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MODERN APPROACH TO CHEMICAL CALCULATIONS

AN INTRODUCTION TO THE MOLE CONCEPT

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CONTENTS

CHAPTER ONE

ELEMENTARY PROBLEMS BASED ON DEFINITION OF MOLE: THE MOLE CONCEPT

The mole concept is an essential tool for the study of the fundamentals of chemical calculations. This concept is simple but its application in problems requires a thorough practice.

The Mole

The 14th General Conference on Weights and Measures (1971) adopted the mole (mol) as the basic SI unit of the amount of a substance.

There are many ways of measuring the amount of a substance, weight and volume being the most common. But the basic unit of chemistry is the atom or a molecule and to measure the number of atoms or molecules is, therefore, of foremost importance.

Mole in Latin means heap or mass or pile. A mole of atoms is a collection of atoms whose total weight is the number of grams equal to the atomic weight. As equal numbers of moles of different elements contain equal numbers of atoms, it is convenient to express amounts of the elements in terms of moles. Just as a dozen means twelve objects, a score means twenty objects, chemists have defined a mole as a 'definite number' of particles, viz., atoms, molecules, ions or electrons, etc. This 'definite number' is called the Avogadro constant, equal to $6{\cdot}022 \times 10^{23}$, in honour of Amedeo Avogadro. However, for many years scientists have made use of the concept of a mole without knowing the value of the Avogadro constant. Thus, a mole of hydrogen atoms or a mole of hydrogen molecules or a mole of hydrogen ions or a mole of electrons means the Avogadro constant of hydrogen atoms, hydrogen molecules, hydrogen ions or electrons respectively.

The value of the Avogadro constant depends on the atomic-weight scale. At present **the mole is defined as the amount of a substance containing as many atoms, molecules, ions, electrons or other elementary entities as there are carbon atoms in exactly 12 g of ^{12}C**. The value of the Avogadro constant was changed by a very small amount in 1961 when the basis of the atomic-weight scale was changed from the naturally occurring mixture of oxygen isotopes at 16 amu to ^{12}C, which put oxygen at 15·9994 amu.

It is quite interesting and surprising to know that the mole is such a big number that it will take 10^{16} years to count just one mole at the rate of one count per second, and the world population would be only of the order of 10^{-14} mole in chemical terminology.

$$\frac{w}{288} \times 184 = \frac{569}{304} \times 184$$
$$w = 539.05 \text{ g.}$$

Ex. 38. *0.75 mole of solid 'A_4' and 2 moles of gaseous O_2 are heated in a sealed vessel, completely using up the reactants and producing only one compound. It is found that when the temperature is reduced to the initial temperature, the contents of the vessel exhibit a pressure equal to half the original pressure. What conclusions can be drawn from these data about the product of the reaction?*

Solution : **First Method** : As both A_4 and O_2 are consumed

$$\frac{\text{moles of } A_4}{\text{moles of } O_2} = \frac{0.75}{2.0}$$
$$\frac{(\text{moles of A})/4}{(\text{moles of O})/2} = \frac{0.75}{2.0}$$
$$\frac{\text{moles of A}}{\text{moles of O}} = \frac{3}{4}$$

Thus, the empirical formula of the product is A_3O_4. Further, as 2 moles of O_2 give 1 mole of A_3O_4 (for gases, pressure $\propto$ mole at constant temperature and volume), A_3O_4 is also the molecular formula of the product.

Second Method : $\underset{0.75 \text{ mole}}{A_4(s)} + \underset{2.0 \text{ moles}}{O_2(g)} \rightarrow \underset{1.0 \text{ mole}}{A_xO_y(g)}$

Applying POAC for A atoms,

$$4 \times \text{moles of } A_4 = x \times \text{moles of } A_xO_y$$
$$4 \times 0.75 = x \times 1 \; ; \; x = 3$$

Applying POAC for O atoms,

$$2 \times \text{moles of } O_2 = y \times \text{moles of } A_xO_y$$
$$2 \times 2 = y \times 1; \; y = 4.$$

In the following chapters, we shall apply the principle of atom conservation (POAC) along with the said rules in tackling the various problems encountered in chemical practice.

PROBLEMS

(Answers bracketed with questions)

1. Find the number of atoms in 48 g of ozone at NTP. ($1{\cdot}8066 \times 10^{24}$)
2. What is the ratio of the volumes occupied by 1 mole of O_2 and 1 mole of O_3 in identical conditions? (1 : 1)
3. Calculate the mass of 5 moles of $CaCO_3$ in grams. (500 g)
4. The vapour density of a gas is 11·2. Calculate the volume occupied by 11·2 g of the gas at NTP.
   [Hint: Mol. wt. $= 2 \times$ VD] (11·2 litres)

5. Calculate the number of oxygen atoms in 0·2 mole of $Na_2CO_3 \cdot 10H_2O$. ($1{\cdot}56 \times 10^{24}$)

6. Calculate the number of moles of $CuSO_4$ contained in 100 mL of 1 M $CuSO_4$ solution. Also, find the number of SO_4^{2-} ions in it. (0·1 mole, 0.6022×10^{23})

7. Find the total number of nucleons present in 12 g of ^{12}C atoms. ($12 \times 6{\cdot}022 \times 10^{23}$)

8. Find (i) the total number of neutrons, and (ii) the total mass of neutrons in 7 mg of ^{14}C. (Assume that the mass of a neutron = mass of a hydrogen atom) ($24{\cdot}088 \times 10^{20}$, 0·004 g)
[Hint: 1 ^{14}C atom contains 8 neutrons.]

9. How many moles are there in 1 metre^3 of any gas at NTP? (1 m^3 = 10^3 litres) (44·6 moles)

10. 3 g of a salt of molecular weight 30 is dissolved in 250 g of water. Calculate the molality of the solution. (0·4 *m*)

11. Calculate the volume occupied by 5·25 g of nitrogen at 26°C and 74·2 cm of pressure. (4·71 litres)

12. Find the ratio of the number of molecules contained in 1 g of NH_3 and 1 g of N_2. (28 : 17)

13. How many molecules of CO_2 are contained in one litre of air if the volume content of CO_2 is 0·03 % at NTP? ($8{\cdot}06 \times 10^{18}$)

14. Is the number of molecules in 1 kg of H_2 and 1 kg of O_2 the same ? What is the ratio of weights of H_2 and O_2, the mixture of which contains equal number of molecules of each gas? (no, 1 : 16)

15. The measured density at NTP of a gaseous sample of a compound was found to be 1·78 g/L. What is the weight of 1 mole of the gaseous sample? (39·9 g)

16. If the concentration of a solution is 2 M calculate the number of millimoles present in 2 litres of the solution.
[Hint: Follow Rule 5.] (4000)

17. How many moles of oxygen are contained in one litre of air if its volume content is 21% at NTP? (0·0093)

18. How many atoms do mercury vapour molecules consist of if the density of mercury vapour relative to air is 6·92? (Hg = 200). The average mass of air is 29 g/mole. (One)

19. Calculate the total number of atoms in 0·5 mole of $K_2Cr_2O_7$.
[Hint: Follow Example 19] ($3{\cdot}31 \times 10^{24}$)

20. What is the volume of 6 g of hydrogen at 1 atm and 0°C? (67·2 litres)

21. What is the density of oxygen gas at NTP?
[Hint: See Example 14] (1·429 g/L)

22. Calculate the total number of electrons present in 18 mL of water. ($10 \times 6{\cdot}022 \times 10^{23}$)

23. Calculate the number of electrons, protons and neutrons in 1 mole of $^{16}O^{-2}$ ion.
$(10 \times 6{\cdot}022 \times 10^{23},\ 8 \times 6{\cdot}022 \times 10^{23},\ 8 \times 6{\cdot}022 \times 10^{23})$

24. Find the mass of the nitrogen contained in 1 kg of (i) KNO_3, (ii) NH_4NO_3, and (iii) $(NH_4)_2\ HPO_4$.
[(i) 138·5 g (ii) 350 g and (iii) 212 g]

25. Find the mass of each element in 7·84 g of $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$. What will be the volume of O_2 at NTP in this sample?
(3·136 litres)

26. The density of solid AgCl is 5·56 g/cc. The solid is made up of a cubic array of alternate Ag^+ and Cl^- ions at a spacing of 2·773 Å between centres. From these data calculate the Avogadro constant.
$(6{\cdot}04 \times 10^{23})$

27. Three atoms of magnesium combine with 2 atoms of nitrogen. What will be the weight of magnesium which combines with 1·86 g of nitrogen?
[Hint: Use Rule 6]
(4·86 g)

28. 600 mL of a mixture of O_3 and O_2 weighs 1 g at NTP. Calculate the volume of ozone in the mixture.
(200 mL)

29. The vapour density (hydrogen = 1) of a mixture consisting of NO_2 and N_2O_4 is 38·3 at 26·7°C. Calculate the number of moles of NO_2 in 100 g of the mixture.
[Hint: Wt. of $NO_2 = x$ g.

$$\therefore \text{obs. mol. wt. (wt./mole)} = \frac{\text{wt. in g}}{\text{total moles}} = \frac{100}{\left(\frac{x}{46} + \frac{100-x}{92}\right)} = 2 \times 38{\cdot}3.\Big]$$

(0·437 mole)

30. A nugget of gold and quartz weighs 100 g. Sp. gr. of gold, quartz and the nugget are 19·3, 2·6 and 6·4 respectively. Calculate the weight of gold in the nugget.
[Hint: $\frac{x}{19{\cdot}3} + \frac{100-x}{2{\cdot}6} = \frac{100}{6{\cdot}4}$; x = wt. of gold]
(68·6 g)

31. The nucleus of an atom of X is supposed to be a sphere with a radius of 5×10^{-13} cm. Find the density of the matter in the atomic nucleus if the atomic weight of X is 19.

$$\left[\textbf{Hint: } \text{Density} = \frac{\text{mass of 1 mole (i.e., at. wt.)}}{\text{vol. of 1 mole}}\right]$$

$(6{\cdot}02 \times 10^{13}$ g/mL)

32. Copper forms two oxides. For the same amount of copper, twice as much oxygen was used to form the first oxide than to form the second one. What is the ratio of the valencies of copper in the first and second oxides?
[Hint: Assume that the oxides are Cu_2O_x and Cu_2O_y and apply Rule 6]
(2 : 1)

33. 105 mL of pure water (4°C) is saturated with NH_3 gas, producing a solution of density 0·9 g/mL. If this solution contains 30% of NH_3 by weight, calculate its volume.

$$\left[\textbf{Hint: } \text{Density} = \frac{\text{total mass}}{\text{total volume}} = \frac{105\,(H_2O) + 45\,(NH_3)}{V}\right]$$

(166·67 mL)

34. How many iron atoms are present in a stainless steel ball bearing having a radius of 0·1 inch (1 inch = 2·54 cm)? The stainless steel contains 85·6% Fe by weight and has a density of 7·75 g/cc.
$(4{\cdot}91 \times 10^{21})$

35. How many litres of liquid CCl_4 ($d = 1.5$ g/cc.) must be measured out to contain 1×10^{25} CCl_4 molecules? (1·61 L.)

36. A sample of potato starch was ground in a ball mill to give a starchlike molecule of lower molecular weight. The product analysed 0·086 % phosphorus. If each molecule is assumed to contain one atom of phosphorus, what is the molecular weight of the material? (3.6×10^4 amu)

37. The dot at the end of this sentence has a mass of about one microgram. Assuming that the black stuff is carbon, calculate the approximate number of atoms of carbon needed to make such a dot. (1 microgram $= 1 \times 10^{-6}$ g) (5×10^{16} atoms)

38. To what volume must 50 mL of 3·50 M H_2SO_4 be diluted in order to make 2 M H_2SO_4? (87·5 mL)
[Hint: Use Rule 5]

39. Sulphur molecules exist under various conditions as S_8, S_6, S_4, S_2 and S.
(a) Is the mass of one mole of each of these molecules the same?
(b) Is the number of molecules in one mole of each of these molecules the same?
(c) Is the mass of sulphur in one mole of each of these molecules the same?
(d) Is the number of atoms of sulphur in one mole of each of these molecules the same? (No, Yes, No, No)

40. Two minerals that contain Cu are $CuFeS_2$ and Cu_2S. What mass of Cu_2S would contain the same mass of Cu as is contained in 125 lb of $CuFeS_2$? (54.2 lb)

41. What is the maximum number of moles of CO_2 that could be obtained from the carbon in 4 moles of $Ru_2(CO_3)_3$? (12 mol)

42. What mass of NaCl would contain the same total number of ions as 245 g of $MgCl_2$? (225 g)

43. An unknown sample weighing 1.5 g was found to contain only Mn and S. The sample was completely reacted with oxygen and it produced 1.22 g of Mn (II) oxide and 1.38 g of SO_3. What is the simplest formula for this compound? (Mns)

44. The two sources of Zn, that is, $ZnSO_4$ and $Zn(CH_3COO)_2 \cdot 2H_2O$, can be purchased at the same price per kilogram of compound. Which is the most economical source of Zn and by how much? ($ZnSO_4$, 35.9%)

45. How many moles of H_2O form when 25.0 mL of 0.10 M HNO_3 solution is completely neutralised by NaOH? (2.5×10^{-3} mole)

46. Which would be larger: an atomic mass unit based on the current standard or one based on the mass of a Be-9 atom set at exactly 9 amu? (latter)

47. The enzyme carbonic anhydrase catalyses the hydration of CO_2. This reaction: $CO_2 + H_2O \rightarrow H_2CO_3$, is involved in the transfer of CO_2 from tissues to the lungs via the bloodstream. One enzyme molecule hydrates 10^6 molecules of CO_2 per second. How many kg of CO_2 are hydrated in one hour in one litre by 1×10^{-6} M enzyme? (0.1584 kg)

48. An oxybromo compound, $KBrO_x$, where x is unknown, is analysed and found to

contain 52.92% Br. What is the value of x? (2)

49. Radium disintegrates at an average rate of 2.24×10^{13} α-particles per minute. Each α-particle takes up two electrons from the air and becomes a neutral helium atom. After 420 days, helium gas collected was 0.5 mL, measured at 27°C and 750 mmHg. Calculate the Avogadro constant. (6.7×10^{23})

Objective Problems

1. The density of chlorine relative to air is
   (a) 2·44 (b) 3
   (c) found only experimentally (d) 4

2. A gaseous oxide contains 30·4 % of nitrogen, one molecule of which contains one nitrogen atom. The density of the oxide relative to oxygen is
   (a) 0·94 (b) 1·44 (c) 1·50 (d) 3·0

3. The mass of an oxygen atom is half that of a sulphur atom. Can we decide on this basis that the density of sulphur vapour relative to oxygen is 2?
   (a) Yes (b) No

4. Density of air is 0·001293 g/cc. Its vapour density is
   (a) 0·001293 (b) 1·293 (c) 14·48 (d) cannot be calculated

5. 5·6 litres of oxygen at NTP is equivalent to
   (a) 1 mole (b) $\frac{1}{2}$ mole (c) $\frac{1}{4}$ mole (d) $\frac{1}{8}$ mole

6. 22·4 litres of water vapour at NTP, when condensed to water, occupies an approximate volume of
   (a) 18 litres (b) 1 litre (c) 1 mL (d) 18 mL

7. Which of the following has the highest mass?
   (a) 1 g-atom of C (b) $\frac{1}{2}$ mole of CH_4
   (c) 10 mL of water (d) $3{\cdot}011 \times 10^{23}$ atoms of oxygen

8. $6{\cdot}022 \times 10^{22}$ molecules of N_2 at NTP will occupy a volume of
   (a) 22·4 litres (b) 2·24 litres (c) 6·02 litres (d) 6·02 mL

9. How many grams are contained in 1 gram-atom of Na?
   (a) 13 g (b) 23 g (c) 1 g (d) $\frac{1}{23}$ g

10. The weight of 350 mL of a diatomic gas at 0°C and 2 atm pressure is 1 g. The wt. of one atom is
    (a) $\frac{16}{N}$ (b) $\frac{32}{N}$
    (c) 16 N (d) 32 N (N is the Av. const.)

11. The number of atoms present in 16 g of oxygen is
    (a) $6{\cdot}02 \times 10^{11{\cdot}5}$ (b) $3{\cdot}01 \times 10^{23}$ (c) $3{\cdot}01 \times 10^{11{\cdot}5}$ (d) $6{\cdot}02 \times 10^{23}$

12. 1 mole of a compound contains 1 mole of C and 2 moles of O. The molecular weight of the compound is
    (a) 3 (b) 12 (c) 32 (d) 44

13. The volume of a gas at 0°C and 700 mm pressure is 760 cc. The number of molecules present in this volume is
(a) $1{\cdot}88 \times 10^{22}$ (b) $6{\cdot}022 \times 10^{23}$ (c) $18{\cdot}8 \times 10^{23}$ (d) $18{\cdot}8 \times 10^{22}$

14. 1 mole of a diatomic element X_2 contains 34 and 40 moles of electrons and neutrons respectively. The isotopic formula of the element is
(a) ${}^{74}_{34}X$ (b) ${}^{37}_{17}X$ (c) ${}^{40}_{34}X$ (d) ${}^{40}_{20}X$

15. 2 moles of H atoms at NTP occupy a volume of
(a) 11·2 litres (b) 44·8 litres (c) 2 litres (d) 22·4 litres

16. No. of electrons in 1·8 mL of H_2O (l) is
(a) $6{\cdot}02 \times 10^{23}$ (b) $3{\cdot}011 \times 10^{23}$ (c) $0{\cdot}6022 \times 10^{23}$ (d) $60{\cdot}22 \times 10^{23}$

17. Molecular weight of a gas, 11·2 litres of which at NTP weighs 14 g, is
(a) 14 (b) 28 (c) $\frac{14}{11{\cdot}2}$ (d) $14 \times 11{\cdot}2$

18. The weight of 1 mole of a gas of density 0·1784 g/L at NTP is
(a) 0·1784 g (b) 1 g (c) 4 g (d) cannot be calculated

19. Number of HCl molecules present in 10 mL of 0·1 N HCl solution is
(a) $6{\cdot}022 \times 10^{23}$ (b) $6{\cdot}022 \times 10^{22}$ (c) $6{\cdot}022 \times 10^{21}$ (d) $6{\cdot}022 \times 10^{20}$

20. Number of atoms in 12 g of ${}^{12}_{6}C$ is
(a) 6 (b) 12 (c) $6{\cdot}022 \times 10^{23}$ (d) $12 \times 6{\cdot}022 \times 10^{23}$

21. 5 moles of a gas in a closed vessel was heated from 300 K to 600 K. The pressure of the gas doubled. The number of moles of the gas will be
(a) 5 (b) 2·5 (c) 10 (d) 20

22. Which of the following contains the greatest number of oxygen atoms?
(a) 1 g of O (b) 1 g of O_2
(c) 1 g of O_3 (d) all have the same number of atoms

23. If the atomic weight of carbon were set at 24 amu, the value of the Avogadro constant would be
(a) $6{\cdot}022 \times 10^{23}$ (b) $12{\cdot}044 \times 10^{23}$ (c) $3{\cdot}011 \times 10^{23}$ (d) none of these

24. If 32 g of O_2 contain $6{\cdot}022 \times 10^{23}$ molecules at NTP then 32 g of S, under the same conditions, will contain,
(a) $6{\cdot}022 \times 10^{23}$S (b) $3{\cdot}011 \times 10^{23}$S (c) $12{\cdot}044 \times 10^{23}$S (d) 1×10^{23}S

25. How many moles of electrons weigh one kilogram?
(a) 6.022×10^{23} (b) $\frac{1}{9.108} \times 10^{31}$ (c) $\frac{6.022}{9.108} \times 10^{54}$ (d) $\frac{1}{9.108 \times 6.022} \times 10^{8}$
[IIT 2002]

Answers

1-a, 2-b, 3-b, 4-c, 5-c, 6-d, 7-a, 8-b, 9-b, 10-a, 11-d, 12-d, 13-a, 14-b, 15-d, 16-a, 17-b, 18-c, 19-d, 20-c, 21-a, 22-d, 23-b, 24-a, 25-d.

PROBLEMS BASED ON EQUATIONS: STOICHIOMETRY

The word 'stoichiometry' is derived from the Greek words *stoicheion*, which means element, and *metrein*, which means to measure. The numerals used to balance a chemical equation are known as stoichiometric coefficients. These numbers are essential for solving problems based on chemical equations. Hence such problems are also called stoichiometric calculations. The mole method is very useful in such calculations.

For stoichiometric calculations, the mole relationships between different reactants and products are required, as from them, the mass–mass, mass–volume and volume–volume relationships between different reactants and products can be obtained.

For a given balanced equation say,

$$2\,KClO_3 = 2\,KCl + 3\,O_2$$

we can get such relationships directly from the stoichiometric coefficients, e.g.,

$$3 \times \text{moles of } KClO_3 = 2 \times \text{moles of } O_2$$

$$2 \times \text{moles of } KClO_3 = 2 \times \text{moles of } KCl$$

and, $$3 \times \text{moles of } KCl = 2 \times \text{moles of } O_2$$

For balanced chemical equations, one can also apply the **Factor-Label Method** (Ex. 38 and 39).

The above equations can also be obtained **from an unbalanced equation say**

$$KClO_3 = KCl + O_2$$

by applying POAC for different atoms as explained in Chapter 1.

Another important method used for solving problems based on chemical equations is the **equivalent (or milli-equivalent) method.** This method is based on the fact that for the different amounts of reactants and products involved in the reaction, the number of equivalents (or milli-equivalents) of each reactant and each product are equal.

For the reaction,

$$VO + Fe_2O_3 = FeO + V_2O_5$$

eq. of VO = eq. of Fe_2O_3 = eq. of FeO = eq. of V_2O_5

or, m.e. of VO = m.e. of Fe_2O_3 = m.e. of FeO = m.e. of V_2O_5.

In this method too, balancing of chemical equations is not required. This method is generally applied in volumetric stoichiometric calculations.

PROBLEMS

(Answers bracketed with questions)

1. Calculate orally
   (i) How many moles of $CaCO_3$ shall be produced from 5 moles of Ca atoms?
   (ii) How many moles of $BaSO_4$ shall be formed from 5 moles of $BaCl_2$?
   (iii) How many moles of Na_2O shall be produced from 5 moles of Na atoms?
   [(i) 5 (ii) 5 (iii) 2·5]
2. What weight of oxygen will react with 40 g of Ca? (16 g)
3. Calculate, without balancing the following equation, the volume of chlorine at NTP produced from 50 g of sodium chloride.
   $$NaCl + MnO_2 + H_2SO_4 \rightarrow NaHSO_4 + MnSO_4 + Cl_2 + H_2O$$ (9·575 litres)
4. Two tonnes of an iron ore containing 94% of Fe_2O_3 produces iron in pure state. Calculate the weight of iron. (1315 kg)
5. Calculate the volume of acetylene at NTP produced by 100 g of CaC_2 with water. (35 litres)
6. How many litres of detonating gas will be produced at NTP in the decomposition of 0·1 mole of water by an electric current? (3·36 litres)
7. Find the mass of $Cu(NO_3)_2 \cdot 3H_2O$ produced by dissolving 10 g of copper in nitric acid and then evaporating the solution. (38 g)
8. 4·90 g of $KClO_3$, on heating, shows a weight loss of 0·384 g. What per cent of the original $KClO_3$ has decomposed? (20%)
9. When the mixture of $MgCO_3$ and $CaCO_3$ was heated for a long time, the weight decreased by 50%. Calculate the percentage composition of the mixture. ($MgCO_3$: 71.59%; $CaCO_3$: 28.41%)
10. How many moles of $Zn(FeS_2)_2$ can be made from 2 g of Zn, 3 g of Fe and 4 g of S? (0·0269 mole)
11. Calculate the weight of V_2O_5 produced from 2 g of VO and 5·75 g of Fe_2O_3.
    $$VO + Fe_2O_3 \rightarrow FeO + V_2O_5.$$ (2·18 g)
    [Hint: Fe_2O_3 is the limiting reagent.]
12. Equal weights of mercury and iodine are allowed to react completely to form a mixture of mercurous and mercuric iodide leaving none of the reactants. Calculate the ratio by weight of Hg_2I_2 and HgI_2 formed. (0·532 : 1)
13. 5·5 g of a mixture of $FeSO_4 \cdot 7H_2O$ and $Fe_2(SO_4)_3 \cdot 9H_2O$ requires 5·4 mL of 0·1 N $KMnO_4$ solution for complete oxidation. Calculate the number of moles of hydrated ferric sulphate in the mixture. (0·0095 mole)
14. Anhydrous sodium sulphate can absorb water vapour and be converted to the decahydrate. By how many grams would the mass of a 1-g sample of the thoroughly dried Na_2SO_4 increase if exposed to sufficient water vapour to be converted to the decahydrate? (1·27 g)

15. A partially dried clay sample contained 50% of silica and 7% of water. The original clay contained 12% of water. Find the percentage of silica in the original sample. (47·3%)

16. 1 g of a sample containing NaCl, NaBr and an inert material, with excess of $AgNO_3$, produces 0·526 g of precipitate of AgCl and AgBr. By heating this precipitate in a current of chlorine, AgBr converted to AgCl and the precipitate then weighed 0·426 g. Find the percentage of NaCl and NaBr in the sample. (NaCl: 4·25%; NaBr: 23·2%)

17. 3·90 g of a mixture of Al and Al_2O_3, when reacted with a solution of sodium hydroxide, produced 840 mL of a gas at NTP. Find the composition of the mixture. (Al: 17·3%)

[Hint: Only Al produces H_2.]

18. To determine the NaCl content in commercial NaOH, 2 g of the latter was dissolved in water and an excess amount of an $AgNO_3$ solution was added to this solution. The precipitate formed was washed and dried. Its mass was 0·287 g. Find the mass of NaCl in the initial sample. (0·117 g)

19. One litre of an acidified solution of $KMnO_4$ containing 15·8 g of $KMnO_4$ is decolourised by passing sufficient amount of SO_2. If SO_2 is produced by roasting of iron pyrites (FeS_2), what will be the amount of pyrites required to produce the necessary amount of SO_2? (15 g)

20. When a mixture of NaBr and NaCl is repeatedly digested with sulphuric acid, all the halogens are expelled and Na_2SO_4 is formed quantitatively. With a particular mixture, it was found that the weight of Na_2SO_4 obtained was precisely the same as the weight of NaBr–NaCl mixture taken. Calculate the ratio of the weights of NaCl and NaBr in the mixture. (1·454 : 1)

21. 25·4 g of iodine and 14·2 g of chlorine are made to react completely to yield a mixture of ICl and ICl_3. Calculate the number of moles of ICl and ICl_3 formed. (0·1 mole, 0·1 mole)

22. An alloy of aluminium and copper was treated with aqueous HCl. The aluminium dissolved according to the reaction:

$$Al + 3H^+ \rightarrow Al^{3+} + \frac{3}{2}H_2,$$

but the copper remained as pure metal. A 0·350-g sample of the alloy gave 415 cc of H_2 measured at 273 K and 1 atm pressure. What is the weight percentage of Al in the alloy? (95·3%)

23. 1 g of dry green algae absorbs 4.7×10^{-3} mole of CO_2 per hour by photosynthesis. If the fixed carbon atoms were all stored after photosynthesis as starch, $(C_6H_{10}O_5)_n$, how long would it take for the algae to double their own weight assuming photosynthesis takes place at a constant rate? (7·88 hours)

[Hint: Wt. of $(C_6H_{10}O_5)_n = 2 - 1 = 1$ g. Apply POAC for C in

$$CO_2 \rightarrow (C_6H_{10}O_5)_n$$

$$\therefore \text{ time} = \frac{\text{moles of } CO_2}{\text{rate of absorption of } CO_2}.\ ]$$

24. Crude calcium carbide is made in an electric furnace by the following reaction:

$$CaO + 3C \rightarrow CaC_2 + CO$$

The product contains 85% of CaC_2 and 15% of unreacted CaO.

(a) How much CaO is to be added to the furnace charge for each 1000 kg of CaC_2 (pure) produced?

(b) How much CaO is to be added to the furnace charge for each 1000 kg of crude product?

[(a) 1051·5 kg; (b) 893·7 kg]

25. 2·5 g of a mixture of BaO and CaO when treated with an excess of H_2SO_4, produced 4·713 g of the mixed sulphates. Find the percentage of BaO present in the mixture. (60%)

26. A mixture of NaI and NaCl, when heated with H_2SO_4, produced the same weight of sodium sulphate as that of the original mixture. Calculate percentage of NaI in the mixture. (28·85%)

27. 7·46 g of KCl was heated with excess of MnO_2 and H_2SO_4. The gas so produced was then passed through a solution of KI. Calculate the weight of iodine.

$$\left[\text{Hint: } KCl \xrightarrow[H_2SO_4]{MnO_2} Cl_2 \xrightarrow{KI} I_2;\ (\text{moles of } Cl_2 = \text{moles of } I_2)\right]$$

(12·7 g)

28. Carnalite is a double chloride of potassium and magnesium containing 38·86% of water. 0·458 g of it gave 0·71 g of AgCl and 0·666 g of it gave 0·27 g $Mg_2P_2O_7$. Find the percentage of KCl in the carnalite. (26·46%)

29. What volume of hydrogen at NTP is needed to reduce 125 g of MoO_3 to the metal? (58·3 litres)

30. How much gas (in litres) will be produced at 0°C and 760 mm of pressure when 10 g of oxalic acid was heated with concentrated sulphuric acid? (4·97 litres)

$$\left[\text{Hint: } (COOH)_2 \xrightarrow{H_2SO_4} CO + CO_2 + H_2O. \text{ Apply POAC for C atoms.}\right]$$

31. A natural gas sample contains 84% (by volume) of CH_4, 10% of C_2H_6, 3% of C_3H_8 and 3% of N_2. If a series of catalytic reactions could be used for converting all the carbon atoms of the gas into butadiene, C_4H_6, with 100% efficiency, how much butadiene could be prepared from 100 g of the natural gas? (82 g)

32. What weights of P_4O_6 and P_4O_{10} will be produced by the combustion of 2 g of P_4 in 2 g of oxygen leaving no P_4 and O_2. (1·996 g, 2·004 g)

33. From the following reactions, $2CoF_2 + F_2 \rightarrow 2CoF_3$

$$(CH_2)_n + 4n\,CoF_3 \rightarrow (CF_2)_n + 2n\,HF + 4n\,CoF_2$$

calculate how much F_2 will be consumed to produce 1 kg of $(CF_2)_n$. (1·52 kg)

34. A mixture containing $KClO_3$, $KHCO_3$, K_2CO_3 and KCl was heated, producing CO_2, O_2 and H_2O gases according to the following equations:

$$2KClO_3(s) \rightarrow 2KCl(s) + 3O_2$$

$$2KHCO_3(s) \rightarrow K_2O(s) + H_2O(g) + 2CO_2(g)$$

$$K_2CO_3(s) \rightarrow K_2O(s) + CO_2(g)$$

The KCl does not react under the conditions of the reaction. If 100.0 g of the mixture produces 1.80 g of H_2O, 13.20 g of CO_2 and 4.0 g of O_2, what was the composition of the original mixture? ($KClO_3$: 10.2 g, $KHCO_3$: 20 g, K_2CO_3: 13.8 g)

Objective Problems

1. In a gaseous reaction of the type, $aA + bB \rightarrow cC + dD$, which statement is wrong?
   (a) *a* litres of A combine with *b* litres of B to give C and D
   (b) *a* moles of A combine with *b* moles of B to give C and D
   (c) *a* g of A combine with *b* g of B to give C and D
   (d) *a* molecules of A combine with *b* molecules of B to give C and D

2. The equation $2Al\,(s) + \frac{3}{2}O_2\,(g) \rightarrow Al_2O_3\,(s)$ shows that
   (a) 2 moles of Al react with $\frac{3}{2}$ moles of O_2 to produce $\frac{7}{2}$ moles of Al_2O_3
   (b) 2 g of Al react with $\frac{3}{2}$ g of O_2 to produce one mole of Al_2O_3
   (c) 2 g of Al react with $\frac{3}{2}$ litre of O_2 to produce 1 mole of Al_2O_3
   (d) 2 moles of Al react with $\frac{3}{2}$ moles of O_2 to produce 1 mole of Al_2O_3

3. If 5 litres of H_2O_2 produce 50 litres of O_2 at NTP, H_2O_2 is
   (a) '50V' (b) '10V' (c) '5V' (d) '250V'

4. 2·76 g of silver carbonate on being strongly heated yields a residue weighing
   (a) 2·16 g (b) 2·48 g (c) 2·32 g (d) 2·64 g

5. Assuming that petrol is octane (C_8H_{18}) and has density 0·8 g/mL, 1·425 litres of petrol on complete combustion will consume
   (a) 50 moles of O_2 (b) 100 moles of O_2
   (c) 125 moles of O_2 (d) 200 moles of O_2

6. 12 g of Mg will react completely with an acid to give
   (a) 1 mole of O_2 (b) $\frac{1}{2}$ mole of H_2 (c) 1 mole of H_2 (d) 2 moles of H_2

7. 10 mL of gaseous hydrocarbon on combustion gives 40 mL of $CO_2(g)$ and 50 mL of H_2O (vap.). The hydrocarbon is
   (a) C_4H_5 (b) C_8H_{10} (c) C_4H_8 (d) C_4H_{10}

8. For complete oxidation of 4 litres of CO at NTP, the required volume of O_2 at NTP is
   (a) 4 litres (b) 8 litres (c) 2 litres (d) 1 litre

9. The minimum quantity in grams of H_2S needed to precipitate 63·5 g of Cu^{2+} will be nearly
   (a) 63·5 g (b) 31·75 g (c) 34 g (d) 20 g

10. If 0·5 mole of $BaCl_2$ is mixed with 0·2 mole of Na_3PO_4, the maximum number of mole of $Ba_3(PO_4)_2$ that can be formed is
   (a) 0·7 (b) 0·5 (c) 0·30 (d) 0·1

11. For the reaction $A + 2B \rightarrow C$, 5 moles of A and 8 moles of B will produce
(a) 5 moles of C
(b) 4 moles of C
(c) 8 moles of C
(d) 13 moles of C

12. A mixture of N_2 and H_2 is caused to react in a closed container to form NH_3. The reaction ceases before either reactant has been totally consumed. At this stage, 2.0 moles each of N_2, H_2 and NH_3 are present. The moles of N_2 and H_2 present originally were respectively,
(a) 4 and 4 moles
(b) 3 and 5 moles
(c) 3 and 4 moles
(d) 4 and 5 moles

Answers

1-c, 2-d, 3-b, 4-a, 5-c, 6-b, 7-d, 8-c, 9-c, 10-d, 11-b, 12-b.

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CHAPTER THREE

EUDIOMETRY OR GAS ANALYSIS

Gaseous reactions are carried out in a special type of tube known as an eudiometer tube. The tube is graduated in millimetres for volume measurement. The reacting gases taken in the eudiometer tube are exploded by sparks, produced by passing electricity through the platinum terminals provided in the tube. The volumes of the products of a gaseous explosion are determined by absorbing them in suitable reagents, e.g., CO_2 and SO_2 are absorbed in KOH solution, O_2 is absorbed in a solution of alkaline pyrogallol, and CO is absorbed in a solution of ammoniacal cuprous chloride. Since H_2O vapour produced during the reaction changes to liquid on cooling, the volume of water is neglected, but while applying POAC, moles of H_2O produced cannot be neglected.

Eudiometry is mainly based on Avogadro's law, which states that equal volumes of all gases under similar conditions of temperature and pressure contain equal number of molecules. Two gases having equal number of molecules, also have equal number of moles. The mole concept may be applied in solving the problems of this chapter, keeping in mind that in a gaseous reaction the relative volumes (measured under identical conditions) of each reactant and product represent their relative numbers of moles.

A(g) +	B(g) →	C(g) +	D(g)
a volumes	*b* volumes	*c* volumes	*d* volumes
a moles	*b* moles	*c* moles	*d* moles

In the following problems we shall again see that the balancing of gaseous reactions are not required if solved by the POAC method.

EXAMPLES

Ex. 1. *What volume of oxygen will be required for the complete combustion of 18·2 litres of propane at NTP?*

Solution :

$$C_3H_8 + O_2 \rightarrow CO_2 + H_2O$$

Applying POAC for C atoms, we have,

moles of C in C_3H_8 = moles of C in CO_2

$3 \times$ moles of $C_3H_8 = 1 \times$ moles of CO_2. ... (1)

Similarly, applying POAC for H and O atoms,

$8 \times$ moles of $C_3H_8 = 2 \times$ moles of H_2O ... (2)

Hence, volume of NO = 44 mL

and volume of $N_2O = (60 - 44)$ mL = 16 mL.

Ex. 22. *A mixture of formic acid and oxalic acid is heated with concentrated H_2SO_4. The gas produced is collected and on its treatment with KOH solution the volume of the gas decreased by one-sixth. Calculate the molar ratio of the two acids in the original mixture.*

Solution : The decomposition of the acids takes place as follows:

$$\underset{a \text{ moles (say)}}{HCOOH} \rightarrow \underset{\substack{a \text{ moles} \\ a \text{ vol.}}}{H_2O} + \underset{\substack{a \text{ moles} \\ a \text{ vol.}}}{CO} \Big\} \text{ after decomposition}$$

$$\underset{b \text{ moles (say)}}{H_2C_2O_4} \rightarrow \underset{\substack{b \text{ moles} \\ b \text{ vol.}}}{H_2O} + \underset{\substack{b \text{ moles} \\ b \text{ vol.}}}{CO} + \underset{\substack{b \text{ moles} \\ b \text{ vol.}}}{CO_2} \Big\} \text{ after decomposition}$$

H_2O is absorbed by H_2SO_4 and CO_2 is absorbed by KOH.

Thus, as given,

$$\frac{\text{volume of } CO_2}{\text{total volume of } (CO + CO_2)} = \frac{b}{a + b + b} = \frac{1}{6}$$

or

$$\frac{a}{b} = 4.$$

The molar ratio of HCOOH and $H_2C_2O_4 = 4 : 1$.

PROBLEMS

(Answers bracketed with questions)

1. Calculate the volume of CO_2 produced by the combustion of 40 mL of acetone in the presence of excess of oxygen. (120 mL)
2. What volume of air will be required to oxidise 210 mL of sulphur dioxide to sulphur trioxide, if the air contains 21% of oxygen? (500 mL)
3. What volume of CO_2 is obtained in the combustion of 2 litres of butane? (8 litres)
4. If a mixture containing 12 litres of hydrogen and 11·2 litres of chlorine is exploded in an eudiometer tube, what will be the composition of the resulting mixture by volume? (HCl = 22·4 litres , H_2 = 0·8 litre)
5. What volume of oxygen is required for complete combustion of 2·2 g of propane at NTP? (5·6 litres)
6. 500 mL of a hydrocarbon gas, burnt in excess of oxygen, yields 2500 mL of CO_2 and 3 litres of water vapour, all volumes being measured at the same temperature and pressure. What is the formula of the hydrocarbon? (C_5H_{12})

7. When 0·02 litre of a mixture of hydrogen and oxygen was exploded, 0·003 litre of oxygen remained. Calculate the initial composition of the mixture in per cent by volume. (O_2 : 44·0%; H_2 : 56%)

8. 12 mL of a gaseous hydrocarbon was exploded with 50 mL of oxygen. The volume measured after explosion was 32 mL. After treatment with KOH the volume diminished to 8 mL. Determine the formula of the hydrocarbon. (C_2H_6)

9. 15 mL of a gaseous hydrocarbon was required for complete combustion in 357 mL of air (21% of oxygen by volume) and the gaseous products occupied 327 mL (all volumes being measured at NTP). What is the formula of the hydrocarbon? (C_3H_8)

10. 0·90 g of a solid organic compound (molecular weight = 90) containing C, H and O was heated with oxygen corresponding to a volume of 224 mL at STP. After the combustion the total volume of the gases was 560 mL at STP. On treatment with KOH the volume decreased to 112 mL. Determine the molecular formula of the compound. ($C_2H_2O_4$)

11. The explosion of a mixture consisting of one volume of a gas being studied and one volume of H_2 yielded one volume of water vapour and one volume of N_2, the volumes being measured under identical conditions. Find the formula of the gas being studied. (N_2O)

12. 5 mL of a gas containing C and H was mixed with an excess of oxygen (30 mL) and the mixture exploded by means of an electric spark. After the explosion the volume of the mixed gases remaining was 25 mL. On adding a concentrated solution of KOH, the volume further diminished to 15 mL, the residual gas being pure oxygen. All volumes have been reduced to NTP. Calculate the molecular formula of the hydrocarbon gas. (C_2H_4)

13. 40 mL of ammonia gas taken in an eudiometer tube was subjected to sparks till the volume did not change any further. The volume was found to increase by 40 mL. 40 mL of oxygen was then mixed and the mixture was further exploded. The gases remained were 30 mL. Deduce the formula of ammonia. (NH_3)

14. 20 mL of a gas containing H and S was heated with tin. When the reaction was over, there was no change in volume. The residual gas was hydrogen. If the molecular weight of the gas is 34, calculate the molecular formula. (H_2S)

15. When a certain quantity of oxygen was ozonised in a suitable apparatus, the volume decreased by 4 mL. On addition of turpentine the volume further decreased by 8 mL. All volumes were measured at the same temperature and pressure. From these data, establish the formula of ozone. (O_3)

16. 1 litre of a sample of ozonised oxygen weighs 1·5 g at 0°C and one atm pressure. 100 mL of this sample reduced to 90 mL when treated with turpentine under the same conditions. Find the molecular weight of ozone. (48)

17. 280 mL of sulphur vapour at NTP weighs 3·2 g. Determine the molecular formula of the sulphur vapour. (S_8)

18. 1 litre of oxygen and 1 litre of hydrogen are taken in a vessel of 2-litre capacity at NTP. The gases are made to combine by applying electric sparks. Assume that

water is formed quantitatively. How many grams of water are formed? What is the other component present in the vessel and in what weight? If the vessel is now heated to 100°C, what will be the pressure inside the vessel in mm of Hg?
(0·8036 g; O_2; 0·7143 g; 778 mm)

19. 20 mL of a mixture of C_2H_2 and CO was exploded with 30 mL of oxygen. The gases after the reaction had a volume of 34 mL. On treatment with KOH, 8 mL of oxygen remained. Calculate the composition of the mixture.
(C_2H_2 : 6 mL; CO : 14 mL)

20. On passing 25 mL of a gaseous mixture of N_2 and NO over heated copper, 20 mL of the gas remained. Calculate the percentage of each in the mixture.
(N_2 : 60%; NO : 40%)

21. 40 mL of a mixture of hydrogen, CH_4 and N_2 was exploded with 10 mL of oxygen. On cooling, the gases occupied 36·5 mL. After treatment with KOH, the volume reduced by 3 mL and again on treatment with alkaline pyrogallol, the volume further decreased by 1·5 mL. Determine the composition of the mixture.
(H_2 : 12·50%; CH_4 : 7·50%; N_2 : 80%)

22. What volume of air is needed for the combustion of 1 metre^3 of a gas having the following composition in percentage volume : 50% of H_2, 35% of CH_4, 8% of CO, 2% of C_2H_4 and 5% of noncombustible admixture? The air contains 21% (by volume) of oxygen.
(5 cubic metre)

23. 38 mL of a mixture of CO and H_2 was exploded with 31 mL of O_2. The volume after the explosion was 29 mL which reduced to 12 mL when shaken with KOH. Find the percentage of CO and H_2 in the mixture. (CO = 44·7% ; H_2 = 55·3%)

24. A mixture of CH_4 and C_2H_2 occupied a certain volume at a total pressure of 63 mm. The sample was burnt to CO_2 and H_2O and the CO_2 alone was collected and its pressure was found to be 69 mm in the same volume and at the same temperature as the original mixture. What fraction of the mixture was methane?
(0·90)

25. A mixture of 20 mL of CO, CH_4 and N_2 was burnt in an excess of oxygen, resulting in reduction of 13 mL of volume. The residual gas was treated with KOH solution when there was a further reduction of 14 mL in volume. Calculate the volumes of CO and CH_4 in the given mixture. (10 mL, 4 mL)

26. A mixture of oxygen and hydrogen is analysed by passing it over hot copper oxide and through a drying tube. Hydrogen reduces the CuO according to the equation, $CuO + H_2 \rightarrow Cu + H_2O$; oxygen then oxidises the copper formed:

$$Cu + \frac{1}{2}O_2 \rightarrow CuO$$

100 cm^3 of the mixture measured at 25°C and 750 mm yields 84·5 cm^3 of dry oxygen measured at 25°C and 750 mm after passing over CuO and a drying agent. What is the mole per cent of H_2 in the mixture?
(10·3%)

[Hint: $\underset{x}{CuO} + \underset{x}{H_2} \rightarrow Cu + H_2O ; \underset{x}{Cu} + \underset{x/2}{\frac{1}{2}O_2} \rightarrow CuO$

If x is moles of H_2 or vol. of H_2 in the mixture, $100 - \left(x + \frac{x}{2}\right) = 84·5$.]

