.

10. The difference between lyophilic and lyophobic colloids is in their

(*a*) Particle size

(*b*) Filterability

(*c*) Behaviour towards dispersion medium

(*d*) None of the above is correct.

11. Alum purifies muddy water by

(*a*) Dialysis (*b*) Coagulation

(*c*) Electrophoresis (*d*) Emulsification.

12. Detergent action of soaps is due to

(*a*) Coagulation (*b*) Emulsification properties

(*c*) Ionisation (*d*) High molecular mass.

13. Ferric chloride is applied to stop bleeding because

(*a*) Fe^{3+} ions coagulate blood which is a negatively charged sol

(*b*) Fe^{3+} ions coagulate blood which is a positively charged sol

(*c*) Cl^- ions coagulate blood which is a negatively charged sol.

(*d*) Cl^- ions coagulate blood which is a positively charged sol

14. Soap is a sodium salt of higher fatty acids. When soap is added to water, the colloidal solution obtained contains ...... colloidal particles.

(*a*) Positively charged (*b*) Negatively charged

(*c*) Neutral in nature (*d*) Not ionized.

15. The hydrophobic colloid among the following is

(*a*) Gelatin (*b*) Starch

(*c*) Sulphur (*d*) Albumin.

16. Cottrell precipitator works on the principle of

(*a*) Distribution law

(*b*) Addition of electrolytes

(*c*) Le-Chatelier's principle

(*d*) Neutralization of charge on colloids.

17. The electrical charge on colloidal particles is indicated by

(*a*) Brownian movement (*b*) Electrophoresis

(*c*) Ultramicroscope (*d*) Tyndall effect.

18. Gold number gives an indication of

(*a*) Protecting power of colloids

(*b*) Purity of gold sol

(*c*) Purity of any sol

(*d*) Strength of gold sol in moles/per litre.

19. Lyophobic colloids have

(*a*) Little interaction with the dispersion medium

(*b*) Strong interaction with the dispersion medium

(*c*) Medium interaction with the dispersion medium

(*d*) None of the above statements is true.

20. Which of the following electrolytes will have minimum coagulation value for aluminium hydroxide sol ?

(*a*) KCl (*b*) KNO_3

(*c*) K_2CrO_4 (*d*) $K_4[Fe(CN)_6]$.

21. Which of the following electrolytes will have maximum coagulating power for arsenious sulphide sol ?

(*a*) NaCl (*b*) $CaCl_2$

(*c*) $MgSO_4$ (*d*) $AlCl_3$.

22. Which of the following processes forms the basis of purification of muddy water by addition of alum ?

(*a*) Flocculation (*b*) Emulsification

(*c*) Peptisation (*d*) Dispersion.

23. In the preparation of AgI sol, the excess of $AgNO_3$ is added to potassium iodide solution. The particles of the sol will acquire

(*a*) negative charge (*b*) positive charge

(*c*) no charge (*d*) unpredictable.

24. Which of the following statements is not true ?

(*a*) Blood is a positively charged sol

(*b*) Soap solution contains ionic micelles as the colloidal particles

(*c*) An oil in water emulsion easily spreads over surface of water

(*d*) Colloidal particles have dimensions in the range 10^{-7} to 10^{-5} cm.

25. Which of the following electrolytes has maximum coagulating power for ferric hydroxide sol ?

(*a*) Na_3PO_4 (*b*) Na_2SO_4

(*c*) $MgCl_2$ (*d*) $AlCl_3$.

26. Which of the following is the correct expression for Freundlich adsorption isotherm ?

(*a*) $\frac{x}{m} = \log k + \frac{1}{n} \log p$ (*b*) $\log p = \log k + \log \frac{x}{m}$

(*c*) $\frac{x}{m} = kp^n$ (*d*) $\frac{x}{m} = kp^{1/n}$.

27. The colloidal system consisting of a liquid adsorbent and a gas adsorbate is termed as (*a*) Aerosol (*b*) Liquid aerosol

(*c*) Foam (*d*) Gel.

28. Which of the following statements is not true for a lyophobic sol ?

(*a*) It is irreversible

(*b*) It is less stable

(*c*) It carries charges

(*d*) Its colloidal particles are highly solvated.

29. Which of the following statements is not true for chemisorption ?

(*a*) It is highly specific

(*b*) Involves strong interactions between adsorbent and adsorbate

(*c*) Extent of adsorption always decreases with increase in temperature

(*d*) Adsorption is restricted to monomolecular layers.