27. When a … over a … not ent…

28. When … reduct… be the… [Hint:

29. One v… 2·5 vo… and … condi…

30. 5·22 … in a … whic… retu… to in… the … gas … [Hi… exc…

27. When a mixture consisting of 10 moles of SO_2 and 15 moles of O_2 was passed over a catalyst, 8 moles of SO_3 was formed. How many moles of SO_2 and O_2 did not enter into the reaction? $\begin{bmatrix} SO_2: 2 \text{ moles} \\ O_2: 11 \text{ moles} \end{bmatrix}$

28. When 100 mL of an O_2–O_3 mixture was passed through turpentine, there was reduction of volume by 20 mL. If 100 mL of such a mixture is heated, what will be the increase in volume? (10 mL)

[**Hint:** O_3 is absorbed by turpentine.]

29. One volume of a compound of carbon, hydrogen and oxygen was exploded with 2·5 volumes of oxygen. The resultant mixture contained 2 volumes of water vapour and 2 volumes of carbon dioxide. All volumes were measured in identical conditions. Determine the formula of the compound. (C_2H_4O)

30. $5{\cdot}22 \times 10^{-4}$ mole of a gas containing H_2, O_2 and N_2 exerted a pressure of 67·4 mm in a certain standard volume. The gas was passed over a hot platinum filament which combined H_2 and O_2 into H_2O which was frozen out. When the gas was returned to the same volume, the pressure was 14·3 mm. Extra oxygen was added to increase the pressure to 44·3 mm. The combustion was repeated, after which the pressure read 32·9 mm. What was the mole fraction of H_2, O_2 and N_2 in the gas sample? (0·638, 0·262, 0·1)

[**Hint:** 2 volumes of H_2 combine with 1 vol. of O_2. In the first combustion H_2 is in excess, while in the second one, O_2 is in excess.]

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CHAPTER FOUR

ATOMIC WEIGHT

The atomic weight of an element is defined as the average weight of the atoms of the element relative to a carbon atom, taken as exactly 12. **Atomic weight in grams is, in fact, the weight of one mole of atoms**, e.g., the atomic weight of oxygen is 16 and so 16 grams is the weight of 1 mole of oxygen atoms. Mathematically,

$$\text{atomic weight} = \frac{\text{weight of atoms in grams}}{\text{number of moles of atoms}}.$$

Atomic weight is measured in atomic mass unit (amu). Atomic mass unit is defined as $\frac{1}{12}$ of the mass of the ^{12}C isotope ($1 \text{ amu} = 1{\cdot}66 \times 10^{-24}$ g). One amu is also called one **dalton**.

We shall see here how the mole method can be applied in solving the problems on atomic weight by on different methods, viz., from Dulong and Petit's law, vapour density of chloride of the elements, law of isomorphism, Cannizzaro's method, etc.

EXAMPLES

Ex. 1. *A sample of pure* Ca *metal weighing* 1·35 *grams was quantitatively converted to* 1·88 *grams of pure* CaO. *What is the atomic weight of* Ca? (O = 16)

Solution : From the formula of CaO,

we know, moles of Ca = moles of O

$$\frac{\text{weight of Ca}}{\text{atomic wt. of Ca}} = \frac{\text{weight of O}}{\text{atomic wt. of O}} \qquad \text{(Rule 2, Chapter 1)}$$

$$\frac{1{\cdot}35}{\text{at. wt. of Ca}} = \frac{1{\cdot}88 - 1{\cdot}35}{16}.$$

Atomic weight of Ca = 40·75.

Ex. 2. *A compound contains* 28% *of nitrogen and* 72% *of a metal by weight.* 3 *atoms of the metal combine with* 2 *atoms of nitrogen. Find the atomic weight of the metal.* (N = 14)

Solution : The formula of the compound is M_3N_2 (M representing the metal)

$2 \times$ moles of M $= 3 \times$ moles of N. (Rule 6, Chapter 1)

Now if the weight of the compound is 1 gram

then weight of M = 0·72 g and weight of N = 0·28 g.

Comparing these values with the moles of X, Y and Z calculated above, we find that moles of X and Y are in excess and therefore, moles of X and Y associated with 0·03 mole of Z are 0·01 and 0·02 mole respectively. Now,

$$\text{wt. of Z + wt. of Y + wt. of Z = wt. of } XY_2Z_3$$

or $0{\cdot}01 \times 60 + 0{\cdot}02 \times$ at. wt. of $Y + 0{\cdot}03 \times 80 = 4{\cdot}4$ (Rule 2, Chapter 1)

$\therefore$ at. wt. of Y = 70 amu.

PROBLEMS

(*Answers bracketed with questions*)

1. 1·5276 grams of $CdCl_2$ was found to contain 0·9367 gram of Cd. Calculate the atomic weight of Cd. (112·4 amu)
2. In air, element X is oxidised to compound XO_2 . If 1·0 gram of X reacts with 0·696 g of oxygen, what is the atomic weight of X? (46 amu)
3. When $BaBr_2$ is heated in a stream of chlorine, it is completely converted to $BaCl_2$. From 1·50 g of $BaBr_2$, just 1·05 g of $BaCl_2$ is obtained. Calculate the atomic weight of Ba from this data. (137·5)
4. Naturally occurring boron consists of two isotopes whose atomic weights are 10·01 and 11·01. The atomic weight of natural boron is 10·81. Calculate the percentage of each isotope in natural boron. (20%; 80%)
5. In an experiment pure carbon monoxide was passed over red hot copper oxide. CO_2, so produced, weighed 0·88 g and the weight of copper oxide was reduced by 0·3232 g. Calculate the atomic weight of carbon. (12·0)
6. 4·008 g of pure $KClO_3$ was quantitatively decomposed to give 2·438 g of KCl and oxygen. KCl was dissolved in water and treated with $AgNO_3$ solution. The result was a precipitate of AgCl weighing 4·687 g. Under further treatment, AgCl was found to contain 3·531 g of Ag. What are the atomic weights of Ag, Cl and K relative to O = 16? (108·0, 35·5, 39·0)
7. From the following data calculate the atomic weight of carbon.

Compound	*Vapour density*	*% of C*
CO	14	42·8
CS_2	38	15·8
C_2H_2	14	85·7
C_3H_4	22	81·4
C_6H_6	39	92·3

(12·0)

8. The vapour density of a volatile chloride of a metal is 74·6. If the specific heat of the metal is 0·55, calculate the exact atomic weight of the metal and the formula of its chloride. (7·2, MCl_4)

9. A sample of a metal chloride weighing 0·22 g required 0·51 g of $AgNO_3$ to precipitate the chloride completely. The specific heat of the metal is 0·057. Find the molecular formula of the chloride if the metal is M. (MCl_3)

10. A hydrated sulphate of a metal contained 8·1% of the metal and 43·2% of SO_4^{2-} by weight. Assuming the specific heat of the metal to be 0·242, determine the formula of the hydrated sulphate. [$M_2(SO_4)_3 \cdot 18\,H_2O$]

11. 0·096 g of stannic chloride gave 25·84 mL of its vapour at 120°C and 350 mm pressure. If the chloride contains 54·6% of chlorine and tin has the valency equal to 4, what will be the atomic weight of tin? (118)

12. A metal forms three volatile chlorides containing 23·6%, 38·2% and 48·3% of chlorine respectively. The vapour densities of the chlorides (H = 1) are 74·6, 92·9 and 110·6 respectively. The specific heat of the metal is 0·055. Find the exact atomic weight of the metal and formulae of its chlorides.
(114·9; MCl; MCl_2; MCl_3)

13. Cu_2S and Ag_2S are isomorphous. The percentages of sulphur in these compounds are 20·14% and 12·94% respectively. If the atomic weight of Cu is 63·5, calculate the atomic weight of Ag. (107·9)

14. The natural titanium oxide, known as rutile and containing 39·95% of oxygen, is isomorphous with SnO_2, known as cassiterite. Calculate the atomic weight of titanium. (48·1)

15. The atomic weight of sulphur was determined by decomposing 6·2984 g of Na_2CO_3 with H_2SO_4 and weighing the resultant Na_2SO_4 formed. The weight was found to be 8·4380 g. Taking the atomic weights of C, O and Na as 12·011, 15·999 and 22·990 respectively, calculate the atomic weight of sulphur. (32·019)

16. 12·5843 grams of a sample of $ZrBr_4$ was dissolved and after several chemical steps, all of the combined bromine was precipitated as AgBr. The silver content of the AgBr was found to be 13·216 g. Calculate the atomic weight of Zr from this experiment. (Ag = 107·868, Br = 79·904) (91·32)

17. In a chemical determination of the atomic weight of vanadium, 2·8934 g of pure $VOCl_3$ was allowed to undergo a set of reactions as a result of which all the chlorine contained in this compound was converted to AgCl which weighed 7·1801 g. Calculate the atomic weight of vanadium. (Ag = 107·868, Cl = 35·453) (50·91)

MOLECULAR WEIGHT

Molecular weight of a compound is defined as the weight of a molecule of the compound relative to a carbon atom, the atomic weight of which is supposed to be exactly 12. The molecular weight when expressed in grams is called gram molecular weight. **The molecular weight in grams is, in fact, the weight of 1 mole of molecules, e.g.,** molecular weight of O_2 is 32 and 32 g is the weight of 1 mole of oxygen molecules. Mathematically,

$$\text{molecular weight} = \frac{\text{weight of molecules in grams}}{\text{number of moles of molecules}}.$$

Molecular weight is measured in atomic mass unit (amu). Atomic mass unit is defined as 1/12 of the mass of the ^{12}C isotope (1 amu $= 1{\cdot}66 \times 10^{-24}$ g). There are various methods to determine the molecular weight of compounds viz., vapour-density method (e.g. Regnault's method, Victor Meyer's method, Dumas method and Hofmann method), depression-in-freezing-point method, elevation-in-boiling-point method, gravimetric method, (silver-salt method of organic acids and platinichloride method for organic bases), volumetric method, etc. The problems on molecular weight based on depression-in-freezing-point and elevation-in-boiling-point methods shall be discussed in Chapter 13 (Dilute Solution and Colligative Propertries).

The mole method is found to be very useful in tackling the problems on molecular weight based on the aforesaid methods.

EXAMPLES

Ex. 1. 96·00 g *of a gas occupies the same volume as* 84 g *of nitrogen under similar conditions of temperature and pressure. Find the molecular weight of the gas.* (N = 14)

Solution : According to Avogadro's principle, equal volumes of all gases under identical conditions of temperature and pressure contain equal numbers of molecules or moles.

$\therefore$ number of moles of N_2 = number of moles of the gas

$$\frac{84}{28} = \frac{96}{M} \quad \left\{\begin{array}{l}\text{say } M = \text{mol. wt. of the gas} \\ N_2 = 28\end{array}\right\}$$

(Rule 1, Chapter 1)

$M = 32.$

Ex. 18. *When 2·96 g of mercuric chloride is vaporised in a 1-litre bulb at 680 K, the pressure is 458 mm. What is the molecular weight and molecular formula of mercuric chloride vapour?* (Hg = 200·6)

Solution : Let M be the molecular weight of mercuric chloride.

No. of moles of the mercuric chloride vapour $= \dfrac{2{\cdot}96}{M}$.

Again from the gas equation $pV = nRT$,

$$\text{no. of moles} = n = \frac{pV}{RT} = \frac{\left(\frac{458}{760}\right) \times 1}{0{\cdot}0821 \times 680}$$

where $p = \dfrac{458}{760}$ atm, V = 1 litre, R = 0·0821 lit. atm K^{-1} mol^{-1} and $T = 680$ K.

Hence
$$\frac{2{\cdot}96}{M} = \frac{\frac{458}{760} \times 1}{0{\cdot}0821 \times 680}$$
$$M = 274.$$

Since $HgCl_2$ has a molecular weight of $(200{\cdot}6 + 2 \times 35{\cdot}5) = 271{\cdot}6$ which is nearly equal to the calculated value of 274, $HgCl_2$ is the molecular formula for mercuric chloride.

PROBLEMS

(*Answers bracketed with questions*)

1. What is the volume of 6 g of hydrogen at 1·5 atm and 273°C? (89·6 litres)

2. A certain gas occupies 0·418 litre at 27°C and 740 mm of Hg. (i) What is its volume at STP? (ii) If the same gas weighs 3·00 g, what is its molecular weight? (0·3704 litre. 181·4)

3. 33·6 cc of phosphorus vapour weighs 0·0625 g at 546°C and 76 cmHg pressure. What is the molecular weight of phosphorous? How many atoms are there in one molecule of phosphorus vapour? (125, 4)

4. The mass of a sulphur atom is double that of an oxygen atom. Can we decide on this basis that the density of sulphur vapour relative to oxygen is two? (No)

5. In a Victor Meyer determination, 0·0926 g of a liquid gave 28·9 mL of gas collected over water and measured at 16°C and 753·6 mm pressure. Calculate molecular weight and vapour density of the substance. (Aq. tension at 16°C = 13·6 mm) (78, 39)

[**Hint:** Find weight of 22400 mL (NTP) of the gas]

6. A Dumas bulb of capacity 200 mL weighs 22·567 g at 120°C. Filled with vapour of a substance at 120°C and 755 mmHg pressure, it weighs 22·8617 g. Find the molecular weight of the substance. (47·8)

7. 0·2704 g of a substance when introduced into a Hofmann tube generated 110 mL of vapours at 99·6°C and 747 mmHg pressure. The height of mercury inside the tube was 285·2 mm. Calculate the molecular weight of the substance. (122·6)

8. 0·607 g of the silver salt of a tribasic acid on combustion deposited 0·37 g of pure silver. Calculate the molecular weight of the acid. (210·16)

9. 0·304 g of a silver salt of a dibasic acid left 0·216 g of silver on ignition. Calculate its molecular weight. (90)

10. 0·66 g of platinichloride of a monoacid base left 0·150 g of platinum. Calculate its molecular weight. (Pt = 195) (221)

11. The chloroplatinate of a diacid base contains 39% platinum. What is the molecular weight of the base? (Pt = 195) (90)

12. A solution containing 3·00 g of a monobasic organic acid was just neutralised by 40 mL of 0·5 N NaOH solution. Calculate the molecular weight of the acid. (150)

13. 0·366 g of an organic base required 15 mL of $\frac{N}{5}$ HCl for exact neutralisation. If the molecular weight of the base is 122, find its acidity. (1)

❑❑❑

CHAPTER SIX

CHEMICAL EQUIVALENCE

Significance of Equivalent Weight

An equivalent of a substance is defined as the amount of it which combines with 1 mole of hydrogen atoms or replaces the same number of hydrogen atoms in a chemical reaction. The weight in grams of 1 equivalent is called the equivalent weight in grams. For example, in the compounds HBr, H_2O and NH_3; one mole of H combines with one mole of Br, ½ mole of O and ⅓ mole of N respectively. Hence the equivalent weights in grams of Br, O and N are the weights of 1 mole of Br, ½ mole of O, ⅓ mole of N respectively. In other words, 1 mole each of Br, O and N contains their 1 equivalent, 2 equivalents and 3 equivalents respectively.

Thus: eq. wt. of Br $= 1 \times 79{\cdot}9 = 79{\cdot}9$

$$\text{eq. wt. of O} = \frac{1}{2} \times 16 = 8{\cdot}0$$

$$\text{eq. wt. of N} = \frac{1}{3} \times 14 = 4{\cdot}67$$

(Atomic weights of Br, O and N are 79·9, 16 and 14 respectively.)

To determine the equivalent weight of an element, it is not necessary to proceed from its hydrogen compound only. Equivalent weight of an element can be calculated using the composition of the compound of the given element with any other element, whose equivalent weight is known by the knowledge of the **Law of Equivalence.** The law states that **one equivalent of an element combines with one equivalent of the other.** Accordingly, the equivalent weight of an element is the weight of its mole combining with one equivalent of another element. It can be further illustrated by the following example:

The equivalent weight of Al in Al_2O_3 can be calculated if it is known that 1 mole of O contains 2 equivalents of it. From the composition of Al_2O_3 we write, 3 moles of O combine with 2 moles of Al, or 6 equivalents of O combine with 2 ... O combines with ⅓ mole of Al.

$\therefore$ eq. wt. of $MnSO_4 = \dfrac{\text{Mol. wt.}}{2}$

Hence the answer is (b).

PROBLEMS

(Answers bracketed with questions)

1. Fe forms two chlorides, $FeCl_2$ and $FeCl_3$. Does Fe have the same value of equivalent weight in its compounds? (No)

2. The equivalent weight of a metal is 12. What is the equivalent weight of its oxide? (20)

3. 0·2 g of oxygen and 3·17 g of a halogen combine separately with the same amount of a metal. What is the equivalent weight of the halogen? (127)

4. Arsenic forms two oxides, one of which contains 65·2% and the other, 75·7% of the element. Determine the equivalent weights of arsenic in both cases. (15, 24·9)

5. 1·80 g of a metal oxide required 833 mL of hydrogen at NTP to be reduced to its metal. Find the equivalent weights of the oxide and the metal. (24·2, 16·2)

6. A certain amount of a metal whose equivalent weight is 28, displaces 0·7 litre of hydrogen measured at NTP from an acid. Calculate the weight of the metal. (1·75 g)

7. 9·44 g of a metal oxide is formed by the combination of 5 g of the metal. Calculate the equivalent weight of the metal. (9·01)

8. 14·7 g of sulphuric acid was needed to dissolve 16·8 g of a metal. Calculate the equivalent weight of the metal and the volume of hydrogen liberated at NTP. (56, 3·36 litres)

9. The salt Na_2HPO_4 is formed when orthophosphoric acid is reacted with an alkali. Find the equivalent weight of orthophosphoric acid. (49)

10. 0·501 g of silver was dissolved in nitric acid and HCl was added to this solution, AgCl so formed weighed 0·6655 g. If the equivalent weight of chlorine is 35·5, what will be the equivalent weight of silver? (108)

11. 5 g of zinc displaced 4·846 g of copper from a copper sulphate solution. If zinc has an equivalent weight of 32·5, find the equivalent weight of copper. (31·5)

12. (i) What is the weight of sodium bromate and molarity of solution necessary to prepare 85·5 mL of 0·672 N solution when the half-cell reaction is

$$BrO_3^- + 6H^+ + 6e \rightarrow Br^- + 3H_2O?$$

(ii) What would be the weight as well as molarity if the cell reaction is

$$2BrO_3^- + 12H^+ + 10e \rightarrow Br_2 + 6H_2O?$$ (IIT 1987)

[(i) 1·4479 g, 0·112 M (ii) 1·7236 g, 0·134 M]

13. 2 g of a metal when dissolved in nitric acid converted to its nitrate. The nitrate was then precipitated to 2·66 g of the metal chloride. Find the equivalent weight of the metal. (107·57)

14. 2 g of anhydrous $BaCl_2$, present in a solution, was quantitatively converted to 2·25 g of $BaSO_4$. Find the equivalent weight of Ba. (64·5)

15. The chloride of a metal 'M' contains 47·23% of the metal. 1 g of this metal displaced from a compound 0·88 g of another metal 'N'. Find the equivalent weight of 'M' and 'N' respectively. (31·77 ; 27·96)

16. What weight of $CuSO_4 \cdot 5H_2O$ must be taken to make 0·5 litre of 0·01 M Cu (II) ion solution? (1·248 g)

17. How many litres of SO_2 taken at NTP have to be passed through a solution of $HClO_3$ to reduce 16·9 g of it to HCl? (13·44 litres)

18. How many grams of H_2S will react with 6·32 g of $KMnO_4$ to produce K_2SO_4 and MnO_2? (0·511 g)

[**Hint:** ON change for Mn, + 7 to + 4 and for S, – 2 to + 6]

19. One gram of the acid $C_6H_{10}O_4$ requires 0·768 g of KOH for complete neutralisation. How many neutralisable hydrogen atoms are in this molecule? (2)

20. What is the weight of 1 gram-equivalent of the oxidising and the reducing agent in the following reaction?

$$5Zn + V_2O_5 \rightarrow 5ZnO + 2V \qquad (V = 50{\cdot}94,\ Zn = 65{\cdot}38 \text{ and } O = 16)$$

[**Hint:** Zn is reducing agent and its ON change = 2; V_2O_5 is oxidising agent and its ON change = 10] (32·69 g, 18·2 g)

21. Write the following oxidising agents in the increasing order of equivalent weight:

$$KMnO_4 \rightarrow Mn^{2+}$$
$$K_2Cr_2O_7 \rightarrow Cr^{3+}$$
$$KMnO_4 \rightarrow MnO_2$$
$$KIO_3 \rightarrow I^-$$
$$KClO_3 \rightarrow Cl^-$$

($KClO_3$, $KMnO_4$, KIO_3, $K_2Cr_2O_7$, $KMnO_4$)

22. Find the equivalent weight of H_3PO_4 in each of the following reactions:

$$H_3PO_4 + OH^- \rightarrow H_2PO_4^- + H_2O$$
$$H_3PO_4 + 2OH^- \rightarrow HPO_4^{2-} + 2H_2O$$
$$H_3PO_4 + 3OH^- \rightarrow PO_4^{3-} + 3H_2O$$

(98, 49, 32·67)

23. Calculate the equivalent weight of SO_2 in the following reactions:

(a) $SO_2 + 2H_2S = 3S + 2H_2O$

(b) $5SO_2 + 2KMnO_4 + 2H_2O = K_2SO_4 + 2MnSO_4 + 2H_2SO_4$ (16, 32)

24. How many equivalents per mole of H_2S are there in its oxidation to SO_2? (6)

□□□

CHAPTER SEVEN

VOLUMETRIC CALCULATIONS

The quantitative analysis in chemistry is primarily carried out by two methods, viz., volumetric analysis and gravimetric analysis. In the first method the mass of a chemical species is measured by measurement of volume, whereas in the second method it is determined by taking the weight.

In the volumetric analysis, the process of determination of strength of a solution by another solution of known strength under volumetric conditions is known as *titration*. Titrations are of various types, viz., acid and base titration, oxidation–reduction titration, iodine titration, etc. The fundamental basis of all titrations is the **law of equivalence** which states that at the end point of a titration the volumes of the two titrants reacted have the same number of equivalents or milliequivalents.

The strength of a solution in volumetric analysis is generally expressed in terms of normality, i.e., number of equivalents per litre but since the volume in the volumetric analysis is generally taken in millilitres (mL), the normality is expressed by milliequivalents per millilitre.

Milliequivalents (m.e.)

From the definition of normality we know,

$$\text{normality of a solution} = \frac{\text{number of equivalents}}{\text{volume in litres}}.$$

$\therefore$ number of equivalents = normality × volume in litres.

If the volume is taken in mL,

number of milliequivalents (m.e.) = normality × vol. in mL.

$$\therefore \quad \frac{\text{number of milliequivalents}}{1000} = \text{number of equivalents}$$

$$\left(\frac{\text{m.e.}}{1000} = \text{equivalents}\right)$$

For a given solution, number of equivalents per litre is the same as the number of milliequivalents per mL.

Milliequivalents and Chemical Reactions

It is important at this stage to mention that for any given reaction, say,

$$A + 2B = 2C + 3D,$$

the stoichiometric coefficients of A, B, C and D represent the molar ratio of A, B, C and D, i.e., 1 mole of A combines with 2 moles of B to produce 2 moles of C and 3 moles of D. But these coefficients do not represent the

$x=4,\ y=2$ and $z=2$.

Ex. 73. 10 mL *of tap water containing* Ca^{2+} *and* Mg^{2+} *in the presence of* HCO_3^- *was properly buffered and the indicator murexide added. The sample was diluted and heated to 60°C. Titration with* 0.01 M EDTA *solution changed the indicator colour at* 7.50 mL. *This complexed* Ca^{2+} *only.*

A second 10-mL *sample was made basic and Erio T indicator added. Titration with* 0.01 M EDTA *solution changed the indicator colour at* 13.02 mL. *Under these conditions both* Ca^{2+} *and* Mg^{2+} *are complexed.*

If the 10 mL *of water sample were to be evaporated to dryness, what weight of* $CaCO_3 + MgCO_3$ *would be formed?*

Solution : All EDTA complexes are formed on a one-to-one basis with dipositive ions.

Mole of $Ca^{2+} + Mg^{2+}$ = mole of $CaCO_3$ + mole of $MgCO_3$

$$= \frac{0.01 \times 13.02}{1000} = 13 \times 10^{-5}$$

Mole of Ca^{2+} = mole of $CaCO_3$

$$= \frac{0.01 \times 7.50}{1000} = 7.50 \times 10^{-5}.$$

$\therefore$ mole of $MgCO_3 = 13 \times 10^{-5} - 7.50 \times 10^{-5} = 5.5 \times 10^{-5}$.

$\therefore$ weight of $CaCO_3 + MgCO_3 = 7.50 \times 10^{-5} \times 100 + 5.5 \times 10^{-5} \times 84$

$= 1.21 \times 10^{-2}$ g.

($CaCO_3 = 100$, $MgCO_3 = 84$)

PROBLEMS

(Answers bracketed with questions)

1. Calculate the strength in g/L of 3 N HCl and $\frac{N}{2}$ H_2SO_4 solutions. (109·5, 24·5)

2. How many mL of 1 M sulphuric acid is required to neutralise 10 mL of 1 M sodium hydroxide solution? (5 mL)

3. 2 litres of ammonia at 13°C and 0·90 atmospheric pressure is neutralised by 134 mL of H_2SO_4 solution. Find the normality of the acid. (0·57 N)

4. What weight of $CuSO_4 \cdot 5H_2O$ must be taken to make 0·5 litre of 0·01 M copper (II) ion solution? (1·248 g)

5. (a) Calculate the molarity of hydrogen chloride in a solution when 0·365 g of it has been dissolved in 100 mL of the solution.

   (b) 3 g of a salt of molecular weight 30 is dissolved in 250 g of water. The molality of the solution is .... [(a) 0·1 M (b) 0·4 m]

6. Derive a formula for the volume of water, V_2, which must be added to V_1 mL of concentrated solution of molarity M_1 to give a solution of molarity M_2.

$$\left[V_2 = \frac{V_1(M_1 - M_2)}{M_2}\right]$$

7. Find the equivalent weight of H_3PO_4 in the reaction
$[Ca(OH)_2 + H_3PO_4 = CaHPO_4 + 2H_2O]$ (49)

8. A 250-mL sample of 0·20 M hydrochloric acid is to be made by diluting the approximate amount of the concentrated reagent 11·7 M. What volume of the latter should be used? (4·27 mL)

9. How many mL of each of two hydrochloric acids of strengths 12 N and 3 N are to be mixed to make one litre of 6 N solution? (333·33 mL, 666·67 mL)

10. What volumes of 2 M and 6 M solutions of HCl have to be mixed to prepare 500 mL of a 3 M solution? Disregard the change in the volume in mixing. (375 mL, 125 mL)

11. 1 litre of a solution contains 18·9 g of HNO_3 and 1 litre of another solution contains 3·2 g of NaOH. In what volume ratio must these solutions be mixed to obtain a solution having a neutral reaction? (1 : 3·75)

12. 10 mL of sulphuric acid solution (sp. gr. = 1·84) contains 98% by weight of pure acid. Calculate the volume of 2·5 N NaOH solution required to just neutralise the acid. (147·2 mL)

13. What is the molarity and molality of a 13% solution (by weight) of H_2SO_4 solution? Its density is 1·090 g/mL. To what volume should 100 mL of this acid be diluted in order to prepare 1·5 N solution? (1·45 M, 1·52 *m*, 193·3 mL)

14. How many mL of concentrated sulphuric acid of sp. gr. 1·84 containing 98% H_2SO_4 solution by weight is required to prepare 200 mL of 0·5 N solution? (2·71 mL)

15. 26 mL of a 1 N Na_2CO_3 solution is neutralised by the acids *A* and *B* in different experiments. The volumes of the acids *A* and *B* required were 10 mL and 40 mL respectively. How many volumes of *A* and *B* are to be mixed in order to prepare 1 litre of normal acid solution? (179·4, 820·6)

16. 25 mL of a solution of Fe^{2+} ions was titrated with a solution of the oxidising agent $Cr_2O_7^{2-}$. 32·45 mL of 0·0153 M $K_2Cr_2O_7$ solution was required. What is the molarity of the Fe^{2+} solution? (0·1192 M)

17. Upon heating a litre of a $\frac{N}{2}$ HCl solution, 2·675 g of hydrogen chloride is lost and the volume of the solution shrinks to 750 mL. Calculate (i) the normality of the resultant solution (ii) the number of milliequivalents of HCl in 100 mL of the original solution. (0·569 N, 50)

18. The reaction $Zn + CuSO_4 = Cu + ZnSO_4$ goes completely to the right. In one experiment 10 g of metallic zinc was added to 200 mL of copper sulphate solution.

After all copper is precipitated it was found that not all the zinc had dissolved. After filtration the total solid at the end of the reaction was 9·810 g. Calculate (i) the weight of copper deposited and (ii) molarity of copper sulphate in the original solution. (Cu = 63·5, Zn = 65·4) (6·35 g, 0·5 M)

19. 0·108 g of finely-divided copper was treated with an excess of ferric sulphate solution until copper was completely dissolved. The solution after the addition of excess dilute sulphuric acid required 33·7 mL of 0·1 N $KMnO_4$ for complete oxidation. Find the equation which represents the reaction between metallic copper and ferric sulphate solution. (Cu = 63·6, Fe = 56)
[$Cu + Fe_2(SO_4)_3 = CuSO_4 + 2FeSO_4$]

20. A commercial sample (2·013 g) of NaOH containing Na_2CO_3 as an impurity was dissolved to give 250 mL of solution. A 10 mL portion of the solution required 20 mL of 0·1 N H_2SO_4 solution for complete neutralisation. Calculate the percentage by weight of Na_2CO_3 in the sample. (2·29%)

21. (i) A solution of a mixture of KCl and KOH was neutralised with 120 mL of 0·12 N HCl. Calculate the amount of KOH in the mixture.

(ii) After titration, the resultant solution was made acidic with HNO_3. Then excess of $AgNO_3$ solution was added to precipitate the AgCl which weighed 3·7 g after drying. Calculate percentage of KOH in the original mixture. (0·806 g, 48·7 %)

22. 10·03 g of vinegar was diluted to 100 mL and a 25 mL sample was titrated with the 0·0176 M $Ba(OH)_2$ solution. 34·30 mL was required for equivalence. What is the percent of acetic acid in the vinegar? (2·90 %)

23. Zinc can be determined volumetrically by the precipitation reaction

$$3\,Zn^{2+} + 2\,[4K^+, Fe(CN)_6^{4+}] \longrightarrow K_2Zn_3[Fe(CN)_6]_2 + 6\,K^+$$

A sample of zinc ore weighing 1·5432 g was prepared for reaction and required 34·68 mL of 0·1043 M $K_4Fe(CN)_6$ for titration. What is the percentage of zinc in the ore? (23 %)

24. 5·5 g of a mixutre of $FeSO_4 \cdot 7H_2O$ and $Fe_2(SO_4)_3 \cdot 9H_2O$ requires 5·4 mL of 0·1 N $KMnO_4$ solution for complete oxidation. Calculate the number of mole of hydrated ferric sulphate in the mixture. (0·0077 mole)

25. A chemist is preparing to analyse samples that will contain no more than 0·5 g of uranium. His procedure calls for preparing the uranium as U^{4+} ion and oxidising it by MnO_4^- in acid solution.

$$5U^{4+} + 2MnO_4^- + 6H_2O \rightarrow 5UO_2^{2+} + 2Mn^{2+} + 4H_3O^+$$

If he wants to react the total U^{4+} sample with a maximum of 50 mL of $KMnO_4$ solution, what concentration should he choose? (0·0168 M)

26. For the standardisation of a $Ba(OH)_2$ solution, 0·2 g of potassium acid phthalate (wt. of one mole = 204·2 g) was weighed which was then titrated with $Ba(OH)_2$ solution. The titration indicated equivalence at 27·80 mL of $Ba(OH)_2$ solution. What

is the molarity of the base? The equation for reaction is

$$2KHC_8H_4O_4 + Ba(OH)_2 \rightarrow 2H_2O + 2K^+ + 2C_8H_4O_4^{2-} + Ba^{2+}$$ (0·0176 M)

27. A sample of magnesium metal containing some magnesium oxide as impurity was dissolved in 125 mL of 0·1 N H_2SO_4. The volume of hydrogen evolved at 27·3°C and 1 atm was 120·1 mL. The resulting solution was found to be 0·02 N with respect to H_2SO_4. Calculate (i) the weight of the sample dissolved and (ii) the percentage by weight of magnesium in the sample. Neglect any change in the volume of the solution.
(0·1235 g; 95·95%)

28. A piece of aluminium weighing 2·7 g is treated with 75 mL of H_2SO_4 (sp. gr. 1·18 containing 24·7% H_2SO_4 by weight). After the metal is completely dissolved, the solution is diluted to 400 mL. Calculate the molarity of free sulphuric acid in the resulting solution.
(0·177 M)

29. 4·00 g of mixture of NaCl and Na_2CO_3 was dissolved in water and the volume made up to 250 mL; 25 mL of this solution required 50 mL of N/10 HCl for complete neutralisation. Calculate percentage composition of the original mixture.
(33·75% ; 66·25%)

30. 1·00 g of a mixture consisting of equal number of moles of carbonates of the two univalent metals, required 44·4 mL of 0·5 N HCl for complete reaction. If the atomic weight of one of the metals is 7, find the atomic weight of the other metal. What will be the total amount of sulphate formed on gravimetric conversion of 1 g of the mixture of sulphates?
(23·1 ; 1·4 g)

31. A mixture containing only Na_2CO_3 and K_2CO_3 weighing 1·22 g was dissolved in water to form 100 mL of a solution. 20 mL of this solution required 40 mL of 0·1 N HCl for neutralisation. Calculate the weight of Na_2CO_3 in the mixture. If another 20 mL portion of the solution is heated with excess of $BaCl_2$, what will be the weight of the precipitate obtained?
(0·53 g ; 0·3946 g)

32. 1·00 g of a moist sample of a mixture of KCl and $KClO_3$ was dissolved in water and made up to 250 mL. 25 mL of this solution was treated with SO_2 to reduce the chlorate to chloride and excess SO_2 was removed by boiling. The total chloride was precipitated as silver chloride. The weight of the precipitate was 0·1435 g. In another experiment, 25 mL of the original solution was heated with 30 mL of 0·2 N solution of ferrous sulphate and unreacted ferrous sulphate required 37·5 mL of 0·08 N solution of an oxidising agent for complete oxidation. Calculate the molar ratio of chlorate to chloride in the given mixture. Fe^{2+} reacts with ClO_3^- according to the reaction

$$ClO_3^- + 6Fe^{2+} + 6H^+ \rightarrow Cl^- + 6Fe^{3+} + 3H_2O$$

($0·5 \times 10^{-3}$ mole ; $0·5 \times 10^{-3}$ mole)

33. 0·6 g of a sample of pyrolusite was boiled with 200 mL of N/10 oxalic acid and excess of dilute H_2SO_4. The liquid was filtered and the residue washed. The filtrate and washings were mixed and made up to 500 mL. 100 mL of this solution required 50 mL of N/30 $KMnO_4$ solution. Calculate the percentage of MnO_2 in the given sample of pyrolusite.
(84·58%)

34. 25 mL of a 0·107 M H_3PO_4 was titrated with a 0·115 M solution of a NaOH solution to the end point identified by the colour change of the indicator, bromocresol green. This required 23·1 mL. The titration was repeated using phenolphthalein indicator. This time 25 mL of 0·107 M H_3PO_4 required 46·8 mL of the 0·115 M NaOH. What is the coefficient n in the equation,

$H_3PO_4 + nOH^- \rightarrow nH_2O + [H_{(3-n)}PO_4]^{n-}$ for each reaction? (1; 2)

35. 9·8 g of $FeSO_4(NH_4)_2SO_4 \cdot xH_2O$ was dissolved in 250 mL of its solution. 20 mL of this solution required 20 mL of $KMnO_4$ solution containing 3·53 g of 90% pure $KMnO_4$ dissolved per litre. Calculate x. (6)

36. 10 mL of H_2O_2 weighs 10·205 g. The solution was diluted to 250 mL, 25 mL of which required 35·8 mL of a decinormal solution of $KMnO_4$. Calculate the weight in grams of H_2O_2 in 100 mL and also the volume strength of the solution. (6·086 g; 20 V)

37. 50 mL of H_2O_2 was treated with excess of KI in presence of dilute sulphuric acid. I_2 so liberated was titrated with 20 mL of 0·1 N hypo solution. Calculate the strength of H_2O_2 in grams per litre. (0·68)

38. Calculate the percentage of available chlorine in a sample of 3·546 g of bleaching powder which was dissolved in 100 mL of water; 25 mL of this solution, on treatment with KI and dilute acid, required 20 mL of 0·125 N sodium thiosulphate solution. (10·01%)

39. (a) A zinc rod weighing 25·00 g was kept in 100 mL of 1 M $CuSO_4$ solution. After a certain time molarity of Cu^{2+} in solution was 0·8 M. What was the molarity of the sulphate ion (SO_4^{2-})? What was the weight of the zinc rod after cleaning?

(b) If the above experiment was done with a copper rod of weight 25 g and 50 mL of 2M zinc sulphate ($ZnSO_4$) solution, what would be the molarity of Zn^{2+} at the end of the same interval? [(a) 1 M, 23·6926 g; (b) 2 M]

40. 25 mL of a mixed solution of Na_2CO_3 and $NaHCO_3$ required 12 mL of N/20 HCl when titrated using phenolphthalein as an indicator. But 25 mL of the same, when titrated separately with methyl orange required 30 mL of N/20 HCl. Calculate the amount of Na_2CO_3 and $NaHCO_3$ in grams per litre. (2·544 g; 1·008 g)

41. 20 mL of a mixed solution of Na_2CO_3 and NaOH required 17·5 mL of N/10 HCl when titrated with phenolphthalein as indicator. But when methyl orange was added, a second end point was observed on the further addition of 2·5 mL of HCl. Calculate the amount of Na_2CO_3 and NaOH in the solution. (0·02648 g, 0·06 g)

42. 0·2 g of a chloride of an element was dissolved in water and then treated with excess of silver nitrate solution resulting in the formation of 0·47 g of silver chloride. Find the equivalent weight of the element. (25·56)

43. A sample of hydrazene sulphate ($N_2H_6SO_4$) was dissolved in 100 mL of water. 10 mL of this solution was reacted with excess of ferric chloride solution and warmed to complete the reaction. Ferrous ion formed was estimated and it required 20 mL of M/50 potassium permanganate solution. Estimate the amount of hydragene sulphate in one litre of the solution. **(IIT 1988)**

Reactions:

$$4Fe^{+++} + N_2H_4 \rightarrow N_2 + 4Fe^{++} + 4H^+$$

$$MnO_4^- + 5Fe^{++} + 8H^+ \rightarrow Mn^{++} + 5Fe^{+++} + 4H_2O$$

(6·5 g/L)

[**Hint** Eq. wt. of $N_2H_4 = \dfrac{\text{mol. wt.}}{4}$]

44. 5 g of bleaching powder was suspended in water and volume made up to half a litre. 20 mL of this suspension when acidified with acetic acid and treated with excess of KI solution, liberated I_2 which required 20 mL of a N/10 hypo solution for titration. Calculate the percentage of available chlorine in bleaching powder.

[**Hint:** See Example 58.]

45. A 10-g mixture of Cu_2S and CuS was treated with 200 mL of 0·75 M MnO_4^- in acid solution producing SO_2, Cu^{2+} and Mn^{2+}. The SO_2 was boiled off and the excess MnO_4^- was titrated with 175 mL of 1 M Fe^{2+} solution. Calculate the percentage of CuS in the original mixture. (57·4%)

[**Hint** $\underset{+2\ -2}{Cu_2S} \rightarrow \underset{+4}{2Cu^{2+}} + \underset{+4}{SO_2}$; eq. wt. of $Cu_2S = \dfrac{\text{mol. wt.}}{8}$]

46. A 0·518-g sample of limestone is dissolved and then Ca is precipitated as CaC_2O_4. After filtering and washing the precipitate, it requires 40 mL of 0·25 N $KMnO_4$ solution acidified with H_2SO_4 to titrate it. What is the percentage of CaO in limestone?

$$MnO_4^- + CaC_2O_4 + H_2SO_4 \rightarrow CaSO_4 + Mn^{2+} + CO_2 + H_2O$$

(54·1%)

47. 20 mL of M/60 solution of $KBrO_3$ was added to a certain volume of SeO_3^{2-} solution. Br_2 evolved was removed by boiling and the excess of $KBrO_3$ was back titrated with 5.1 mL of $\frac{M}{25}$ solution of $NaAsO_2$. Calculate the weight of SeO_3^{2-} in the solution. (0.084 g)

[**Hint** $\underset{+4}{SeO_3^{2-}} + \underset{+5}{BrO_3^-} + H^+ \rightarrow \underset{+6}{SeO_4^{2-}} + \underset{0}{Br_2} + H_2O$

$\underset{+5}{BrO_3^-} + \underset{+3}{AsO_2^-} + H_2O \rightarrow \underset{-1}{Br^-} + \underset{+5}{AsO_4^{3-}} + H^+$]

48. Concentrated HCl solution is 37.0% HCl and has a density of 1.19 g/mL. A dilute solution of HCl is prepared by diluting 4.50 mL of this concentrated HCl solution to 100 mL with water. Then 10 mL of this dilute HCl solution reacts with an $AgNO_3$ solution. Calculate the volume of 0.108 M $AgNO_3$ solution required to precipitate all the chloride as AgCl(s).