30. Which of the following statements is true for physical adsorption ?

(*a*) It is also known as Langmuir adsorption

(*b*) Heat of adsorption is about 100 kJ mol^{-1}

(*c*) Extent of adsorption increases with increase in temperature

(*d*) It is not specific.

31. The STEM (Scanning Transmission Electron Microscope) is used to determine

(*a*) Charge of the colloid (*b*) Size of the colloid

(*c*) Colour of the colloid (*d*) Nature of the colloid.

32. Which of the following statements is not true ?

(*a*) Milk is an example of an emulsion

(*b*) Boot-polish is an example of a gel

(*c*) Clouds are an example of liquid aerosol

(*d*) Cheese is an example of solid sol.

33. Migration of colloidal particles under the influence of an electric field is known as

(*a*) Electro-dialysis (*b*) Electro-osmosis

(*c*) Electrophoresis (*d*) None of these.

34. Which of the following statements is not correct for lyophobic sols ?

(*a*) They have surface tension and viscosity similar to that of medium

(*b*) Their particles are easily detected under ultra-microscope

(*c*) The particles migrate in one direction in an electric field

(*d*) Electrolytes cannot cause their coagulation.

35. Which of the following statements is not correct for lyophilic sols ?

(*a*) Surface tension of a lyophilic sol is often lower than that of the medium

(*b*) Viscosity is much higher than that of medium

(*c*) The particles may migrate in either direction or not at all in an electric field

(*d*) Their particles can be easily detected under ultra-microscope.

36. Which of the following statements is not correct ?

(*a*) Foam consists of gas as dispersed phase liquid as dispersion medium

(*b*) Smoke, dust, fog, mist and cloud are examples of aerosols

(*c*) Sols of metals, metal sulphides, sulphur, acidic dyes are negatively charged.

(*d*) Among gelatin, gum arabic and potato starch, gelatin has the highest gold number.

37. Colloidal solution of metals like gold, platinum, etc. can be obtained by

(*a*) Bredig's arc method

(*b*) Peptisation

(*c*) Hydrolysis of their salts

(*d*) Oxidation of their salts.

38. Which of the following is homogeneous ?

(*a*) an emulsion (*b*) a sol

(*c*) a suspension (*d*) none of these.

39. For adsorption of a gas on the solid adsorbent

(*a*) ΔH is positive

(*b*) ΔS is positive

(*c*) ΔH is negative and ΔS is positive

(*d*) Both ΔH as well as ΔS are negative.

40. In physical adsorption the gas molecules are bound on the solid surface by

(*a*) Chemical forces (*b*) Electrostatic forces

(*c*) Graphical forces (*d*) van der Waal's forces.

41. If dispersed phase is a liquid and the dispersion medium is a solid, the colloid is known as

(*a*) A sol (*b*) A gel

(*c*) An emulsion (*d*) A foam.

42. Which of the following can form colloidal solution with water ?

(*a*) NaCl (*b*) Glucose

(*c*) Starch (*d*) Barium nitrate.

43. Gels on standing exude small amount of liquid. This phenomenon is known as

(*a*) Efflorescence (*b*) Synerisis

(*c*) Thixotropy (*d*) Adsorption.

44. The ability of an ion to bring about coagulation of a given colloid depends upon

(*a*) Its size

(*b*) The magnitude of its charge only

(*c*) The sign of its charge alone

(*d*) Both magnitude and sign of its charge.

45. Freundlich adsorption isotherm is applicable to adsorptions involving

(*a*) Unimolecular layers (*b*) Multimolecular layers

(*c*) Both of the above (*d*) None of these.

46. Butter is an example of a/an

(*a*) Emulsion (*b*) Gel

(*c*) Solid foam (*d*) Sol.

47. $Fe(OH)_3$ sol is prepared in the presence of a little excess of $FeCl_3$, the charge on the colloidal particles would be

(*a*) Negative (*b*) Positive

(*c*) Neutral (*d*) None of these.

48. Metallic sols are generally prepared by Bredig's arc method. The method involves

(*a*) Dispersion

(*b*) Condensation

(*c*) Dispersion followed by condensation

(*d*) Condensation followed by dispersion.

49. Coagulation value of an electrolyte is expressed in units of

(*a*) moles per litre (*b*) millimoles/litre

(*c*) milligrams per litre (*d*) millimoles per millilitre.

50. Some gels are semi-solid when at rest but change to liquid sol on agitation. This reversible sol-gel transformation is known as

(*a*) Synerisis (*b*) Swelling

(*c*) Thixotropy (*d*) Flocculation.

51. Which of the following is less than zero during adsorption ?

(*a*) ΔG (*b*) ΔS

(*c*) ΔH (*d*) All of the above.

52. For adsorption of a gas on a solid, the plot of log x/m *vs* log P is linear with slope equal to (n being whole number)

(*a*) k (*b*) log k

(*c*) n (*d*) $\frac{1}{n}$.

53. Which is adsorbed in maximum amount by activated charcoal ?

(*a*) N_2 (*b*) CO_2

(*c*) Cl_2 (*d*) O_2.

54. Which of the following constitute irreversible colloidal system in water as dispersion medium

(*a*) Clay (*b*) Platinum

(*c*) $Fe(OH)_3$ (*d*) All of the above.

55. A colloidal solution is subjected to an electrical field. The particles move towards anode. The coagulation of same sol is studied using NaCl, $BaCl_2$ and $AlCl_3$ solutions. Their co-agulating power should be

(*a*) $NaCl > BaCl_2 > AlCl_3$ (*b*) $BaCl_2 > AlCl_3 > NaCl$

(*c*) $AlCl_3 > BaCl_2 > NaCl$ (*d*) $BaCl_2 > NaCl > AlCl_3$.

56. The stability of lyophilic colloid is due to which of the following ?

(*a*) Charge on their particles

(*b*) Large size of their particles

(*c*) Small size of their particles

(*d*) A layer of dispersion medium.

57. Which of the following is the most effective in the coagulation of gold sol ?

(*a*) $NaNO_3$ (*b*) $MgCl_2$

(*c*) Na_3PO_4 (*d*) $K_4[Fe(CN)_6]$.

58. Which colloid is used in treating eye disease ?

(*a*) Colloidal sulphur (*b*) Colloidal antimony

(*c*) Colloidal gold (*d*) Colloidal silver.

59. In coagulating the colloidal solution of As_2S_3 which has the minimum coagulating value ?

(*a*) NaCl (*b*) KCl

(*c*) $BaCl_2$ (*d*) $AlCl_3$.

60. Cod liver oil is

(*a*) Fat dispersed in water

(*b*) Water dispersed in fat

(*c*) Water dispersed in oil

(*d*) Fat dispersed in fat.

61. Colloidal silver is obtained by reduction of silver nitrate solution with

(*a*) Glucose (*b*) Fructose

(*c*) Sucrose (*d*) Hydrogen (H_2).

62. The Rubin number which was proposed by Ostwald as an alternative to the Gold number in order to measure the protective efficiency of a lyophilic colloid may be defined as the

(*a*) mass in milligrams of a colloid per 100 c.c. of solution which just prevents the colour change of standard sol of dye Congo-Rubin from red to violet when 0.16 g eq. KCl is added to it.

(*b*) mass in grams of a colloid per 100 c.c. of solution which just prevents the colour change of standard sol of dye Congo-Rubin from red to violet when 0.1 M KCl is added to it.

(*c*) mass in grams of a colloid per 100 c.c. of solution which just prevents the colour change of standard sol of dye Congo-Rubin from red to violet when 0.2 M KCl is added to it

(*d*) mass in grams of a colloid per 100 c.c. of solution which just prevents the colour change of standard sol of dye Congo-Rubin from red to violet when 1 M KCl is added to it.

63. The ability of an ion to bring about coagulation of a given colloid depends on

(*a*) its size

(*b*) the magnitude of its charge

(*c*) the sign of the charge alone

(*d*) both magnitude and sign of its charge.

64. At CMC the surfactant molecules

(*a*) decompose (*b*) become completely soluble

(*c*) associate (*d*) dissociate.

65. Which of the following kinds of catalysis can be explained by the adsorption theory ?

(*a*) Homogeneous catalysis (*b*) Acid-base catalysis

(*c*) Heterogeneous catalysis (*d*) Enzyme catalysis.

66. In which of the following, Tyndall effect is not observed ?

(*a*) Suspensions (*b*) Emulsions

(*c*) Sugar solution (*d*) Gold sol.

67. Which one of the following will have the highest coagulating power for a ferric hydroxide sol ?

(*a*) NaCl (*b*) $BaCl_2$

(*c*) K_2CrO_4 (*d*) $K_3[Fe(CN)_6]$.