49. 0.9546 g of a Rochelle salt, $NaKC_4H_4O_6 \cdot 4H_2O$, on ignition, gave $NaKCO_3$, which was treated with 41.72 mL of 0.1307 N H_2SO_4. The unreacted H_2SO_4 was then neutralised by 1.91 mL of 0.1297 N NaOH. Find the percentage purity of the Rochelle salt in the sample. (76.87%)

50. A mixture of $KMnO_4$ and $K_2Cr_2O_7$ weighing 0.24 g on being treated with KI in acid solution liberates just sufficient I_2 to react with 60 mL of 0.1 N $Na_2S_2O_3$ solution. Calculate percentage of Cr and Mn in the mixture. (20.83%, 14.17%)

[Hint $\underset{+7}{KMnO_4} \rightarrow \underset{+2}{Mn^{2+}}$ and $\underset{+12}{K_2Cr_2O_7} \rightarrow \underset{+6}{2Cr^{3+}}$]

51. Federal regulations set an upper limit of 50 parts per million (ppm) of NH_3 in the air in a work environment (that is, 50 mL NH_3 per 10^6 mL of air). The density of $NH_3(g)$ at room temperature is 0.771 g/L. Air from a manufacturing operation was drawn through a solution containing 100 mL of 0.0105 M HCl. The NH_3 reacts with HCl as follows:

$$NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(aq)$$

After drawing air through the acid solution for 10 minutes at a rate of 10 litres/min, the acid was titrated. The remaining acid required 13.1 mL of 0.0588 M NaOH to reach the equivalence point.

(a) How many grams of NH_3 were drawn into the acid solution?

(b) How many ppm of NH_3 were in the air?

(c) Is this manufacturer in compliance with regulations?

[(a) 0.00475 g (b) 61.6 ppm (c) No]

Objective Problems

1. Normality of a solution is defined as
   (a) number of eq./litre of solution (b) number of eq./litre of solvent
   (c) number of mole/kg of solvent (d) number of mole/kg of solution

2. In the reaction $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$, the eq. wt. of $Na_2S_2O_3$ is equal to its
   (a) mol. wt. (b) mol. wt./2 (c) 2 × mol. wt. (d) mol. wt./6

3. In the reaction $VO + Fe_2O_3 \rightarrow FeO + V_2O_5$, the eq. wt. of V_2O_5 is equal to its
   (a) mol. wt. (b) mol. wt./8 (c) mol. wt./6 (d) none of these

4. In the reaction $Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$, the eq. wt. of Na_2CO_3 is
   (a) 53 (b) 106 (c) 10·6 (d) 5·3

5. The eq. wt. of iodine in $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$ is equal to its
   (a) mol. wt. (b) mol. wt./2 (c) mol. wt./4 (d) none of these

6. The eq. wt. of K_2CrO_4 as an oxidising agent in acid medium is
   (a) mol. wt./2 (b) $\frac{2 \times \text{mol. wt.}}{3}$ (c) $\frac{\text{mol. wt.}}{3}$ (d) $\frac{\text{mol. wt.}}{6}$

7. In alkaline condition $KMnO_4$ reacts as follows:

$$2KMnO_4 + 2KOH \rightarrow 2K_2MnO_4 + H_2O + O,$$

the eq. wt. of $KMnO_4$ is

(a) 52·7 (b) 158 (c) 31·6 (d) 79

8. 0·126 g of an acid requires 20 mL of 0·1 N NaOH for complete neutralisation. Eq. wt. of the acid is

(a) 45 (b) 53 (c) 40 (d) 63

9. H_3PO_4 is a tribasic acid and one of its salt is NaH_2PO_4. What volume of 1 M NaOH solution should be added to 12 g of NaH_2PO_4 to convert it into Na_3PO_4?

(a) 100 mL (b) 200 mL (c) 80 mL (d) 300 mL

10. 2 g of a base whose eq. wt. is 40 reacts with 3 g of an acid. The eq. wt. of the acid is

(a) 40 (b) 60 (c) 10 (d) 80

11. In a reaction 4 moles of electrons are transferred to one mole of HNO_3 when acted as an oxidant. The possible reduction product is

(a) (1/2) mole of N_2 (b) (1/2) mole of N_2O

(c) 1 mole of NO_2 (d) 1 mole of NH_3

12. Normality of 1% H_2SO_4 solution is nearly

(a) 2·5 (b) 0·1 (c) 0·2 (d) 1

13. What volume of 0·1N HNO_3 solution can be prepared from 6·3 g of HNO_3?

(a) 1 litre (b) 2 litres (c) 0·5 litre (d) 5 litres

14. The volume of water to be added to 200 mL of seminormal HCl solution to make it decinormal is

(a) 200 mL (b) 400 mL (c) 600 mL (d) 800 mL

15. 0·2 g of a sample of H_2O_2 required 10 mL of N $KMnO_4$ in a titration in the presence of H_2SO_4. Purity of H_2O_2 is

(a) 25% (b) 85% (c) 65% (d) 95%

16. 100 mL of 0·5 N NaOH solution is added to 10 mL of 3 N H_2SO_4 solution and 20 mL of 1 N HCl solution. The mixture is

(a) acidic (b) alkaline (c) neutral (d) none of these

17. Which of the following has the highest normality?

(a) 1 M H_2SO_4 (b) 1 M H_3PO_3 (c) 1 M H_3PO_4 (d) 1 M HNO_3

18. Eq. wt. of a metal, x g of which reacts with 1 eq. of an acid, is

(a) 1 (b) $x/2$ (c) $2x$ (d) x

19. The molarity of 98% H_2SO_4 ($d = 1·8$ g/mL) by wt. is

(a) 6 M (b) 18 M (c) 10 M (d) 4 M

20. 0·7 g of $Na_2CO_3 \cdot xH_2O$ is dissolved in 100 mL of water, 20 mL of which required 19·8 mL of 0·1 N HCl. The value of x is

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

21. The normality of 10 mL of a '20 V' H_2O_2 is

(a) 1·79 (b) 3·58 (c) 60·86 (d) 6·086

(a) 1·79 (b) 3·58 (c) 60·86 (d) 6·086

22. If 8·3 mL of a sample of H_2SO_4 (36 N) is diluted by 991·7 mL of water, the approximate normality of the resulting solution is
(a) 0·4 (b) 0·2 (c) 0·1 (d) 0·3

23. 10 mL of an HCl solution gave 0·1435 g of AgCl when treated with excess of $AgNO_3$. The normality of the resulting solution is
(a) 0·1 (b) 3 (c) 0·3 (d) 0·2

24. 500 mL of a 0·1 N solution of $AgNO_3$ is added to 500 mL of a 0·1 N KCl solution. The concentration of nitrate in the resulting mixture is
(a) 0·1 N (b) 0·05 N (c) 0·01 N (d) 0·2 N

25. The ratio of amounts of H_2S needed to precipitate all the metal ions from 100 mL of 1 M $AgNO_3$ and 100 mL of 1 M $CuSO_4$ is
(a) 1 : 2 (b) 2 : 1 (c) zero (d) infinite

26. If 0·5 mole of $BaCl_2$ is mixed with 0·2 mole of Na_3PO_4, the maximum number of mole of $Ba_3(PO_4)_2$ that can be formed is
(a) 0·7 (b) 0·5 (c) 0·30 (d) 0·1

27. 0·45 g of an acid of molecular weight 90 was neutralised by 20 mL of 0·5 N caustic potash. The basicity of the acid is
(a) 1 (b) 2 (c) 3 (d) 4

28. 1 litre of 18 molar H_2SO_4 has been diluted to 100 litres. The normality of the resulting solution is:
(a) 0·09 N (b) 0·18 N (c) 1800 N (d) 0·36 N

29. The best indicator for detection of end point in titration of a weak acid and a strong base is
(a) methyl orange (3 to 4) (b) methyl red (4 to 6)
(c) bromothymol blue (6 to 7·5) (d) phenolphthalein (8 to 9·6)
NB Figures in the brackets show the pH range of the indicator. (IIT 1985)

30. In a compound A_xB_y,
(a) moles of A = moles of B = moles of A_xB_y
(b) eq. of A = eq. of B = eq. of A_xB_y
(c) $y \times$ moles of $A = y \times$ moles of $B = (x + y) \times$ moles of A_xB_y
(d) $y \times$ moles of $A = y \times$ moles of B

31. The volume strength of 1·5 N H_2O_2 solution is
(a) 4·8 (b) 8·4 (c) 3·0 (d) 8·0

32. The number of moles of $KMnO_4$ that will be needed to react completely with one mole of ferrous oxalate in acidic solution is (IIT 1997)
(a) 3/5 (b) 2/5 (c) 4/5 (d) 1

33. The number of moles of $KMnO_4$ that will be needed to react with one mole of sulphite ions in acidic solution is (IIT 1997)
(a) 2/5 (b) 3/5 (c) 4/5 (d) 1

34. Which of the following reactions is not a disproportionation reaction?
(a) $2NO_2 + H_2O = HNO_3 + HNO_2$
(b) $Cl_2 + H_2O = HCl + HClO$
(c) $3K_2MnO_4 + 2H_2O = 2KMnO_4 + MnO_2 + 4KOH$
(d) $2FeSO_4 + 2H_2O = Fe_2(OH)_2SO_4 + H_2SO_4$

Answers

1-a, 2-a, 3-c, 4-b, 5-b, 6-c, 7-b, 8-d, 9-b, 10-b, 11-b, 12-c, 13-a, 14-d, 15-b, 16-c, 17-c, 18-d, 19-b, 20-c, 21-b, 22-d, 23-a, 24-b, 25-a, 26-d, 27-b, 28-d, 29-d, 30-b, 31-b, 32-a, 33-a, 34-d.

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CHAPTER EIGHT

ELECTROLYSIS AND ELECTROLYTIC CONDUCTANCE

The electrical and chemical concepts are interdependent. A flow of electricity through a substance may produce a chemical reaction, and also, a chemical reaction may cause a flow of electricity through some external circuit. The former involves the study of electrolysis and conductance, while the latter, the measurement of electromotive force. In this chapter we shall deal with the phenomena of electrolysis and conductance.

ELECTROLYSIS

Faraday's Laws

The quantitative relationship between the amount of electricity passed through a cell and the amount of substances discharged at the electrodes was systematised by Michael Faraday in the form of the following laws:

First law: The amount of substance discharged (deposited or dissolved) at an electrode is proportional to the quantity of the electricity passing through the electrolyte.

Mathematically:

$$\left.\begin{aligned} &w \propto q \\ &w \propto I.t \quad (q = I.t) \\ &w = z.I.t \end{aligned}\right\} \qquad \ldots (1)$$

where w is the weight of the substance discharged at an electrode in grams; q is the charge in coulombs, t is the time of flow of electricity in seconds, I is the current in amperes and z is a constant known as the electrochemica

number of grams of the substanc

Since x is very small,

$$K_a = 0.05x^2 = 0.05 \times (0.0188)^2$$
$$= 1.76 \times 10^{-5} \text{ mole/litre.}$$

Ex. 45. *The specific conductance of a saturated solution of AgCl at 25°C after subtracting the specific conductance of conductivity of water is* 2.28×10^{-6} mho cm^{-1}. *Find the solubility product of AgCl at 25°C.*
($\Lambda^\circ_{AgCl} = 138.3$ mho cm^2)

Solution : For equilibrium,

$$AgCl = Ag^+ + Cl^-$$
$$K_{sp} = [Ag^+][Cl^-]$$

If the solubility of AgCl in water is, say, x moles/litre or x eq./L,

$$K_{sp} = x \cdot x = x^2.$$

$\therefore$ volume containing 1 eq. of AgCl $= \dfrac{1000}{x}$

$$\Lambda_{AgCl} = \text{sp. cond.} \times V$$
$$= 2.28 \times 10^{-6} \times \frac{1000}{x}.$$

Since AgCl is sparingly soluble in water, $\Lambda_{AgCl} = \Lambda^\circ_{AgCl} = 138.3$.

$$\therefore\ 2.28 \times 10^{-6} \times \frac{1000}{x} = 138.3$$

$$x = 1.644 \times 10^{-5} \text{ eq./litre or mole/litre.}$$
$$K_{sp} = x^2 = (1.644 \times 10^{-5})^2$$
$$= 2.70 \times 10^{-10} \text{ (mole/litre)}^2.$$

PROBLEMS

(Answers bracketed with questions)

1. Molten $AlCl_3$ is electrolysed with a current of 0.5 amp to produce 27.0 g Al. (i) How many g eq. of Al were produced? (ii) How many gram-atoms of Al were produced? (iii) How many atoms of Al were produced? (iv) How many electrons were required? (v) What is the no. of faradays of electricity consumed? (vi) How long did the electrolysis take place? (vii) How many litres of Cl_2 at NTP were produced?
{(i) 3 g eq (ii) 1 (iii) Av. constant (iv) 3 × Av. constant
(v) 3 F (vi) 160 h 50 min (vii) 33.6 litres}

2. In the electrolysis of an aqueous $Cr_2(SO_4)_3$ solution using a current of 2 amp, the mass of cathode is increased by 8 g. How long was electrolysis conducted? (6.19 h)

3. A spoon used as a cathode is dipped in $AgNO_3$ solution and a current of 0·2 amp is passed for one hour. Calculate
(a) how much silver plating has occurred?
(b) how many electrons were involved in the process?
(c) what amount of copper would have been plated under similar conditions?
(0·805 g, $4·5 \times 10^{21}$, 0·237 g)

4. A steady current passing through a solution of $AgNO_3$ solution deposits 0·50 g of Ag in 1 h. Calculate the number of coulombs. What volume of hydrogen at 27°C and 750 mm pressure would the same current liberate in one hour?
(446·7 coulombs, 57·7 mL)

5. At the Nangal fertilizer plant in Punjab, hydrogen is produced by the electrolysis of water. The hydrogen is used for the production of ammonia and nitric acid (by oxidation of ammonia). If the average production of ammonium nitrate is 5000 kg/day, estimate the daily consumption of electricity per day.
($2·8 \times 10^5$ amp/day)

6. In an electrolysis experiment, current was passed for 5 hours through two cells connected in series. The first cell contains a solution of gold and second contains $CuSO_4$ solution. 9·85 g of gold was deposited in the first cell. If the oxidation number of gold is +3, find the amount of Cu deposited on the cathode of the second cell. Also calculate the magnitude of the current in ampere. (1 F = 96500 coulomb) (Au = 197, Zn = 65·4)
(4·765 g, 0·8037 amp)

7. A constant current flowed for 2 hours through a potassium iodide solution oxidising the iodide ion to iodine ($2I^- \rightarrow I_2 + 2e^-$).
At the end of the experiment, the iodine was titrated with 21·75 mL of 0·0831 M sodium thiosulphate solution

$$(I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}).$$

What was the average rate of current flow in amperes? (0·0242 amp)

8. During the electrolysis of $CrCl_3$, chlorine gas is evolved at the anode and chromium is deposited at the cathode. How many grams of Cr and how many litres of chlorine (at NTP) are produced, when a current of 6 amperes is passed for one hour?
(3·88 g, 2·507 litres)

9. A current passes through two cells containing respectively—(i) $CuSO_4$ solution between Cu electrode and (ii) $AgNO_3$ solution between Pt electrodes. Calculate the loss or gain in weight of the different electrodes in the time in which 40 cc of oxygen at NTP collects in the second cell.
(Ag = 108 ; Cu = 63·5)

First cell { 0·228 g Cu deposited at cathode.
0·228 g Cu dissolved out from anode.

Second cell { 0·778 g of Ag deposited at cathode.
Wt. of anode does not change .

10. What weight of water will be decomposed by a current of 100 amp in 12 h?
(403 g)

11. How many grams of H_2 and O_2 are produced during the electrolysis of water under a 1·30 amp of current for 5 hours? What volumes of dry gases are produced at NTP?

$$\begin{Bmatrix} H_2 - 0{\cdot}245\text{ g}, O_2 - 1{\cdot}94\text{ g} \\ H_2 - 2{\cdot}72\text{ L}, O_2 - 1{\cdot}36\text{ L} \end{Bmatrix}$$

12. The water is electrolysed in a cell, hydrogen is liberated at one electrode and oxygen is simultaneously liberated at the other. In a particular experiment hydrogen and oxygen so produced were collected together and the total volume measured 16·8 mL at NTP. How many coulombs were passed through the cell in the experiment?

(96·5 coulombs)

13. Ag is electrodeposited on a metallic vessel of surface area 800 cm^2 by passing a current of 0·2 amp for three hours. Calculate the thickness of silver deposited, given its density is 10·47 g/cc.

($2{\cdot}88 \times 10^{-4}$ cm)

14. 50 mL of hydrogen gas was collected over at 23°C, 740 mmHg barometric pressure. H_2 was produced by the electrolysis of water. The voltage was constant at 2·1 volts, the current averaged 0·50 amp for 12 minutes and 20 seconds. Calculate Avogadro constant.

($5{\cdot}85 \times 10^{23}$)

15. A current of 0·5 amp is sent through a solution of $CuSO_4$ for 20 minutes using Pt electrodes.

(a) Calculate the weight of Cu deposited.

(b) Find out the total number of copper atoms deposited.

(Cu = 63·57, Av. constant = $6{\cdot}022 \times 10^{23}$, 1 F = 96500 coulombs) (0·1976 g; $1{\cdot}87 \times 10^{21}$)

16. What current is required to pass 1 mole of electrons per hour through an electrolytic bath? How many grams of Al and Cd will be liberated by 1 mole of electrons?

(26·8 amp, Al – 8·99 g, Cd – 56·2 g)

17. How many hours are required for a current of 3 amp to decompose electrolytically 18 g of water? (18 hours)

18. 50 mL of a 0·1 M $CuSO_4$ solution is electrolysed for 12 minutes, at a current of 0·06 amp. If Cu is produced at one electrode and O_2 at the other, what will be the pH of the final solution? For $HSO_4^- = H^+ + SO_4^{2-}$, $K_{diss} = 1{\cdot}3 \times 10^{-2}$. (2·95)

19. For the electrolytic production of $NaClO_4$ from $NaClO_3$ as per reactions:

$$ClO_3^- + H_2O \rightarrow ClO_4^- + 2H^+ + 2e^-$$

(i) How many faradays of electricity would be required to produce 1 mole of $NaClO_4$?

(ii) What volume of H_2 at STP would be liberated at the cathode in the time that it takes to form 12·25 g of $NaClO_4$? (2 F, 2·24 litres)

20. Electric current is passed through two cells 'A' and 'B' in series. Cell 'A' contains an aqueous solution of Ag_2SO_4 and platinum electrodes. The cell 'B' contains aqueous solution of $CuSO_4$ and Cu electrodes. The current is passed till 1·6 g of oxygen is liberated at the anode of cell 'A'.

(i) Give ... electrode.

(ii) Calculate the quantities of substances deposited at the cathodes of the two cells. (Ag = 108, Cu = 63·5)

[(i) In cell 'A'; $2H_2O \rightarrow O_2(g) + 4H^+ + 4e$ at anode
$Ag^+ + e \rightarrow Ag$ at cathode
In cell 'B'; $Cu \rightarrow Cu^{2+} + 2e$ at anode
$Cu^{2+} + 2e \rightarrow Cu$ at cathode
(ii) Ag = 21·6 g; Cu = 6·35 g]

21. One hundred millilitres of 0·8 M copper sulphate is electrolysed for 30 minutes by passing a current of 5 amp. Calculate the amount of copper sulphate in grams in the solution. (5·32 g)

22. Anthracene can be oxidised anodically to anthraquinone. What weight of anthraquinone can be produced by the passage of a current of 1 amp for 60 minutes if the current efficiency is 100%? (1·2932 g)

[**Hint:** $C_{14}H_{10} + 3O \rightarrow C_{14}H_8O_2 + H_2O$

$$\text{Eq. wt. of } C_{14}H_8O_2 = \frac{\text{mol. wt.}}{6}$$]

23. To reduce nitrobenzene to aniline, 20 g of $C_6H_5NO_2$, 30 cc of an alcohol, 250 cc of water, 11 g of HCl and 1 g of $SnCl_2 \cdot 2H_2O$ were placed in the cathode space. After passing current at a rate of 26·5 amp-hour through the lead cathode electrolytic cell, 12·76 g of aniline was produced. Determine the current yield. (84·38%)

[**Hint:** See Example 13]

24. 0·2964 g of Cu was deposited on passage of a current of 0·5 amp for 30 min through a solution of copper sulphate. Calculate the atomic weight of Cu. (63·56)

25. Most of the copper used to make wire has been electrically refined by depositing it from copper salts solution (divalent) on to a cathode. What is the cost of electrical energy required per kg of copper if the cost of electricity is Rs. 0·25 per kWh and the cell operates at 0·2 volt? The electrochemical equivalent of copper is 0·00033 g/coulomb. (4·2 p)

[**Hint:** No. of eq. in 1 kg of Cu × 0·25 /no. of eq. of Cu deposited by 1 kWh = cost in rupees.]

26. How long should a current of 0·5 amp be passed through 50 mL of a 0·10 M NaCl solution in order to make its pH 12, assuming no volume change? (97 s)

27. Lake Cayuga has a volume of water estimated to be 8.2×10^{12} litres. A power station not so far above Cayuga's waters produces electricity at the rate of 1.5×10^6 coulombs per second at an appropriate voltage. How long would it take to electrolyse the lake? (1·9 million years)

28. A 200-watt, 110-volt incandescent lamp is connected in series with an electrolytic cell of negligible resistance containing a solution of zinc chloride. What weight of zinc will be deposited from the solution on passing the current for 30 minutes? (Zn = 63·5; 1 faraday = 96500 coulombs) (1·075 g)

29. 40 mL of 0·125 M of $NiSO_4$ solution is electrolysed by a current of 0·05 amp for 40 minutes. (i) Write the equation for the reactions occurring at each electrode. (ii) How many coulombs of electricity passed through the solution? (iii) How many grams of the product deposited on the cathode? (iv) How long will the same current have to pass through the solution to remove completely the metal ions from the solution? (v) At the end of electrolysis how many grams of the product would appear at the anode? [120, 0·037 g, 19300 s, 0·08 g]

30. An electric current is passed through a solution of (i) silver nitrate, (ii) solution of 10 g of copper sulphate ($CuSO_4 \cdot 5H_2O$) crystals in 500 mL of water, platinum electrodes being used in each case. After 30 minutes it was found that 1·307 g of silver has been deposited. What was the concentration of copper, expressed as grams of copper per litre in the copper sulphate solution after electrolysis? (4·32 g/litre)

31. In a fuel cell hydrogen and oxygen react to produce electricity. In the process hydrogen gas is oxidised at the anode and oxygen at the cathode. If 67·2 litres of H_2 at STP react in 15 minutes, what is the average current produced? If the entire current is used for electrodeposition of copper from Cu (II) solution, how many grams of copper will be deposited?

Anode reaction: $H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$

Cathode reaction: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ **(IIT 1988)** (643·34 amp, 190·5 g)

[**Hint:** Eq. of hydrogen = no. of faradays of electricity = eq. of Cu deposited]

32. 3 amp of current was passed through an aqueous solution of an unknown salt of Pd for 1 hour. 2·977 g of Pd^{n+} was deposited at the cathode. Find n. (Pd = 106·4) (4)

33. A total of 69500 C of electricity was required to reduce 37.7 g of M^{3+} to the metal. What is M? (M = 157)

34. A solution containing Cu(I), Ni and Zn cyanide complexes was electrolysed and a deposit of 0.175 g was obtained. The deposit contained 72.8% Cu, 4.3% Ni and 22.9% Zn. No other element was released. Calculate the number of coulombs passed through the solution. (335·9 C)

35. Calculate the minimum number of kWh of electricity required to produce 1.0 kg of Mg from electrolysis of molten $MgCl_2$ if the applied emf is 5.0 V. (1 kWh = 3.6×10^6 J) (11.0 kWh)

36. A sample of Al_2O_3 dissolved in a molten fluoride bath is electrolysed using a current of 1.20 A. What is the rate of production of Al in g/hour? The oxygen liberated at the positive carbon electrode reacts with the carbon to form CO_2. What mass of CO_2 is produced per hour? (0·403, 0·4924 g/h)

37. The specific conductance of an N/10 KCl solution at 18°C is $1{\cdot}12 \times 10^{-2}$ mho cm^{-1}. The resistance of the solution contained in the cell is found to be 65 ohms. Calculate the cell constant. (0·728 cm^{-1})

38. When a solution of ... 1.342 mho metre^{-1} was placed in a conductivity

cell with parallel electrodes, the resistance was found to be 170·5 ohm. The area of the electrodes is $1{\cdot}86 \times 10^{-4}$ sq metre. Calculate the distance between the two electrodes in metres. ($4{\cdot}25 \times 10^{-2}$ metres)

39. The resistances of two electrolytes, X and Y, were found to be 45 and 100 ohms respectively when equal volumes of both the solutions were taken in the same cell in two different experiments. If equal volumes of these solutions are mixed in the same cell, what will be the conductance of the mixture? (0·016 mho)
[Hint: See Example 34]

40. The resistance of an aqueous solution containing 0·624 g of $CuSO_4 \cdot 5H_2O$ per 100 cm^3 of the solution in a conductance cell of cell constant 153·7 per metre is 520 ohms at 298 K. Calculate the molar conductivity.
($CuSO_4 \cdot 5H_2O = 249{\cdot}5$) (118·2 mho cm^2)

41. An aqueous solution of 0·02 M KCl solution is filled in a 25-cm-long capillary tube of internal radius 0·01 cm. The solution was found to have a specific conductance of 0·0027 mho cm^{-1}. What will be the current in amp when a potential of 2 volts is applied across the capillary tube? ($6{\cdot}78 \times 10^{-8}$ amp)

42. Given the equivalent conductance of sodium butyrate, sodium chloride and hydrogen chloride as 83, 127 and 426 mho cm^2 at 25°C respectively. Calculate the equivalent conductance of butyric acid at infinite dilution. (382 mho cm^2)

43. A dilute solution of KCl was placed between two platinum electrodes 10 cm apart, across which a potential of 6 volts was applied. How far would the K^+ ion move in 2 hours at 25°C? Ionic conductance of K^+ ion at infinite dilution at 25°C is 73·52 mho cm^2. (3·29 cm)

44. For 0·0128 N solution of acetic acid at 25°C, equivalent conductance of the solution is 1·4 mho cm^2 eq^{-1} and $\Lambda_0 = 391$ mho cm^2 eq^{-1}. Calculate dissociation constant (K_a) of acetic acid. ($1{\cdot}6 \times 10^{-5}$)

45. The specific conductance at 25°C of a saturated solution of AgCl in water is $1{\cdot}826 \times 10^{-6}$ mho cm^{-1}. If Λ°_{AgCl} is equal to 138·26 mho cm^2, find out the solubility of AgCl in water in grams per litre. ($1{\cdot}89 \times 10^{-3}$ g/L)

46. Specific conductance of pure water at 25°C is $0{\cdot}58 \times 10^{-7}$ mho cm^{-1}. Calculate ionic product of water (K_w) if ionic conductances of H^+ and OH^- ions at infinite dilution are 350 and 198 mho cm^2 respectively at 25°C. (1×10^{-14}) $(mole/litre)^2$

Objective Problems

1. The number of electrons involved in the reaction when one faraday of electricity is passed through an electrolyte is
   (a) 12×10^{46} (b) 96,500
   (c) 6×10^{23} (d) 8×10^{16}

2. Number of electrons involved in the electrodeposition of 63·5 g of Cu from a

solution of $CuSO_4$ is
(a) 6.022×10^{23} (b) 3.011×10^{23}
(c) 12.044×10^{23} (d) 6.022×10^{22}

3. Faraday's laws of electrolysis are related to the
(a) atomic number of the cation
(b) atomic number of the anion
(c) equivalent weight of the electrolyte
(d) speed of the cation
(IIT 1985)

4. The electric charge for electrodeposition of 1 eq. of a substance is
(a) one ampere per second (b) 96500 coulombs per second
(c) one ampere for one hour (d) charge on one mole of electrons

5. 1 coulomb of electricity produces m kg of a substance X. Electrochemical equivalent of X is
(a) m (b) $m \times 10^3$ (c) $m \times 10^{-3}$ (d) all wrong

6. Electrochemical equivalent of a substance is ·0006735; its eq. wt. is
(a) 65 (b) 67·35
(c) 130 (d) cannot be calculated

7. When electricity is passed through a solution of $AlCl_3$, 13·5 g of Al is deposited. The number of faradays must be
(a) 1·0 (b) 1·5 (c) 0·5 (d) 2·0

8. 3·17 g of a substance was deposited by the flow of 0·1 mole of electrons. The equivalent weight of the substance is
(a) 3·17 (b) 0·317 (c) 317 (d) 31·7

9. A current of 0·5 ampere when passed through $AgNO_3$ solution for 193 seconds deposited 0·108 g of Ag. The equivalent weight of Ag is
(a) 10·8 (b) 108 (c) 54 (d) 1

10. In the electrolysis of an aqueous solution of a salt, the pH in the space near one of the electrodes increased. A solution of which of the following salts was electrolysed?
(a) $Cu(NO_3)_2$ (b) $CuCl_2$ (c) KCl

11. In the electrolysis of $CuCl_2$ solution (aq) with Cu electrodes, the weight of cathode increased by 3·2 g. In the anode,
(a) 0·05 mole of Cu^{2+} will go into the solution
(b) 560 mL of O_2 will be liberated
(c) 112 mL of Cl_2 will be liberated
(d) 3·2 mole of Cu^{2+} will go into the solution

12. The current required to displace 0·1 g of H_2 in 10 seconds will be
(a) 9·65 amp (b) 1·988 amp (c) 198 amp (d) 965 amp

13. The charge of an electron is 1.6×10^{-19} coulomb. How many electrons per second pass through a cross section of a Cu wire carrying 10^{-16} amp?
(a) 300 (b) 1800 (c) 1200 (d) 600

14. 96500 coulombs deposit 107·9 g of Ag from its solution. If $e = 1{\cdot}6 \times 10^{-19}$ coulomb, calculate the number of electrons per mole of electrons

(a) 96500 (b) $1{\cdot}6 \times 10^{-19}$ (c) $6{\cdot}02 \times 10^{23}$ (d) $6{\cdot}02 \times 10^{-23}$

15. A current of 2 amp passing for 5 hours through a molten tin salt deposits 22·2 g of tin. The oxidation state of the tin in the salt is

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

16. The cost at 5 paise/kWh of operating an electric motor for 8 hours which takes 15 amp at 110 V is

(a) Rs 66 (b) 66 paise

(c) 37 paise (d) Rs 6·60

[Hint: $W = I.V$]

17. One faraday of current was passed through the electrolytic cells placed in series containing solutions of Ag^+, Ni^{++} and Cr^{+++} respectively. The amounts of Ag (at. wt. = 108), Ni (at. wt. = 59) and Cr (at. wt. = 52) deposited will be

	Ag	Ni	Cr
(a)	108 g	29·5 g	17·4 g
(b)	108 g	59·0 g	52·0 g
(c)	108 g	108·0 g	108·0 g
(d)	108 g	117·5 g	166·0 g

18. 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

(a) 320 min (b) 160 min (c) 80 min (d) 40 min

19. In the electrolysis of H_2SO_4, 9·72 litres and 2·35 litres of H_2 and O_2 were liberated. Number of equivalent of persulphuric acid ($H_2S_2O_8$) produced is

(a) 0·448 (b) 0·224 (c) 0·868 (d) 0·42

[Hint: Reactions are $2H_2SO_4 \rightarrow H_2S_2O_8 + H_2$

$$2H_2O \rightarrow 2H_2 + O_2$$]

20. In the electrolysis of H_2O, 11·2 litres of H_2 was liberated at cathode at NTP. How much O_2 will be liberated at anode under the same conditions?

(a) 11·2 litres (b) 22·4 litres (c) 32 g (d) 5·6 litres

21. A galvanic cell was operated under almost ideally reversible conditions at a current of 10^{-16} amp. How long would it take to deliver 1 mole of electrons?

(a) $9{\cdot}65 \times 10^{20}$ s (b) 96,500 s

(c) $9{\cdot}65 \times 10^{-12}$ s (d) none of these

22. The time required for a current of 3 amp to decompose electrolytically 18 g of H_2O is

(a) 18 hours (b) 36 hours (c) 9 hours (d) 18 seconds

23. A constant current of 1.50 amp is passed through an electrolytic cell containing 0.10 N solution of $AgNO_3$ and a silver anode and a platinum cathode are used. After some time, the concentration of the $AgNO_3$ solution may be

(a) equal to 0.10 M
(b) less than 0.10 M
(c) greater than 0.10 M

24. Which of the following processes is used in the extraction metallurgy of Mg?
(a) Fused salt electrolysis
(b) Self-reduction
(c) Aqueous solution electrolysis
(d) Thermite reduction **(IIT 2002)**

25. In which of the following aqueous solutions, H_2 and O_2 are not liberated at cathode and anode respectively on electrolysis using inert electrodes?
(a) H_2SO_4 solution
(b) NaOH solution
(c) Na_2SO_4 solution
(d) $AgNO_3$ solution

[Hint: Read text for preferential discharge of ions.)

26. The aqueous solutions of the following substances were electrolysed. In which case, the pH of the solution does not change if inert electrodes are used.
(a) $AgNO_3$ (b) $CuSO_4$ (c) NaCl (d) K_2SO_4

27. Electrolytic conduction is due to the movement of
(a) molecules (b) atoms (c) ions (d) electrons

28. Which of the following equations is correct?
(a) Cond. = sp. cond. × cell constant
(b) Eq. cond. = sp. cond. × cell constant
(c) Cond. = eq. cond. × cell constant
(d) Cell constant = sp. cond./cond.

29. Which of the following solutions of KCl has the lowest value of specific conductance?
(a) 1 M (b) 0·1 M (c) 0·01 M (d) 0·001 M

30. Which of the following solutions of KCl has the lowest value of equivalent conductance?
(a) 1 M (b) 0·1 M (c) 0·01 M (d) 0·001 M

31. Under which of the following conditions, conductance, sp. conductance and eq. conductance are all equal?
(a) 1000 cc of the solution contains 1 eq. of the electrolyte
(b) 100 cc of the solution contains 1 eq. of the electrolyte
(c) 10 cc of the solution contains 1 eq. of the electrolyte
(d) 1 cc of the solution contains 1 eq. of the electrolyte

32. Which of the following is the unit of eq. conductance?
(a) mho (b) mho cm^2 (c) mho cm^{-1} (d) mho cm^{-2}

33. If V, in the equation $\Lambda = \text{sp. cond.} \times V$, is the volume in cc containing 1 eq. of the electrolyte; V for a $\frac{N}{10}$ solution will be
(a) 10 cc (b) 100 cc (c) 1000 cc (d) 10,000 cc

34. At infinite dilution, the eq. conductances of CH_3COONa, HCl and CH_3COOH are 91, 426 and 391 mho cm^2 respectively at 25°C. The eq. conductance of NaCl at infinite dilution will be
(a) 126 (b) 209 (c) 391 (d) 908

Answers

1-c, 2-c, 3-c, 4-d, 5-b, 6-a, 7-b, 8-d, 9-b, 10-c, 11-a, 12-d, 13-d, 14-c, 15-c, 16-b, 17-a, 18-c, 19-a, 20-d, 21-a, 22-a, 23-a, 24-a, 25-d, 26-d, 27-c, 28-d, 29-d, 30-a, 31-d, 32-b, 33-d, 34-a.

ESTIMATION OF ELEMENTS IN ORGANIC COMPOUNDS

In the estimation of elements in organic compounds, the atoms of the element to be estimated, present in the organic compound are quantitatively converted to another compound and then the number of moles of atoms of the element in that compound is calculated by the mole method, e.g., C and H in the organic compound are converted to CO_2 and H_2O respectively. The moles of C in CO_2 and the moles of H in H_2O are calculated which give the moles of C and H present in the organic compound. The same method is applied to the estimation of other elements, the moles of which are calculated as given below:

$C \xrightarrow{\text{combustion}} CO_2$; moles of C in $CO_2 = 1 \times$ moles of CO_2

($\because$ 1 mole of CO_2 contains 1 mole of C)

$H \longrightarrow H_2O$; moles of H in $H_2O = 2 \times$ moles of H_2O

($\because$ 1 mole of H_2O contains 2 moles of H)

Halogen (X) (Carius method) $\longrightarrow AgX$; moles of X in $AgX = 1 \times$ moles of AgX

($\because$ 1 mole of AgX contains 1 mole of X)

$S \xrightarrow[\text{(Carius method)}]{} BaSO_4$;

moles of S in $BaSO_4 = 1 \times$ moles of $BaSO_4$

($\because$ 1 mole of $BaSO_4$ contains 1 mole of S)

$P \xrightarrow[\text{(Carius method)}]{} Mg_2P_2O_7$; moles of P in $Mg_2P_2O_7$

$= 2 \times$ moles of $Mg_2P_2O_7$

($\because$ 1 mole of $Mg_2P_2O_7$ contains 2 moles of P)

$N \xrightarrow[\text{(Dumas method)}]{} N_2$ gas at NTP;

moles of $N = 2 \times$ moles of $N_2 = \dfrac{2 \times \text{volume (NTP)}}{22400}$

($\because$ 1 mole of N_2 contains 2 moles of N)

$N \xrightarrow[\text{Kjeldahl method}]{} NH_3$; moles of N in $NH_3 = 1 \times$ moles of NH_3

($\because$ 1 mole of NH_3 contains 1 mole of N)

Solution : Moles of P in $Mg_2P_2O_7 = 2 \times$ moles of $Mg_2P_2O_7$

$$= 2 \times \frac{0.444}{222} = 0.004 \text{ g.}$$

$$\text{Weight of P} = 0.004 \times 31 \text{ g}$$
$$= 0.124 \text{ g.}$$

$$\text{percentage of P} = \frac{0.124}{0.248} \times 100 = 50\%.$$

PROBLEMS

(Answers bracketed with questions)

1. 0·3 g of a compound on combustion gave 0·54 g of water and 0·88 g of carbon dioxide. Find the percentages of carbon and hydrogen in the compound. (80%, 20%)

2. 0·2475 g of an organic compound on combustion gave 0·4950 g of CO_2 and 0·2025 g of H_2O. Calculate the percentage of oxygen in the compound. (36·37%)

3. 0·2060 g of a substance gave 18·8 mL of moist nitrogen at 17°C and 756 mm pressure. If the vapour tension at 17°C is 14·5 mm, find the percentage of nitrogen in the compound. (10·56%)

4. An organic compound of molecular formula C_3H_7N was analysed for nitrogen by Dumas method. Find the volume (in mL) of nitrogen evolved at NTP from 2 g of the substance. (393 mL)

5. 0·788 g of a substance after digestion with H_2SO_4 was distilled with an excess of NaOH. The liberated NH_3 was absorbed in 100 mL of N H_2SO_4 solution. The remaining acid required 73·7 mL of N NaOH solution for neutralization. Find the percentage of nitrogen in the compound. (46·7%)

6. Find the percentage of nitrogen in an organic compound analysed by Kjeldahl method. 1·61 g of the compound produced NH_3 which was absorbed in 250 mL of $\frac{N}{2}$ H_2SO_4 solution. The remaining acid was then diluted to one litre, 25 mL of which required 25·5 mL of N/10 NaOH for exact neutralization. (20%)

7. An organic compound contains C, H, N and O. 0·135 g of this compound on combustion produced 0·198 g of CO_2 and 0·108 g of H_2O while the same amount gave 16·8 mL of nitrogen at 0°C and 76 cm of pressure. Calculate the percentage of oxygen in the compound. (35·44%)

8. 0·1890 g of an organic compound gave 0·2870 g of silver chloride by Carius method. Find the percentage of chlorine in the compound. (37·57%)

9. 0·123 g of an organic compound produced 0·099 g of CO_2 and 0·0507 g of H_2O. 0·185 g of the same compound produced 0·319 g of AgBr. Find the percentages of carbon, hydrogen and bromine in the compound. (21·96%, 4·48%, 73·36%)

10. 0·2595 g … percenta…

11. 1·5 g of … 2·5090 … compo…

10. 0·2595 g of an organic compound yielded quantitatively 0·35 g of BaSO4. Find the percentage of sulphur in the compound. (Ba = 137·3, S = 32, O = 16) (18·5%)

11. 1·5 g of an organic compound in a quantitative determination of phosphorus gave 2·5090 g of $Mg_2P_2O_7$. Calculate the percentage of phosphorus in the compound. (46·71%)

❑❑❑

CHAPTER TEN

EMPIRICAL, MOLECULAR AND STRUCTURAL FORMULAE

The utility of the mole concept is further illustrated by the problems of determining the empirical and molecular formulae of the compounds. Empirical formula represents the simplest set of whole numbers expressing the relative numbers of atoms in the compound and anything that can be said about relative numbers of atoms may be said about the relative numbers of moles of atoms. A calculation of the relative numbers of moles of each element in the compound will, therefore, lead us to the empirical formula of the compound. The empirical formula implies nothing about how many moles of atoms are actually in one mole of the compound. In fact, **the molecular formula expresses the actual numbers of moles of atoms of each element present in one mole of the compound.**

The molecular formula weight is the whole number multiple of the empirical formula weight for a given compound.

$$\frac{\text{Molecular formula weight}}{\text{Empirical formula weight}} = n \text{ (say)}$$

Thus if X represents the empirical formula of a compound, its molecular formula will be represented as $(X)_n$.

EXAMPLES

Ex. 1. *Find the empirical formula of chromium oxide containing 68·4% of chromium.* (Cr = 52, O = 16)

Solution : Let the weight of chromium oxide be 100 g.

∴ weight of chromium = 68·4 g

and weight of oxygen = 31·6 g.

$$\left.\begin{aligned} \therefore \quad \text{moles of chromium} &= \frac{68 \cdot 4}{52} = 1 \cdot 32 \\ \text{and} \quad \text{moles of oxygen} &= \frac{31 \cdot 6}{16} = 1 \cdot 98. \end{aligned}\right\} \quad \ldots \text{(Eqn. 2)}$$

Relative numbers of moles of Cr and O atoms

$$= \frac{\text{moles of Cr}}{\text{moles of O}} = \frac{1 \cdot 32}{1 \cdot 98} = \frac{132}{198} = \frac{2 \times 66}{3 \times 66} = \frac{2}{3} \text{ (by inspection only).}$$

The empirical formula is Cr_2O_3.

Calculation of empirical formula weight and molecular formula of the acid (C):

Moles of $C = \frac{0.39}{44} = 0.0088.$

Wt. of $C = 0.0088 \times 12 = 0.1064$ g.

Moles of $H = \frac{2 \times 0.08}{18} = 0.0088.$

Wt. of $H = 0.0088 \times 1 = 0.0088$ g.

$\therefore$ wt. of $O = [0.4 - (0.1064 + 0.0088)] = 0.2848.$

Moles of $O = \frac{0.2848}{16} = 0.0178.$

$\therefore$ moles of C : H : O $= 0.0088 : 0.0088 : 0.0178 = 1 : 1 : 2.$

$\therefore$ empirical formula is CHO_2 (45).

As the mol. wt. is 90, molecular formula is $(COOH)_2$.