68. Point out the false statement

(*a*) Brownian movement and Tyndall effect is shown by colloidal systems

(*b*) Gold number is a measure of the protective power of a lyophilic colloid

(*c*) The colloidal solution of a liquid in liquid is called gel

(*d*) Hardy-Schulze rule is related with coagulation.

ANSWERS

QUESTION BANK (Level I)

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

QUESTION BANK (Level II)

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

33. (*c*) **34.** (*d*) **35.** (*d*) **36.** (*d*) **37.** (*a*) **38.** (*d*) **39.** (*d*) **40.** (*d*)
41. (*b*) **42.** (*c*) **43.** (*b*) **44.** (*d*) **45.** (*a*) **46.** (*b*) **47.** (*b*) **48.** (*c*)
49. (*b*) **50.** (*c*) **51.** (*d*) **52.** (*d*) **53.** (*b*) **54.** (*d*) **55.** (*c*) **56.** (*d*)
57. (*d*) **58.** (*d*) **59.** (*a*) **60.** (*c*) **61.** (*a*) **62.** (*a*) **63.** (*d*) **64.** (*c*)
65. (*c*) **66.** (*c*) **67.** (*d*) **68.** (*c*).

HINTS/SOLUTIONS

QUESTION BANK (Level I)

1. (*b*) self explanatory.
2. (*a*) Factual.
3. (*d*) Sugar solution is a true solution.
4. (*a*) See Important terms, fact and formulae.
5. (*c*) Factual.
6. (*a*) Arsenious sulphide sol is negatively charged sol. Smaller the charge on the positive ion, smaller is the coagulating power.
7. (*c*) Physisorption does not need any activation energy.
8. (*a*) Soap sol contains negatively charged ionic micelles.
9. (*c*) Colloidal solutions pass through the filter paper.
10. (*b*) The colloidal formed has a fluid like appearance.
11. (*a*) $Fe(OH)_3$ is a positively charged sol. Comparing the charge on negative ions, Cl^- has least charge and hence least coagulating power and maximum coagulation value.
12. (*b*) Self explanatory answer.
13. (*d*) Factual questions.
14. (*b*) Adsorption is exothermic process due to attractive forces between adsorbate and adsorbent.
16. (*b*) See summary.
17. (*b*) In fog water (liquid) is dispersed in air (gas).
18. (*a*) Self explanatory.
19. (*c*) Colloidal sols have particle size in the range 1-100 nm.
20. (*b*) Salts in the sea-water coagulate the colloidal particles present in the river-water.
21. (*d*) Starch is soluble in water.
22. (*b*) During electrophoresis colloidal particles may go to cathode or anode depending on the charge on them.
23. (*c*) It is used as a stabilizer.
24. (*c*) Sulphide sol is –vely charged.
25. (*b*) Sodium reacts with water violently.
26. (*b*) See summary (terms, facts etc.)
27. (*d*) Charcoal is good adsorbent for easily liquifiable gases.
28. (*a*) Factual.
29. (*d*) Lyophilic sols are reversible.
30. (*d*) For adsorption ΔH, ΔS and ΔG all are negative.
31. (*b*) Molecules move haphazardly.
32. (*c*) Adsorption is mono molecular due formation of chemical bonds.
33. (*d*) Factual (see summary).
34. (*d*) See summary.
35. (*a*) Adsorption decreases with increase in temperature.
36. (*d*) Gel is a system with liquid as disperse phase and solid as dispersion medium.
37. (*b*) The average molecular mass of bigger particles is determined by study of osmotic pressure as it is the only colligative property which is measurable for solutions containing such macro particles.
38-41. Self explanatory and factual question.
42. (*b*) Chemisorption needs activation energy and hence does not occur at very low temperature.
43-45. Self explanatory and factual question.
46. (*b*) Charge on colloidal particles would be negative due to adsorption of I^- ions on AgI.
47. (*d*) Factual.
48. (*b*) It is a fact.
49. (*a*) Hydroxide sol carries a positive charge. More in the –ve charge on additive more is the coagulating power (Hardy Schulze rule).
50-52. Self explanatory and factual question.
53. (*a*) Apply Hardy Schulze rules.
54. (*c*) Hydroxide sols carry a positive charge due to adsorption of + ve ions on the precrpitate.
55. (*a*) See summary.
56. (*c*) 0.25 g = 250 mg.
57. According to Hardy Schulze rules coagulating power of an ion depends on type of charge and magnitude of charge.
58. (*a*) Factual.
59. (*b*) See summary.
60-69. Self explanatory and factual question.
70. (*a*) These are heterogeneous.
71. (*d*) Factual.

72. (*c*) $Fe(OH)_3$ sol carries a positive charge. The additive with least –ve charge will be least effective in coagulation.
74-77. Self explanatory and factual question.
78. (*d*) Due to different size light of different colours is scattered.
79. (*d*) $[Fe(CN)_6]^{4-}$ is most effective according to Hardy Schulze rule.
80. (*d*) Fact.

QUESTION BANK (Level II)

1. (*d*) The substance that gets adsorbed.
2. (*c*) 1 nm (= 10^{-7} cm) – 100 nm = (10^{-5} cm)
3. (*c*) Tyndall effect.
4. (*c*) Apply Hardy Schulze rules. As_2C_3 is a negative sol.
5. (*a*) A substance is classified on the basis of molecular size as macromolecular, multimolecular and associated colloids.
6. (*a*) PO_4^{3-} has maximum coagulating power for $Fe(OH)_3$, a positively charged sol.
7. (*a*) Crystallisation cannot seperate colloidal substances from impurities.
8-9. Self explanatory and factual question.
10. (*c*) Answer itself is an explanation.
11. (*b*) Electrolytes coagulate colloidal solutions.
12. (*b*) Soap emulsifies greasy impurities.
13. (*a*) Self explanatory.
14. (*b*) Soap sol contains negatively charged ionic micelles.
15. (*c*) Sulphur (S_8) is insoluble in water.
16-17. Self explanatory and factual question.
18. (*a*) See summary.
19. (*a*) Answer itself is an explanation.
20. (*d*) $Al(OH)_3$ sol is a positively charged sol. $[Fe(CN)_6]^{4-}$ has maximum charge and hence has maximum coagulating power and minimum coagulation value.
21. (*d*) Apply Hardy Schulze rule.
22. (*a*) Precrpitation is also called flocculation.
23. (*b*) AgI particles acquire positive charge due to adsorption of Ag^+ ions from excess $AgNO_3$.
24. (*a*) Blood is a negatively charged sol.
25. (*a*) Apply Hardy Schulze rules. Phosphate ion has 3 unit negative charge.
26. (*d*) See summary.
27. (*c*) Answer itself is an explanation.
28. (*d*) Colloidal particles in lyophobic sols have little interaction with the dispersion medium and hence their particles are not solvated.
29. (*c*) Chemisorption needs activation energy. Therefore, at lower temperatures, it shows an increase in extent of adsorption with increase in temperature.
30-35. Self explanatory and factual question.
36. (*d*) Among gelatin, gum arabic and starch, gelatin has maximum protecting power and hence least gold number.
37. (*a*) These cannot be changed to colloidal solutions by simple methods.
38. (*d*) Emulsion, sol and suspension are all heterogeneous.
39. (*d*) For spontaneous process ΔH = – ve but as the gas molecules adsorb therefore ΔS is also – ve.
40-41. Self explanatory.
42. (*c*) Glucose NaCl + $Ba(NO_3)_2$ in water produces a true solution.
43. (*b*) Self explanatory.
44. (*d*) Hardy Schulze rules.
45. (*a*) Factual.
46. (*b*) It has a rigid apearance.
47. (*d*) Due to adsorption of Fe^{3+} ions, colloidal particles would acquire positive charge.
48. (*c*) In Bredig's arc method, the metal first gets vaporised (dispersed) and then the vapours are condensed in cold water to form colloidal solution.
49-52. See summary.
53. (*b*) Easily liquifiable gases adsorb more.
54. (*d*) Self explanatory.
55. (*c*) Apply Hardy Schulze rules.
56. (*d*) See facts, terms.
57. (*b*) Gold sol is negatively charged. Mg^{2+} has maximum charge among the given cations.
59. (*a*) The positive ion with least charge shall be required in more amount.
61. (*a*) Glucose has aldehydic group therefore shall produce colloidal Ag.
62. (*a*) Self explanatory. It is a term.
63. (*d*) According to Hardy Schulze rules coagulating power of an ion depends on type of charge and magnitude of charge.
65. (*c*) Heterogeneous catalysis can be explained on the basis of adsorption.
66. (*c*) Sugar solution is a true solution.
67. (*d*) The colloidal solution of a liquid in liquid is emulsion and not gel.
68. (*c*) Liquid in liquid colloidal is an emulsion.