As the acid (C) is now known, the reaction sequence may be represented as

$$\underset{(B)}{NaOH + CO\,(gas)} \rightarrow HCOONa \rightarrow \underset{(C)}{(COOH)_2}$$

$$\uparrow$$

$$\underset{(A)}{HCOOH}$$

PROBLEMS

(Answers bracketed with questions)

1. A sulphide of Fe contains 46·5% of Fe by weight. Find the empirical formula of the sulphide. (FeS_2)

2. 1·60 g of an oxide of iron, on heating in a stream of hydrogen gas, completely converted to 1·12 g of iron. Find the empirical formula of the oxide. (Fe_2O_3)

3. Carbon combines with hydrogen to form three compounds, A, B and C. The percentages of hydrogen in A, B and C are 25%, 14·3% and 7·7% respectively. Find the empirical formula of the compound. (CH_4, CH_2, CH)

4. A compound of carbon, hydrogen and nitrogen contains three elements in the respective weight ratio of 9 : 1 : 3. Calculate its empirical formula. If its molecular weight is 108, what is its molecular formula? (C_3H_4N, $C_6H_8N_2$)

5. A hydrated salt of iron sulphate weighing 2 g, contains 0·9065 g of water of crystallisation. Find the formula of the hydrated salt. ($FeSO_4 \cdot 7H_2O$)

6. An iron compound yielded C = 64·4%, H = 5·5% and Fe = 29·9%. What is the simple formula of the compound? ($C_{10}H_{10}Fe$)

7. 1·763 g of hydrated $BaCl_2$ was heated to dryness. The anhydrous salt remained was 1·505 g. What is the formula of the hydrate? ($BaCl_2 \cdot 2H_2O$)

8. A boron–hydrogen compound weighing 0·0553 g created a pressure of 0·658 atm in a bulb of 40·7 mL volume at 100°C. Analysis showed it to be 85·7% boron. What is its molecular formula? (B_5H_9)

9. A mixture of one volume of gas and two volumes of oxygen, on explosion form two volumes of CO_2 and one volume of N_2 under the identical conditions of temperature and pressure. Find the formula of the gas. (C_2N_2)

10. 9 volumes of a gaseous mixture consisting of a gaseous organic compound A and just sufficient amount of oxygen required for complete combustion yielded on burning 4 volumes of CO_2, 6 volumes of water vapour and 2 volumes of N_2, all volumes measured at the same temperature and pressure. If the compound has only C, H and N,

(i) how many volumes of oxygen are required for complete combustion?

(ii) what is the molecular formula of the compound A? (7 vol., $C_2H_6N_2$)

[**Hint:** See Example 13]

11. A sample of gaseous hydrocarbon occupying 1·12 litres at NTP when completely burnt in air produced 2·2 g of CO_2 and 1·8 g of H_2O. Calculate the weight of the compound and the volume of the oxygen at NTP required for its burning. Find the molecular formula of the compound. (0·8 g, 2·24 litres, CH_4)

12. 0·21 g of an organic compound containing C, H, O and N gave upon combustion 0·462 g of CO_2 and 0·1215 g of H_2O. The ammonia produced on distillation of 0·104 g of this compound with NaOH, required 15 mL of N/20 H_2SO_4 for neutralisation. Find the empirical formula of the compound. ($C_7H_9NO_2$)

13. An organic compound on qualitative analysis was found to contain C, H, N and O. 1·0 g of it on oxidation with CuO and oxygen gave 1·239 g of CO_2 and 0·1269 g of H_2O. 2 g of the sample was digested with concentrated sulphuric acid and the residue was distilled after the addition of excess solution of sodium hydroxide. The ammonia evolved was absorbed in 50 mL of 1·0 N sulphuric acid. The resulting solution was diluted to 500 mL in a measuring flask. 25 mL of this solution required 21·8 mL of 0·05 N NaOH for complete neutralisation. Calculate the empirical formula of the compound. (C_2HNO_2)

14. 0·2614 g of an organic compound gave upon combustion 0·2324 g of CO_2 and 0·0950 g of H_2O. 0·1195 g of this compound gave 0·3470 g of AgCl. If the vapour density of the substance is 49·5, calculate its molecular formula. ($C_2H_4Cl_2$)

15. A dibasic anhydrous acid produced upon combustion 0·195 g of CO_2 and 0·04 g of H_2O. 0·5 g of the salt of this acid when ignited, converted to 0·335 g of pure silver. Find the molecular formula of the dibasic acid. [$(COOH)_2$]

16. A monoacid organic base gave the following results on analysis:

(i) 0·10 g of the base gave 0·2882 g of CO_2 and 0·0756 g of H_2O.

(ii) 0·20 g of the base produced 21·8 mL of N_2 at 15°C and 760 mm pressure.

(iii) 0·40 g of the platinichloride left 0·125 g of Pt.
Calculate the molecular formula of the base. (C_7H_9N)

17. An organic compound containing C, H, O and S gave the following data on analysis:

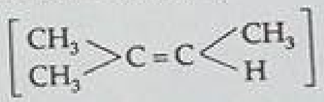
(a) The combustion of 0·1668 g of the compound resulted in the formation of 0·4540 g and 0·0663 g of CO_2 and H_2O respectively.

(b) 0·1254 g of the compound on heating with HNO_3 and $BaCl_2$ yielded 0·1292 g of $BaSO_4$.
Calculate the empirical formula of the organic compound. ($C_{14}H_{10}SO$)

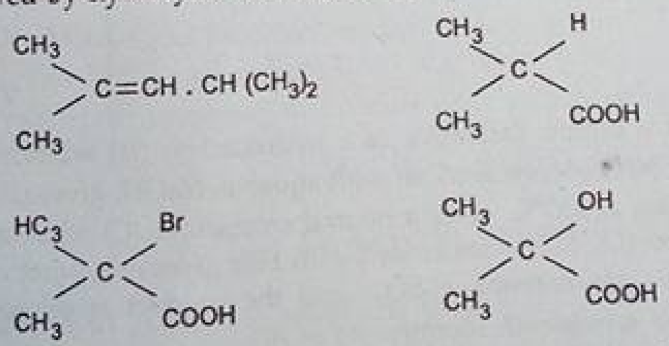
18. An organic compound containing 92·3% of C, 7·7% of H had the molecular weight 26. When treated with bromine, it gave a product containing 92·5% of bromine but when treated with HBr, it gave a product containing 85·1% of bromine. What is the structural formula of the organic compound? ($CH \equiv CH$)

19. An organic aromatic compound (X) containing 52·2% of C, 3·7% of H and 44·1% of chlorine on oxidation with alkaline $KMnO_4$ gave a monobasic acid (Y), the sodium salt of which on distillation with soda lime gave benzene. What is the structural formula of (X) and (Y)? ($C_6H_5CH \cdot Cl_2$, C_6H_5COOH)

20. One mole of hydrocarbon (A) reacts with one mole of bromine giving a dibromocompound, $C_5H_{10}Br_2$. Substance (A) on treatment with cold, dilute alkaline $KMnO_4$ solution forms a compound $C_5H_{12}O_2$. On ozonolysis, (A) gives equimolar quantities of propanone and ethanal. Deduce the structural formula of (A).



21. An alkene (A), on ozonolysis yields acetone and an aldehyde. The aldehyde is easily oxidised to an acid (B). When (B) is treated with bromine in presence of phosphorus, it yields compound (C) which on hydrolysis gives a hydroxy acid (D). The acid can also be obtained from acetone by the reaction with hydrogen cyanide followed by hydrolysis. Identify the compounds (A), (B), (C) and (D).



22. An aromatic hydrocarbon (A), containing 91·3% of C and 8·7% of H, on treatment with chlorine gave 3 isomeric monochlorocompounds (B), (C) and (D), each having 28% of chlorine. On oxidation with permanganate, all the three gave a monobasic acid. The acid from (B) on distillation with soda lime gave benzene while those

from (C) and (D) gave monochlorobenzene on the same treatment. Assign formulae to (A), (B), (C) and (D).

[(A) $C_6H_5 \cdot CH_3$ (B) $C_6H_5CH_2Cl$
(C) $C_6H_4(CH_3)Cl$ (ortho) (D) (para)]

23. 0·15 g of an organic compound (A) gave 0·33 g of CO_2 and 0·18 g of H_2O. The molecular weight of (A) is 60. The compound (A) on dehydration gave a hydrocarbon (B) containing 85·7% of C. (B), on successive treatment with hydriodic acid and silver hydroxide gave a product (C), isomeric with (A). Find structural formulae of (A), (B) and (C).

[(A) $CH_3CH_2CH_2OH$
(B) $CH_3CH=CH_2$
(C) $CH_3CH(OH)CH_3$]

24. Compound (A) with molecular weight 108, contained 88·89% C and 11·11% H. It gave a white precipitate with ammoniacal silver nitrate. Complete hydrogenation atom of (A) gave another compound (B) with molecular weight 112. Oxidation of (A) gave an acid with equivalent weight 128. Decarboxylation of this acid gave cyclohexane. Give structures of (A) and (B).

[$\underset{(A)}{C_6H_{11}C \equiv CH}$, $\underset{(B)}{C_6H_{11}CH_2-CH_3}$]

25. A compound (X) containing only C, H and O is unreactive towards sodium. It does not add bromine. It does not react with Schiff reagent. On refluxing with an excess of hydriodic acid, (X) yields only one organic product (Y). On hydrolysis, (Y) yields a new compound (Z) which can be converted to (Y) by reaction with red phosphorous and iodine. The compound (Z), on oxidation with $KMnO_4$ gives a carboxylic acid. The equivalent weight of this acid is 60. What are the compounds (X), (Y) and (Z). Write chemical equation leading to the conversion of (X) to (Y).

[$C_2H_5OC_2H_5$, C_2H_5I, C_2H_5OH
$C_2H_5OC_2H_5 + 2HI \rightarrow 2C_2H_5I + H_2O$]

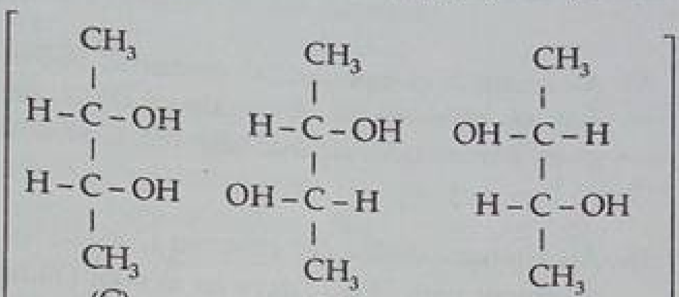
26. 448 mL of a hydrocarbon (A) having C (87·80%), H (12·19%) weigh 1·64 g at NTP. On hydrogenation it gives 2 methyl pentane. Treatment of (A) with acidic $HgSO_4$ gives a new compound (B) of molecular weight $C_6H_{12}O$. Compound (A) does not react with ammoniacal $AgNO_3$. What is the structure of (A)?

[$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-C\equiv C-CH_3$]

27. 0·369 g of a bromo derivative of a hydrocarbon (A) when vaporised occupied 67·2 mL at NTP. (A), on reaction with aqueous NaOH, gives (B). (B), when passed over alumina at 250°C, gives a neutral compound (C) while at 300°C, it gives a hydrocarbon (D). (D), when heated with HBr gives an isomer of (A). When (D) is treated with concentrated H_2SO_4 and the product is diluted with water and distilled, (E) is obtained. Identify (A) to (E).

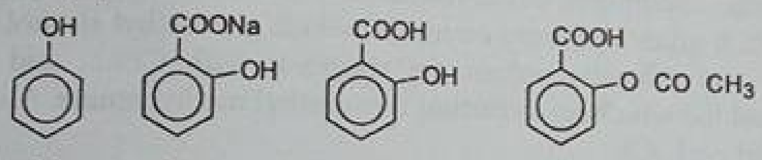
[(A) $CH_3 \cdot CH_2CH_2Br$ (B) $CH_3 \cdot CH_2CH_2OH$
(C) $C_3H_7 \cdot O \cdot C_3H_7$ (D) $CH_3-CH=CH_2$
(E) $\begin{matrix} CH_3 \\ CH_3 \end{matrix} \!\!> CH-OH$]

28. When 0·90 g of an organic compound $C_4H_{10}O_2$ (A) was treated with Na, 224 mL of H_2 were evolved at NTP, compound (A) could be separated into two fractions (B) and (C) by crystallisation, of which fraction (B) could be resolved into optical isomers, (D) and (E). Write down the structural formulae for (C), (D) and (E) with proper reasoning.



(C) (D) (E)

29. An organic compound (A) has 76·6% C and 6·38% H. Its vapour density is 47. It gives characteristic colour with aqueous $FeCl_3$ solution. (A), when heated with CO_2 and NaOH at 140°C under pressure, gives (B) which, on being acidified gives (C). (C) reacts with acetyl chloride to give (D) which is a well-known painkiller. Identify (A), (B), (C) and (D).



(A) (B) (C) (D)

30. An unknown compound of C, H and O contains 69·77% C and 11·63% H and has a molecular weight of 86. It does not reduce Fehling's solution but forms a bisulphite addition compound and gives a positive iodoform test. What are the possible structures?

[CH_3, C_3H_7 > CO, C_2H_5, C_2H_5 > CO]

[Hint: See Example 25]

31. An organic compound (mol. wt. = 44) (X) contains 54·54% of C and 9·09% of H. With PCl_5, (X) gives a compound of molecular weight 99. On oxidation it gives an acid of molecular weight 60. What is (X)? (CH_3CHO)

32. A ketone (A) which undergoes haloform reaction gives compound (B) on reduction. (B) on heating with H_2SO_4 gives compound (C), which forms monozonide (D). (D) on hydrolysis in the presence of Zn dust gives only acetaldehyde. Identify (A), (B) and (C).

[(A) $CH_3COCH_2CH_3$ (B) $CH_3CH(OH)CH_2CH_3$ (C) $CH_3CH=CH_2CH_3$]

33. An organic compound (A) having molecular weight, 58, contained 62·06% of C and 10·35% of H and rest, oxygen. (A), on reduction gave (B) which gave iodoform test. (B), on dehydration, gave an unsaturated hydrocarbon (C) having molecular weight 42. Find (A), (B) and (C).

($CH_3 \cdot CO \cdot CH_3$; $CH_3CH(OH)CH_3$; $CH_3 \cdot CH=CH_2$)

34. An aromatic compound (X) contains C (79·25 %) and H (5·66 %). (X) on treatment with alkali, gave a neutral product (Y) containing C (77·78 %) and H (7·41%) and the sodium salt of an aromatic organic acid (Z) which on distillation with soda lime gave benzene. Assign structural formulae to (X), (Y) and (Z).

(C_6H_5CHO, $C_6H_5CH_2OH$, C_6H_5COOH)

35. An aromatic compound (X) contained 58·5% of C, 4·1% of H and 11·4% of N. (X) may be obtained by the action of HNO_3 on a compound (Y). (X), on reduction, gives a monoacid organic base (Z). Give structural formulae of (X), (Y) and (Z).

($C_6H_5NO_2$, C_6H_6, $C_6H_5NH_2$)

36. An aliphatic amine (X) contains C (61·01%), H (15·25%) and N (23·74%). (X), on treatment with HNO_2, gave an alcohol (Y) having C(60%) and H (13·33%). (Y), on careful oxidation gave (Z) of vapour density 29. (Z) gave iodoform test. Assign structural formulae to (X), (Y) and (Z).

$$\left[{CH_3 \atop CH_3} \!>\! CH\cdot NH_2 ;\ {CH_3 \atop CH_3} \!>\! CH\cdot OH ;\ {CH_3 \atop CH_3} \!>\! CO \right]$$

37. An organic compound (A) contains C = 32%, H = 6·66% and N = 18·67%. On reduction, it gives a primary amine (B) which gives ethyl alcohol with nitrous acid. (B) gives an offensive odour on warming with $CHCl_3$ and KOH and gives compound (C) which on reduction forms ethyl methyl amine. Assign the structures of (A), (B) and (C).

[(A) $C_2H_5NO_2$
(B) $C_2H_5NH_2$
(C) C_2H_5NC]

(**Hint:** See Example 28)

38. Compound (A) gives positive Lucas test in 5 minutes. When 6 g of (A) is treated with Na metal, 1120 mL of H_2 is evolved at STP. Assuming (A) to contain one atom of oxygen per molecule, write the structural formula of (A).

[$CH_3\cdot CH(OH)\cdot CH_3$]

39. An organic compound (A) of molecular weight 140·5 has 68·32% C, 6·4% H and 25·26% Cl. Hydrolysis of (A) with dilute acid gives compound (B), $C_8H_{10}O$. Compound (B) can be oxidised under mild condition to compound (C), C_8H_8O. Compound (C) forms a phenyl hydrazone (D) with $PhNHNH_2$ and gives a positive iodoform test. Give the structures of compounds (A) to (D).

[(A) $C_6H_5\ CH\cdot Cl\ CH_3$ (B) ${C_6H_5 \atop CH_3} \!>\! CH\cdot OH$
(C) ${C_6H_5 \atop CH_3} \!>\! CO$ (D) $C_6H_5-\underset{\displaystyle CH_3}{\underset{|}{C}}=N\cdot NH\cdot C_6H_5$]

40. 10 g of a mixture of hexane and ethanol are reacted with Na to give 200 mL of hydrogen at 27°C and 760 mmHg pressure. What is the percentage of ethanol in the mixture.

(7·475%)

[**Hint** $2C_2H_5OH + 2Na \rightarrow 2C_2H_5ONa + H_2$]

41. A mixture of 0·535 g of ethanol and acetaldehyde when heated with Fehling's solution gave 1·2 g of a red precipitate. What is the percentage of acetaldehyde in the mixture? (Cu = 63·5) (34·50%)

[**Hint:** Acetaldehyde reduces Fehling's solution to red cuprous oxide (Cu_2O) and $CH_3CHO + [O] \rightarrow CH_3COOH$]

42. An organic compound, (A) containing C, H, N and O, on analysis gives 49·32% carbon, 9·59% hydrogen and 19·18% nitrogen. (A) on boiling with NaOH gives off NH_3 and a salt which on acidification gives a monobasic nitrogen-free acid (B). The silver salt of (B) contains 59·67% silver. Deduce the structures of (A) and (B).
(IIT 1988) [(A) $C_2H_5CONH_2$ (B) C_2H_5COOH]

43. A certain compound was known to have a formula which would be represented as $[PdC_xH_yN_z](ClO_4)_2$. Analysis showed that the compound contained 30·15% C and 5·06% H. When converted to the corresponding thiocyanate, $[PdC_xH_yN_z](SCN)_2$, the analysis was 40·412% C and 5·94% H. Find x, y and z. (14, 28, 4)

❑❑❑

CHAPTER ELEVEN

ATOMIC STRUCTURE AND RADIOACTIVITY

ATOMIC STRUCTURE

An atom consists of an extremely small and dense nucleus and an extranuclear space. The nucleus contains positively charged protons and neutral neutrons, and these particles are collectively called nucleons. In the extranuclear space, negatively charged electrons revolve around the nucleus. As the magnitude of the charge of an electron is the same as that of a proton, the number of electrons is equal to that of protons in an atom, the atom being neutral.

The number of protons present in the nucleus of an atom is termed as the atomic number of the element (Z). The sum of the number of protons and neutrons is called the mass number (A). The term 'nuclide' refers to a nucleus having a specific atomic number and specific mass number.

Since each proton and each neutron has a mass approximately equal to 1 (amu) on the atomic weight scale, the atomic weight of an element is approximately equal to the mass number. The electron has a negligible mass compared to the proton and neutron. The mass of an electron on the atomic weight scale is approximately equal to 1/1837 amu (1 amu $= 1{\cdot}66 \times 10^{-24}$ g or $1{\cdot}66 \times 10^{-27}$ kg).

To calculate the radius (r) and energy (E) of a permissible orbit for one-electron species like H, He^{+}, Li^{2+}, etc., Bohr derived equations based on the following postulates.

Bohr's Postulates

1. The electrons revolve around the nucleus in certain orbits without losing energy because the energy in a fraction of a quantum can neither be lost nor gained.
2. Energy is absorbed or emitted only when an electron in an atom jumps from one orbit to another.
3. The electron is restricted to those orbits in which its angular momentum is an integral multiple of $h/2\pi$.

Angular momentum $= mvr = n \times \dfrac{h}{2\pi}$ where n is an integer.

The following equations were derived:

$$r = \frac{n^2 h^2}{4\pi^2 mZe^2} \qquad \ldots (1)$$

$$\frac{N_1}{N_2} = \frac{\lambda_2 - \lambda_1}{\lambda_1}. \quad \text{... (Eqn. 31)}$$

Now,

$$\lambda_1 = \frac{0{\cdot}6932}{(t_{\frac{1}{2}})_1} = \frac{0{\cdot}6932}{1{\cdot}913 \times 365} = 9{\cdot}927 \times 10^{-4}\ \text{d}^{-1}$$

$$\lambda_2 = \frac{0{\cdot}6932}{(t_{\frac{1}{2}})_2} = \frac{0{\cdot}6932}{3{\cdot}64} = 0{\cdot}1900\ \text{d}^{-1}.$$

Thus,

$$\frac{N\,(\text{Th})}{N\,(\text{Ra})} = \frac{0{\cdot}1900 - 9{\cdot}927 \times 10^{-4}}{9{\cdot}927 \times 10^{-4}} = 190.$$

Ex. 70. *Consider*

$$^{224}\text{Ra} \xrightarrow{-\alpha} {}^{220}\text{Rn} \xrightarrow{-\alpha} {}^{216}\text{Po}$$

where $t_{\frac{1}{2}}$ *(Ra)* = 3·64 yr, $t_{\frac{1}{2}}$ *(Rn)* = 55 s. *Determine the* N *(Ra)/*N *(Rn) ratio once secular equilibrium in which* $t_{\frac{1}{2}}$ *(parent)* >> $t_{\frac{1}{2}}$ *(daughter) or* λ *(parent)* << λ *(daughter) has been established.*

Solution : We have,

$$\frac{N_1}{N_2} = \frac{\lambda_2}{\lambda_1}. \quad \text{... (Eqn. 32)}$$

Now,

$$\lambda_1 = \frac{0{\cdot}6932}{(t_{\frac{1}{2}})_1} = \frac{0{\cdot}6932}{3{\cdot}64 \times 60 \times 60} = 2{\cdot}20 \times 10^{-6}\ \text{s}^{-1}$$

$$\lambda_2 = \frac{0{\cdot}6932}{(t_{\frac{1}{2}})_2} = \frac{0{\cdot}6932}{55} = 1{\cdot}26 \times 10^{-2}\ \text{s}^{-1}.$$

Thus,

$$\frac{N\,(\text{Ra})}{N\,(\text{Rn})} = \frac{1{\cdot}26 \times 10^{-2}}{2{\cdot}20 \times 10^{-6}} = 5727.$$

PROBLEMS

(Answers bracketed with questions)

1. Using Bohr theory, calculate the radii of the first and the tenth orbits in the hydrogen atom. ($r_1 = 0{\cdot}53 \times 10^{-8}$ cm, $r_{10} = 0{\cdot}53 \times 10^{-6}$ cm)

   [Hint: See examples 1 and 2.]

2. Calculate the velocities of the electron in the first and the tenth orbits of the hydrogen atom. ($v_1 = 21 \cdot 9 \times 10^7$ cm/s)

3. Calculate the energy in calories required to produce, from neutral He atoms, 1 mole of (a) He^+ ions (b) 'He^{++} ions using Bohr's equations. [(b) 1,821000 cal]

4. Calculate the energy in eV required to ionise 1 mole of hydrogen.
[Hint: See Ex. 8.] ($8 \cdot 189 \times 10^{24}$ eV)

5. Calculate the frequency of the spectral line when an electron from the fifth orbit jumps to the second orbit in a hydrogen atom. (R = 109737 cm^{-1}) ($6 \cdot 91 \times 10^{14}$)

6. Find (i) the total number of neutrons (ii) the total mass of neutrons in 7 mg of ^{14}C. (Assume the mass of a neutron = mass of a hydrogen atom)
[(i) $24 \cdot 08 \times 10^{20}$ (ii) 4 mg)]

7. Calculate the wave number and frequency of radiation having wavelength 5800 Å.
(172400 cm^{-1}, $5 \cdot 172 \times 10^{14}$ cycles s^{-1})

8. What total amount of energy in calories would be required to shift all the electrons from the first Bohr orbit to the sixth Bohr orbit in 1 mole of hydrogen?
Through what distance would each electron have to move?
What frequency of radiation would be emitted if the electrons returned to their initial state? (304800 calories)

9. The ionisation energy of hydrogen atom is 13·6 eV. What will be the ionisation energy of He^+ and Li^{2+} ions? (54·4 eV, 122·4 eV)

10. Calculate the frequency, energy and wavelength of the radiation corresponding to the spectral line of lowest frequency in Lyman series in the spectra of hydrogen atom. Also, calculate the energy for the corresponding line in the spectra of Li^{2+} ($R_H = 1 \cdot 09678 \times 10^7\ m^{-1}$, $c = 3 \times 10^8$ m/s, $h = 6 \cdot 625 \times 10^{-34}$ J · s.)
($2 \cdot 176 \times 10^{-18}$ J, $1 \cdot 958 \times 10^{-17}$ J)

11. Considering the shape of a Ca nucleus like a sphere, calculate the density of the nucleus of Ca of mass number 40. ($1 \cdot 8 \times 10^{14}$ g cm^{-3})

12. For He^+ and Li^{2+}, the energies are related to the quantum number, n, through an expression

$$E_n = -\frac{Z^2 B}{n^2}$$

where Z is the atomic number of species and $B = 2 \cdot 179 \times 10^{-18}$ J.
(a) What is the energy of the lowest level ($n = 1$) of a He^+ ion?
(b) What is the energy of the level $n = 3$ of a Li^{2+} ion?
{(a) $8 \cdot 716 \times 10^{-18}$ J; (b) $2 \cdot 179 \times 10^{-18}$ J}

13. The line at 434 nm in the Balmer series of the hydrogen spectrum corresponds to a transition of an electron from the n^{th} to second Bohr orbit. What is the value of n? ($n = 5$)

[Hint: $\nu = 3{\cdot}2881 \times 10^{15}\ s^{-1}\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$]

14. What change in molar energy in joule would be associated with an atomic transition giving rise to radiation at 1 Hz? ($h = 6{\cdot}626 \times 10^{-34}$ J · s) ($3{\cdot}99 \times 10^{-10}$ J · mol^{-1})
[Hint: 1 Hz = s^{-1}, $\Delta E = Nh\nu$ and $\nu = 1$]

15. Calculate the uncertainty in the position of a particle when the uncertainty in the momentum is zero. (∞)

16. Calculate the uncertainty in the velocity of a wagon of mass 2000 kg, whose position is known to an accuracy of ± 10 metre. ($5{\cdot}25 \times 10^{-31}$ m s^{-1})

17. Calculate the uncertainty in velocity of an electron when the uncertainty in position is 0·1 nm. ($5{\cdot}786 \times 10^5$ m s^{-1})

18. For the gaseous reaction $K + F \rightarrow K^+ + F^-$, ΔH was calculated to be 19 kcal under conditions where the cations and anions were prevented by electrostatic separation from combining with each other. The ionisation potential of K is 4·3 eV. Find electron affinity of F. (3·47 eV)
[Hint: See Ex. 27]

19. The prominent yellow line in the spectrum of sodium vapour lamp has a wavelength of 590 nm. What minimum accelerating potential is needed to excite this line in an electron tube containing sodium vapour.
($h = 6{\cdot}63 \times 10^{-34}$ J · s, $c = 3 \times 10^8$ m/s) (2·11 V)
[Hint: 1 eV = $1{\cdot}602 \times 10^{-19}$ J, $E = \frac{hc}{\lambda}$
and 1 eV = energy of 1 electron being accelerated by 1 volt.]

20. If the energy difference between the ground state of an atom and its excited state is $4{\cdot}4 \times 10^{-19}$ J, what is the wavelength of the photon required to produce this transition? ($4{\cdot}5 \times 10^{-7}$ m)
[Hint: $\lambda = \frac{hc}{\Delta E}$]

21. A body weighing $3{\cdot}0 \times 10^3$ kg is moving and its speed can be measured with an accuracy of ± 0·0025 mile per hour and its position with an accuracy of ± 0·01 mile. Is the uncertainty principle valid? (No)

22. An electron is accelerated by applying potential difference of 1000 eV. What is the de Broglie's wavelength associated with it? 1 eV = $1{\cdot}6 \times 10^{-12}$ erg.
($h = 6{\cdot}627 \times 10^{-27}$ erg s, $m_e = 9{\cdot}1 \times 10^{-28}$ g) ($3{\cdot}87 \times 10^{-9}$ cm)

23. A large object weighing $1{\cdot}0 \times 10^3$ kg is moving with a velocity of 50 km per hour. Does it have a wave motion? (λ is very low hence no)

24. Is it possible to locate the electron within 0·005 nm? (Use the standard values of h and m.) (not possible)

[**Hint:** Δv would be nearly as large as the velocity of light.]

25. Assume that 10^{-17} J of light energy is needed by the interior of the human eye to see an object. How many photons of green light ($\lambda = 495$ nm) are needed to generate this minimum energy?
(25)

26. How are a 1s orbital and a 2s orbital in an atom similar? How do they differ? How are a $2p_x$ orbital and a $2p_y$ orbital in an atom similar? How do they differ?
(read text)

27. What is the maximum number of electrons in an atom in which the last electron, filled, has the following quantum numbers?
(a) $n = 3$ (b) $n = 3$, and $l = 1$ (c) $n = 3, l = 1$ and $m = -1$
(d) $n = 3, l = 1, m = -1$ and $s = +\frac{1}{2}$ [(a) 30, (b) 18 (c) 16 (d) 13]

28. Which of the following equations describe(s) particle-like behaviour? Which describe(s) wavelike behaviour? Do any involve both types of behaviour?
(a) $C = \gamma\lambda$ (b) $E = mc^2$ (c) $\gamma = \frac{n^2 a_0}{Z}$ (d) $E = h\gamma$ (e) $\lambda = \frac{h}{mv}$
[Wavelike: (a) & (d), particle-like: (b) & (c), Both: (e)]

29. The quantum numbers listed below are for four different electrons in the same atom. Arrange them in order of increasing energy. Indicate whether any two have the same energy.
(a) $n = 4, l = 0, m = 0$ and $s = +\frac{1}{2}$
(b) $n = 3, l = 2, m = +1$ and $s = +\frac{1}{2}$
(c) $n = 3, l = 2, m = -2$ and $s = -\frac{1}{2}$
(d) $n = 3, l = 1, m = +1$ and $s = -\frac{1}{2}$
((d) < (a) < (b) = (c))

30. When compounds of barium are heated in a flame, green light of wavelength 554 nm is emitted. How much energy is lost when one mole of barium atoms each emit one photon of this wavelength?
(216 kJ)

31. What is the energy in J evolved when 1 mole of He-4 nuclei is produced from protons and neutrons? How many litres of C_2H_6(g) at 25°C and 725 mmHg are needed to evolve the same quantity of energy when C_2H_6 is burnt in O_2? (neutron = 1·008867 amu, proton = 1·00728 amu, He = 4·0015 amu, $\Delta H_{comb.}(C_2H_6) = -1427{\cdot}81$ kJ/mol)
($2{\cdot}732 \times 10^{12}$ J, $4{\cdot}9 \times 10^{7}$ L)

32. A 1·0-mg sample of Tc–99 has an activity of $1{\cdot}7 \times 10^{-5}$ curie, decaying by β-emission. Calculate the decay constant.
($1{\cdot}0 \times 10^{-13}\ s^{-1}$)

33. Tritium, $^{3}_{1}H$ is a radioactive nucleus of hydrogen. It is used in luminous watch dials. Tritium decays by β-emission with $t_{1/2} = 12.3$ years. What is the activity in curie of a sample containing 2·5 μg of tritium? The atomic mass of tritium is 3·02 amu.
(0·024 Ci)

34. Predict the type of radioactive decay process that is likely for each of the following nuclides.

(a) $^{228}_{92}U$ (b) $^{8}_{5}B$ (c) $^{68}_{29}Cu$

((a) α (b) β^+ or *K*–capture (c) β emission)

35. If 28·0% of a sample of Ag-112 decays in 1·52 h, what is the half-life of this isotope? (3·21 h)

36. $^{232}_{90}Th$ disintegrates to $^{x}_{y}Pb$ by emitting six α- and four β-particles. Find *x* and *y*. (208, 82)

37. The uranium (mass no. 238 and at. no. 92) emits an α-particle, the product has the mass no. and at. no.:

(a) 236 and 92 (b) 234 and 90 (c) 238 and 90 (d) 236 and 90 [b]

38. To which series will the following elements belong?

$^{257}_{103}Lr$, $^{254}_{99}Es$, $^{243}_{95}Am$ $(4n+1,\ 4n+2,\ 4n+3)$

39. A sample of carbon from an ancient frame gives 7 counts of ^{14}C per minute per gram of carbon. If freshly cut wood gives 15·3 counts of ^{14}C per minute per gram, what is the age of the frame? (Half-life period of ^{14}C = 5770 years)
[Hint: $N^0 = 15{\cdot}3,\ N = 7$] (6520 years)

40. Calculate the number of atoms disintegrating per minute in a mass of 0·001g of radium which is an α-emitter with a half-life period of 1620 years. $(2{\cdot}16\times10^9)$

41. In a sample of pitchblende the atomic ratio is $^{206}Pb : {}^{238}U = 0{\cdot}23 : 1$. Calculate the age of the mineral, if half-life of uranium is taken as $4{\cdot}5\times10^9$ years. All lead originated from uranium. $(1{\cdot}34\times10^9$ years)

42. A sample of radon emitted initially 7×10^4 α-particles per second. After some time, the emission rate became $2{\cdot}1\times10^4$. If $t_{\frac{1}{2}}$ for radon is 3·8 days, find the age of the sample. (6·6 days)

43. ^{222}Rn has a half-life period of 3·83 days. What fraction of the sample will remain undecomposed at the end of 10 days? (0·164)

44. The number of α-particles emitted per second by 1 g of radium is $3{\cdot}608\times10^{10}$. Calculate decay constant and $t_{\frac{1}{2}}$.

$$\begin{Bmatrix} 1{\cdot}35\times10^{-11}\ s^{-1} \\ 5{\cdot}13\times10^{10}\ s \end{Bmatrix}$$

45. The rate of radioactive decomposition corresponding to $3{\cdot}7\times10^{10}$ disintegration per second is called a curie. What weight of ^{226}Ra, whose $t_{\frac{1}{2}} = 1620$ yr, will be required to yield 1 millicurie of radiation? $(1\times10^{-3}$ g)

46. Calculate the weight of $^{14}C\left(t_{\frac{1}{2}} = 5720\ yr\right)$ atoms which will give $3{\cdot}70\times10^7$ disintegrations per second (dps). (0·2234 mg)

47. Calculate the number of disintegrations which 1 g of $^{226}Ra\left(t_{\frac{1}{2}} = 1600 \text{ yr}\right)$ would undergo per second. What quantity of $Na^{24}\left(t_{\frac{1}{2}} = 15 \text{ hours}\right)$ would undergo the same no. of disintegrations per second. ($3{\cdot}658 \times 10^{10}$ dps, $1{\cdot}37 \times 10^{-7}$ g)

48. A piece of wood was found to have $^{14}C/^{12}C$ ratio 0·7 times that in a living plant. Calculate the period (in years) when the plant died.
$\left(t_{\frac{1}{2}} \text{ for } C^{14} = 5760 \text{ yr}\right)$ (2964 yr)

49. 10·0 gram-atom of an α-active radioisotope is disintegrating in a sealed container. In one hour, the He gas collected at STP is 11·2 litres. Calculate the half-life of the isotope supposing each nucleus yielding one He atom. (13·49 h)

50. The disintegration rate for a sample containing $^{60}_{27}Co$ as the only radioactive nuclide, is found to be 240 atoms/minute. $t_{\frac{1}{2}}$ of Co is 5·2 years. Find the number of atoms of Co in the sample. How long must this radioactive sample be maintained before the rate falls to 100 disintegrations/minute. ($9{\cdot}6 \times 10^8$, 6·6 years)

51. Sample containing $^{234}_{88}Ra$, which decays by α-particle emission, is observed to disintegrate at the following rate expressed as counts per minute (cpm). Calculate half-life of this nuclide. $t = 0$, 1000 cpm; $t = 1$ h, 992 cpm; $t = 10$ h, 924 cpm; $t = 100$ h, 452 cpm; $t = 250$ h, 138 cpm. (3·63 days)

52. The thorium radioactive decay series produces one atom of ^{208}Pb as the final disintegration product of an atom of ^{232}Th. $t_{\frac{1}{2}}$ of ^{232}Th is $1{\cdot}39 \times 10^{10}$ years. A certain rock is found to have a mass ratio of ^{208}Pb and ^{232}Th as ·14 : 1. Determine the age of the rock. ($2{\cdot}97 \times 10^9$ years)

53. The ratio of the number of atoms of two radioactive elements *A* and *B*, in equilibrium with each other, is $3{\cdot}1 \times 10^9 : 1$. If $t_{\frac{1}{2}}$ of element *B* is 6·45 yrs, calculate that of element *A*. (2×10^{10})

54. Which nucleus has higher binding energy per nucleon : $^{58}_{28}Ni$ (57·941 amu) or $^{55}_{25}Mn$ (54·939 amu)? Mass of neutron is 1·00867 amu and that of proton is 1·00728 amu. (Ni)

55. For $^{238}_{92}U$ the binding energy per nucleon is 7·576 MeV. What is the atomic weight of this isotope? Use the mass of neutron and proton from Ex. 60.
[Hint: See Ex. 60] (239·93 amu)

Objective Problems

1. The frequency of a green light is 6×10^{14} Hz. Its wavelength is
   (a) 500 nm (b) 5 nm
   (c) 5000 nm (d) none of these

[Hint: 1 nm = 10^{-9} m]

2. The ratio of energy of a photon of 2000 Å wavelength radiation to that of 4000 Å radiation is
(a) 1/4 (b) 4 (c) 1/2 (d) 2

3. The values of charge on the oil droplets experimentally observed were -1.6×10^{-19}, -2.4×10^{-19} and -4×10^{-19} coulomb. The value of the electronic charge, indicated by these results is
(a) -1.6×10^{-19} (b) -2.4×10^{-19} (c) -4×10^{-19} (d) -0.8×10^{-19}
[Hint: Find the highest common factor.]

4. Which of the following statements is/are correct?
(a) A photon is a positively charged nuclear particle.
(b) A photon is a particle of light energy.
(c) A photon is a quantum of light.
(d) A photon is a bundle of energy of definite magnitudes but not necessarily light energy.

5. For which of the following species, Bohr theory does not apply?
(a) H (b) H^+ (c) He^+ (d) Li^{2+}

6. The radius of the first Bohr orbit of hydrogen atom is r. The radius of the 3rd orbit would be
(a) $3r$ (b) $9r$ (c) $27r$ (d) none of these

7. The electronic velocity in the fourth Bohr orbit of hydrogen is v. The velocity of the electron in the first orbit would be
(a) $4v$ (b) $16v$ (c) $v/4$ (d) $v/16$

8. The ionisation potential of hydrogen atom is 13·6 eV. The energy required to remove an electron in the $n = 2$ state of hydrogen atom is
(a) 27·2 eV (b) 13·6 eV (c) 6·8 eV (d) 3·4 eV.

9. The energy of the second Bohr orbit in the hydrogen atom is -3.41 eV. The energy of the second Bohr orbit of He^+ ion would be
(a) -0.85 eV (b) -13.64 eV (c) -1.70 eV (d) -6.82

10. The ratio of the radii of the first three Bohr orbits is
(a) 1 : 5 : 33 (b) 1 : 2 : 3 (c) 1 : 4 : 9 (d) 1 : 8 : 27

11. The ratio of the difference in energy between the first and second Bohr orbits to that between the second and third Bohr orbit is
(a) 1/2 (b) 1/3 (c) 4/9 (d) 27/5

12. For $l = 3$, which value of m is not possible?
(a) 4 (b) 0 (c) –3 (d) –1

13. The designation of an orbital with $n = 4$ and $l = 1$, is
(a) 4d (b) 4s (c) 4f (d) 4p

14. Which of the following orbitals is meaningless?
(a) 6f (b) 2d (c) 7s (d) 3d

15. Which of the following sets of quantum numbers is possible for an electron in a 4*f* orbital

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

(c) $n=4, l=3, m=+1, s=-\frac{1}{2}$ (d) $n=4, l=3, m=4, s=+\frac{1}{2}$

16. The maximum number of electrons in an atom with quantum numbers $n=3, l=2$ is

(a) 2 (b) 6 (c) 10 (d) 30

17. The number of orbitals in $n=3$ are

(a) 1 (b) 4 (c) 9 (d) 16

18. If the nitrogen atom had electronic configuration $1s^7$, it would have energy lower than that of the normal ground state configuration $1s^2, 2s^2 2p^3$, because the electrons would be closer to the nucleus. Yet, $1s^7$ is not observed because it violates

(a) Heisenberg uncertainty principle
(b) Hund Rule
(c) Pauli exclusion principle
(d) Bohr postulate of stationary orbits (IIT 2002)

19. Rutherford's experiment, which establishes the nuclear model of the atom, used a beam of

(a) β-particles, which impinged on a metal foil and got absorbed
(b) γ-rays, which impinged on a metal foil and ejected electrons
(c) helium atoms, which impinged on a metal foil and got scattered
(d) helium nuclei, which impinged on a metal foil and got scattered (IIT 2002)

20. Total number of nodal planes are same in

(a) 3*s*, 4*d* (b) 4*s*, 3*p* (c) 5*s*, 4*d* (d) 4*s*, 4*p*

21. The number of waves made by an electron moving in an orbit having maximum quantum number (*m*) +3 is

(a) 3 (b) 4 (c) 5 (d) 6

[Hint: $l=3$ and $n=4$]

22. The electronic transition from $n=2$ to $n=1$ will produce shortest wavelength in

(a) Li^{2+} (b) He^+ (c) H (d) H^+

23. The first emission line of Balmer series in He^+-spectrum has the wave no. in cm^{-1} equal to (*R*-Rydberg constant)

(a) $\frac{3R}{4}$ (b) $\frac{20R}{36}$ (c) $\frac{5R}{36}$ (d) $\frac{R}{6}$

24. If the radius of first Bohr orbit is *r*, the wavelength of an electron in the third orbit of a hydrogen atom is equal to

(a) $6\pi r$ (b) $2\pi r$ (c) $9\pi r$ (d) $3r$

25. If the shortest λ of hydrogen atom in Lyman series is *x*, the longest λ in Balmer series of He^+ is

(a) $\frac{x}{4}$ (b) $\frac{5x}{9}$ (c) $\frac{6x}{5}$ (d) $\frac{9x}{5}$

26. Consider a large number of hydrogen atoms with electrons randomly distributed in the $n = 1, 2, 3,$ and 4 orbits. How many different wavelengths of light are emitted by these atoms as the electrons fall into lower energy orbits.
(a) 1 (b) 3 (c) 6 (d) 9

27. How many times larger is a hydrogen atom than the radius of an H atom in its ground state if the H atom with an electron characterised by a quantum number of 106?
(a) 106 (b) 212 (c) 11236 (d) none of these

28. Which is larger, an He^+ ion with an electron in an orbit with $n = 3$ or an Li^{2+} ion with an electron in an orbit with $n = 5$?
(a) He^+ (b) Li^{2+} (c) both equal

29. Which of the following sets of quantum numbers is permissible for an electron in an atom?
(a) $n = 1, l = 1, m = 0, s = +\frac{1}{2}$ (b) $n = 3, l = 1, m = -2, s = -\frac{1}{2}$
(c) $n = 2, l = 1, m = 0, s = +\frac{1}{2}$ (d) $n = 2, l = 0, m = 0, s = 1$

30. Number of stable isotopes is least when the number of neutrons and that of protons in the isotopes are respectively
(a) odd and odd (b) even and odd
(c) odd and even (d) even and even

31. A radioactive nuclide generally disintegrates by α-emission when its N/P ratio is
(a) less than 1 (b) equal to one (c) equal to 1·2 (d) greater than 1·5

32. $^{x}_{8}X$ atom is isotone to $^{17}_{9}Y$ atom. The value of x is
(a) 8 (b) 16 (c) 9 (d) 17

33. If 5 g of a radioactive substance has a $t_{\frac{1}{2}}$ = 14 h, 20 g of the same substance will have a $t_{\frac{1}{2}}$ equal to
(a) 56 h (b) 3·5 h (c) 14 h (d) 28 h

34. The designations of a proton and neutron are $^{1}_{1}H$ and $^{1}_{0}n$ respectively. Are the two particles of equal mass?
(a) Yes, both proton and neutron have the same mass, i.e., 1 amu.
(b) No, mass numbers reflect actual masses only to the nearest amu. The precise masses of proton and neutron are 1·0072765 and 1·008665 amu.

35. The nuclides $^{40}_{18}Ar$ and $^{41}_{19}K$ are
(a) isotopes (b) isobars (c) isotones (d) none of these

36. Which of the following nuclides are isobars?
(a) $^{40}_{21}Sc$ and $^{42}_{21}Sc$ (b) $^{40}_{18}Ar$ and $^{40}_{21}Sc$ (c) $^{40}_{18}Ar$ and $^{41}_{19}K$ (d) none of these

37. To what stable isotope would $^{257}_{103}Lr$ decay?
(a) $^{208}_{82}Pb$ (b) $^{209}_{83}Bi$ (c) $^{206}_{82}Pb$ (d) $^{207}_{82}Pb$

[Hint: $^{257}_{103}Lr$ belongs to $(4n + 1)$ series]

38. The half-life of a radioactive isotope is 1·5 hours. The mass of it that remains undecayed after 6 hours is (if the initial mass of the isotope was 32 g)
(a) 32 g (b) 16 g (c) 4 g (d) 2 g

39. The radioactivity due to C-14 isotope $\left(t_{\frac{1}{2}} = 6000 \text{ yr}\right)$ of a sample of wood from an ancient tomb was found to be nearly half that of fresh wood; the tomb is, therefore, about
(a) 3000 years old (b) 6000 years old
(c) 9000 years old (d) 12000 years old

40. The half-life period of a radioactive nuclide is 3 hours. In 9 hours its activity will be reduced by a factor of
(a) 1/9 (b) 1/8 (c) 1/27 (d) 1/6
[Hint: Cal. N/N°]

41. If 3/4 quantity of a radioactive element disintegrates in two hours, its half-life would be
(a) 1 hour (b) 45 m (c) 30 m (d) 15 m

42. A sample of rock from moon contains equal number of atoms of uranium and lead $\left(t_{\frac{1}{2}} \text{ for } U = 4{\cdot}5 \times 10^9 \text{ years}\right)$. The age of the rock would be
(a) $4{\cdot}5 \times 10^9$ years (b) 9×10^9 years
(c) $13{\cdot}5 \times 10^9$ years (d) $2{\cdot}25 \times 10^9$ years

43. A radioactive isotope having a half-life of 3 days was received after 12 days. It was found that there were 3 g of the isotope in the container. The initial weight of the isotope when packed was
(a) 12 g (b) 24 g (c) 36 g (d) 48 g

44. If N^0 is the initial number of nuclei, number of nuclei remaining undecayed at the end of n^{th} half-life is
(a) $2^{-n} N^0$ (b) $2^n N^0$ (c) $n^{-2} N^0$ (d) $n^2 N^0$

45. A radioactive substance is decaying with $t_{\frac{1}{2}} = 30$ days. On being separated into two fractions, one of the fractions, immediately after separation, decays with $t_{1/2} = 2$ days. The other fraction, immediately after separation, would show
(a) constant activity (b) increasing activity
(c) decay with $t_{1/2}$ = 30 days (d) decay with $t_{1/2} = 28$ days

46. A radioactive substance has a constant activity of 2000 disintegrations/minute. The material is separated into two fractions, one of which has an initial activity of 1000 disintegrations per minute while the other fraction decays with $t_{\frac{1}{2}}$ = 24 hours. The total activity in both samples after 48 hours of separation is
(a) 1500 (b) 1000 (c) 1250 (d) 2000

47. The orbital angular momentum of an electron in 2s orbital is
(a) $+\frac{1}{2} \cdot \frac{h}{2\pi}$ (b) zero (c) $\frac{h}{2\pi}$ (d) $\sqrt{2}\,\frac{h}{2\pi}$

[Hint: $L = \sqrt{l\,(l+1)}\,\frac{h}{2\pi}$]

48. For a *d*-electron, the orbital angular momentum is

(a) $\sqrt{6}\,\hbar$ (b) $\sqrt{2}\,\hbar$ (c) $\hbar$ (d) $2\,\hbar$

[Hint: $L = \sqrt{l\,(l+1)}\,\hbar$; $l = 0, 1, 2, \ldots$; $\hbar = \frac{h}{2\pi}$; $\hbar$ is called Dirac h] **(IIT 1997)**

49. $^{27}_{13}Al$ is a stable isotope. $^{29}_{13}Al$ is expected to disintegrate by

(a) α-emission (b) β-emission

(c) positron emission (d) proton emission **(IIT 1996)**

50. Which of the following relates to light both as wave motion as well as particle?

(a) Diffraction and interference (b) Photoelectric effect

(c) $E = mc^2$ (d) $E = h\nu$

Answers

1-a, 2-d, 3-d, 4-b,c, 5-b, 6-b, 7-a, 8-d, 9-b, 10-c, 11-d, 12-a 13-d, 14-b, 15-c, 16-d, 17-c, 18-c, 19-d, 20-d, 21-b, 22-a, 23-b, 24-a, 25-d, 26-c, 27-c, 28-b, 29-c, 30-a, 31-d, 32-b, 33-c, 34-b, 35-c, 36-b, 37-b, 38-d, 39-b, 40-b, 41-a, 42-a, 43-d, 44-a, 45-b, 46-d, 47-b, 48-a, 49-b, 50-d.

❑❑❑

PROPERTIES OF GASES

The Ideal Gas Laws

1. Avogadro's Law

One mole of any substance contains the Avogadro constant ($6{\cdot}022 \times 10^{23}$) of molecules. It was Avogadro who discovered the law of nature for gases. This law is known as Avogadro's law, which states:

The volumes of the same number of moles of all gases measured at constant temperature and pressure are the same. That is, at the same temperature and pressure equal volumes of all gases contain equal number of moles or molecules.

Mathematically, at constant temperature and pressure:

Volume $\propto$ Number of moles

Volume $= K \times$ number of moles

Thus, for the same value of number of moles at constant temperature and pressure the proportionality constant, K will be a universal constant for all gases. When temperature and pressure are taken as 0°C and 1 atm respectively, K for 1 mole of the gas then represents the standard molar volume which is equal to 22·4 litres per mole or $22{\cdot}4 \times 10^{-3}$ metre^3 mole^{-1} (SI).

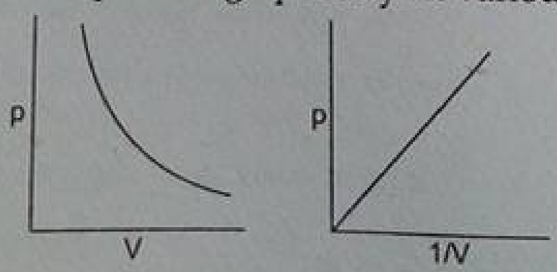
2. Boyle's Law

For a gas at constant temperature the pressure is inversely proportional to the volume, provided number of moles (n) of the gas does not change during the experiment.

$$p \propto \frac{1}{V};\ pV = \text{constant} \qquad \ldots (1)$$

$$p_1V_1 = p_2V_2 \quad (\text{T and } n \text{ are constant})$$

Boyle's law can be expressed graphically in various ways:



$$= \frac{5}{16 \times (0.36 \times 10^{-9})^2} \left(\frac{5.314 \times 10^{-26} \times 1.38 \times 10^{-23} \times 273}{22/7} \right)^{1/2}$$

$$= 1.926 \times 10^{-5} \text{ Pa s.}$$

PROBLEMS

(Answers bracketed with questions)

1. 1 g of helium gas is confined in a two-litre flask under a pressure of 2·05 atm. What is its temperature? (200 K)

2. The density of He is 0·1784 kg/m^3 at STP. If a given mass of He at STP is allowed to expand to 1·5 times its initial volume by changing the temperature and pressure, compute its resultant density. (0·1189 kg/m^3)

   [**Hint** 1 kg/m^3 = 1 g/L. Density is reduced by 1·5 times]

3. The density of an ideal gas A is 1·43 g/L at STP. Determine the density of A at 17°C and 700 torr (mm). (1·24 g/L)

4. A container has 3·2 g of a certain gas at NTP. What would be the mass of the same gas contained in the same vessel at 200°C and 16 atm pressure. (29·534 g)

   [**Hint:** Mol. wt. $(M) = \frac{3.2}{V} \times 22.4$; V = vol. in lit. Apply $pV = \frac{w}{M}RT$;

   w = wt. of the gas in g at 473 K and 16 atm]

5. Calculate the volume occupied by 5 g of acetylene gas at 50°C and 740 mm pressure. **(IIT 1991)** (5·2375 litres)

6. A bottle is heated with its mouth open from 15°C to 100°C. What fraction of air originally contained in the vessel is expelled? (23·5%)

7. An underwater bubble with a radius of 0·5 cm at the bottom of a tank, where the temperature is 5°C and the pressure is 3 atm., rises to the surface where the temperature is 25°C and pressure is 1 atm. What will be the radius of the bubble when it reaches the surface? (0·74 cm)

8. A good vacuum produced in common laboratory apparatus corresponds to 10^{-6} mm pressure at 25°C. Calculate number of molecules per cc at this pressure and temperature. (3.2×10^{10})

9. A sample of nitrogen gas is bubbled through liquid water at 25°C and then collected in a volume of 750 cc. The total pressure of the gas which is saturated with water vapour, is found to be 740 mm at 25°C. The vapour pressure of water at this temperature is 24 mm. How many moles of nitrogen are in the sample? (0·028)

10. A flask of volume 1 litre contains vapour of CH_3OH at a pressure of 1 atm and 25°C. The flask was then evacuated till the final pressure dropped to 10^{-4} mm. Find the number of molecules of methyl alcohol left in the flask. (3.2×10^{15})

11. Estimate the number of molecules left in a volume of the size of a pinhead about 1 cubic mm when the air is pumped out to give a vacuum of 10^{-6} mmHg at 25°C. (3.24×10^7)

12. A 500-cc bulb weighs 38·734 grams when evacuated and 39·3135 grams when filled with air at 1 atm pressure and 24°C. Assuming that air behaves as an ideal gas at this pressure, calculate effective mass of 1 mole of air. (28·2 g)

13. A desiccator of internal volume of 1 litre and containing nitrogen at 1 atm pressure is partially evacuated to a final pressure of 7·6 mm of Hg while the temperature remains constant. What is the volume of the gas at this stage? (1·00 litre)

14. A litre of air weighs 1·293 grams at NTP. At what temperature will a litre of air weigh 1 gram, the pressure being 72 cm? (61·3′c)

15. The vapour of a hydrocarbon is 2·47 times heavier than that of oxygen. What is its molecular weight? (79·04)

16. A gas cylinder contains 370 g of O_2 at 30 atm and 25°C. What mass of O_2 would escape if first the cylinder were heated to 75°C and then the valve were held open until the gas pressure was 1 atm, the temperature being maintained at 75°C? (359 g)

[**Hint:** First calculate the volume of the cylinder and then wt. of O_2 present at 1 atm and 75°C using $pV = nRT$]

17. A gaseous compound is composed of 85·7% by weight of C and 14·3% by weight of H. Its density is 2·28 g/L at 300 K and 1 atm pressure. Calculate the molecular formula of the compound. (C_4H_8)

18. A balloon filled with helium rises to a certain height at which it gets fully inflated to a volume of 1×10^5 litres. If at this altitude temperature and atmospheric pressure is 268 K and 2×10^{-3} atm respectively, what weight of helium will be required to fully inflate the balloon? (36·36 g)

19. Find the total pressure exerted by 1·6 g of methane and 2·2 g of CO_2 contained in a four-litre flask at 27°C. (0·9236 atm)

20. At 100°C and 1 atm pressure the density of water vapour is 0·0005970 g/cc.
(a) What is the molar volume and how does this compare with ideal gas value?
(b) What is the compressibility factor 'Z'?
[V (obs.) = 30·18 lit, and V (ideal) = 30·621 litres; Z = 0·986]

21. A box is divided by a thin partition into equal compartments and they are filled with an equal number of hydrogen and heavy hydrogen molecules respectively. If the pressure in the hydrogen compartment is 1 cm of Hg, what is the pressure in the other compartment? What will be the pressure if the partition is removed? (1 cm of Hg; 1 cm of Hg)

22. 1 g of N_2 and 1 g of O_2 are put in a two-litre flask at 27°C. Calculate partial pressure of each gas, the total pressure and the composition of the mixture in mole percentage. (0·44 atm.; 0·82 atm; 53·3%; 46·7%)

23. Into a gas bulb of 2·83 litres, are introduced 0·174 g of H_2 and 1·365 g of N_2 which can be assumed to behave ideally. The temperature is 0°C. What are the partial pressures of H_2 and N_2 and what is the total gas pressure? What are the mole fractions of each gas? What are pressure fractions? ($pH_2/p = nH_2/n$ = 0·639)

24. 100 cm^3 of NH_3 diffuses through a fine hole in 32·5 seconds. How much time will 60 cc of N_2 take to diffuse under the same conditions? (25 s)

25. A gas 'X' diffuses five times as rapidly as another gas 'Y'. Calculate the ratio of molecular weights of 'X' and 'Y'. (1/25)

26. The rate of diffusion of methane at a given temperature is twice that of a gas X. The molecular weight of X is
(A) 64 (B) 32 (C) 4 (D) 8 (IIT 1990) (A)

27. A mixture containing 1·12 litres of H_2 and 1·12 litres of D_2 at NTP is taken inside a bulb connected to another bulb by a stopcock with a small opening. The second bulb is fully evacuated, the stopcock opened for a certain time and then closed. The first bulb is now found to contains 0·05 g H_2. Determine the percentage composition by weight of the gases in the second bulb. (41·6; 58·33)

[Hint: H = 1, D = 2, Apply Eqn. 9]

28. A mixture consisting of 80 mole per cent hydrogen and 20 mole per cent deuterium at 25°C and a total pressure of 1 atm is permitted to effuse through a small orifice of area 0·20 mm^2. Calculate composition of the initial gas that passes through. (5·65 : 1)

[Hint: mole % = vol. %.]

29. A straight glass tube has two inlets 'X' and 'Y' at the two ends. The length of the tube is 200 cm. HCl gas through inlet X and NH_3 gas through inlet Y are allowed to enter the tube at the same time. White fumes first appear at a point P inside the tube. Find the distance of P from X. (81·1 cm)

30. A mixture of hydrogen and oxygen in 3 : 1 volume ratio is allowed to diffuse through a porous partition. What should be the composition of the initial gas diffusing out of the vessel? (12 : 1)

31. The time required by a certain volume of oxygen to diffuse through a small hole is 3600 seconds. Calculate the time required by the same volume of chlorine to diffuse through the same hole. (5360 s)

32. Calculate the relative rates of diffusion of 235 UF_6 and 238 UF_6 in the gaseous form. (1·0043 : 1)

33. The rate of diffusion of a sample of ozonised oxygen is 0·98 times more than that of pure oxygen. Find the percentage (by volume) of ozone in the ozonised sample. (8·25%)

34. The pressure in a vessel that contained pure oxygen dropped from 2000 mm to 1500 mm in 47 minutes as the oxygen leaked through a small hole into vacuum. When the same vessel was filled with another gas, the pressure dropped from 2000 mm to 1500 mm in 74 minutes. What is the molecular weight of the gas? (79)

35. A vessel of volume 100 mL contains 10% of oxygen and 90% of an unknown gas. The gases diffuse in 86 seconds through a small hole of the vessel. If pure oxygen, under the same conditions, diffuses in 75 seconds, find the molecular weight of the unknown gas. (43·2)

36. A balloon having a capacity of 10000 metre^3 is filled with helium at 20°C and 1 atm pressure. If the balloon is loaded with 80% of the load that it can lift at ground level, at what height will the balloon come to rest? Assume that the volume of the balloon is constant, the atmosphere is isothermal, 20°C, the molecular weight of air is 28·8 and the ground level pressure is 1 atm. The mass of the balloon is $1{\cdot}3 \times 10^6$ g.

[**Hint:** Use Eqn. 11.]

37. The density of hydrogen at 0°C and 760 mmHg pressure is 0·00009 g/cc. What is the rms speed of hydrogen molecules? ($183{\cdot}8 \times 10^3$ cm/s)

38. A one-litre gas bulb contains $1{\cdot}03 \times 10^{23}$ H_2 molecules. If the pressure exerted by these molecules is 760 mmHg, what must be average squared molecular speed? ($9{\cdot}43 \times 10^4$ cm/s)

39. At what temperature the rms speed of hydrogen is equal to escape velocity from the surface of the earth?

[**Hint:** Escape vel. $= \sqrt{2gR}$; R = earth's radius $= 6{\cdot}37 \times 10^6$ cm.] (100·2 K)

40. At what temperature, hydrogen at 1 atm pressure has the same rms speed as that of oxygen at NTP? (–256°C)

41. Compute rms speed of (i) O_2 at 15°C and 77 cm pressure, (ii) NH_3 molecules at NTP, and (iii) average speed of CH_4 at 500°C.
($47{\cdot}3 \times 10^3$ cm/s, $6{\cdot}8 \times 10^4$ cm/s, $10{\cdot}9 \times 10^4$ cm/s)

42. Show that the ideal gas law can be written as $p = \frac{2}{3}E$, where E is the kinetic energy per unit volume.

43. At what temperature would the most probable speed of CO molecules be twice that at 0°C? (819°C)

44. At what temperature would N_2 molecules have the same average speed as He atoms at 300 K? (2100 K)

45. Calculate the kinetic energy of Avogadro constant of gaseous molecules at 0°C. ($3{\cdot}4 \times 10^{10}$ erg)

46. Calculate the average kinetic energy per mole of CO_2 gas at 27°C in different units.
($3{\cdot}74 \times 10^{10}$ ergs, 3742 joules, 894 calories)

47. A gas of molecular weight 40 has a specific heat 0·075 cal/g/deg at a constant volume. What is the C_v value for it and what is the atomicity of the gas?
(3 cal/mole, monoatomic)

48. At 627°C and 1 atm, SO_3 partially dissociates into SO_2 and O_2. One litre of the equilibrium mixture weighs 0·94 g under the above conditions. Calculate the partial pressures of the constituent gases in the mixture.

[Hint: See Example 53] (0·5986, 0·2676, 0·1338 atm)

49. The degree of dissociation of N_2O_4 according to the equation $N_2O_4 = 2NO_2$ at 70°C and atmospheric pressure is 65·6%. Calculate the apparent molecular weight of N_2O_4 under the above conditions. (55·56)

[Hint: $\underset{1-x}{\overset{1}{N_2O_4}} \rightleftharpoons \underset{2x}{2NO_2}$; approx. mol. wt. $= \dfrac{92(1-x)+46(2x)}{1+x}$.]

50. 1 mole of a gas is changed from its initial state (15 lit ; 2 atm) to final state (4 lit, 10 atm) reversibly. If this change can be represented by a straight line in p–V curve, calculate maximum temperature, the gas attained. (698 K)

[Hint: Eqn. for the line is $\dfrac{p-2}{10-2} = \dfrac{V-15}{4-15}$; $11p + 8V = 142$

For $(pV)_{max}$, $11p = \dfrac{142}{2} = 71$ and $8V = \dfrac{142}{2} = 71$

or $p = \dfrac{71}{11}$ and $V = \dfrac{71}{8}$ then apply

$(pV)_{max} = nRT_{max}$.]

51. Calculate the volume occupied by 7 g of N_2 under a pressure of 100 atm at 27°C ($a = 1·39$ atm lit^2 mole^{-2}, $b = 0·391$ lit mole^{-1}) (58·8 mL)

52. The van der Waals constant b for a gas is $4·2 \times 10^{-2}$ lit mole^{-1}. How close the nuclei of the two molecules come together? ($3·2 \times 10^{-8}$ cm)

53. Find the temperature at which 3 moles of SO_2 will occupy a volume of 10 litres at a pressure of 15 atms.

($a = 6·71$ atm lit^2 mole^{-2}),

($b = 0·0564$ lit mole^{-1}) (351°C)

54. A 2·55 g sample of NH_4NO_2 is heated in a test tube.

$$NH_4NO_2(s) \rightarrow N_2(g) + 2H_2O(g)$$

What volume of N_2 will be collected in the flask when the water and gas temperature is 26°C and barometric pressure is 745 mmHg? (1·013 L)

55. How is the rms speed of N_2 molecules in a gas sample changed by

(a) an increase in temperature?

(b) an increase in volume of sample?

(c) mixing with an Ar sample at the same temperature?

[(a) increases (b) no effect (c) no effect]

56. Nickel carbonyl, $Ni(CO)_4$, is one of the most toxic substances known. The present maximum allowable concentration in laboratory air during an 8-hr work day is 1

part in 10^9. Assume 24°C and 1 atm pressure what mass of $Ni(CO)_4$ is allowable in a laboratory that is 110 m^2 in area, with a ceiling height of 2·7 m? $(3{\cdot}53 \times 10^{-4}$ g)

57. A sample of gas has a molar volume of 10·1 L at a pressure of 745 mmHg and a temperature of −138°C. Is the gas behaving ideally? (No)

58. Cyanogen is 46·2% C and 53·8% N by mass. At a temperature of 25°C and a pressure of 750 mmHg, 1·0 g of cyanogen gas occupies 0·476 L. Find the formula of cyanogen. (C_2N_2)

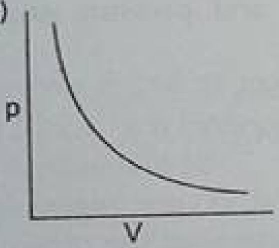
59. Two containers of the same volume, one containing the gas *A* and the other containing the gas *B*, have the same number of molecules of each gas. The mass of the molecule *A* is twice the mass of the molecule *B*. The rms speed of *A* is also twice that of *B*. Calculate the pressure ratio of the gases *A* and *B*. (8 : 1)

60. Calculate the percentage of free volume available in 1 mole gaseous water at 1 atm pressure and 373 K. (99·94%)

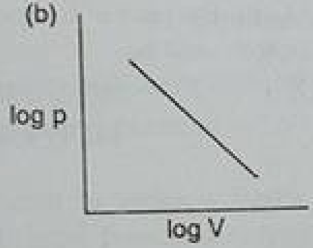
Objective Problems

1. Which of the following curves does not represent Boyle's law?

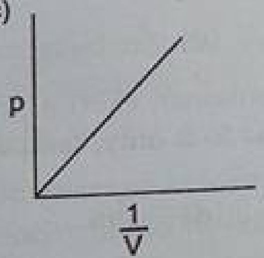
(a)



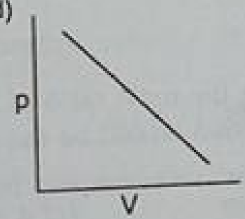
(b)



(c)



(d)



2. The temperature of 20 litres of nitrogen was increased from 100 K to 300 K at a constant pressure. Change in volume will be
(a) 80 litres (b) 60 litres (c) 40 litres (d) 20 litres

3. If the volume of a given mass of a gas at constant temperature becomes three times, the pressure will be
(a) $3p$ (b) $p/3$ (c) $9p$ (d) p

4. If the pressure of a given mass of a gas is reduced to half and temperature is doubled simultaneously, the volume will be
(a) same as before (b) twice as before
(c) four times as before (d) one-fourth as before

5. 10 g of a gas at NTP occupies a volume of 2 litres. At what temperature will the volume be double, pressure and amount of the gas remaining same?
(a) 273 K (b) 546 K (c) −273°C (d) 546°C

6. If 1 litre of N_2 at 27°C and 760 mm contains N molecules, 4 litres of O_2, under the same conditions of temperature and pressure, shall contain
(a) N molecules (b) $2N$ molecules (c) $\frac{N}{4}$ molecules (d) $4N$ molecules

7. Under identical conditions of temperature the density of a gas X is three times that of gas Y while molecular mass of gas Y is twice that of X. The ratio of pressures of X and Y will be
(a) 6 (b) 1/6 (c) 2/3 (d) 3/2

8. The molecules of a gas A travel four times faster than the molecules of gas B at the same temperature. The ratio of molecular weights (M_A/M_B) will be
(a) 1/16 (b) 4 (c) 1/4 (d) 16

9. The volume occupied by 22·4 g of a gas (vap. density = 11·2) at NTP is
(a) 22·4 litres (b) 11·2 litres (c) 44·8 litres (d) 1 litres

10. 32 g of oxygen and 3 g of hydrogen are mixed and kept in a vessel of 760 mm pressure and 0°C. The total volume occupied by the mixture will be nearly
(a) 22·4 litres (b) 33·6 litres (c) 56 litres (d) 44·8 litres

11. A pre-weighed vessel was filled with oxygen at NTP and weighed. It was then evacuated, filled with SO_2 at the same temperature and pressure and again weighed. The weight of oxygen will be
(a) the same as that of SO_2 (b) 1/2 that of SO_2
(c) twice that of SO_2 (d) 1/4 that of SO_2

12. A closed vessel contains equal number of nitrogen and oxygen molecules at a pressure of p mm. If nitrogen is removed from the system then the pressure will be
(a) p (b) $2p$ (c) $p/2$ (d) p^2

13. Two gases A and B, having the mole ratio of 3 : 5 in a container, exert a pressure of 8 atm. If A is removed, what would be the pressure due to B only, temperature remaining constant?
(a) 1 atm (b) 2 atm (c) 4 atm (d) 5 atm

14. Equal weight of methane and oxygen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by oxygen is
(a) 1/3 (b) 1/2 (c) 2/3 (d) $\frac{1}{3}\times\frac{273}{298}$

15. In two separate bulbs containing ideal gases A and B respectively, the density of gas A is twice that of gas B while molecular weight of gas A is half that of gas B at the same temperature, pressure ratio P_A/P_B will be
(a) 1/4 (b) 1/2 (c) 4 (d) 1

16. If 1 litre of a gas A at 600 mm and 0·5 litre of gas B at 800 mm are taken in a 2-litre bulb, the resulting pressure is
(a) 1500 mm (b) 1000 mm (c) 2000 mm (d) 500 mm

17. If the ratio of the rates of diffusion of the two gases A and B is 4 : 1, the ratio of their densities is
(a) 1 : 16 (b) 1 : 4 (c) 1 : 8 (d) 1 : 2

18. Since the atomic weights of C, N and O are 12, 14 and 16 respectively, among the following pair of gases, the pair that will diffuse at the same rate is
(a) carbon dioxide and nitrous oxide
(b) carbon dioxide and nitrogen peroxide
(c) carbon dioxide and carbon monoxide
(d) nitrous oxide and nitrogen peroxide

19. Two grams of hydrogen diffuse from a container in 10 minutes. How many grams of oxygen would diffuse through the same container in the same time under similar conditions?
(a) 0·5 g (b) 4 g (c) 6 g (d) 8 g

20. Four rubber tubes are respectively filled with H_2, O_2, N_2 and He. The tube which will be required to be reinflated first is
(a) H_2-filled tube (b) O_2-filled tube (c) N_2-filled tube (d) He-filled tube

21. Equal weights of methane and hydrogen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by hydrogen is
(a) 1/2 (b) 8/9 (c) 1/9 (d) 16/17

22. The specific gravity of CCl_4 vapour at 0°C and 76 cmHg in grams/litre is
(a) 11·2 (b) 77
(c) 6·88 (d) cannot be calculated

23. The rms speed of gas molecules at a temperature 27 K and pressure 1·5 bar is 1×10^4 cm/s. If both temperature and pressure are raised three times, the rms speed of the gas will be
(a) 9×10^4 cm/s (b) 3×10^4 cm/s
(c) $\sqrt{3} \times 10^4$ cm/s (d) 1×10^4 cm/s

24. The ratio of rms velocity to average velocity of gas molecules at a particular temperature is
(a) 1·086 : 1 (b) 1 : 1·086 (c) 2 : 1·086 (d) 1·086 : 2

25. The average velocity of an ideal gas molecule at 27°C is 0·3 m/s. The average velocity at 927°C will be
(a) 0·6 m/s (b) 0·3 m/s (c) 0·9 m/s (d) 3·0 m/s
(IIT 1986)

26. Kinetic energy per mole of an ideal gas
(a) is proportional to temperature (b) inversely proportional to temperature
(c) is independent of temperature (d) is zero at 0°C

27. The temperature of a sample of a gas is raised from 127°C to 527°C. The average kinetic energy of the gas
(a) does not change (b) is doubled
(c) is halved (d) cannot be calculated

28. The kinetic energy of N molecules of O_2 is x joule at −123°C. Another sample of O_2 at 27°C has a kinetic energy of $2x$ joules. The latter sample contains
(a) N molecules of O_2 (b) $2N$ molecules of O_2
(c) $N/2$ molecules of O_2 (d) none of these

29. A helium atom is two times heavier than a hydrogen molecule at 298 K, the average kinetic energy of helium is
(a) two times that of hydrogen molecules
(b) same as that of hydrogen molecules
(c) four times that of hydrogen molecules
(d) half that of hydrogen molecules

30. The kinetic energy of any gas molecule at 0°C is
(a) $5{\cdot}66 \times 10^{-21}$ J (b) 3408 J (c) 2 cal (d) 0

31. The ratio of the average molecular kinetic energy of UF_6 to that of H_2, both at 300 K, is
(a) 1 : 1 (b) 7 : 2 (c) 176 : 1 (d) 2 : 7

32. At what temperature will hydrogen molecules have the same kinetic energy as nitrogen molecules have at 35°C?
(a) $\left(\frac{28 \times 35}{2}\right)$°C (b) $\left(\frac{2 \times 35}{28}\right)$°C (c) $\left(\frac{2 \times 28}{35}\right)$°C (d) 35°C

33. A monoatomic gas, a diatomic gas and a triatomic gas are mixed, taking one mole of each. C_p/C_v for the mixture is
(a) 1·40 (b) 1·428 (c) 1·67 (d) 1·33

34. When 1 mole of a monoatomic ideal gas is heated to raise its temperature through 1°C, the fraction of the heat energy supplied which increases the kinetic energy of the gas is
(a) 2/5 (b) 3/5 (c) 3/7 (d) 5/7

35. The values of van der Waals constant '*a*' for the gases O_2, N_2, NH_3 and CH_4 are 1·36, 1·39, 4·17 and 2·253 L^2 atm $mole^{-2}$ respectively. The gas which can most easily be liquefied is
(a) O_2 (b) N_2 (c) NH_3 (d) CH_4 **(IIT 1989)**

36. One mole of an ideal monoatomic gas is mixed with 1 mole of an ideal diatomic gas. The molar specific heat of the mixture at constant volume is
(a) 3 cal (b) 4 cal (c) 8 cal (d) 5 cal

37. According to kinetic theory of gases, for a diatomic molecule,
(a) the pressure exerted by the gas is proportional to the mean velocity of the molecule
(b) the pressure exerted by the gas is proportional to the root mean square velocity of the molecule
(c) the root mean square velocity of the molecule is inversely proportional to the temperature
(d) the mean translational kinetic energy of the molecule is proportional to the absolute temperature **(IIT 1991)**

38. The ratio between the rms velocity of H_2 at 50 K and that of O_2 at 800 K is
(a) 4 (b) 2 (c) 1 (d) 1/4 **(IIT 1996)**

39. The compressibility factor for an ideal gas is
(a) 1·5 (b) 1·0 (c) 2·0 (d) ∞ **(IIT 1997)**

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

(a) 10 seconds : He
(b) 20 seconds : O_2
(c) 25 seconds : CO
(d) 55 seconds : CO_2 **(IIT 1996)**

41. One mole of N_2O_4 (g) at 300 K is kept in a closed container under one atmosphere. 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 atm (d) 1 atm **(IIT 1996)**

42. A column of air 1 m^2 in cross section extending through the atmosphere has a mass of roughly 10,000 kg. The atmospheric pressure at the surface of the earth is

(a) 1×10^5 N (b) 1×10^2 k Pa (c) 1×10^5 k Pa (d) 1 atmosphere

43. If the product of the gas constant *R* i.e., ·0821 lit atm/K/mole and NTP temperature in kelvin equals 22·4, the compressibility factor of the gas at 1 atmospheric pressure is

(a) > 1 (b) < 1 (c) = 1 (d) = 0

44. The graph of the quantity d/p against pressure is extrapolated to zero pressure to obtain a limiting value. If this limiting d/p value for a certain nonideal gas is found to be 2·86 g/L-atm at 0°C, the molar mass of the gas will be

(a) 2·86 (b) 64·06 (c) 22·4 (d) none of these

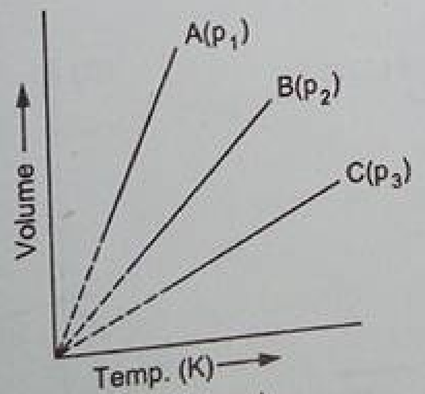
45. The rms speed of N_2 molecules in a gas sample can be changed by

(a) an increase in volume of sample
(b) mixing with Ar sample
(c) an increase in pressure on the gas
(d) an increase in temperature

46. How high must a column of water be to exert a pressure equal to that of a column of Hg that is 760 mm high

(a) 760 mm (b) 55·9 mm (c) 74480 mm (d) 10336 mm

47. In the following graph in which volume is plotted versus temperature, the lines *A*, *B* and *C* represent the same mass of the same ideal gas at different pressures p_1, p_2 and p_3 respectively.



The correct relationship of pressures is

(a) $p_1 > p_2 > p_3$ (b) $p_1 = p_2 = p_3$ (c) $p_3 > p_2 > p_1$ (d) $p_1 > p_2 < p_3$

48. A 5·0-L reaction vessel contain hydrogen at a partial pressure of 0·588 atm and oxygen gas at a partial pressure of 0·302 atm. The limiting reactant in the following reaction:

$$2H_2 + O_2 = 2H_2O$$

is

(a) H_2 (b) O_2 (c) None (d) both

49. When a gas is passed through a small hole at a temperature greater than its critical temperature, Joule–Thomson effect will show

(a) cooling of the gas (b) warming of the gas
(c) no change in temperature (d) first cooling and then warming

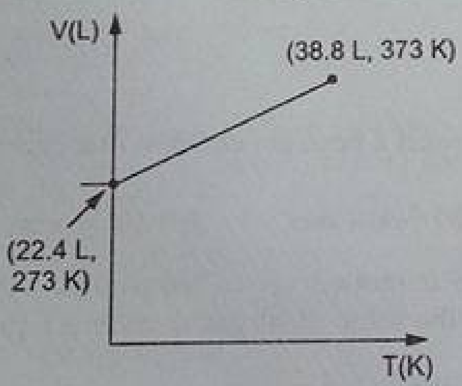
50. Which of the following statements is wrong?

(a) Critical temperature is the highest temperature at which condensation of a gas is possible.
(b) Critical pressure is the highest pressure at which a liquid will boil when heated.
(c) Boyle temperature is the temperature at which the second virial coefficient is zero.
(d) Inversion temperature is the temperature above which the gas becomes cooler during Joule–Thomson expansion.

51. Which of the following choice (s) is (are) correct for a gas?

(a) $P_{ideal} > P_{real}$ (b) $V_{ideal} > V_{real}$
(c) $P_{ideal} < P_{real}$ (d) $V_{ideal} < V_{real}$

52. Which of the following volume (V) – temperature (T) plots represents the behaviour of one mole of an ideal gas at one atmospheric pressure?

(a)


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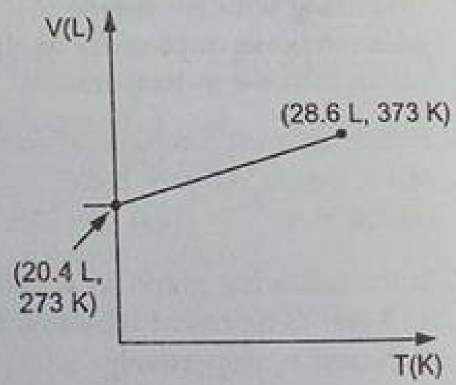

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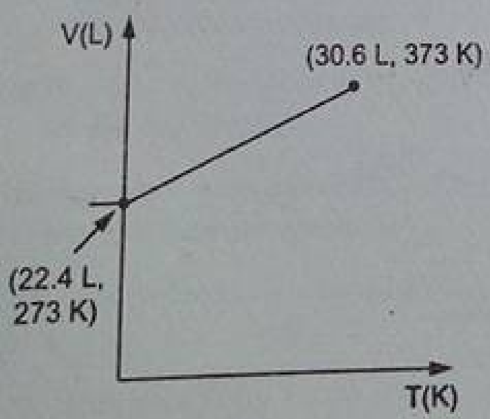

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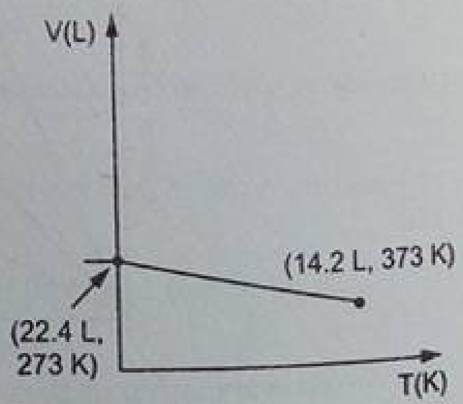


Answers

1-d, 2-c, 3-b, 4-c, 5-b, 6-d, 7-a, 8-a, 9-a, 10-c, 11-b, 12- c, 13-d, 14-a, 15-c, 16-d, 17-a, 18-a, 19-d, 20-a, 21-b, 22-c, 23-c, 24-a, 25-a, 26-a, 27-b, 28-a, 29-b, 30-a, 31-a, 32-d, 33-b, 34-b, 35-c, 36-b, 37-d, 38-c, 39-b, 40-b, 41-b, 42-b, 43-c, 44-b, 45-d, 46-d, 47-c, 48-a, 49-b, 50-d, 51-a & d, 52-c.

❑❑❑

DILUTE SOLUTION AND COLLIGATIVE PROPERTIES

A solution is a homogeneous mixture of chemical species. The solutions are of several types but we shall discuss here mainly the solutions containing a solid solute and a liquid solvent. The distinction between a solute and a solvent is an arbitrary one. However, the constituent present in the greater amount is generally known as the solvent, while those present in relatively smaller amounts are called the solutes.

Concentration Units

The concentrations of solutions may be expressed in the following common sets of units.

1. **Molarity:** The molarity of a solution is the number of moles of solute present in one litre of the solution. It is expressed by 'M'.

2. **Demal unit:** The concentrations are also expressed in Demal units. One demal unit represents one mole of solute present in one litre of the solution at 0°C. It is expressed by 'D'.

3. **Molality:** The molality is defined as the number of moles of the solute present in 1000 g of the solvent. It is symbolised by '*m*'.

4. **Normality:** The normality is the number of equivalents of solute present in one litre of the solution. It is expressed by 'N'.

5. **Formality:** The formality is the number of gram-formula weights of the solute per litre of the solution. It is expressed by 'F'.

6. **Mole fraction:** The ratio of the number of moles of the solute to the total number of moles of the solution is known as mole fraction of the solute. Similarly, the ratio of the number of moles of the solvent to the total number of moles of the solution is called mole fraction of the solvent.

If x_1 and x_2 represent the mole fraction of the solute and the solvent respectively, we have,

$$x_1 = \frac{n_1}{n_1 + n_2} \quad \text{and} \quad x_2 = \frac{n_2}{n_1 + n_2}$$

where n_1 and n_2 are the number of moles of the solute and the solvent respectively present in a solution.

7. **Percentage:** The concentration in percentage is generally expressed in three ways:

(i) weight of solute in grams per 100 mL of solution the multiplication of n with the rate constant k' gives another constant k, which may also be called rate constant, though not according to its definition.]

Let us now calculate x to get the value of k from Equation (1).

When 0·525 mole of a solute is added, polymerisation stops and x moles of A remain. Just before the addition of the solute,

moles of solvent $A = x$

moles of solvent $B = 12$

$\therefore$ vapour pressure of the mixture of solvents $= x_A p_A^0 + x_B p_B^0$

$$p^0 = \frac{x}{x+12} \times 300 + \frac{12}{x+12} \times 500 \qquad \cdots (2)$$

Vapour pressure of the solution, $p = 400$ ... (3)

(after the addition of 0·525 mole of a solute).

Applying Raoult's law,

$$\frac{p^0 - p}{p^0} = \text{mole fraction of the solute}$$

$$= \frac{0{\cdot}525}{0{\cdot}525 + (x+12)}. \qquad \cdots (4)$$

Solving equations (2), (3) and (4), we get

$$x = 2{\cdot}84.$$

Substituting $x = 2{\cdot}84$, $t = 100$ m and $a = 10$ in Equation (1)

$$k = \frac{2{\cdot}303}{100} \log \frac{10}{2{\cdot}84} = 1{\cdot}2 \times 10^{-2}\ \text{min}^{-1}.$$

PROBLEMS

(Answers bracketed with questions)

1. Calculate mole fractions of urea and water if 2·0 g of urea is dissolved in 31·4 g of aqueous solution. (0·02, 0·98)

2. Under what condition will the molality of a solute not be equal to its molarity?
[Hint: Consider density of the solvent.]