PART–B

INORGANIC CHEMISTRY

10

CHEMICAL FAMILIES — PERIODIC PROPERTIES

Important Terms, Facts and Formulae

LONG FORM OF PERIODIC TABLE

- Long form of periodic table is based on modern periodic law.
- **Modern periodic law** was proposed by **H.G.J. Moseley**. It states that **the properties of elements are periodic function of their atomic numbers.**
- **Group.** A vertical column of elements in the periodic table.
- **Period.** A horizontal row of elements in the periodic table.
- **Long Form of Periodic Table** has 18 groups and 7 periods. Sixth period is the longest and first period is the smallest. The number of elements in the first six periods are 2, 8, 8, 18, 18 and 32 respectively.
- **s-Block Elements.** Elements of groups 1 and 2. Their general electronic configuration is $\mathbf{ns^{1-2}}$.
- **p-Block Elements.** Elements of groups 13, 14, 15, 16, 17 and 18. Their general electronic configuration is $\mathbf{ns^2\,np^{1-6}}$.
- **d-Block Elements.** Elements of groups 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12. Also known as transition elements. Their general electronic configuration is $\mathbf{(n-1)d^{1-10}\,ns^{1-2}}$. $_{46}$**Pd** is exception ($4d^{10}\,5s^0$).
- **f-Block Elements.** The two horizontal rows of elements at the bottom of the table. Also known as inner transition elements. Their general electronic configuration is $\mathbf{(n-2)\,f^{1-14}\,(n-1)\,d^{0-1}\,ns^2}$.

ATOMIC VOLUME

- **Atomic Volume** is defined as the volume occupied by one mole atoms of the element in solid state.

$$\textbf{Atomic volume} = \frac{\textbf{Gram atomic mass}}{\textbf{Density in solid state}}$$

- A graph showing variation of atomic volume with atomic weight was plotted by Lothar Meyer.
- Atomic volume increases on moving down the group. Across a period atomic volume first decreases and then starts increasing.
- Alkali metals have the highest atomic volumes in their respective periods.

ATOMIC SIZE

- Distance between the centre of the nucleus and the outermost shell of electrons is called **atomic radius.**
- **Covalent Radius.** Half of the internuclear distance between two atoms of the elements held by a single covalent bond.
- **van der Waal's Radius.** Half of the internuclear distance between two nearest atoms belonging to two adjacent molecules in solid state.
- **Metallic Radius.** Half of the internuclear distance between two nearest atoms in the metallic lattice.
- van der Waal's radius > Metallic radius > Covalent radius.
- Atomic radius decreases on moving across the period and increases on moving down the group.

IONIC RADIUS

- Size of anion > Size of atom > Size of cation.
- **Isoelectronic ions.** The ions having same number of electrons but different nuclear charge. Examples :

  (*i*) N^{3-}, O^{2-}, F^-, Na^+, Mg^{2+}, Al^{3+}

  (*ii*) P^{3-}, S^{2-}, Cl^-, K^+, Ca^{2+}, Sc^{3+}.
- Among isoelectronic ions, greater the nuclear charge smaller is the size. For example, ionic sizes of the following isoelectronic ions vary in the order :

  (*i*) $N^{3-} > O^{2-} > F^- > Na^+ > Mg^{2+} > Al^{3+}$

  (*ii*) $P^{3-} > S^{2-} > Cl^- > K^+ > Ca^{2+} > Sc^{3+}$.

IONISATION ENERGY (I.E.)

- The energy required to remove the outermost electron from an isolated gaseous atom of the element is called **ionisation energy.**

$$A(g) + IE \longrightarrow A^+(g) + e^-$$

- Ionisation energy in general increases on moving along the period and decreases on going down the group.

- Be, Mg, N, P and noble gases have relatively higher values of I.E. due to their stable electronic configurations.
- Alkali metals have the least and noble gases have the highest ionisation energies in the respective periods.
- Helium (He) has the highest IE among all the elements.
- Caesium (Cs) has the least IE among all the elements (except Fr which is radioactive).
- Successive ionisation energies are always greater than the first ionisation energy.

$$IE_3 > IE_2 > IE_1$$

- **Some trends** among the elements of second and third periods are given below :

$$IE_1 : Li < B < Be < C < O < N < F < Ar$$
$$IE_1 : Na < Al < Mg < Si < S < P < Cl < Ar$$
$$IE_2 : Li > C > B > Be$$
$$IE_2 : O > F > N > C$$
$$IE_2 : Na > Al > Mg$$
$$IE_3 : Mg > Na > Al$$

- While comparing IE_2, consider the electronic configuration of A^+ ion, keeping in mind the stability of electronic configuration with half filled and fully filled subshells.