3. A sugar syrup of weight 214·2 g contains 34·2 g of sugar ($C_{12}H_{22}O_{11}$). Calculate (i) molal concentration, and (ii) mole fraction of sugar in the syrup. **(IIT 1988)** (0·556 m, 0·0099)

4. Calculate mole fraction of solute in an aqueous 4 m solution assuming the density of the solution as 1·0 g/mL. (0·0674)
[Hint: See Example 6]

5. Nitric acid (70%) has a specific gravity of 1·42. Find the normality and molarity of the acid. (15·8 N, 15·8 M)

6. 1 g of NaCl is dissolved in 10 g of a solution, the density of which is 1·07 g/cc. Find the molality and molarity of NaCl. (1.899 *m*, 1.829 M)
[Hint: See Example 6]

7. Calculate mole fraction, molarity and molality of C_2H_5OH solution which is 50% by weight of C_2H_5OH in H_2O and has a density of ·9144 g per cc.
(0·281, 9·93 M, 21·7 *m*)

8. The molarity and molality of a solution are M and m respectively. If the molecular weight of the solute is M', calculate the density of the solution in terms of M, m and M'.
$$\left[D = M\left(\frac{1}{m} + \frac{M'}{1000}\right)\right]$$

9. When 400 g of a 20% solution was cooled, 50 g of the solute precipitated. What is the per cent concentration of the remaining solution? (8·6%)

10. In what mass of water must 25 g of $CuSO_4 \cdot 5H_2O$ be dissolved to obtain an 8% solution of $CuSO_4$? (174·775 g)

11. One litre of water was added to 500 mL of 32% HNO_3 of density 1·20 g/mL. What is the per cent concentration of HNO_3 in the solution obtained? (12·8%)

12. Determine the per cent concentration of a solution obtained by mixing 300 g of a 25% and 400 g of a 40% solution. (33·6%)

13. Calculate the per cent concentration of a 9·28 N NaOH solution of density 1·31 g/mL. (28·3%)

14. The pressure of the water vapour of a solution containing a nonvolatile solute is 2% below that of the vapour of pure water. Determine the molality of the solution.
(1·134 *m*)

15. What is the vapour pressure at 100°C of a solution containing 15·6 g of water and 1·68 g of sucrose ($C_{12}H_{22}O_{11}$)? (75·57 cm)

16. The vapour pressure of an aqueous solution of cane sugar (mol. wt. 342) is 756 mm at 100°C. How many grams of sugar are present per 1000 g of water? (99·94 g)

17. At 20°C the vapour pressure of ether is 442 mm of Hg. When 6·1 g of a substance is dissolved in 50 g of ether (mol. wt. 74), the vapour pressure falls to 410 mm. What is the molecular weight of the substance? (115·4)

18. 0·5 g of a nonvolatile organic compound (mol. wt. 65) is dissolved in 100 mL of CCl_4. If the vapour pressure of pure CCl_4 is 143 mm, what would be the vapour pressure of the solution? (Density of CCl_4 solution is 1·58 g/cc). (141·93 mm)

19. Which of the following aqueous solutions has a higher vapour pressure if the density of water is 1 g/cc?
(a) Solution having mole fraction of cane sugar = 0·1
(b) Solution having molal concentration = 1 *m* (b)

20. An aqueous solution containing 20% by weight of liquid X (mol. wt. = 140) has a vapour pressure 160 mm at 60°C. Calculate the vapour pressure of pure liquid 'X' if the vapour pressure of water is 150 mm at 60°C. (470·5 mm)

21. At 25°C, benzene and toluene have densities 0·879 and 0·867 g/cc respectively. Assuming that benzene–toluene solutions are ideal, establish the equation for the density of the solution.

$$d = \frac{1}{100}[0{\cdot}879\ V + 0{\cdot}867\ (100 - V)]$$

where V is the volume per cent of benzene.

22. Ethanol and methanol form a solution that is very nearly ideal. The vapour pressure of ethanol is 44·5 mm and that of methanol is 88·7 mm at 20°C.

(a) Calculate the mole fraction of methanol and ethanol in a solution obtained by mixing 60 g of ethanol with 40 g of methanol.

(b) Calculate the partial pressure and the total vapour pressure of this solution and the mole fraction of ethanol in the vapour. [(a) 0·49, 0·51 (b) 22·7, 43·5, 0·34]

23. The vapour pressure of pure benzene is 22 mm and that of pure toluene is 75 mm at 20°C. What is the composition of the solution of these two components that has a vapour pressure of 50 mm at this temperature? What is the composition of vapour in equilibrium with this solution?

[Hint: Use equations 3 and 5] (0·47 : 0·53 : 0·20 : 0·80)

24 A solution containing ethyl alcohol and propyl alcohol has a vapour pressure of 290 mm at 30°C. Find the vapour pressure of pure ethyl alcohol if its mole fraction in the solution is 0·65. The vapour pressure of propyl alcohol is 210 mm at the same temperature. (333·12 mm)

25. What are partial and total vapour pressures at 25°C above the solution having equal numbers of molecules of benzene and toluene? The vapour pressures of benzene and toluene at this temperature are 95·1 and 28·4 mmHg respectively. What is the composition of the vapour in equilibrium with benzene–toluene solution? [47·6, 14·2, 61·8 mm Hg; 0·77 and 0·23]

[Hint: Mole fraction of each is 0·5.]

26. Benzene and toluene form nearly ideal solutions. If at 27°C the vapour pressures of pure toluene and pure benzene are 32·06 mm and 103·01 mm respectively,

(a) calculate the vapour pressure of a solution containing 0·60 mole fraction of toluene

(b) calculate the mole of fraction of toluene in vapour for this composition of the liquid [(a) 60·44 mm (b) 0·318]

27. At 50°C the vapour pressures of pure water and ethyl alcohol are, respectively 92·5 mm and 219·9 mm of Hg. If 6 g of nonvolatile solute of mol. wt. 120 is dissolved in 150 g of each of these solvents, what will be the relative vapour pressure lowerings in the two solvents? (0·006, 0·015)

28. Calculate the molecular weight of a substance, 10 g of which in 1 litre of solution exerts an osmotic pressure of 81 mmHg at 27 K. (207·99)

29. The water vapour pressure at 293 K is 2338 Pa and the vapour pressure of an aqueous solution is 2295·8 Pa. Determine its osmotic pressure at 313 K if the

solution density at this temperature is 1010 kg/m^3. The molecular weight of the solute is 60.

(2.56×10^6 Pa)

30. What is the osmotic pressure of a solution of 4·48 g of a substance of molecular weight 286 in 100 cm^3 water at 298 K?
(R = 82·1 cm^3 atm/deg/mole) (3·83 atm)

31. 10·1 g of a volatile liquid occupies a volume of 4 litres when vaporised at 100°C and 70 cm pressure. What would be the osmotic pressure of a 2% (grams per 100 cc) solution of this substance at 0°C? (5·34 atm)

32. The average osmotic pressure of human blood is 7·7 atm at 40°C.
(a) What should be the total concentration of various solutes in the blood?
(b) Assuming this concentration to be essentially the same as the molality, find the freezing point of blood. [K_f (H_2O) = 1·86] (0·29 mole/litre, −0·539°C)

33. A solution containing 10·2 g of glycerene per litre is found to be isotonic with a 2% solution of glucose. Calculate the molecular weight of glycerene (mol. wt. of glucose = 180). (91·8)

34. The osmotic pressure of an aqueous solution containing 45 g of sucrose (343) per litre of solution is 2·97 atm at 0°C. Find the value of the gas constant and compare the result with the accepted value. (0·0826 lit · atm/K/mole)

35. What is the freezing point of a solution containing 6·84 g of sucrose per 500 g of water? K_f for water is 1·86°C · m^{-1}. (−0·074°C)

36. What weight of glycerol would have to be added to 1000 g of water in order to lower its freezing point by 10°C? K_f = 1·86. (495 g)

37. An aqueous solution contains 10% by weight of urea (60·00) and 5% by weight of glucose (180·00). What will be its freezing point? K_f for water is 1·86. (−4·254°C)

38. If glycerene, $C_3H_5(OH)_3$, and methyl alcohol, CH_3OH, are sold at the same price per kg, which would be cheaper for preparing an antifreeze solution for the radiator of an automobile? (CH_3OH)

39. How much ice will separate if a solution containing 25 g of ethylene glycol [$C_2H_4(OH)_2$] in 100 g of water is cooled to −10°C ? $K_f(H_2O)$ = 1·86. (25·05 g)

40. What approximate proportions by volume of water (d = 1 g/cc) and ethylene glycol $C_2H_6O_2$ (d = 1·12 g/cc) must be mixed to ensure protection of an automobile cooling system to −10°C? (10 : 3)

41. At 25°C a solution containing 0·2 g of polyisobutylene in 100 cc of benzene, developed a rise of 2·4 mm at osmotic equilibrium. Calculate the molecular weight of polyisobutylene if the density of the solution is 0·88 g/cc

[Hint OP = $\frac{0.24 \times 0.88}{\ldots}$ cm (Hg)] (2.4×10^5)

42. 0·1 g of an unknown substance was dissolved in 5 g of camphor and it was found that the melting point of camphor was depressed by 5·3°C. If K_f is 39·7, find the weight of 1 mole of the solute. (150)

43. 1·23 g of a substance dissolved in 10 g of water raised the boiling point of water to 100·39°C. Calculate the molecular weight of the substance. ($K_b = 0{\cdot}52°C\ m^{-1}$) (164)

44. Two elements '*A*' and '*B*' form compounds having formulae AB_2 and AB_4. When dissolved in 20 g of benzene, 1 g of AB_2 lowers the freezing point by 2·3°C whereas 1 g of AB_4 lowers the freezing point by 1·3°C. Calculate the atomic weights of *A* and *B*. (K_f for benzene $= 5{\cdot}1°C\ m^{-1}$) (25·57, 42·65)

45. When 45 g of glucose was dissolved in 500 g of water, the solution has a freezing point of –0·93°C.

(a) What is the molecular weight of glucose?

(b) If the simplest formula is CH_2O, what is its molecular formula? (180; $C_6H_{12}O_6$)

46. Calculate K_b of water when 1 mole of the solute is dissolved in 1000 g of water. The latent heat of vaporisation of water is 539·9 calories per gram. (0·514)

47. Molal elevation constant of chloroform is 3·88. 0·3 g of camphor added to 25·2 g of chloroform raised the boiling point of the solvent by 0·299°C. Calculate the molecular weight of camphor. (154)

48. Calculate the molal depression constant of water. Latent heat of fusion of ice at 0° is 80 calories per gram. (1·84°)

49. K_b for CCl_4 is 5·02. The boiling point of pure CCl_4 is 76·8°C. Calculate the boiling point of a 1 molal solution of naphthalene ($C_{10}H_8$) in CCl_4. (81·8°C)

50. Calculate the K_b for chloroform from the following data:

(a) Boiling point of pure $CHCl_3 = 61{\cdot}3°C$.

(b) The solution containing 5·02 g of naphthalene ($C_{10}H_8$) in 18 g of $CHCl_3$ boils at 69·5°C.

($3{\cdot}8°C\ m^{-1}$)

51. A solution containing 1·23 g of $Ca(NO_3)_2$ in 10 g of water boils at 100·975°C. Calculate the degree of ionisation of the nitrate ($K_b = 0{\cdot}52$). (75%)

52. A 0·5% aqueous solution of KCl was found to freeze at 272·76 K. Calculate the van't Hoff factor and the degree of dissociation of KCl at this concentration. $K_f(H_2O) = 1{\cdot}86°C\ m^{-1}$. (1·92, 0·92)

53. When 60·26 g of VCl_4 was added to 1000 g of solvent CCl_4, the freezing point of CCl_4 was depressed by 5·415°C. K_f for CCl_4 is 29·9. Compare the number of moles of particles with the number predicted by the formula. Calculate the number of dimers, V_2Cl_8 present.

[Hint: $2VCl_4 \rightarrow V_2Cl_8$]

$$\begin{pmatrix} V_2Cl_8 = 0{\cdot}134 \text{ mole} \\ VCl_4 = 0{\cdot}0473 \text{ mole} \end{pmatrix}$$

54. At 25°C, a 0·1 m solution of CH_3COOH is 1·35% dissociated. Calculate the freezing point and osmotic pressure of the solution. Compare your results with those expected under conditions of no dissociation. K_f for water $= 1{\cdot}86°C\ m^{-1}$.
[Hint : See Example 48] (–0·19°C, 2·47 atm)

55. The vapour pressure of a 0·01 m solution of a weak base BOH in water at 20°C is 17·536 mm. Calculate K_b for the base. Aq. tension at 20°C = 17·54 mm. $(9{\cdot}7 \times 10^{-4})$

$$[\text{Hint : } i = \frac{\text{obs. lowering in v.p.}}{\text{cal . lowering in v.p.}} = \frac{p - p_{\text{obs.}}}{p^0 \cdot \frac{n}{N}} = \frac{17{\cdot}540 - 17{\cdot}536}{17{\cdot}54 \times \frac{0{\cdot}01}{1000/18}}.$$

Then apply $i = 1 + x$ and $K_b = \dfrac{0{\cdot}01x^2}{1 - x}$]

56. In an Ostwald–Walker experiment, dry air was first blown through a solution containing a certain amount of solute ($M = 278$) in 150 g of water, and then also through pure water. The loss in mass of water was found to be 0·0827 g while the mass of water absorbed in sulphuric acid was 3·317 g. Calculate the amount of the solute. (0·57 g)

57. Pheromones are compounds secreted by the females of many insect species to attract males. One of these compounds contains 80·78% C, 13·56% H, and 5·66% O. A solution of 1·0 g of this substance in 8·50 cc of benzene freezes at 3·37°C. What are the molecular weight and molecular formula of the compound?
(f.p. of $C_6H_6 = 5{\cdot}5°C$, $K_f(C_6H_6) = 5{\cdot}12°C/m$) (282, $C_{19}H_{38}O$)

58. The vapour pressure of pure water at 25°C is 23·62 mm Hg. What will be the vapour pressure of a solution of 1·5 g of urea in 50 g of water? (23·41 mmHg)

Objective Problems

1. A molal solution is one that contains one mole of a solute in
   (a) 1000 g of the solvent (b) one litre of solvent
   (c) one litre of solution (d) 22·4 litres of solution **(IIT 1986)**

2. Vapour pressure of a solvent is 17·5 mm (Hg) while that of its dilute solution is 17·45. The mole fraction of the solvent is
   (a) 0·997 (b) 0·075 (c) 17·48 (d) 1·05

3. Which of the following is not a colligative property?
   (a) Vapour pressure (b) Depression in f.p.
   (c) Elevation in b.p. (d) Osmotic pressure

4. When an ideal binary solution is in equilibrium with its vapour, molar ratio of the two components in the solution and in the vapour phases is
   (a) same (b) different
   (c) may or may not be same depending upon volatile nature of the two components

5. The osmotic pressure of a solution is given by the relation
(a) $p = \frac{RT}{c}$ (b) $p = \frac{cT}{R}$ (c) $p = \frac{Rc}{T}$ (d) $\frac{p}{c} = RT$
(c is the concentration in moles/litre)

6. The osmotic pressure of a solution at 0°C is 4 atm. What will be its osmotic pressure at 546 K under similar conditions?
(a) 4 atm (b) 2 atm (c) 8 atm (d) 1 atm

7. Which of the following aqueous solutions has osmotic pressure nearest to that of an equimolar solution of $K_4[Fe(CN)_6]$?
(a) Na_2SO_4 (b) $BaCl_2$ (c) $Al_2(SO_4)_3$ (d) $C_{12}H_{22}O_{11}$

8. 0·1 M solution of urea, at a given temperature, is isotonic with
(a) 0·1 M NaCl solution (b) 0·1 M glucose solution
(c) 0·02 M KCl solution (d) 0·1 M $BaCl_2$ solution

9. Which one of the following pairs of solution can we expect to be isotonic at the same temperature?
(a) 0·1 M urea and 0·1 M NaCl (b) 0·1 M urea and 0·2 M $MgCl_2$
(c) 0·1 M NaCl and 0·1 M Na_2SO_4 (d) 0·1 M $Ca(NO_3)_2$ and 0·1 M Na_2SO_4

10. Which statement is incorrect about osmotic pressure (p), volume (V) and temperature (T)?
(a) $p \propto 1/V$ if T is constant (b) $p \propto T$ if V is constant
(c) $p \propto V$ if T is constant (d) pV is constant if T is constant

11. Equal volume of 0·1 M urea and 0·1 M glucose are mixed. The mixture will have
(a) lower osmotic pressure (b) same osmotic pressure
(c) higher osmotic pressure (d) none of these

12. The factor $\Delta T_f / K_f$ represents
(a) molarity (b) formality (c) normality (d) molality

13. The f.p. of 1% solution of $Ca(NO_3)_2$ in water will be
(a) below 0°C (b) 0° (c) 1°C (d) 2°C

14. Which has the highest f.p. at 1 atm?
(a) 0·1 M NaCl solution (b) 0·1 M $BaCl_2$ solution
(c) 0·1 M sugar solution (d) 0·1 M $FeCl_3$ solution

15. Which of the following 0·1 M aqueous solution will have the lowest f.p.?
(a) K_2SO_4 (b) NaCl
(c) Urea (d) Glucose
(IIT 1989)

16. An aqueous solution contains 5% and 10% of urea and glucose respectively (by wt.). If K_f for water is 1·86, the f.p. of the solution is
(a) 3·03 K (b) 3·03°C (c) −3·03°C (d) −3·03 K

17. When 1 mole of a solute is dissolved in 1 kg of H_2O, boiling point of solution was found to be 100·5°C. K_b for H_2O is
(a) 0·5 (b) 100 (c) 100·5 (d) 95·5

18. An aqueous solution of NaCl shall boil at
(a) 100°C (b) below 100°C (c) above 100°C (d) 99·9°C

19. Which solution will have the highest b.p.?
(a) 1% solution of $C_6H_{12}O_6$
(b) 1% solution of NaCl
(c) 1% solution of $ZnSO_4$
(d) 1% solution of $(NH_2)_2CO$

20. Which solution will have the highest b.p.?
(a) 1 M $C_6H_{12}O_6$ solution
(b) 1 M NaCl solution
(c) 1 M $BaCl_2$ solution
(d) 1 M $(NH_2)_2CO$ solution

21. The temperature at which the vapour pressure of a liquid equals external pressure is called
(a) f.p. (b) b.p. (c) m.p. (d) critical temp.

22. The ratio of the value of any colligative property for KCl solution to that for sugar solution is nearly
(a) 1·0 (b) 0·5 (c) 2·0 (d) 2·5

23. For an aqueous solution of NaCl, the observed molecular weight of NaCl will be
(a) less than 58·5 (b) more than 58·5 (c) 58·5 (d) $58{\cdot}5^2$

24. The weight of water in 1 litre of 2 M NaCl solution of density 1·117 g/mL is
(a) 1117 g (b) 1000 g (c) 117 g (d) 883 g

25. Glucose is added to 1 litre of water to such an extent that $\Delta T_f / K_f$ becomes equal to 1/1000. The wt. of glucose added is
(a) 180 g (b) 18 g (c) 1·8 g (d) 0·18 g

26. Which of the following colligative properties is associated with the concentration term 'molarity'?
(a) Lowering of vap. pressure
(b) Osmotic pressure
(c) Depression in f.p.
(d) Elevation in b.p.

27. Which of the following experimental methods is adopted to determine osmotic pressure?
(a) Berkley–Hartley's method
(b) Beckmann's method
(c) Landsberger's method
(d) Differential method

28. Which of the following solutes will produce the largest total molality of solute particles upon addition to 1 kg of water?
(a) 1·0 mole $Co(NO_3)_2$
(b) 2·0 mole KCl
(c) 3·0 mole C_2H_5OH
(d) 3·0 mole of sugar

Answers

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

CHEMICAL THERMODYNAMICS

The various laws of thermodynamics are based on human experience about the behaviour of macroscopic systems (assemblage of a large number of molecules). Thermodynamics is concerned with the **equilibrium states** of the systems. An equilibrium state is one in which the macroscopic properties of the system, such as its temperature, density and chemical composition, are well defined and do not change with time. Thus, the subject of thermodynamics does not concern itself with the time element in any transformation and, therefore, has no valid application in the study of reaction kinetics.

The First Law of Thermodynamics

The first law of thermodynamics is a statement of the principle of conservation of energy. This law may be stated in various ways as given below:

(1) Energy can neither be created nor be destroyed. It can only be converted from one form of energy to another.

(2) Since energy and mass are interlinked by Einstein's equation $E = mc^2$, the total mass and energy of an isolated system remain unchanged.

(3) The conclusion of all the statements of the first law of thermodynamics is that it is impossible to construct a perpetual motion machine, i.e., a machine that can work without consuming energy.

Mathematical Formulation of the First Law

The amount of heat 'q' given to a closed system is used to increase the internal energy 'E' of the system and also to produce work 'W' in such a way that:

Heat absorbed = increase in internal energy + work done by the system.

$$q = \Delta E - W$$

or $$\Delta E = q + W \qquad \text{... (1)}$$

W is taken negative as the work is done by the system. The first law of thermodynamics states that the change in internal energy of a system, ΔE, equals q plus W.

The heat absorbed by a closed system in a process in which no work is done is equal to the internal energy of the system.

$$\Delta E = q$$

Ex. 65. *Compute the heat of formation of liquid methyl alcohol in kilojoules per mole using the following data. The heat of vaporisation of liquid methyl alcohol = 38 kJ/mole. The heats of formation of gaseous atoms from the elements in their standard states:* H, 218 kJ/mole; C, 715 kJ/mole; O, 249 kJ/mole.

Average bond energies: C—H = 415 kJ/mole

C—O = 356 kJ/mole

O—H = 463 kJ/mole (IIT 1997)

Solution : $C + 2H_2 + \frac{1}{2}O_2 \rightarrow CH_3OH$; $\Delta H = ?$

For reactants:

Heat of atomisation of 1 mole of C = 715 kJ

Heat of atomisation of 4 moles of H = 4 × 218 kJ

Heat of atomisation of 1 mole of O = 249 kJ

For products:

Heat of formation of 3 moles of C—H bonds = −3 × 415 kJ

Heat of formation of 1 mole of C—O bonds = −356 kJ

Heat of formation of 1 mole of O—H bonds = −463 kJ

Heat of condensation of 1 mole of CH_3OH to liquid = −38 kJ

On adding, we get ΔH of formation of CH_3OH (l).

$\Delta H = -266 \text{ kJ mole}^{-1}$.

PROBLEMS

(*Answers bracketed with questions*)

1. Find the work done when 1 mole of hydrogen expands isothermally from 15 to 50 litres against a constant pressure of 1 atm at 25°C. (−718 cal)
2. 100 g of argon is allowed to expand from a pressure of 10 atm to 0·1 atm at 100°C. Calculate the heat which is absorbed, assuming ideal behaviour. (8580 cal)
3. The molar volumes of ice and water are respectively 0·0196 and 0·0180 litres per mole at 273 K. If ΔH for the transition of ice to water is 1440 calories per mole at 1 atm pressure, find ΔE. (1440 cal)
4. For the reaction, $C_{graphite} + \frac{1}{2}O_2(g) = CO(g)$ at 298 K and 1 atm, $\Delta H = -26416$ cal. If the molar volume of graphite is 0·0053 litre, calculate ΔE. (− 26712 cal)
5. One mole of an ideal gas at 300 K expands isothermally and reversibly from 5 to 20 litres. Calculate the work done and heat absorbed by the gas. (−832 kJ, 832 kJ)
6. Calculate the heat of formation of ethylene from the following data at 20°C:

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$; $\Delta H = -65$ kcal

$C(s) + O_2(g) \rightarrow CO_2(g)$; $\Delta H = -97$ kcal

$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$; $\Delta H = -340$ kcal (16 kcal)

7. Calculate the heat of formation of carbon monoxide from the following data:

$$C\,(s) + O_2\,(g) \rightarrow CO_2\,(g);\ \Delta H = -94\ \text{kcal}$$

$$2CO\,(g) + O_2\,(g) \rightarrow 2CO_2\,(g);\ \Delta H = -136\ \text{kcal}$$

(– 26 kcal)

8. The heat of combustion of ethyl alcohol is 330 kcal. If the heats of formation of CO_2 (g) and H_2O (l) are 94·3 and 68·5 kcal respectively, calculate the heat of formation of ethyl alcohol.

(–64·1 kcal)

9. The heats of formation of CO_2 (g) and H_2O (l) are – 94·05 kcal and –68·32 kcal respectively. The heat of combustion of methyl alcohol (l) is –173·65 kcal. Calculate the heat of formation of liquid methyl alcohol.

(–57·04 kcal)

10. At constant volume at 27°C,

$$2C_6H_6\,(g) + 15O_2\,(g) \rightarrow 12CO_2\,(g) + 6H_2O\,(l);\ \Delta E = -1600\ \text{kcal}$$

$$2C_2H_2\,(g) + 5O_2\,(g) \rightarrow 4CO_2\,(g) + 2H_2O\,(l);\ \Delta E = -620\ \text{kcal}$$

Calculate the heat of polymerisation of acetylene to benzene at constant pressure.

(–131·2 kcal)

11. Calculate the heat of formation of CH_3COOH (l) at 25°C from the following data:

$$CH_3COOH\,(l) + 2O_2\,(g) \rightarrow 2CO_2 + 2H_2O\,(l);\ \Delta H = -208{\cdot}34\ \text{kcal}$$

$$C\,(s) + O_2\,(g) \rightarrow CO_2\,(g);\ \Delta H = -94{\cdot}05\ \text{kcal}$$

$$H_2\,(g) + \frac{1}{2}O_2 \rightarrow H_2O\,(l);\ \Delta H = -68{\cdot}32\ \text{kcal}$$

(–116·4 kcal)

12. For the reaction at 25°C,

$$NH_3\,(g) \rightarrow \frac{1}{2}N_2\,(g) + \frac{3}{2}H_2\,(g);\ \Delta H^0 = 11{\cdot}04\ \text{kcal}$$

calculate ΔE^0 of the reaction at the given temperature. (10·44 kcal)

13. From the following equations, calculate the standard molar heat of formation of AgCl at 25°C.

$$Ag_2O\,(s) + 2HCl\,(g) \rightarrow 2AgCl\,(s) + H_2O(l);\ \Delta H^0 = -77{\cdot}61\ \text{kcal}$$

$$2Ag\,(s) + \frac{1}{2}O_2\,(g) \rightarrow Ag_2O\,(s);\ \Delta H^0 = -73{\cdot}1\ \text{k cal}$$

$$\frac{1}{2}H_2\,(g) + \frac{1}{2}Cl_2\,(g) \rightarrow HCl\,(g);\ \Delta H^0 = -22{\cdot}06\ \text{kcal}$$

$$H_2\,(g) + \frac{1}{2}O\,(g) \rightarrow H_2O\,(l);\ \Delta H^0 = -68{\cdot}32\ \text{kcal}$$

(–63·20 kcal)

14. Calculate the enthalpy of formation of HBr (g) from the following data:

$$SO_2\,(aq) + \frac{1}{2}O_2\,(g) \rightarrow SO_3\,(aq);\ \Delta H = -63{\cdot}7\ \text{kcal}$$

$$2Br\,(g) + SO_2\,(aq) + H_2O\,(l) \rightarrow 2HBr\,(aq) + SO_3\,(aq);\ \Delta H = -54\ \text{kcal}$$

$$H_2\,(g) + \frac{1}{2}O_2\,(g) \rightarrow H_2O\,(l);\ \Delta H = -68{\cdot}4\ \text{kcal}$$

$$HBr\,(g) + aq \rightarrow HBr\,(aq);\ \Delta H = -20\ \text{kcal}$$

(–9·4 kcal)

15. Calculate the enthalpy of formation of $Ca(OH)_2$ (s) from the following data:

$$H_2\,(g) + \frac{1}{2}O_2\,(g) \rightarrow H_2O\,(l);\ \Delta H = -68{\cdot}3\ \text{kcal}$$

$$CaO\,(s) + H_2O(l) \rightarrow Ca(OH)_2\,(s);\ \Delta H = -15{\cdot}3 \text{ kcal}$$

$$Ca\,(s) + \frac{1}{2}O_2\,(g) \rightarrow CaO\,(s);\ \Delta H = -151{\cdot}8 \text{ kcal}$$

(−235·4 kcal)

16. Calculate the heat of formation of KOH from the following data:

$$K + H_2O + aq \rightarrow KOH\,(aq) + \frac{1}{2}H_2;\ \Delta H = -48{\cdot}4 \text{ kcal}$$

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O;\ \Delta H = -68{\cdot}44 \text{ kcal}$$

$$KOH + aq \rightarrow KOH\,(aq);\ \Delta H = -14{\cdot}01 \text{ kcal}$$

(−102·46 kcal)

17. Calculate the heat of formation of C_6H_6, given that the heats of combustion of benzene, carbon and hydrogen are 754, 94 and 68 kcal respectively. (−14 kcal)

18. Calculate the enthalpy change for the reaction

$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$; from the following data:

$$2Fe + \frac{3}{2}O_2 \rightarrow Fe_2O_3;\ \Delta H = -177{\cdot}1 \text{ kcal}$$

$$C + \frac{1}{2}O_2 \rightarrow CO;\ \Delta H = -32{\cdot}8 \text{ kcal}$$

$$C + O_2 \rightarrow CO_2;\ \Delta H = -94{\cdot}3 \text{ kcal}$$

(−8·4 kcal)

19. The heats of formation of $Na_2B_4O_7$ (s) and $Na_2B_4O_7 \cdot 10H_2O$ (s) are −742 and −1460 kcal respectively. Calculate the heat of hydration of $Na_2B_4O_7$ in forming decahydrate. (−718 kcal)

20. The heats of combustion of graphite and diamond at 298 K are −393 and −395 kJ/mole respectively. The specific heats of these substances are 720 and 505 J $kg^{-1}K^{-1}$ respectively. Calculate the heat of transformation of graphite into diamond at 273 K.

(2·0645 kJ $mole^{-1}$)

[**Hint:** $\Delta H = \{-393 - (395)\} + (0{\cdot}720 - 0{\cdot}505) \times \frac{12}{1000} \times (298 - 273)$]

21. The enthalpies of neutralisation for CH_3COOH with NaOH and NH_4OH with HCl are −50·6 and − 51·4 kJ eq^{-1} respectively. Calculate the enthalpy of neutralisation of CH_3COOH with NH_4OH.

(−44·74 kJ $eq.^{-1}$)

22. Calculate the fuel efficiency in kJ/gram of C_2H_4 and C_4H_{10}. The heats of formation of C_2H_4, C_4H_{10}, CO_2 and H_2O are 52·3, −126·1, −393·5 and −285·8 kJ $mole^{-1}$ respectively.

(50·39 and 49·6 kJ g^{-1})

23. The heat of formation of Fe_2O_3 is − 821·32 kJ $mole^{-1}$ at 298 K and 1 atm and that of Al_2O_3 is 1675·60 kJ $mole^{-1}$ under the same condition. Calculate the heat of reaction of reduction of 1 mole of Fe_2O_3 with metallic aluminium. (−854·28 kJ)

24. A gas is enclosed in a cylinder with a piston. Weights are added to the piston, giving a total mass of 2·20 kg. As a result the gas is compressed and the weights

are lowered 0·25 m. At the same time, 1·50 J of heat evolved from the system. What is the change in internal energy of the system? (3·89 J)

25. Calculate ΔG^0 for the reaction

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$$

Given that, ΔG_f^0 $(CaF_2(s)) = -1162$ kJ/mole.

ΔG_f^0 $(Ca^{2+}(aq)) = -553{\cdot}0$ and ΔG_f^0 $(F^-(aq)) = -276{\cdot}5$ kJ/mole.

Also calculate K_{sp} for this reaction at 25°C.

(56 kJ, 2×10^{-10})

26. To what temperature must magnesium carbonate be heated to decompose it to MgO and CO_2 at 1 atm? Given:

	$MgCO_3(s)$	$MgO(s)$	$CO_2(g)$
ΔH_f^0	–1112	–601·2	–393·5 kJ
S^0	65·9	26·9	213·7 J/K

(671 K)

27. Predict the direction in which ΔG^0 for the equilibrium

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); \ \Delta G_{298}^0 = -33{\cdot}32 \text{ kJ}$$

will change with increase in temperature. Calculate ΔG^0 at 500°C, assuming that ΔH and ΔS do not change with temperature, that is, $\Delta H_{298}^0 = \Delta H_{793}$ and $\Delta S_{298}^0 = \Delta S_{793}$.

$$\Delta H^0 = -92{\cdot}38 \text{ kJ} \quad \text{and} \quad \Delta S^0 = -198{\cdot}2 \text{ J/K}$$

(The eqn. shifts .o left with increase in temp., +60·83 kJ)

28. A heat pump is used to draw water from a well. The temperature of the water is 15°C and that of the atmosphere is 40°C. If the amount of water drawn is 10 kg from the depth of 12 m, calculate the amount of heat supplied to the well. (14·72 kJ)

29. Given the following reactions with their enthalpy changes, at 25°C,

$$N_2(g) + 2O_2(g) \rightarrow 2NO_2(g); \ \Delta H = 16{\cdot}18 \text{ kcal}$$

$$N_2(g) + 2O_2(g) \rightarrow N_2O_4(g); \ \Delta H = 2{\cdot}31 \text{ kcal}$$

calculate the enthalpy of dimerisation of NO_2. Is N_2O_4 apt to be stable with respect to NO_2 at 25°C?

(–13·87 kcal, N_2O_4 stable only at low temp.)

30. A system is changed from an initial state to a final state by a manner such that $\Delta H = q$. If the same change from the initial state to the final state were made by a different path, would ΔH be the same as that of the first path? Would q?

(same, most probably different)

31. Two moles of an ideal gas are held by a piston under 10 atm pressure at 273 K. The pressure is suddenly released to 0·4 atm and the gas is allowed to expand isothermally. Calculate $W, q, \Delta E$ and ΔH. (–4358 J, 4358 J, 0, 0)

[Hint: The gas expands irreversibly.)

32. If the equation of state for 1 mole of a gas is

$$p(V - b) = RT,$$

prove that dp is an exact differential and p is a state function.

33. Show that the differential $d\overline{V}$ of the molar volume of an ideal gas is an exact differential and hence $\overline{V}$ is a state function.

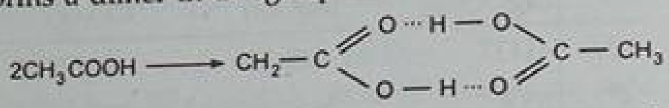
[Hint: $\overline{V} = \frac{RT}{p}$; $\overline{V} = f(p, T)$]

34. Assume that the only change in volume is due to the production of hydrogen and calculate the work done in joules when 2·0 moles of Zn dissolve in hydrochloric acid, giving H_2 at 35°C and 1 atm.

$$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$ ($-5{\cdot}12 \times 10^3$ J)

[Hint: $W = -p\Delta V = -\Delta n_{H_2}RT$]

35. Acetic acid forms a dimer in the gas phase



The dimer is held together by two hydrogen bonds with a total strength of 66·5 kJ per mole of dimer. At 25°C, the equilibrium constant for the dimerisation is $1{\cdot}3 \times 10^3$ (pressure in atm). What is ΔS^0 for the reaction? Assume that ΔH does not vary with temperature. ($-0{\cdot}11$ kJ/mol· K)

36. A Carnot engine has an efficiency of 40%. If the temperature of the reservoir is 280 K, what is the temperature of the source? (466·6 K)

37. A Carnot engine whose temperature of the source is 400 K takes 200 cal of heat at this temperature and rejects 150 cal of heat to the sink. Calculate the temperature of the sink and the efficiency of the engine. (300 K, 25%)

38. One mole of an ideal gas at 22·4 litres is expanded isothermally and reversibly at 300 K to a volume of 224 litres at a constant pressure. Calculate $W, q, \Delta H, \Delta G$ and ΔS.

($-5{\cdot}74$ kJ, 5·74 kJ, 0, $-5{\cdot}74$ kJ, +19·1 J/K)

39. K_{sp} of AgCl at 25°C is $1{\cdot}782 \times 10^{-10}$. At 35°C, K_{sp} is $4{\cdot}159 \times 10^{10}$. What are ΔH^0 and ΔS^0 for the reaction: $AgCl(s) = Ag^+(aq) + Cl^-(aq)$? ($\Delta H^0 = 64{\cdot}655$ kJ, $\Delta S^0 = 30{\cdot}3$ J)

40. For the reaction

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

$\Delta H^0 = -393{\cdot}51$ kJ/mole and $\Delta S^0 = 2{\cdot}86$ J/mole · K at 25°C. Does the reaction become more or less favourable as the temperature increases? (more favourable)

41. The $\Delta H^0, \Delta G^0$ and ΔS^0 values for the reaction

$$2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$$

at 25°C are $-196{\cdot}0$ kJ/mole, $-233{\cdot}6$ kJ/mole and +125·6 J/mole · K respectively. Is there any temperature at which $H_2O_2(l)$ is stable at 1 atm? Assume that ΔH and ΔS values do not change with temperature. (theoretically at -1586 K)

42. For each of the following processes, tell whether the entropy of the system increases, decreases or remains constant.

(a) Melting one mole of ice to water at 0°C

(b) Freezing one mole of water to ice at 0°C

(c) Freezing one mole of water to ice at -10°C

(d) Freezing one mole of water to ice at 0°C and then cooling it to –10°C

((a) increases (b) decreases (c) decreases (d) decreases)

43. The heat of formation of ethane is –20·3 kcal. Calculate the bond energy of C—C bond in ethane if the heats of atomisation of carbon and hydrogen are respectively 170·9 and 52·1 kcal per mole and bond energy of C—H bond is 99·0 kcal.

(80·7 kcal)

44. The heat of reaction of $N_2 + 3H_2 \rightarrow 2NH_3$ is –20 kcal. If the bond energies of H—H and N—H bonds are 104 and 93 kcal/mole respectively, calculate the bond energy of $N \equiv N$ bond.

(226 kcal)

45. Calculate the heat of formation of acetone from the following data:

$$\frac{1}{2}H_2(g) \rightarrow H(g);\ \Delta H = 52{\cdot}1 \text{ kcal}$$

$$\frac{1}{2}O_2(g) \rightarrow O(g);\ \Delta H = 59{\cdot}16 \text{ kcal}$$

$$C(s) \rightarrow C(g);\ \Delta H = 171{\cdot}7 \text{ kcal}$$

Bond energies:

C—H = 99 kcal

C—C = 80 kcal

C=O = 81 kcal

(51·86 kcal)

46. Calculate the heat of formation of methyl alcohol (liquid) from the following data:

Heat of atomisation of C = 170·9 kcal

Heat of atomisation of H = 52·1 kcal

Heat of atomisation of O = 59·6 kcal

Bond energies: C—H = 99 kcal

C—O = 84 kcal

O—H = 110·55 kcal

Heat of liquefaction of 1 mole of CH_3OH = –8·4 kcal.

(–61·0 kcal)

47. Calculate the heat of the following gaseous reaction:

$$CH_4 + 4F_2 \rightarrow CF_4 + 4\,HF$$

The bond energies of C—H; F—F; C—F and H—F bonds are 99·3; 38; 116 and 135 kcal/mole respectively.

(–454·8 kcal)

48. Estimate the heat of formation of gaseous isoprene

$$(H_2C = \overset{\overset{CH_3}{|}}{C} - \overset{\overset{H}{|}}{C} = CH_2)$$ from the following data:

Bond energies:

C—H = 98·8 kcal/mole

H—H = 104·0 kcal/mole

C—C = 83·1 kcal/mole

C=C = 147·0 kcal/mole

(23·9 kcal)

Heat of sublimation of carbon (s) = 171·7 kcal per mole.

49. Using the required bond-energies data from the above problems, calculate the heat of hydrogenation of ethene to ethane. (–29·7 kcal)

50. Calculate the heat of the following homogeneous gaseous reaction

$$CH_3COCH_3 + 2O_2 \rightarrow CH_3COOH + CO_2 + H_2O$$

from the following data:

Bond energies (kJ):

C—H = 414·49	C—O = 967·13
C—C = 347·92	Resonance energy:
C=O = 724·32	— COOH = 117·23
O=O = 494·04	CO_2 = 138·16
O—H = 462·64	

(–554·33 kJ)

51. Calculate the resonance energy of N_2O from the following data:

$$\Delta H_f^0 \text{ of } N_2O = 82 \text{ kJ mole}^{-1}$$

Bond energies of N≡N, N = N, O = O and N = O bonds are 946, 418, 498 and 607 kJ mole^{-1} respectively. (–88 kJ)

Objective Problems

1. The heat of formation of HCl (g) from the reaction

$$H_2(g) + Cl_2(g) = 2HCl(g);\ \Delta H = -44 \text{ kcal is}$$

(a) +44 kcal (b) –44 kcal (c) +22 kcal (d) –22 kcal

2. Given $N_2(g) + 3H_2(g) = 2NH_3(g)$; $\Delta H^0 = -22$ kcal. The standard enthalpy of formation of NH_3 gas is

(a) –11 kcal/mole (b) 11 kcal/mole
(c) –22 kcal/mole (d) 22 kcal/mole

3. If for $H_2(g) = 2H(g)$; $\Delta H = 104$ kcal, heat of atomisation of hydrogen is

(a) 52 kcal (b) 104 kcal (c) 208 kcal (d) none of these

4. Heats of combustion of CH_4, C_2H_4, C_2H_6 are –890, –1411 and –1560 kJ/mole respectively. Which has the lowest fuel value in kJ/g?

(a) CH_4 (b) C_2H_4 (c) C_2H_6 (d) all same

5. 2·1 g of Fe combines with S evolving 3·77 kJ. The heat of formation of FeS in kJ/mole is

(a) –3·77 (b) –1·79 (c) –100·5 (d) none of these

6. When a certain amount of ethylene was combusted, 6226 kJ of heat was evolved. If the heat of combustion of ethylene is 1411 kJ, the volume of O_2 (at NTP) that entered into the reaction is

(a) 296·5 mL (b) 296·5 litres (c) 6226 × 22·4 litres (d) 22·4 litres

7. $\left[\begin{array}{l} H_2(g) + \frac{1}{2}O_2(g) = H_2O(g);\ \Delta H = -241.8\ kJ \\ CO(g) + \frac{1}{2}O_2(g) = CO_2(g);\ \Delta H = -283\ kJ \end{array}\right]$

The heat evolved in the combustion of 112 litres of water gas (mixture of equal volumes of H_2 and CO) is

(a) 241·8 kJ (b) 283 kJ (c) 1312 kJ (d) 1586 kJ

8. $\left[\begin{array}{l} H_2(g) + \frac{1}{2}O_2(g) = H_2O(g);\ \Delta H = -241.8\ kJ \\ C_2H_2(g) + 2\frac{1}{2}O_2(g) = 2CO_2(g) + H_2O(g);\ \Delta H = -1300\ kJ \end{array}\right]$

Equal volumes of C_2H_2 and H_2 are combusted under identical conditions. The ratio of heats evolved in the two cases is

(a) 5·37/1 (b) 1/5·37 (c) 1/1 (d) none of these

9. The heat of neutralisation of a strong dibasic acid in dilute solution by NaOH is nearly

(a) –27·4 kcal/eq (b) 13·7 kcal/mole
(c) –13·7 kcal/eq (d) –13·7 kcal/mole

10. The temperature of 5 mL of a strong acid increases by 5° when 5 mL of a strong base is added to it. If 10 mL of each is mixed, the temperature should increase by

(a) 5° (b) 10° (c) 15° (d) cannot be known

11. The heat of neutralisation of a strong acid by a strong base is equal to ΔH of:

(a) $H^+ + OH^- = H_2O$
(b) $H_2O + H^+ = H_3O^+$
(c) $2H_2 + O_2 = 2H_2O$
(d) $CH_3COOH + NaOH = CH_3COONa + H_2O$

12. In which case of mixing of a strong acid and a base, each being of 1 N concentration, the increase in temperature is the highest?

(a) 20 mL acid and 30 mL alkali (b) 10 mL acid and 40 mL alkali
(c) 25 mL acid and 25 mL alkali (d) 35 mL acid and 15 mL alkali

13. The heat of neutralisation of HCl by NaOH is –55·9 kJ/mole. If the heat of neutralisation of HCN by NaOH is –12·1 kJ/mole, the energy of dissociation of HCN is

(a) –43·8 kJ (b) 43·8 kJ (c) 68 kJ (d) –68 kJ

14. The dissociation energy of CH_4 and C_2H_6 are respectively 360 and 620 kcal/mole. The bond energy of C—C is

(a) 260 kcal/mole (b) 180 kcal/mole
(c) 130 kcal/mole (d) 80 kcal/mole

15. In which of the following cases does entropy decrease?

(a) Solid changing to liquid (b) Expansion of a gas
(c) Crystals dissolve (d) Polymerisation

16. In which of the following reactions is ΔS positive?

(a) $H_2O(l) \rightarrow H_2O(s)$ (b) $3O_2(g) \rightarrow 2O_3(g)$

(c) $H_2O\,(l) \rightarrow H_2O\,(g)$ (d) $N_2\,(g) + 3H_2\,(g) \rightarrow 2NH_3\,(g)$

17. In the process of ice melting at $-15°C$
(a) $\Delta G < 0$ (b) $\Delta G > 0$ (c) $\Delta G = 0$

18. In a reaction, ΔH and ΔS both are more than zero. In which of the following cases would the reaction be spontaneous?
(a) $\Delta H > T\Delta S$ (b) $T\Delta S > \Delta H$ (c) $\Delta H = T\Delta S$

19. In which case is a reaction possible at any temperature?
(a) $\Delta H < 0,\ \Delta S > 0$ (b) $\Delta H < 0,\ \Delta S < 0$
(c) $\Delta H > 0,\ \Delta S > 0$ (d) in none of the cases

20. In which case is a reaction impossible at any temperature?
(a) $\Delta H > 0,\ \Delta S > 0$ (b) $\Delta H > 0,\ \Delta S < 0$
(c) $\Delta H < 0,\ \Delta S < 0$ (d) in all cases

21. The difference between the heats of reaction at constant pressure and constant volume for the reaction
$2C_6H_6\,(l) + 15\,O_2\,(g) \rightarrow 12CO_2\,(g) + 6H_2O\,(l)$ at 25° C in kJ is
(a) $-7{\cdot}43$ (b) $+3{\cdot}72$ (c) $-3{\cdot}72$ (d) $+7{\cdot}43$ (IIT 1991)

22. Molar heat capacity of water in equilibrium with ice at constant pressure is
(a) zero (b) ∞
(c) $40{\cdot}45\ kJ\,K^{-1}\,mol^{-1}$ (d) $75{\cdot}48\ J\,K^{-1}\,mol^{-1}$ (IIT 1997)

23. Standard molar enthalpy of formation of CO_2 is equal to
(a) zero
(b) the standard molar enthalpy of combustion of gaseous carbon
(c) the sum of standard molar enthalpies of formation of CO and O_2
(d) the standard molar enthalpy of combustion of carbon (graphite) (IIT 1997)

24. When steam condenses to water at 90°C, the entropy of the system decreases. What must be true if the second law of thermodynamics is to be satisfied?
(a) Entropy of the universe also decreases.
(b) Entropy of the surroundings also decreases.
(c) Entropy of the surroundings increases to the same extent to which entropy of the system decreases.
(d) Increase in entropy in the surroundings is greater than decrease in entropy of the system.

[Hint: For a spontaneous process $\Delta S_{universe}$ must be positive.]

25. A certain reaction is spontaneous at 85°C. The reaction is endothermic by 34 kJ. The minimum value of ΔS for the reaction is
(a) $497{\cdot}2$ J/K (b) $-497{\cdot}2$ J/K
(c) $+2094$ J/K (d) cannot be calculated

26. For the reaction,

$$\frac{1}{2}A_2 + \frac{1}{2}B_2 \rightarrow AB;\ \Delta H = -50\ \text{kcal}.$$

If the bond energies of A_2, B_2 and AB are respectively $x, \frac{x}{2}$ and x kcal, the value of x is

(a) 50 (b) 100 (c) 200 (d) 400

27. One mole of a nonideal gas undergoes a change of state (2·0 atm, 3·0 L, 95 K) → (4 atm, 5 L, 245 K) with a change in internal energy, $\Delta E = 30{\cdot}0$ L atm. The change in enthalpy, ΔH, of the process in L. atm is

(a) 40·0 (b) 42·3 (c) 44·0

(d) not defined, because pressure is not constant **(IIT 2002)**

[Hint: $\Delta H = \Delta E + (p_2V_2 - p_1V_1)$**]**

28. Which of the following thermodynamic variables is extensive?

(a) Pressure (b) Density (c) Temperature (d) Mass

29. Which of the following is an intensive property?

(a) Volume (b) Internal energy
(c) Entropy (d) Mass/volume

30. Which of the following is an intensive property?

(a) emf (b) Volume (c) Mass (d) Enthalpy

31. Which of the following is not a thermodynamic state function?

(a) Work (b) Internal energy
(c) Free energy (d) Temperature

32. Which of the following is not an exact differential?

(a) dq (b) dG (c) dV (d) dS

33. Which of the following is a state function and also an extensive property?

(a) Internal energy (b) Pressure
(c) Molar heat capacity (d) Temperature

34. Which of the following is not equal to zero in a cyclic process?

(a) ΔG (b) ΔW (c) ΔS (d) ΔH

Answers

1-d, 2-a, 3-a, 4-b, 5-c, 6-b, 7-c, 8-a, 9-c, 10-a, 11-a, 12-c, 13-b, 14-d, 15-d, 16-c, 17-b, 18-b, 19-a, 20-b, 21-a, 22-b, 23-d, 24-d, 25-a, 26-c, 27-c, 28-d, 29-d, 30-a, 31-a, 32-a, 33-a, 34-b

CHEMICAL EQUILIBRIUM

In the study of any chemical reaction, two types of information are of vital importance, viz, how far a reaction would go, and how fast would it reach its goal. The answer to the first question forms the subject matter of this chapter.

Chemical Equilibrium and Equilibrium Constant

The reactions are generally reversible, that is, they can proceed both ways. A reaction is said to have attained equilibrium when the rate of the forward reaction equals that of the backward reaction.

Let us consider a general case of a reversible reaction,

$$aA + bB \rightleftharpoons mM + nN$$

Applying the law of mass action:

Rate of the forward reaction $\propto [A]^a\ [B]^b$

or rate of the forward reaction $= k_1\ [A]^a\ [B]^b$.

Rate of backward reaction $\propto [M]^m\ [N]^n$

or rate of backward reaction $= k_2\ [M]^m\ [N]^n$.

At equilibrium:

Rate of forward reaction = rate of backward reaction

$$k_1\ [A]^a\ [B]^b = k_2\ [M]^m\ [N]^n$$

$$\frac{k_1}{k_2} = \frac{[M]^m\ [N]^n}{[A]^a\ [B]^b}$$

or

$$^{*}K_c = \frac{k_1}{k_2} = \frac{[M]^m\ [N]^n}{[A]^a\ [B]^b} \qquad \ldots (1)$$

[ ] represents concentration in moles per litre. Here, all concentrations are at equilibrium. k_1 and k_2 are known as the rate constants of the forward and backward reactions respectively.

Chemical equilibrium is dynamic in the sense that individual molecules are continually reacting, even though the overall composition of the reaction mixture does not change. The other criteria of a chemical equilibrium are: the

* When there is no subscript on K, it is understood to be K_c. In thermodynamics the equilibrium constant is defined in terms of activities rather than

Now the temperature above which the forward reaction will be spontaneous is actually the temperature at which the reaction attains equilibrium, that is, when $K = 1$ or $\log K = 0$.

$$\therefore \quad \Delta G^0 = -2.303\, RT \log K$$
$$= -2.303\, RT \log 1.0$$
$$= 0.$$

From thermodynamics, we have

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$
$$0 = 33025 - T \times 102.96$$

or $\quad T = 320.75$ K.

PROBLEMS

(*Answers bracketed with questions*)

1. K_c for the equilibrium $N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$ at 298° C is 5.7×10^{-9}. Which species has a higher concentration at equilibrium? (N_2O_4).

2. The equilibrium constant of an equilibrium represented by A (g) $\rightleftharpoons$ B (g) is 1·1. Which of the two gases A and B has a molar concentration greater than 1 at equilibrium? (B)

3. At a particular temperature, the equilibrium constant for

$$2NO_2\,(g) \rightleftharpoons N_2O_4\,(g)$$

is one. The same reaction is carried out in a container of volume just half of the former. Will the value of $[N_2O_4]/[NO_2]^2$ be equal to 1 if no reaction occurred? Will the equilibrium constant change by this change in volume? (No. No)

4. Would you expect the equilibrium constant for the reaction $I_2\,(g) \rightleftharpoons 2I\,(g)$ to increase or decrease as temperature increases? Why?
[**Hint:** The forward reaction is endothermic as energy is required to break I_2 into I.]

5. For the reaction NOBr (g) $\rightleftharpoons$ NO (g) + $\frac{1}{2}Br_2$ (g); $K_p = 0.15$ atm at 90°C. If 0·50 atm of NOBr, 0·40 atm of NO, and 0·20 atm of Br_2 are mixed at this temperature, will Br_2 be consumed or formed? (Consumed)
[**Hint:** Use eqns. 8, 9 and 10.]

6. The ammonia in equilibrium with a 1 : 3 N_2–H_2 mixture at 20 atm and 427°C amounts to 16%. Calculate K_p and K_c for (3.49×10^{-2}; 2)

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3$$

7. State whether the following statement is false or true. If the equilibrium constant for $A_2 + B_2 \rightleftharpoons 2AB$ is K, the equilibrium constant for $AB \rightleftharpoons \frac{1}{2}A_2 + \frac{1}{2}B_2$ is $1/K$. (False)

8. One mole of N_2 and 3 moles of PCl_5 are placed in a 100-litre vessel heated to 227°C. The equilibrium pressure is 2·05 atm. Assuming ideal behaviour, calculate the degree of dissociation for PCl_5 and K_p for the reaction:

$$PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$$ (0·33; 0·205 atm)

[Hint: While calculating partial pressure, include moles of N_2 in the total moles]

9. Twenty grams of HI is heated at 327°C in a bulb of 1-litre capacity. Calculate the volume percentage of H_2, I_2 and HI at equilibrium. Given that the mass law constant for the equation $2HI \rightleftharpoons H_2 + I_2$ is 0·0559 at 327°C when concentrations are expressed in moles/litre. ($HI = 67{\cdot}9\%$, $H_2 = I_2 = 16{\cdot}05\%$)

10. 25 mL of H_2 and 18 mL of I_2 vapours were heated in a sealed tube at 456°C, when at equilibrium 30·8 mL of HI was formed. Calculate the degree of dissociation of pure HI at 456°C. (24·5%)

11. Bodenstein found that at 443°C the dissociation of HI according to the equation $2\,HI \rightleftharpoons H_2 + I_2$ was 21·98%. For experiments at the same temperature, starting with varying amounts of H_2 and I_2, the amount of HI present when equilibrium was attained is given by the following numbers:

I_2 (mL) (vap.) initial	H_2 (mL) (vap.) initial	HI (mL) (vap.) at equib.
2·94	8·10	5·65
9·27	8·07	13·46
33·10	7·89	15·41

Verify whether the amounts of HI obtained are according to the law of mass action.

12. HI is introduced into three identical 500-mL bulbs at 350°C. Each bulb is opened at different time intervals and analysed for I_2 by titrating with 0·015 M hypo solution.

$$(I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI)$$

Bulb number	Initial mass of HI	Time of opening bulb	Vol. of hypo required
1	0·3 g	2	20·96 mL
2	0·406 g	20	41·50 mL
3	0·28 g	40	28·68 mL

Calculate K_c for $2HI \rightleftharpoons H_2 + I_2$ at 350°C. ($1{\cdot}49 \times 10^{-2}$)

[Hint: Moles of $I_2 = \frac{1}{2}$(moles of $Na_2S_2O_3$)

$= \frac{1}{2}$(molarity × vol. in L)]

13. Five grams of PCl_5 (molecular wt. 208·5) was completely vapourised to an equilibrium state at 250°C in a vessel of 1·9-litre capacity. The equilibrium mixture

exerted a pressure of 1 atm. Calculate degree of dissociation, K_c and K_p for the reaction.

(84·6 %, 0·0587, 2·53)

14. Ammonia under a pressure of 15 atm at 27°C is heated to 347°C in a closed vessel in the presence of a catalyst. Under these conditions NH_3 is partially decomposed according to the equation

$$2NH_3 \rightleftharpoons N_2 + 3H_2$$

The vessel is such that the volume remains effectively constant, whereas pressure increases to 50 atm. Calculate the percentage of NH_3 actually decomposed. Pressure of NH_3 at 27°C or 300 K = 15 atm.

(61·3%)

15. In a gaseous reaction of the type $A + 2B \rightleftharpoons 2C + D$, the initial concentration of B was 1·5 times that of A. At equilibrium the equilibrium concentrations of A and D were equal. Calculate the equilibrium constant. (4)

16. A mixture of SO_2 and O_2 at 1 atm in the mole ratio of 2 : 1 is passed through a catalyst at 1170°C at a rate sufficient for attainment of equilibrium. The existing gas, suddenly chilled and analysed, is found to contain 87% SO_3 by volume. Calculate K_p for the reaction: $SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3$

(57·76)

17. For the reaction:

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

$K_c = 9{\cdot}14 \times 10^{-6}$ at 25°C. If the initial concentrations of the ions are: $[Fe^{3+}] = 0{\cdot}5$ M, $[Hg_2^{2+}] = 0{\cdot}5$ M, $[Fe^{2+}] = 0{\cdot}03$ M and $[Hg^{2+}] = 0{\cdot}03$ M, what will be the ionic concentrations at equilibrium?

$$\left[\begin{array}{l} [Fe^{3+}] = 0{\cdot}497\ M,\ [Hg_2^{2+}] = 0{\cdot}499\ M \\ [Fe^{2+}] = 3{\cdot}27 \times 10^{-2}\ M,\ [Hg^{2+}] = 3{\cdot}27 \times 10^{-2}\ M \end{array}\right]$$

[Hint: Calculate reaction quotient and compare with K_c to establish the direction *of the reaction*.]

18. In a 1-litre vessel at 1000 K are introduced 0·1 mole each of NO and Br_2 and 0·01 mole of NOBr

$$2NO(g) + Br_2(g) \rightleftharpoons 2NOBr(g); \qquad K_c = 1{\cdot}32 \times 10^{-2}$$

Determine the direction of the net reaction and calculate the partial pressure of NOBr in the vessel at equilibrium.

(Reverse, 0·30 atm)

19. An air sample containing 21 : 79 of O_2 and N_2 (mole ratio) is heated to 2400°C. If the mole per cent of NO at equilibrium is 1·8%, calculate K_p for the reaction $N_2 + O_2 \rightleftharpoons 2NO$.

($2{\cdot}1 \times 10^{-3}$)

20. In phosgene gas reaction at 400°C, the initial pressures are $p_{CO} = 342$ mm and $p_{Cl_2} = 352$ mm and the total pressure at equilibrium is 440 mm.

$$CO + Cl_2 \rightleftharpoons COCl_2$$

Calculate percentage dissociation of phosgene at 400°C at 1 atm.

(20·6%)

21. If the heat of reaction at constant volume exceeds that at constant pressure for an endothermic reaction at 25°C by 1190 cal, what is the value of the ratio $\frac{K_p}{K_c}$?

[Hint: Apply $q_p = q_v + \Delta nRT$ and $K_p = K_c \cdot (RT)^{\Delta n}$

We get, $\frac{K_p}{K_c} = (RT)^{-2} = (0{\cdot}082 \times 298)^{-2}$ in atm and litre units]

22. At 400°C for the gas-phase reaction:

$$2H_2O\ (g) + 2Cl_2\ (g) \rightleftharpoons 4HCl\ (g) + O_2\ (g)$$

the K_p is 0·035 when partial pressures are measured in atmospheric units. Calculate K_c value for it, concentration being measured in mole per litre units. State the unit. ($6{\cdot}35 \times 10^{-4}$ mole per litre)

23. One mole each of acetic acid and ethyl alcohol are mixed at 25°C. When the mixture attains equilibrium it is found that 12 g of water is formed. Find the value of K_c. What weight of ethyl acetate will be formed when two moles of ethyl alcohol are further added and the equilibrium is attained? (4, 79·2 g)

24. The equilibrium constant of the ester formation of propionic acid with ethyl alcohol is 7·36 at 50°C. Calculate the weight of ethyl propionate, in grams, existing in an equilibrium mixture when 0·5 mole of propionic acid is heated with 0·5 mole of ethyl alcohol at 50°C. (37·29 g)

25. 0·1 mole of each of ethyl alcohol and acetic acid are allowed to react and at equilibrium the acid was exactly neutralised by 100 mL of 0·85 N NaOH. If no hydrolysis of ester is supposed to have undergone, find the equilibrium constant. (0·031)

26. The K_p value for the equilibrium $H_2\ (g) + I_2\ (s) \rightleftharpoons 2HI\ (g)$ is 871 at 25°C. If the vapour pressure of iodine is 4×10^{-4} atm, calculate the equilibrium constant in terms of partial pressures at the same temperature for the reaction; $H_2\ (g) + I_2\ (s) \rightleftharpoons 2HI\ (g)$. (0·3484 atm)

27. In the reaction $CuSO_4 \cdot 3H_2O \rightleftharpoons CuSO_4 \cdot H_2O + 2H_2O$ (vap.), the dissociation pressure is 7×10^{-3} atm at 25°C and $\Delta H^0 = 2700$ cal. What will be the dissociation pressure at 127°C? ($1{\cdot}247 \times 10^{-2}$ atm)

28. Under what pressure conditions will $CuSO_4 \cdot 5H_2O$ be efflorescent at 25°C? How good a drying agent is $CuSO_4 \cdot 3H_2O$ at the same temperature? For the reaction

$$CuSO_4 \cdot 5H_2O\ (s) \rightleftharpoons CuSO_4 \cdot 3H_2O\ (s) + 2H_2O\ (g)$$

$K_p = 1{\cdot}086 \times 10^{-4}$ atm^2 at 25°C. Vapour pressure of water at 25°C is 23·8 mm (Hg).

[Efflorescence occurs when partial press. of H_2O vap. in air is less than 7·92 mm. $CuSO_4 \cdot 3H_2O$ can reduce moisture when partial press. of H_2O vap. in air is 7·92 mm.]

[Hint: An efflorescent salt is one that loses water to the atmosphere.

$$K_p = p^2_{H_2O} = 1.086 \times 10^{-4};$$

$$p_{H_2O} = 1.042 \times 10^{-2} \text{ atm} = 7.92 \text{ mm.}]$$

29. Vapour density of N_2O_4 which dissociated according to the equation $N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$ is 25·67 at 100°C and a pressure of 1 atm. Calculate the degree of dissociation and K_p for the reaction. (0·792, 6·7)

30. Equilibrium constant (K_p) for the reaction

$$2H_2S\,(g) \rightleftharpoons 2H_2\,(g) + S_2\,(g)$$

is 0·0118 at 1065°C and heat of dissociation is 42·4 kcal. Find equilibrium constant at 1132°C. (0·025)

31. In the gaseous reaction $2A + B \rightleftharpoons A_2B$, $\Delta G^0 = 1200$ cal at 227°C. What total pressure would be necessary to produce 60% conversion of B into A_2B when 2 : 1 mixture is used?

[Hint : Use Equation 12] (5·02 atm)

32. Equilibrium constants (K_p) for the reaction $\frac{3}{2}H_2\,(g) + \frac{1}{2}N_2\,(g) \rightleftharpoons NH_3\,(g)$ are 0·0266 and 0·0129 at 350°C and 400°C respectively. Calculate the heat of formation of gaseous ammonia. (12140 cal)

33. Equilibrium constant K_c for the equilibrium

$$A\,(g) \rightleftharpoons B\,(g) + C\,(g) \text{ is } 0.45 \text{ at } 200°C.$$

One litre of a container contains 0·2 mole of A, 0·3 mole of B and 0·3 mole of C at equilibrium. Calculate the new equilibrium concentrations of A, B and C if the volume of the container is (a) doubled (b) halved at 200°C.

$$\begin{bmatrix} \text{(a) } [A] = 0.07 \text{ M}, [B] = [C] = 0.18 \text{ M} \\ \text{(b) } [A] = 0.52 \text{ M}, [B] = [C] = 0.48 \text{ M} \end{bmatrix}$$

34. A 2-litre vessel contains 0·48 mole of CO_2, 0·48 mole of H_2, 0·96 mole of H_2O and 0·96 mole of CO at equilibrium.

$$[CO_2\,(g) + H_2\,(g) \rightleftharpoons H_2O\,(g) + CO\,(g)]$$

(a) How many moles and how many grams of H_2 must be added to bring the concentration of CO to 0·60 M?

(b) How many moles and how many grams of CO_2 must be added to bring the CO concentration to 0·60 M?

(c) How many moles of H_2O must be removed to bring the CO concentration to 0·60 M?

$$\left\{\begin{array}{l} \text{(a) } H_2 - 1.2 \text{ mole, } 2.4 \text{ g} \\ \text{(b) } CO_2 - 1.2 \text{ mole, } 53 \text{ g} \\ \text{(c) } H_2O - 1 \text{ mole} \end{array}\right\}$$

35. For the reaction $F_2 \rightleftharpoons 2F$, calculate the degree of dissociation and density of fluorine at 4 atm and 1000 K, when $K_p = 1.4 \times 10^{-2}$ atm.

If $K_p\,(760°) = 2 \times 10^{-5}$ atm and $K_p\,(960°) = 4 \times 10^{-3}$ atm, calculate ΔH^0 for the dissociation of fluorine. (0·03, 18·46)

36. From the following data at 1000 K

$$COCl_2\,(g) \rightleftharpoons CO\,(g) + Cl_2\,(g); \qquad K_1 = 0{\cdot}329$$

$$2CO\,(g) + O_2\,(g) \rightleftharpoons 2CO_2\,(g); \qquad K_2 = 2{\cdot}24 \times 10^{22}$$

Calculate equilibrium constant at 1000 K for

$$2COCl_2\,(g) + O_2\,(g) \rightleftharpoons 2CO_2\,(g) + 2Cl_2\,(g)$$ ($2{\cdot}43 \times 10^{21}$)

37. For the equilibrium $COCl_2\,(g) \rightleftharpoons CO(g) + Cl_2\,(g)$, $K_{1000\,K}$ is 0·329. Suppose that x moles of $COCl_2$ is allowed to reach equilibrium in a one-litre container. What will be the value of x that must be used in order that half the chlorine atoms remain as $COCl_2$? (0·658 mole)

38. N_2O_4 is 25% dissociated at 37°C and 1 atm pressure. Calculate (i) K_p, and (ii) the percentage dissociation at 0·1 atm and 37°C.
[Hint: See Example 14] **(IIT 1988)** (0·267, 63·27%)

39. Sulphide ion in alkaline solution reacts with solid sulphur to form polysulphide ions having formulae S_2^{2-}, S_3^{2-}, S_4^{2-}, and so on. The equilibrium constant for the formation of S_2^{2-} is 12 and for the formation of S_3^{2-} is 130, both from S and S^{2-}. Find the equilibrium constant for the formation of S_3^{2-} from S_2^{2-} and S. (10·83)

[Hint: $S\,(s) + S^{2-} = S_2^{2-}; \quad K_1 = [S_2^{2-}]/[S^{2-}]$

$2S\,(s) + S^{2-} = S_3^{2-}; \quad K_2 = [S_3^{2-}]/[S^{2-}]$

$S\,(s) + S_2^{2-} = S_3^{2-}; \quad K_3 = [S_3^{2-}]/[S_2^{2-}] = \dfrac{K_2}{K_1}$**]**

40. The equilibrium constant K_p at 80°C is 1·57 for the reaction,

$$PH_3BCl_3(s) \rightleftharpoons PH_3(g) + BCl_3(g)$$

(a) Calculate the equilibrium pressures of $PH_3(g)$ and $BCl_3(g)$ if a sample of PH_3BCl_3 is placed in a closed vessel at 80°C and allowed to decompose until equilibrium is attained.
(b) What is the minimum amount of PH_3BCl_3 that must be placed in a 0·5-litre vessel at 80°C if equilibrium is to be attained? (1·253 atm; 4·568 g)

41. A mixture of 3·0 moles of SO_2, 4·0 moles NO_2, 1·0 mole of SO_3 and 4·0 moles of NO is placed in a 2·0-litre vessel.

$$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$$

At equilibrium, the vessel is found to contain 1·0 mole of SO_2.
(a) Calculate the equilibrium concentrations of SO_2, NO_2, SO_3 and NO.
(b) Calculate the value of K_c. (0·5 M, 1·0 M, 1·5 M, 3·0 M; 9·0)

42. When 20·0 g of $CaCO_3$ in a 10·0-litre flask is heated to 800°C, 35% of it did not dissociate, calculate K_p for the equilibrium

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$ (1·145 atm)

43. At 298 K, 550 g of D_2O (20 g/mole, density 1·10 g/mL) and 498·5 g of H_2O (18 g/mole, density 0·997 g/mL) are mixed. The volumes are additive. 47·0% of the H_2O reacts to form HDO. Calculate K_c at 298 K for the reaction

$$H_2O + D_2O \rightleftharpoons 2HDO$$

(3·18)

44. At 300 K, the equilibrium constant for the reaction

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

is $6{\cdot}98 \times 10^{24}$. Calculate ΔG^0 of the reaction and $\Delta G_f^0(SO_3)$. Given that $\Delta G_f^0(SO_2) = -300{\cdot}12$ kJ/mole.

(142·7 kJ/mole, 371·5 kJ/mole)

45. What kind of equilibrium constant can be calculated from a ΔG^0 value for a reaction involving only gases?

(K_p)

46. Calculate K_p for the reaction

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

if at a particular temperature and a total pressure of 112·0 atm, the equilibrium mixture consists of 56·6 mole per cent SO_2, 10·6 mole per cent O_2, and 32·8 mole per cent SO_3.

(0·0283)

47. The standard Gibbs free energy change for the reaction :

$$2AB \rightleftharpoons A_2 + B_2$$

is 11·8 kJ at 230 K and 1 atm. Calculate the degree of dissociation of HI at 230 K.

(0·084)

48. Determine the equilibrium concentrations that result from the reaction of a mixture of 0·10 mole of H_2 and 0·050 mole of F_2 in a 1·0-litre flask according to the equation

$H_2(g) + F_2(g) \rightleftharpoons 2HF(g)$; K = 115 ($[H_2] = 0{\cdot}052$, $[F_2] = 0{\cdot}002$, $[HF] = 0{\cdot}097$ M)

49. A stream of gas containing H_2 at an initial partial pressure of 0·20 atm is passed through a tube in which CuO is kept at 500 K. The reaction

$$CuO(s) + H_2(g) \rightleftharpoons Cu(s) + H_2O(g)$$

comes to equilibrium. For this reaction, $K_p = 1{\cdot}6 \times 10^9$. What is the partial pressure of H_2 in the gas leaving the tube? Assume that the total pressure of the stream is unchanged.

(negligibly small)

50. At 973 K, K_p is 1·50 for the reaction

$$C(s) + CO_2(g) \rightleftharpoons 2CO(g)$$

Suppose the total gas pressure at equilibrium is 1·0 atm. What are the partial pressures of CO and CO_2?

(CO–0·686 atm, CO_2–0·314 atm)

51. A flask contains $NH_4Cl(s)$ in equilibrium with its decomposition products.

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$$

For this reaction, $\Delta H = 176$ kJ/mole. How is the mass of NH_3 in the flask affected by each of the following disturbances?

(a) The temperature is decreased
(b) NH_3 is added
(c) HCl is added
(d) NH_4Cl is added with no appreciable change in volume
(e) A large amount of NH_4Cl is added decreasing the volume available to the gases.

((a) Increase (b) Increase (c) Decrease (d) No effect (e) Decrease)

52. Chlorine molecules are 1·0% dissociated at 975 K at a pressure of 1·0 atm (1·0% of the pressure is due to Cl atoms).

$$Cl_2(g) \rightleftharpoons 2Cl$$

Calculate K_p and K_c. ($1{\cdot}01 \times 10^{-4}$, $1{\cdot}26 \times 10^{-6}$)

53. Show that: $2{\cdot}303 \log K = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$

[**Hint:** Use equations 12 and 22 (Ch. 14)]

54. Calculate the equilibrium ratio of C to A if 2·0 moles each of A and B were allowed to come to equilibrium at 300 K

$$A + B \rightleftharpoons C + D; \Delta G^0 = 460 \text{ cal}$$

(0·679)

55. Calculate ΔE^0 for the reaction:

$$2A(g) + B(g) \rightleftharpoons A_2B(g)$$

for which $\Delta S^0 = 5{\cdot}0$ J/K, $K = 1{\cdot}0 \times 10^{-10}$ and $T = 300$ K

[**Hint:** Apply $\Delta G^0 = 2{\cdot}303\, RT \log K$, $\Delta H^0 = \Delta G^0 + T\Delta S^0$ and then $\Delta E^0 = \Delta H^0 - \Delta n_g RT$]

(63·8 kJ)

Objective Problems

1. 120 g of urea is dissolved in 5 litres. The active mass of urea is
   (a) 0·08 (b) 0·4 (c) 120/5 (d) 5/120

2. For the equilibrium $A + B \rightleftharpoons C + D$, equilibrium constant may be equal to
   (a) $\frac{[C]\cdot[A]}{[D]\cdot[B]}$ (b) $\frac{[A]\cdot[B]}{[C]\cdot[D]}$ (c) $\frac{[C]+[D]}{[A]+[B]}$ (d) all wrong

3. For which of the following reactions, K_p may be equal to 0·5 atm?
   (a) $2HI \rightleftharpoons H_2 + I_2$ (b) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$
   (c) $N_2 + 3H_2 \rightleftharpoons 2NH_3$ (d) $2NO_2 \rightleftharpoons N_2O_4$

4. Which of the following is correct?
   (a) K_p will always have some unit
   (b) K_c will always have some unit
   (c) K_x will never have any unit
   (d) When $\Delta n = 0$, $K_p = K_c = K_x$ then all the three Ks have the same unit

5. K_p/K_c for the reaction $CO + \frac{1}{2}O_2 \rightleftharpoons CO_2$ is
   (a) RT (b) $1/\sqrt{RT}$ (c) $\sqrt{RT}$ (d) 1

6. If the initial number of moles/L of N_2, H_2 and NH_3 are 1, 2 and 3 respectively, their concentrations at equilibrium will be

N_2	+ $3H_2$	$\rightleftharpoons$ $2NH_3$
(a) $(1 - x)$	$(2 - 3x)$	$2x$
(b) $(1 - x/3)$	$(2 - x)$	$2x/3$
(c) $(1 - x)$	$(2 - x)$	$(3 + x)$
(d) $(1 - x)$	$(2 - 3x)$	$(3 + 2x)$

7. A 1-litre container contains 2 moles of PCl_5 initially. If at equilibrium, K_c is found to be 1, the degree of dissociation of PCl_5 is

(a) 1 (b) –1 (c) $\frac{1}{2}$ (d) 50

8. The vapour density of undecomposed N_2O_4 is 46. When heated, the vapour density decreases to 24·5 due to its dissociation to NO_2. The percentage dissociation of N_2O_4 at the final temperature is

(a) 87 (b) 60 (c) 40 (d) 70

9. If the equilibrium constants of the following equilibrium

$$SO_2 + 1/2O_2 \rightleftharpoons SO_3 \quad \text{and} \quad 2SO_3 \rightleftharpoons 2SO_2 + O_2$$

are given by K_1 and K_2 respectively, which of the following relations is correct?

(a) $K_2 = \left(\frac{1}{K_1}\right)^2$ (b) $K_1 = \left(\frac{1}{K_2}\right)^3$ (c) $K_2 = \frac{1}{K_1}$ (d) $K_2 = (K_1)^2$

10. For the reactions

$$A \rightleftharpoons B \qquad K_c = 2$$
$$B \rightleftharpoons C \qquad K_c = 4$$
$$C \rightleftharpoons D \qquad K_c = 6$$

K_c for the reaction $A \rightleftharpoons D$ is

(a) $(2+4+6)$ (b) $\frac{2\times4}{6}$ (c) $\frac{4\times6}{2}$ (d) $2\times4\times6$

11. For the equilibrium $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, which of the following expressions is correct?

(a) $K_p = \frac{[CaO].[CO_2]}{[CaCO_3]}$ (b) $K_p = \frac{p_{CaO} \times p_{CO_2}}{p_{CaCO_3}}$

(c) $K_p = p_{CO_2}$ (d) $K_p = \frac{p_{CaO} + p_{CO_2}}{p_{CaCO_3}}$

12. For the reaction $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$, the partial pressures of CO_2 and CO are respectively 4 and 8 atm. K_p for the reaction is

(a) 16 (b) 2 (c) 0·5 (d) 4

13. K_c for $A + B \rightleftharpoons 3C$ is 20 at 25°C. If a 2-litre vessel contains 1, 2 and 4 moles of A, B and C respectively, the reaction at 25°C shall

(a) proceed from left to right (b) proceed from right to left
(c) be at equilibrium (d) not occur

14. K_c for $A + B \rightleftharpoons C + D$ is 10 at 25°C. If a container contains 1, 2, 3 and 4 moles of A, B, C and D respectively at 25°C, the reaction shall

(a) proceed from left to right (b) proceed right to left
(c) be at equilibrium (d) not occur

15. A 1-litre vessel contains 2 moles each of gases A, B, C and D at equilibrium. If 1 mole each of A and B are removed, K_c for $A + B \rightleftharpoons C + D$ will be

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

16. Two samples of HI each of 5 g were taken separately in two vessels of volume 5 and 10 litres respectively at 27°C. The extent of dissociation of HI will be
(a) more in the 5-litre vessel (b) more in the 10-litre vessel
(c) equal in both vessels (d) nil at both

17. For a reversible reaction if the concentrations of the reactants are doubled, the equilibrium constant will be
(a) doubled (b) halved
(c) one-fourth (d) the same

18. If one-third of HI decomposes at a particular temperature, K_c for $2HI \rightleftharpoons H_2 + I_2$ is
(a) 1/16 (b) 1/4 (c) 1/6 (d) 1/2

19. 28 g of N_2 and 6 g of H_2 were mixed. At equilibrium 17 g NH_3 was produced. The weights of N_2 and H_2 at equilibrium are respectively
(a) 11 g, 0 g (b) 1 g, 3 g
(c) 14 g, 3 g (d) 11 g, 3 g

20. For the reaction: $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, the equilibrium constant K_p changes with
(a) total pressure (b) catalyst
(c) the amount of H_2 and I_2 present (d) temperature

21. The oxidation of SO_2 by O_2 to SO_3 is an exothermic reaction. The yield of SO_3 will be maximum if
(a) temperature is increased and pressure is kept constant
(b) temperature is reduced and pressure is increased
(c) both temperature and pressure are increased
(d) both temperature and pressure are reduced.

22. For the gas phase reaction $C_2H_4 + H_2 \rightleftharpoons C_2H_6$ ($\Delta H = -32.7$ kcal) carried out in a vessel, the equilibrium concentration of C_2H_4 can be increased by
(a) increasing the temperature (b) decreasing the pressure
(c) removing some H_2 (d) adding some C_2H_6

23. Pure ammonia is placed in a vessel at a temperature where its dissociation constant is appreciable. At equilibrium,
(a) K_p does not change significantly with pressure
(b) α does not change with pressure
(c) concentration of NH_3 does not change with pressure
(d) concentration of H_2 is less than that of N_2

24. An example of a reversible reaction is
(a) $Pb(NO_3)_2\,(aq) + 2NaI\,(aq) = PbI_2\,(s) + 2NaNO_3\,(aq)$
(b) $AgNO_3\,(aq) + HCl\,(aq) = AgCl\,(s) + HNO_3\,(aq)$
(c) $2Na\,(s) + H_2O\,(l) = 2NaOH\,(aq) + H_2\,(g)$
(d) $KNO_3\,(aq) + NaOH\,(aq) = KOH\,(aq) + NaNO_3\,(aq)$ (IIT 1985)

25. When $NaNO_3$ is heated in a closed vessel, O_2 is liberated and $NaNO_2$ is left behind. At equilibrium

(a) addition of $NaNO_2$ favours reverse reaction
(b) addition of $NaNO_3$ favours forward reaction
(c) increasing temperature favours forward reaction
(d) increasing pressure favours forward reaction

(IIT 1986)

26. The equilibrium $SO_2Cl_2\,(g) \rightleftharpoons SO_2(g) + Cl_2\,(g)$ is attained at 25°C in a closed container and an inert gas, helium, is introduced. Which of the following statements are correct?
(a) Concentrations of SO_2, Cl_2 and SO_2Cl_2 change
(b) More Cl_2 is formed
(c) Concentration of SO_2 is reduced
(d) More SO_2Cl_2 is formed

(IIT 1989)

27. The decomposition of N_2O_4 into NO_2 is carried out at 280 K in chloroform. When equilibrium has been established, 0·2 mole of N_2O_4 and 2×10^{-3} mole of NO_2 are present in 2 litres of 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}

28. The equilibrium constants for the reaction $Br_2 \rightleftharpoons 2Br$ at 500 K and 700 K are 1×10^{-10} and 1×10^{-5} respectively. The reaction is
(a) endothermic (b) exothermic
(c) fast (d) slow

29. Which oxide of nitrogen is most stable at 273 K?
(a) $2N_2O_5 \rightleftharpoons 2N_2 + 5O_2$; $K_c = 1 \times 10^{34}$
(b) $2N_2O \rightleftharpoons 2N_2 + O_2$; $K_c = 1 \times 10^{32}$
(c) $2NO \rightleftharpoons N_2 + O_2$; $K_c = 1 \times 10^{30}$
(d) $2NO_2 \rightleftharpoons N_2 + 2O_2$; $K_c = 1 \times 10^{15}$

30. If a chemical reaction is at equilibrium, which of the following is not correct?
(a) $\Delta G^0 = 0$ (b) $K_p = 1$
(c) $K_c = 1$ (d) $\Delta G^0 = 1$

31. If pressure is applied to the equilibrium system of solid $\rightleftharpoons$ liquid, the melting point of the solid
(a) will not change
(b) may increase or decrease depending upon its nature
(c) will always increase
(d) will always decrease

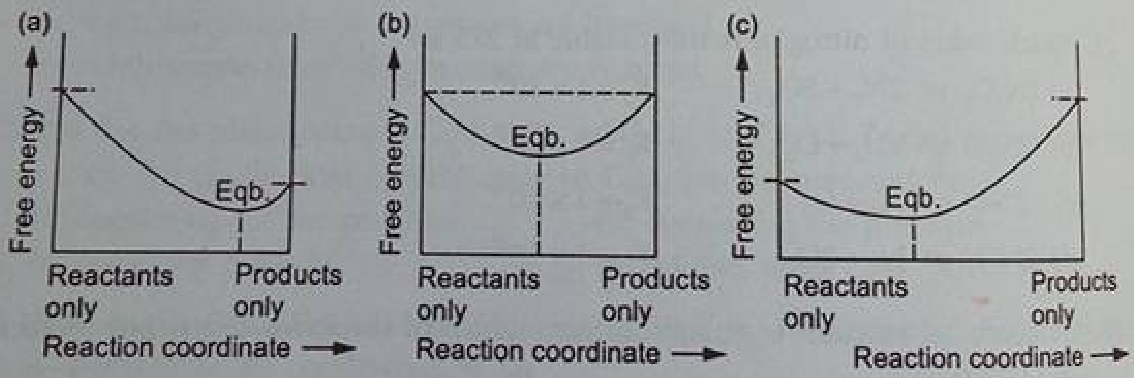
32. If pressure is applied to the following equilibrium of liquid $\rightleftharpoons$ vapour, the boiling point of the liquid
(a) will decrease (b) will increase
(c) may increase or decrease (d) will not change

33. For the equilibrium $PCl_5 \rightleftharpoons PCl_3 + Cl_2$, $K_p = \frac{\alpha^2}{(1-\alpha)V}$; temperature remaining constant,
(a) K_p will increase with the increase in volume
(b) K_p will increase with the decrease in volume
(c) K_p will not change with the change in volume
(d) K_p may increase or decrease with the change in volume

34. When $CaCO_3$ is heated at a constant temperature in a closed container, the pressure due to CO_2 produced will
(a) change with the amount of $CaCO_3$ taken
(b) change with the size of the container
(c) remain constant so long as temperature is constant
(d) remain constant even if temperature is changed

35. 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 chlorine gas at constant volume
(c) introducing an inert gas at constant pressure
(d) increasing the volume of the container
(e) introducing PCl_5 at constant volume

36. Which of the following curves represents a very rare standard reaction at equilibrium?



37. Which of the curves given in Q. 36 represents a standard reaction spontaneous in forward direction?

38. Which of the curves given in Q. 36 represents a standard reaction for which $\Delta G^0 > 0$?

39. Which of the curves given in Q. 36 represents a standard reaction with $K = 1$?

40. Each of the mixtures listed below was placed in a closed container and allowed to stand. Which of the following mixtures is not capable of attaining the equilibrium: $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$?
(a) Pure $CaCO_3$
(b) CaO and a pressure of CO_2 greater than K_p

(c) Some $CaCO_3$ and a pressure of CO_2 greater than K_p
(d) $CaCO_3$ and CaO

41. Consider the following equilibrium in a closed container:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

At a fixed temperature, the volume of the reaction container is halved. For this change which of the following statements holds true regarding the equilibrium constant (K_p) and degree of dissociation (α)?

(a) Neither K_p nor α changes
(b) Both K_p and α change
(c) K_p changes, but α does not change
(d) K_p does not change but α changes

(IIT 2002)

42. The value of the reaction quotient before any reaction occurs is
(a) ∞ (b) -1 (c) 0 (d) 1

43. What is the minimum mass of $CaCO_3$, below which it decomposes completely, required to establish equilibrium in a 6·50-litre container for the reaction: $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$?