ELECTRON AFFINITY OR ELECTRON GAIN ENTHALPY (ΔH_{eg})

- The energy released when an isolated atom of the element in gaseous state accepts an electron to form univalent negative ion is called **electron affinity**.

$$X(g) + e^- \longrightarrow X^-(g) \quad \Delta H = \Delta H_{eg}$$

- It is measured in eV/atom or kJ/mole.
- The energy change in the process of addition of an electron to monovalent negative ion of the element in gaseous state is called second electron affinity (EA_2).

$$X^-(g) + e^- \longrightarrow X^{2-}(g) \Delta H = (\Delta H_{eg})_2$$

- EA, in general, increases on moving across the period and decreases on going down the group.
- **Be, Mg, N and P** have exceptionally low values of EA due to their stable electronic configurations.
- **Noble Gases** (He, Ne, Ar, Kr, Xe, Rn) have negative values of EA due to their stable electronic configurations.
- **Halogens** have the highest EA in their respective periods.
- Among halogens, fluorine has lower EA than chlorine due to greater interelectronic repulsions in small sized 2-*p* subshell.
- Chlorine has the highest EA among all the elements.
- **Some trends** in the values of electron affinities :

$$EA_1 : Cl > F > Br > I$$
$$EA_1 : S > O > Se > Te$$
$$EA_1 : C > B > Li > Be$$
$$EA_1 : Si > Al > Na > Mg$$
$$EA_1 : F > O > N > Ne.$$

VALENCY

- The combining capacity of an element is called **valency**.
- For elements of short periods (Period 2 and 3), the valency with respect to hydrogen increases from 1 to 4 and then decreases from 4 to 1 as we move across the period from left to right. However, the valency with respect to oxygen increases from 1 to 7.
- Valencies of noble gases are zero.
- All the elements of the same group, generally, have same valency.

ELECTRONEGATIVITY

- The tendency of an atom to attract the shared pair of electrons towards itself, in a molecule, is called **electronegativity.**
- Unlike ionisation energy and electron affinity, electronegativity is the property of the element in bonded state.
- Electronegativity increases on moving across the period from left to right and decreases in moving down the group from top to bottom.
- Fluorine is the most electronegative element.
- In a period, the highest electronegativity is of halogens and the lowest is of alkali metals.

ELECTROPOSITIVITY OR METALLIC CHARACTER

- The tendency of an atom of the element to lose valence electrons and form positive ion is called **electropositivity.**
- Greater the electropositive character, greater is the metallic character.
- Electropositive character decreases on moving across the period and increases on moving down the group.
- Alkali metals are the **most electropositive** and halogens are the **least electropositive** elements in their respective periods.

OXIDISING AND REDUCING POWER

- The elements having low ionisation energy are expected to be stronger reducing agents whereas the elements having high electron affinity are expected to be stronger oxidising agents.

- In moving across a period from left to right the reducing power, in general, decreases whereas oxidising power increases.
- Alkali metals are the strongest reducing agents whereas halogens the strongest oxidising elements in their respective periods.
- In moving down a group, from top to bottom, the reducing character, in general, increases whereas the oxidising character decreases.
- Among alkali metals, the strongest reducing agent in solution is lithium. This is due to greater $\Delta H_{\text{hydration}}$ for Li^+.
- Among halogens, the strongest oxidising agent in solution is fluorine. This is due to greater $\Delta H_{\text{hydration}}$ for F^-.

NATURE OF OXIDES

- In a period, from left to right, the basic character of oxides decreases and acidic character of oxides increases.
- In a group, from top to bottom, the basic character of oxides increases whereas acidic character of oxides decreases.
- Generally, oxides of metals are basic whereas oxides of non-metals are acidic

$$\underbrace{Na_2O, MgO,}_{\text{Basic}}\ \underbrace{Al_2O_3,}_{\text{Amphoteric}}\ \underbrace{SiO_2, P_2O_5, SO_3, Cl_2O_7}_{\text{Acidic}}$$

SOME TRENDS :

(*i*) Melting points : $NaF > NaCl > NaBr > NaI$

(*ii*) Melting points : $NaCl > KCl > RbCl > CsCl > LiCl$

(*iii*) Basic strength : $LiOH < NaOH < KOH < RbOH < CsOH$

(*iv*) Basic strength : $Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$

(*v*) Thermal stability :

$$BaCO_3 > SrCO_3 > CaCO_3 > MgCO_3$$

(*vi*) Thermal stability :

$$BaSO_4 > SrSO_4 > CaSO_4 > MgSO_4$$

(*vii*) Solubility in water :

$$BaSO_4 < SrSO_4 < CaSO_4 < MgSO_4$$

(*viii*) Solubility in water :

$$Ba(OH)_2 > Sr(OH)_2 > Ca(OH)_2 > Mg(OH)_2.$$

QUESTION BANK

Level I

Choose the correct answer from the four alternatives given in each of the following questions :

1. The law of triads is applicable to
(*a*) Lithium, beryllium, boron
(*b*) Fluorine, chlorine, bromine
(*c*) Chlorine, bromine, iodine
(*d*) Sodium, potassium, rubidium.

2. Law of octaves was proposed by
(*a*) Lothar Meyer (*b*) D.I. Mendeleev
(*c*) J.A.R. Newlands (*d*) J.W. Dobereiner.

3. Lothar Meyer plotted a graph showing variation of
(*a*) Atomic volume with increase in atomic weight
(*b*) Atomic radii with increase in atomic weight
(*c*) Atomic volume with increase in atomic number
(*d*) Atomic radii with increase in atomic number.

4. The concept of telluric helix was developed by
(*a*) Lothar Meyer (*b*) A.E. de Chancourtois
(*c*) Newlands (*d*) Dobereiner.

5. As we go from left to right in period 3, the gram atomic volume of the elements
(*a*) Increases regularly
(*b*) Decreases regularly
(*c*) First decreases and then increases
(*d*) Remains almost constant.

6. The number of elements in each of the long periods of periodic table is
(*a*) 32 (*b*) 18
(*c*) 8 (*d*) 36.

7. Lanthanum is a member of
(*a*) *s*-Block (*b*) *p*-Block
(*c*) *d*-Block (*d*) *f*-Block.

8. Which block of the periodic table contains maximum number of metals ?
(*a*) *s*-Block (*b*) *p*-Block
(*c*) *d*-Block (*d*) *f*-Block.

9. The variable valency is generally observed in case of
(*a*) Transition elements (*b*) Inert gases
(*c*) Normal elements (*d*) Metallic elements.

10. Inert gases except helium belong to
(*a*) *s*-Block (*b*) *p*-Block
(*c*) *d*-Block (*d*) *f*-Block.

11. A property which gradually increases on moving down a group in the periodic table is
(*a*) Ionisation energy (*b*) Electronegativity
(*c*) Electron affinity (*d*) Atomic size.

12. The element having electronic configuration $[Kr]\ 4d^{10}, 4f^{14}, 5s^2, 5p^6, 5d^1, 6s^2$ belongs to
(*a*) *s*-Block (*b*) *p*-Block
(*c*) *d*-Block (*d*) *f*-Block.

13. Which of the following sets of elements would have nearly same atomic radii ?
(*a*) Na, K, Rb, Cs (*b*) Na, Mg, Al, Si
(*c*) Fe, Co, Ni, Cu (*d*) F, Cl, Br, I.

14. Which of the following elements would have the lowest first ionization energy (IE_1) ?
(*a*) Mg (*b*) Rb
(*c*) Li (*d*) Ca.

15. The magnitude of electron affinity depends on
(*a*) Atomic size (*b*) Nuclear charge
(*c*) Electronic configuration (*d*) All the above.

16. The ionization energy of nitrogen is more than that of oxygen because
(*a*) Nitrogen has half-filled *p*-orbitals
(*b*) Nitrogen atom is smaller in size than oxygen atom
(*c*) Nitrogen contains less number of electrons
(*d*) Nitrogen is less electronegative.

17. The most electronegative element of the third period is
(*a*) F (*b*) P
(*c*) Br (*d*) Cl.

18. In the long form of periodic table, elements are arranged according to
(*a*) increasing atomic number
(*b*) decreasing atomic number
(*c*) increasing atomic mass
(*d*) decreasing atomic mass.

19. In the Mendeleev's periodic table, elements are arranged in the ascending order of their
(*a*) number of neutrons (*b*) atomic number
(*c*) atomic mass (*d*) atomic volume.

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