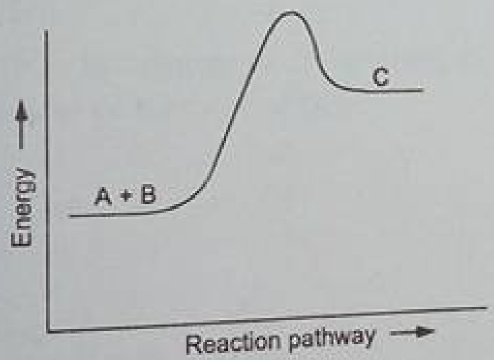
($K_c = 0{\cdot}05$ mole/litre)

(a) 32·5 g (b) 24·6 g (c) 40·9 g (d) 8·0 g

44. The energy profile of the reaction:

$$A + B \rightleftharpoons C$$

is shown as,



The equilibrium constant for the said equilibrium
(a) increases with the increase in temperature
(b) decreases with the increase in temperature
(c) does not change with the change in temperature
(d) is equal to the rate constant of the forward reaction

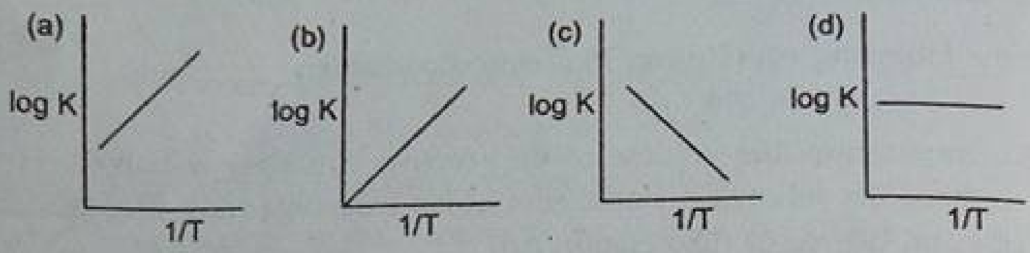
45. NiO is to be reduced to Ni in an industrial process by the use of the reaction

$$NiO(s) + CO(g) \rightleftharpoons Ni(s) + CO_2(g)$$

At 1600 K, the equilibrium constant for the reaction is 600. If a CO pressure of 150 mmHg is to be employed in the furnace and the total pressure never exceeds 760 mmHg, will the reduction occur?

(a) Yes (b) No

46. Which of the following curves between log K and $\frac{1}{T}$ is correct?



Answers

1-b, 2-b, 3-b, 4-c, 5-b, 6-d, 7-c, 8-a, 9-a, 10-d, 11-c, 12-a, 13-a, 14-a, 15-b, 16-c, 17-d, 18-a, 19-c, 20-d, 21-b, 22-All correct, 23-a, 24-d, 25-c, 26-All wrong, 27-c, 28-a, 29-d, 30-d, 31-b, 32-b, 33-c, 34-c, 35-c, d and e, 36-b, 37-a, 38-c, 39-b, 40-c, 41-d, 42-c, 43-a, 44-a, 45-a, 46-c.

❑❑❑

IONIC EQUILIBRIUM IN AQUEOUS SOLUTIONS

This chapter is an extension to the previous chapter 'Chemical Equilibrium'. Here, only such chemical equilibria shall be considered which involve ions in aqueous solutions, and so only K_c (not K_p) is considered as equilibrium constant. In ionic equilibria, for different types of reactions, K_c is expressed by different notations, viz., K_a, K_b, K_w, K_{sp}, etc. These constants will thus have the same physical significance as that of K_c. Let us now discuss different types of ionic equilibria.

Relative Strengths of Acids and Bases

The relative strengths of acids and bases are generally determined by their dissociation constants K_a and K_b respectively.

For an acid of the type HA

$$\begin{array}{ccccccl} c & & 0 & & 0 & & \text{Initial concentrations} \\ HA & \rightleftharpoons & H^+ & + & A^- & & \\ c(1-x) & & cx & & cx & & \text{Concentration at equilibrium} \end{array}$$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{cx \cdot cx}{c(1-x)} = \frac{cx^2}{1-x}$$

$$= cx^2 \text{ (if } x \text{, i.e., degree of dissociation, is very small).}$$

Similarly, for a base of the type of BOH

$$\begin{array}{ccccc} c & & 0 & & 0 \\ BOH & \rightleftharpoons & B^+ & + & OH^- \\ c(1-x) & & cx & & cx \end{array}$$

$$K_b = \frac{[B^+][OH^-]}{[BOH]} = \frac{cx \cdot cx}{c(1-x)} = \frac{cx^2}{(1-x)} = cx^2 \quad \text{(if } x \text{ is very small).}$$

K_a and K_b are just the equilibrium constants and hence depend only on temperature. The greater the value of dissociation constant of the acid (K_a), the more is the strength of the acid and similarly, the greater the value of dissociation constant (K_b), the more is the strength of the base.

The strengths of acids and bases depend on the roles of the solvents used. The greater the tendency of the solvent to accept protons, the more will be the strength of the acid giving protons. Acids like HCl, H_2SO_4, etc., dissociate completely in water (solvent) as water accepts all their protons. Thus, these acids in water have equal acid strength (levelling effect). But the same acids, when taken in acetic acid (solvent), dissociate partially and act as weak acids.

where, $pH = \frac{(pH)_1 + (pH)_2}{2} = \frac{2\cdot286 + 9\cdot719}{2} = 6\cdot003.$

PROBLEMS

(Answers bracketed with questions)

1. Calculate the degree of ionisation of 0·4 M acetic acid in water. Dissociation constant of acetic acid is $1\cdot8 \times 10^{-5}$. $(6\cdot71 \times 10^{-3})$

2. Calculate the degree of dissociation of 0·2 N of a monobasic acid at 25°C. The dissociation constant of acetic acid at this temperature is $1\cdot8 \times 10^{-5}$. What will be the H^+ concentration? $(9\cdot48 \times 10^{-3}, 1\cdot89 \times 10^{-3}$ M)

   [Hint: $K = \frac{0\cdot2x^2}{(1-x)} = 1\cdot8 \times 10^{-5}$; $[H^+] = 0\cdot2x$, x is the degree of dissociation]

3. Calculate $[OH^-]$ for a solution whose pH is 6·2. $(1\cdot6 \times 10^{-8}$ M)

4. The dissociation constant of HCN is $4\cdot8 \times 10^{-10}$. What is the concentration of H_3O^+, OH^- and HCN in a solution prepared by dissolving 0·16 mole of NaCN in 450 mL of water at 25°C? $([OH^-] = [HCN] = 2\cdot72 \times 10^{-3}$ M)

   [Hint: Apply Equation 11(a).]

5. At what concentration of the solution will the degree of dissociation of nitrous acid be 0·2? K_a for HNO_2 is 4×10^{-4}. (0·008 M)

6. The degree of dissociation of acetic acid in a 0·1 N solution is $1\cdot32 \times 10^{-2}$. At what concentration of nitrous acid will its degree of dissociation be the same as that of acetic acid? $\{K_a (HNO_2) = 4 \times 10^{-4}\}$ (2·3 mole/litre)

7. Calculate the pH of the following aqueous solutions:
   (i) 5×10^{-8} M HCl (ii) 5×10^{-10} M HCl
   (iii) 10^{-8} M NaOH (iv) 10^{-10} M NaOH (6·89, 7, 7·02, 7)

8. Compute the pH of a solution at 25°C which is twice as alkaline as pure water. (7·3)

9. How many times is the H^+ concentration in the blood (pH = 7·36) greater than in the spinal fluid (pH = 7·53)? (1·5 times)

10. Calculate the pH of an NaOH solution, the concentration of which is 0·1 g/L. Assume the dissociation of NaOH to be complete. (11·40)

11. Find the pH of a 0·01 M solution of acetic acid, dissociating to the extent of 4·2%. (3·38)

12. Determine the pH value of a solution obtained by mixing 25 mL of 0·2 M HCl and 50 mL of 0·25 N NaOH solutions. (13)

13. Calculate how many H^+ ions are present in one millionth part of 1 mL of pure water. The ionic product of water is $1 \times 10^{-14}\ (\text{mol/L})^2$ (60·3 million)

14. Assuming the first step of dissociation to be complete, find the concentrations of all species in a 0·1 M H_2SO_4 solution. $K_2 = 1{\cdot}2 \times 10^{-2}$.

($[H_2SO_4] = 0\ M$, $[HSO_4^-] = 0{\cdot}09\ M$, $[H^+] = 0{\cdot}11\ M$)

15. Calculate the concentrations of various species in a 0·1 M H_2S saturated solution. $K_1 = 1 \times 10^{-7}$ and $K_2 = 1{\cdot}3 \times 10^{-13}$.

$$\begin{bmatrix} [H_2S] \approx 0{\cdot}1\ M \\ [S^{2-}] = 1{\cdot}3 \times 10^{-13}\ M \\ [HS^-] = 1 \times 10^{-4}\ M \\ [H^+] = 1 \times 10^{-4}\ M \end{bmatrix}$$

16. A weak base BOH of concentration 0·02 mole/litre has a pH value of 10·45. If 100 mL of this base is mixed with 10 mL of 0·1 M HCl, what will be the pH of the mixture? (8·59)

17. How will the pH increase if 0·05 mole of sodium acetate is added to 1 litre of a 0·005 M acetic acid solution? $K_a\ (CH_3COOH) = 1{\cdot}8 \times 10^{-5}$. (pH increases by 2·21)

18. Calculate the pH of 0·1 M acetic acid solution if its dissociation constant is $1{\cdot}8 \times 10^{-5}$. If 1 litre of this solution is mixed with 0·05 mole of HCl, what will be pH of the mixture? (2·87, 1·3)

19. 2·05 g of sodium acetate was added to 100 mL of 0·1 M HCl solution. Find the H^+ ion concentration of the resulting solution. If 6 mL of 1 M HCl is further added to it, what will be the new H^+ concentration? ($1{\cdot}23 \times 10^{-5}$ M, $1{\cdot}36 \times 10^{-5}$ M)

20. Calculate the pH of a buffer solution prepared by dissolving 30 g of Na_2CO_3 in 500 mL of an aqueous solution containing 150 mL of 1 M HCl.
$K_a(H_2CO_3) = 4{\cdot}2 \times 10^{-7}$; $K_a(HCO_3^-) = 4{\cdot}8 \times 10^{-11}$ (10·3)

21. The pH of a buffer solution containing 0·1 M CH_3COOH and 0·1 M CH_3COONa is 4·74. What will be the pH if 0·05 mole of HCl is added to one litre of this buffer solution? $K_a\ (CH_3COOH) = 1{\cdot}8 \times 10^{-5}$. (4·27)

22. The concentration of hydrogen ion in a 0·2 M solution of formic acid is $6{\cdot}4 \times 10^{-3}$ mole per litre. To this solution sodium formate is added so as to adjust the concentration of sodium formate to one mole per litre. What will be the pH of this solution? The dissociation constant of formic acid is $2{\cdot}4 \times 10^{-4}$ and the degree of dissociation of sodium formate is 0·75. **(IIT 1985)** (4·19)

23. When 0·20 M acetic acid is neutralised with 0·20 M NaOH in 0·50 litre of solution, the resulting solution is slightly alkaline. Calculate the pH of the resulting solution. $K_a\ (CH_3COOH) = 1{\cdot}8 \times 10^{-5}$. (9·02)

24. The pH of a 0·1 M solution of NH_4Cl is 5·13. Find the dissociation constant of NH_4OH. $(1{\cdot}8 \times 10^{-5})$

25. A buffer solution is prepared by dissolving 0·2 mole of sodium formate and 0·25 mole of formic acid in approximately 200 (± 50) mL of water. What will be the concentration of H^+ and OH^-? K_a (HCOOH) = $1{\cdot}8 \times 10^{-4}$ $([OH^-] = 4{\cdot}4 \times 10^{-11})$

26. A buffer solution was prepared by dissolving 0·05 mole formic acid and 0·06 mole sodium formate in enough water to make 1 litre of solution. $K_a(HCOOH) = 1{\cdot}8 \times 10^{-4}$.
(a) Calculate the pH of the solution.
(b) If this solution were diluted to 10 times its volume, what would be the pH? (3·83, 3·83)

27. How many gram moles of HCl will be required to prepare one litre of a buffer solution (containing NaCN and HCl) of pH 8·5 using 0·01 gram-formula weight of NaCN? $K_{dissociation}$ (HCN) = $4{\cdot}1 \times 10^{-10}$ (IIT 1988) (0·0088 mole)

28. The pK_a of acetyl salicylic acid (aspirin) is 3·5. The pH of gastric juice in the human stomach is about 2–3 and the pH in the small intestine is about 8. Aspirin will be
(a) un-ionised in the small intestine and in the stomach
(b) completely ionised in the small intestine and in the stomach
(c) ionised in the stomach and almost un-ionised in the small intestine
(d) ionised in the small intestine and almost un-ionised in the stomach
(IIT 1988) (d)

29. Calculate the degree of hydrolysis of an N/10 KCN solution at 25°C. K_a (HCN) = $7{\cdot}2 \times 10^{-10}$; $K_w = 1 \times 10^{-14}$. (1·18%)

30. Calculate the degree of hydrolysis of CH_3COOK in 0·1 M and the pH of the solution. $K_a(CH_3COOH) = 1{\cdot}8 \times 10^{-5}$ $(7{\cdot}5 \times 10^{-5}$; 8·88)

31. Calculate the hydrolysis constant of NH_4Cl; determine the degree of hydrolysis of this salt in 0·01 M solution and the pH of the solution. $(5{\cdot}6 \times 10^{-10}$, $2{\cdot}4 \times 10^{-4}$, 5·63)
$K_b(NH_4OH) = 1{\cdot}8 \times 10^{-5}$

32. A 0·02 M solution of CH_3COONa in water at 25°C is found to have an H^+ concentration of 3×10^{-9} g ionic weight per litre. What is the hydrolytic constant of the salt? $K_w = 1{\cdot}01 \times 10^{-14}$, K_a $(CH_3COOH) = 1{\cdot}75 \times 10^{-5}$. $(5{\cdot}68 \times 10^{-10})$

33. Calculate the hydrolysis constant of the reaction

$$HCO_2^- + H_2O \rightleftharpoons HCO_2H + OH^-$$

and find the concentrations of H_3O^+, OH^-, HCO_2^- and HCO_2H in a solution of 0·15 M HCO_2Na. K_a (HCOOH) ⇌ $1{\cdot}8 \times 10^{-4}$. $(5{\cdot}56 \times 10^{-11})$
[Hint: See equations 10 and 11.]

34. Calculate the pH of each of the following solutions:

(a) 100 mL 0·1 M CH_3COOH mixed with 100 mL of 0·1 M NaOH

(b) 100 mL of 0·1 M CH_3COOH mixed with 50 mL of 0·1 M NaOH

(c) 50 mL of 0·1 M CH_3COOH mixed with 100 mL of 0·1 M NaOH

(K_a (CH_3COOH) $= 1{\cdot}8 \times 10^{-5}$, $K_w = 1 \times 10^{-14}$) [(a) 8·72 (b) 4·75 (c) 12·52]

[Hint: (a) Calculate pH due to hydrolysis of CH_3COONa produced.

(b) Calculate pH of the buffer solutions of CH_3COOH and CH_3COONa produced.

(c) Calculate pH only due to NaOH remained.]

35. Determine the solubility of AgCl (in mole/litre) in water.

K_{sp} (AgCl) $= 1{\cdot}8 \times 10^{-10}$. ($1{\cdot}3 \times 10^{-5}$ mole/litre)

36. What is the solubility product of Ag_2CrO_4 if 0·0166 g of the salt dissolves in 500 mL of water at 18°C? [K_{sp} (Ag_2CrO_4) $= 4 \times 10^{-12}$]

37. The solubility of lead sulphate in water is $1{\cdot}03 \times 10^{-4}$. Calculate its solubility in a centinormal solution of H_2SO_4 · K_{sp} ($PbSO_4$) $= 1{\cdot}6 \times 10^{-8}$. ($2{\cdot}1 \times 10^{-6}$)

38. The solubility of bismuth sulphide in water at 20°C is $1{\cdot}7 \times 10^{-15}$ mol/L. Calculate the value of K_{sp}. ($1{\cdot}5 \times 10^{-72}$)

39. Calculate the solubility of $Mg(OH)_2$ in 0·05 M NaOH.

K_{sp} ($Mg(OH)_2$) $= 8{\cdot}9 \times 10^{-12}$. ($3{\cdot}6 \times 10^{-9}$ mole/litre)

40. Equal volumes of 0·02 N solutions of $CaCl_2$ and Na_2SO_4 are mixed. Will there be a formation of $CaSO_4$ precipitate? K_{sp} ($CaSO_4$) $= 1{\cdot}3 \times 10^{-4}$. (No)

41. 450 mL of 0·001 N solution of $AgNO_3$ is added to 50 mL of 0·001 N solution of HCl. Will there be a formation of precipitate of AgCl?

K_{sp} (AgCl) $= 1{\cdot}8 \times 10^{-10}$. (Yes)

42. The solubility of CaF_2 in water at 18°C is $2{\cdot}04 \times 10^{-4}$ mole/litre. Calculate K_{sp} of CaF_2 and its solubility in 0·01 molar NaF solution.

($3{\cdot}4 \times 10^{-11}$; $3{\cdot}4 \times 10^{-7}$ mole/litre)

43. Will a precipitate of silver sulphate form if equal volumes of 1 N H_2SO_4 and 0·02 M $AgNO_3$ solutions are mixed? K_{sp} (Ag_2SO_4) $= 2 \times 10^{-5}$. (Yes)

44. Will a precipitate of $CaSO_4$ form if

(i) equal volumes of 0·02 M $CaCl_2$ and 0·0004 M Na_2SO_4 solutions are mixed?

(ii) equal volumes of 0·08 M $CaCl_2$ and 0·02 M Na_2SO_4 are mixed?

K_{sp} ($CaSO_4$) $= 2{\cdot}4 \times 10^{-5}$. [(i) No (ii) Yes]

45. A solution containing 0·01 mole/litre of $CaCl_2$ and 0·01 mole/litre of $SrCl_2$ is slowly added to a 0·01 N solution of H_2SO_4. Which substance begins to precipitate earlier? (a) $SrSO_4$ (b) $CaSO_4$. $K_{sp}(SrSO_4) = 3{\cdot}2 \times 10^{-7}$; $K_{sp}(CaSO_4) = 1{\cdot}3 \times 10^{-4}$. ($SrSO_4$)

46. If the solubility product of silver oxalate is 1×10^{-11}, what will be the weight of $Ag_2C_2O_4$ in 2·5 litres of a saturated solution? (0·103 g)

47. Find the solubility of CaF_2 in 0·05 M solution of $CaCl_2$ and water. How many times is the solubility in the second case greater than in the first? $K_{sp}(CaF_2) = 4 \times 10^{-11}$.
($1{\cdot}4 \times 10^{-5}$, $2{\cdot}15 \times 10^{-4}$ mole/litre; 15·4 times)

48. How will the concentration of Ag^+ in a saturated solution of AgCl diminish if such an amount of HCl is added to it that the concentration of the Cl^- in the solution becomes equal to 0·03 mole/litre? $K_{sp}(AgCl) = 1{\cdot}8 \times 10^{-10}$.
$\left(\frac{1}{2230}\text{ of its initial value}\right)$

49. How does the solubility of CaC_2O_4 in a 0·1 M solution of $(NH_4)_2C_2O_4$ decrease in comparison with its solubility in water? Assume that the ionisation of $(NH_4)_2C_2O_4$ is complete. $K_{sp}(CaC_2O_4) = 2 \times 10^{-9}$.
$\left(\frac{1}{2200}\text{ of its solubility in water}\right)$

50. Solid $AgNO_3$ is gradually added to a solution containing Cl^- and I^-. If K_{sp} values of AgCl and AgI are respectively $1{\cdot}7 \times 10^{-10}$ and $1{\cdot}5 \times 10^{-16}$, which one will precipitate first? Also, find the relative concentration of $[I^-]$ to $[Cl^-]$ just before the precipitation of AgCl.
$\left(\text{AgI}, \frac{[I^-]}{[Cl^-]} = 10^{-6}\right)$

51. Given that 2×10^{-4} mole each of Mn^{2+} and Cu^{2+} was contained in one litre of a 0·003 M $HClO_4$ solution, and this solution was saturated with H_2S. Determine whether or not each of these ions, Mn^{2+} and Cu^{2+}, will precipitate as sulphide. The solubility of H_2S, 0·1 mole per litre, is assumed to be independent of the presence of other materials in the solution.

$$K_{sp}(MnS) = 3 \times 10^{-14},\ K_{sp}(CuS) = 8 \times 10^{-37}.$$

K_1 and K_2 for H_2S are 1×10^{-7} and $1{\cdot}1 \times 10^{-14}$ respectively. Also, calculate the percentage of Cu remaining unprecipitated. Will MnS precipitate if the above solution is made neutral by lowering the $[H^+]$ to 10^{-7} M?
(CuS precipitates; $3{\cdot}27 \times 10^{-14}$ %; MnS precipitates)

52. What pH must be maintained in a solution saturated in H_2S (0·1 M) and 10^{-3} M in Zn^{2+} to prevent ZnS from precipitating? (pH < 2)
$K_{sp}(ZnS) = 1 \times 10^{-21}$, $K_a(H_2S) = 1{\cdot}1 \times 10^{-21}$.

53. Should FeS precipitate from a solution that is saturated in H_2S (0·1 M), 0·002 M in Fe^{2+} and at a pH = 3·5?
K_{sp} (FeS) = $6{\cdot}3 \times 10^{-18}$, K_a (H_2S) = $1{\cdot}1 \times 10^{-21}$. (No)

54. A buffer solution is 0·25 M CH_3COOH – 0·15 M CH_3COONa, saturated in H_2S (0·1 M) and has $[Mn^{2+}] = 0{\cdot}015$ M. K_a (CH_3COOH) = $1{\cdot}74 \times 10^{-5}$,
K_a (H_2S) = $1{\cdot}1 \times 10^{-21}$ and K_{sp} (MnS) = $2{\cdot}5 \times 10^{-13}$.
(a) Will MnS precipitate?
(b) Which buffer component should be increased in concentration and to which minimum value to just start precipitation of MnS?
[(a) No (b) $[CH_3COO^-] = 1{\cdot}7$ M]

55. When equal volumes of the following solutions are mixed, precipitation of AgCl ($K_{sp} = 1{\cdot}8 \times 10^{-10}$) will occur only with
(a) 10^{-4} M (Ag^+) and 10^{-4} M (Cl^-)
(b) 10^{-5} M (Ag^+) and 10^{-5} M (Cl^-)
(c) 10^{-6} M (Ag^+) and 10^{-6} M (Cl^-)
(d) 10^{-10} M (Ag^+) and 10^{-10} M (Cl^-) (IIT 1988) (a)

56. How much NH_3 must be added to a 0·004 M Ag^+ solution to prevent the precipitation of AgCl when $[Cl^-]$ reaches 0·001 M? K_{sp} (AgCl) = $1{\cdot}8 \times 10^{-10}$. Dissociation constant for $Ag(NH_3)_2^+ = 6{\cdot}0 \times 10^{-8}$. (0·044 mole/litre)

57. Calculate the simultaneous solubility of CaF_2 and SrF_2.
K_{sp} (CaF_2) = $3{\cdot}9 \times 10^{-11}$.
K_{sp} (SrF_2) = $2{\cdot}9 \times 10^{-9}$.
$\begin{bmatrix} 1{\cdot}2 \times 10^{-5} \text{ mole/litre} \\ 9 \times 10^{-4} \text{ mole/litre} \end{bmatrix}$

58. Aniline is a weak organic base in aqueous solutions. Suggest a solvent in which aniline would become a strong base. (Acetic acid)

59. Distinguish between acid strength and acid concentration. (Read text)

60. Liquid NH_3, like water, is an amphiprotic solvent. Write the equation for the auto-ionisation of NH_3 ($2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$)

61. Calculate the sulphate ion concentration in 0·15 M H_2SO_4. $K_2 = 1{\cdot}02 \times 10^{-2}$
(**Hint:** First ionisation of H_2SO_4 is 100%) ($8{\cdot}9 \times 10^{-3}$)

62. A 50·0 mL sample of a 0·01 M solution of HCOOH was titrated with 0·10 M NaOH. Calculate the pH of the solution when 10 mL of NaOH was added.
K_a for HCOOH = $1{\cdot}772 \times 10^{-4}$ (11·92)

63. What is the pH of a 0·10 M solution of ethylenediaminetetraacetic acid (edta).
$K_{a_1} = 1 \times 10^{-2}$, $K_{a_2} = 2{\cdot}1 \times 10^{-3}$, $K_{a_3} = 6{\cdot}9 \times 10^{-7}$ and $K_{a_4} = 5{\cdot}5 \times 10^{-11}$. (1·54)

[Hint: The only two major contributions to the concentration of H^+ are from the first two ionisation steps]

64. A concentrated strong acid is added to a solid mixture of 0·015-mole samples of $Fe(OH)_2$ and $Ca(OH)_2$ placed in one litre of water. At what value of pH will the dissolution of each hydroxide be complete? (Assume negligible volume change)

$$K_{sp}[Fe(OH)_2] = 7{\cdot}9 \times 10^{-15} \text{ and } K_{sp}[Cu(OH)_2] = 1{\cdot}6 \times 10^{-19}$$

(7·86)

Objective Problems

1. Dissociation constant of H_2O at 25°C is
   (a) 1×10^{-14} (b) 1×10^{14} (c) 14 (d) $1{\cdot}8 \times 10^{-16}$

2. K_a value for the acid HA is 1×10^{-6}. The value of K for
   $$A^- + H_3O^+ = HA + H_2O \text{ is}$$
   (a) 1×10^{-6} (b) 1×10^{12} (c) 1×10^{-12} (d) 1×10^{6}

3. pK_a of a base ($K_b = 1 \times 10^{-5}$) is
   (a) 5 (b) – 9 (c) – 5 (d) 9

4. What molar concentration of NH_3 provides a $[OH^-]$ of $1{\cdot}5 \times 10^{-3}$?
   ($K_b = 1{\cdot}8 \times 10^{-5}$.)
   (a) 0·125 (b) $(0{\cdot}125 + 1{\cdot}5 \times 10^{-3})$
   (c) $(0{\cdot}125 - 1{\cdot}5 \times 10^{-3})$ (d) $(1{\cdot}5 \times 10^{-3})$
   [Hint: $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$]

5. In which of the following cases is the acid strength highest?
   (a) $K_a = 10^{-6}$ (b) $pK_a = 5$ (c) $pK_b = 10$ (d) $K_b = 10^{-11}$

6. The values of K_w in 0·1 M NaOH and 0·1 M NaCl are
   (a) same (b) different (c) same only at 25°C

7. At 90°C, pure water has $[H_3O^+] = 10^{-6}$ mole/litre. The value of K_w at 90°C is
   (a) 10^{-6} (b) 10^{-8} (c) 10^{-12} (d) 10^{-14} **(IIT 1984)**

8. The pH of a 0·01 N monobasic acid is 4. The acid must be
   (a) strong (b) weak

9. 10^{-2} mole of KOH is dissolved in 10 litres of water. The pH of the solution is
   (a) 12 (b) 2 (c) 3 (d) 11

10. The pH of the solution containing 0·1 N HCl and 0·1 N CH_3COOH is
    (a) 1 (b) 0·7 (c) 2 (d) 1·3

11. The pH of a 10^{-8} M HCl solution is
    (a) 8 (b) 7·02 (c) 7 (d) 6·98

12. pH of 10^{-11} M HCl is
    (a) 11 (b) 3 (c) 6·8 (d) 7

13. If pH of a 0·01 N monobasic acid is 2·0, the acid must be
(a) strong (b) weak

14. If the temperature of water is increased from 25°C to 45°C, the pH of water at 45°C will be
(a) 7 (b) slightly greater than 7
(c) < 7 (d) 8

15. pH of a 10^{-3} M NaCl solution (aq) at 25°C is
(a) 7 (b) 11 (c) 3 (d) all wrong

16. pH of an aq. NaCl solution at 85°C should be
(a) 7 (b) > 7 (c) < 7 (d) 0

17. The pH of 7×10^{-8} M CH_3COOH is ($K_w = 1 \times 10^{-14}$)
(a) 8·1 (b) 7·9 (c) 7·1 (d) 6·85

18. The dissociation constant of an acid HA is 1×10^{-5}. The pH of 0·1 molar solution of the acid will be approximately
(a) 3 (b) 5 (c) 1 (d) 6

19. 1 cc of 0·1 N HCl is added to 999 cc solution of NaCl. The pH of the resulting solution will be
(a) 7 (b) 4 (c) 2 (d) 1

20. If a solution has a pOH value of 14 at 25°C, H^+ concentration should be
(a) 0 (b) 10 (c) 1 (d) none of these

21. What will be the hydrogen ion concentration in mole/litre of a solution of pH = 0?
(a) 0 (b) 10^{-7} (c) 10^0 (d) pH cannot be zero

22. Which of the following would decrease the pH of 25 cm^3 of a 0·01 M solution of HCl?
(a) The addition of Mg
(b) The addition of 25 cm^3 of 0·02 M HCl
(c) The addition of 25 cm^3 of 0·005 M HCl
(d) None of these

23. The pH of a 0·1 M NH_3 solution ($K_b = 1.8 \times 10^{-5}$) is
(a) 11·13 (b) 1 (c) 13 (d) none of these

[**Hint:** $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$, $K_b = \dfrac{[NH_4^+][OH^-]}{[NH_3]}$]

24. The pH of a buffer solution of 0·1 M NH_4OH and 0·1 M NH_4Cl is ($pK_b = 4·0$)
(a) 1 (b) 4 (c) 10 (d) 13

25. In a buffer solution of a weak acid and its salt, if the ratio of the concentration of the salt to that of the acid is increased ten times, the pH of the buffer
(a) increases by 1 (b) increases 10 times
(c) decreases 10 times (d) decreases by 1

26. The process of hydrolysis is
(a) always exothermic (b) always endothermic

(c) either exothermic or endothermic (d) neither exothermic nor endothermic

27. When a salt of a weak acid and a weak base is dissolved in water at 25°C, the pH of the resulting solution will always
(a) be 7 (b) be greater than 7
(c) be less than 7 (d) depend upon K_a and K_b values

28. The degree of hydrolysis of a salt of a weak acid and a weak base in its 0·1 M solution is found to be 50%. If the molarity of the solution is 0·2 M, the percentage hydrolysis of the salt should be
(a) 100% (b) 50% (c) 25% (d) none of these

29. If a salt of a strong acid and a weak base hydrolyses appreciably, which of the following formulae is to be used to calculate degree of hydrolysis 'X'?
(a) $X = \sqrt{\frac{K_w}{K_a \cdot a}}$ (b) $X = \sqrt{\frac{K_w}{K_b \cdot a}}$ (c) $X = \sqrt{\frac{K_w}{K_a \cdot K_b}}$ (d) none of these

30. K_{sp} for AgCl in water at 25°C is $1{\cdot}8 \times 10^{-10}$. If 10^{-5} mole of Ag^+ ions are added to this solution, K_{sp} will be
(a) $1{\cdot}8 \times 10^{-15}$ (b) $1{\cdot}8 \times 10^{-10}$ (c) $1{\cdot}8 \times 10^{-5}$ (d) none of these

31. In which of the following cases is the solution of AgCl unsaturated?
(a) $[Ag^+][Cl^-] < K_{sp}$ (b) $[Ag^+][Cl^-] > K_{sp}$
(c) $[Ag^+][Cl^-] = K_{sp}$

32. If the solubility of $Al(OH)_3$ is S moles/litre, the solubility product is
(a) S^3 (b) $27S^4$ (c) S^2 (d) $4S^3$

33. The volume of water needed to dissolve 1g of $BaSO_4$ ($K_{sp} = 1{\cdot}1 \times 10^{-10}$) at 25°C is
(a) 820 litres (b) 450 litres (c) 205 litres (d) none of these

34. The solubility of $BaSO_4$ in water is 0·00233 g per litre at 30°C. The solubility of $BaSO_4$ in 0·1 M $(NH_4)_2SO_4$ solution at the same temperature is
(a) 10^{-5} mole/litre (b) 10^{-6} mole/litre (c) 10^{-8} mole/litre (d) 10^{-9} mole/litre

35. When equal volumes of the following solutions are mixed, precipitation of AgCl ($K_{sp} = 1{\cdot}8 \times 10^{-10}$) will occur only with
(a) 10^{-4} M (Ag^+) and 10^{-4} M (Cl^-) (b) 10^{-5} M (Ag^+) and 10^{-5} M (Cl^-)
(c) 10^{-6} M (Ag^+) and 10^{-6} M (Cl^-) (d) 10^{-10} M (Ag^+) and 10^{-10} M (Cl^-)
(IIT 1988)

36. If the salts M_2X, QY_2 and PZ_3 have the same solubilities ($< \frac{4}{27}$), their K_{sp} values are related as
(a) $K_{sp}(M_2X) = K_{sp}(QY_2) > K_{sp}(PZ_3)$ (b) $K_{sp}(M_2X) > K_{sp}(QY_2) = K_{sp}(PZ_3)$
(c) $K_{sp}(M_2X) = K_{sp}(QY_2) = K_{sp}(PZ_3)$ (d) $K_{sp}(M_2X) > K_{sp}(QY_2) > K_{sp}(PZ_3)$

37. If pK_b for fluoride ion at 25°C is 10·83, the ionisation constant of hydrofluoric acid in water at this temperature is

(a) 1.74×10^{-5} (b) 3.52×10^{-3} (c) 6.75×10^{-4} (d) 5.38×10^{-2}

(IIT 1997)

38. The solubility of A_2X_3 is y mol/dm³. Its solubility product is
(a) $6y^4$ (b) $64y^4$ (c) $36y^5$ (d) $108y^5$ (IIT 1997)

39. Which of the following statements about buffer solutions is wrong?
(a) Weak acids and their salts are better as buffers for pH < 7.
(b) Weak bases and their salts are better as buffers for pH > 7.
(c) A buffer solution has generally lost its usefulness when one component of the buffer pair is less than about 10% of the other.
(d) For most effective buffering in the acid range or basic range, the two components of the buffer should have almost the same mass per unit volume.

40. 10 mL of 0·1 M HCl is titrated with 0·1 M NaOH. When the volume of NaOH added from the burette is from 9·99 mL to 10·01 mL, the pH jumps approximately from
(a) 4 to 10 (b) 6 to 8 (c) 6·9 to 7·1 (d) 1 to 14

41. When one drop of a concentrated HCl solution is added to one litre of pure water at 25°C, the pH drops suddenly from 7 to about 4. When the second drop of the same acid is added, the pH of the solution further drops to about
(a) 3·7 (b) 2·0 (c) 1·0 (d) 0

42. In which of the following aqueous solutions is the degree of dissociation of water maximum?
(a) NH_4Cl solution (b) CH_3COONa solution
(c) CH_3COONH_4 solution (d) NaCl solution

43. pH of an aqueous 1×10^{-8} M NaOH solution is
(a) 8 (b) 7·02 (c) 7 (d) 6

44. The pH of 1×10^{-3} M H_2O_2 solution ($K_a = 2.2 \times 10^{-12}$) is
(a) ≈ 3 (b) slightly less than 7
(c) slightly greater than 7 (d) = 7

45. The pH of an aqueous solution of 0·01 M CH_3COONH_4 at 25°C is

$$(K_a(CH_3COOH) = K_b(NH_4OH) = 1.8 \times 10^{-5})$$

(a) > 7 (b) < 7 (c) 7

Answers

1-d, 2-d, 3-d, 4-b, 5-d, 6-a, 7-c, 8-b, 9-d, 10-a, 11-d, 12-d, 13-a, 14-c, 15-a, 16-c, 17-d, 18-a, 19-b, 20-c, 21-c, 22-b, 23-a, 24-c, 25-a, 26-b, 27-d, 28-b, 29-d, 30-b, 31-a, 32-b, 33-b, 34-d, 35-a, 36-a, 37-c, 38-d, 39-d, 40-a, 41-a, 42-c, 43-b, 44-b, 45-c.

□□□

CHEMICAL KINETICS

In the chapter 'Chemical Equilibrium' we have discussed how far a reaction would proceed to attain equilibrium but nothing has been said about how fast that equilibrium would be attained. This will be the subject matter of the present chapter.

For a reaction at equilibrium the net reaction rate is zero, i.e., the forward rate is equal to the reverse rate. In this section we shall limit ourselves mainly to a forward reaction which is yet to reach equilibrium.

Qualitative Measurement of the Rate of a Reaction; Differential Rate Law and Rate Constant

The rate of a reaction is defined as the change in concentration of any of the reactants or products per unit time. For a reaction

$$A + B \rightarrow C + D$$

the rate of the reaction is equal to the decrease in concentration of either A or B, or increase in concentration of either C or D per unit time.

Let us consider the general reaction

$$aA + bB \rightarrow cC + dD$$

The stoichiometric coefficients *a*, *b*, *c* and *d* signify that for the disappearance of *a* moles of A and *b* moles of B at any instant, *c* moles of C and *d* moles of D will appear. **The rate may, therefore, be more accurately defined as the rate of disappearance of A or B per mole, which in turn, is equal to the rate of appearance of C or D per mole.**

Thus, the rate of the general reaction

= rate of disappearance of A or B per mole

= rate of appearance of C or D per mole

or

$$\text{rate} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt}$$

$$= +\frac{1}{c}\frac{d[C]}{dt} = +\frac{1}{d}\frac{d[D]}{dt} \quad \text{... (1)}$$

[ ] represents the concentration in mole per litre, whereas '*d*' represents an infinitesimally small change in concentration. The negative sign shows that the concentrations of the reactants A and B are decreasing, whereas the positive sign indicates the increase in concentration of the products C and D with the progress of the reaction.

Note that the rate of disappearance or appearance of different reactants and products may be same or different depending on the stoichiometry of

Ex. 61. *From the following reaction scheme, write the rate law for the disappearance of A, B and C.*

1. $A + B \xrightarrow{k_1} C + D$

2. $C + D \xrightarrow{k_2} A + B$

3. $B + C \xrightarrow{k_3} E + D$

Solution : The reactant A is removed in Step 1 and produced in Step 2.

$$\therefore \quad -\frac{d[A]}{dt} = k_1[A][B] - k_2[C][D]$$

Similarly,

$$-\frac{d[B]}{dt} = k_1[A][B] + k_3[B[C] - k_2[C][D]$$

and, $$-\frac{d[C]}{dt} = k_2[C][D] + k_3[B[C] - k_1[A][B].$$

PROBLEMS

(*Answers bracketed with questions*)

1. A first order reaction takes 69·3 minutes for 50% completion. How much time will be needed for 80% completion? (160·9 minutes)

2. In a certain first order reaction, half the reaction was decomposed in 500 seconds. How long will it be until one-tenth is left? (1661 seconds)

3. Find the value of the rate constant for the reaction $A + B \rightarrow AB$, if the rate of the reaction is 5×10^{-5} (mol/L) min^{-1} and [A] and [B] are respectively 0·05 and 0·01 mol/L. [0·1 (mol/L)$^{-1}$ (min)$^{-1}$]

4. For three reactions of first, second and third order, $k_1 = k_2 = k_3$, when concentration is expressed in mol/L. What will be relation among k_1, k_2 and k_3 if the concentration is expressed in mol/mL? $(k_1 = k_2 \times 10^{-3} = k_3 \times 10^{-6})$

5. How many times will the rate of the reaction $2A + B \rightarrow A_2B$ change if the concentration of substance A is doubled and that of substance B is halved? (increase twofold)

6. The rate law for the reaction

$$RCl + NaOH(aq) \rightarrow ROH + NaCl$$

is given by

rate $= k_1$ [RCl], the rate of reaction will be

(a) doubled on doubling the concentration of NaOH

(b) halved on reducing the concentration of RCl to one-half

(c) increased on increasing the temperature of the reaction

(d) unaffected by increasing the temperature of the reaction

[Hint: See Example 14]

(IIT 1988) (b)

7. How many times must the concentration of substance B_2 in the system $2A_2(g) + B_2(g) \rightarrow 2A_2B(g)$ be increased for the rate of the forward reaction to remain unchanged when the concentration of substance A_2 is lowered to one-fourth of its initial value?

(16 times)

8. The order of the reaction $2A + B + C \rightarrow$ Product, is found to be 1, 2 and 0 w.r.t. A, B and C respectively. If the concentration of each reactant is increased by two times, what will be the effect on the rate of the reaction?

[Hint: See solved example 15]

(8 times)

9. In the thermal decomposition of C_2H_5Br to C_2H_4 and HBr, the pressure changed from an initial value of 200 mmHg to 390 mmHg at the end of the reaction. What fraction remained unchanged when the pressure of the mixture was 300 mmHg?

(0·47)

10 Catalytic decomposition of nitrous oxide by gold at 900°C at an initial pressure of 200 mm was 50% in 53 minutes and 73% in 100 minutes. Find the order of the reaction. How much will it decompose in 100 minutes at the same temperature but at an initial pressure of 600 mm? (First, 73%)

11. A certain reaction is of first order. After 540 seconds, 32·5% of the reactant remains.

(a) Calculate the rate constant.

(b) How long would it require for 25% of the reactant to be decomposed?

($2{\cdot}08 \times 10^{-3}\,s^{-1}$; 139 s)

12. The specific reaction rate constant for a first order reaction is $1 \times 10^{-2}\,s^{-1}$. If the initial concentration is 1 M, find the initial rate. What is the reaction rate after two minutes?

($1 \times 10^{-2}, 3 \times 10^{-3}$)

13. For the nonequilibrium process $A + B \rightarrow P$, the reaction is of first order with respect to A and of second order with respect to B. If 1 mole each of A and B are introduced into a 1-litre flask, and the initial rates were 1×10^{-2} mole/litre · s, calculate the rate when half the reactants have converted to the product.

($1{\cdot}2 \times 10^{-3}$ mole $L^{-1}\,s^{-1}$)

14. The rate law for the reaction,

$$CH_3COOC_2H_5 + H_2O \xrightarrow{[H^+]} CH_3COOH + C_2H_5OH$$

is

$$\frac{dx}{dt} = k\,[CH_3COOC_2H_5]\,[H_2O]^{\circ}$$

What will be the effect on the rate if

(i) the concentration of the ester is doubled?

(ii) the concentration of H^+ is tripled?

[(i) Rate doubles (ii) No effect]

15. Prove that the half-life period of a reaction of nth order in a reaction of the type $A \rightarrow$ Product, is inversely proportional to the $(n-1)$th power of the initial concentration.

16. A living plant acquires a definite fraction of $^{14}_{6}C$ nuclei in carbon content. If a freshly cut piece of wood gives 16·1 counts per minute per gram and an old wooden bowl gives 9·6 counts per minute per gram of carbon, calculate the age of the wooden bowl. The half-life of $^{14}_{6}C$ is 5770 years. (4304 years)

17. The following data gives pressure of a gaseous N_2O_5 as a function of time at 45°C. Plot them first in $1/p$ vs t and then as p vs t. Determine the order and rate constant.

t (s)	p (mm)	t (s)	p (mm)
0	348	3600	58
600	247	4800	33
1200	185	6000	18
2400	105	7200	10

(First order, $k_1 = 5 \times 10^{-4} s^{-1}$)

18. A substance decomposes according to second order rate law. If the rate constant is $6{\cdot}8 \times 10^{-4}$ L mole^{-1} s^{-1}, calculate half-life of the substance, if the initial concentration is (i) 0·05 mole/L and (ii) 0·01 mole/L. ($2{\cdot}94 \times 10^4$ s; $1{\cdot}47 \times 10^5$ s)

19. For a certain reaction, it takes 5 minutes for the initial concentration of 0·5 mole/L to become 0·25 mole/L and another 5 minutes to become 0·125 mole/L. What is the order and specific rate constant of the reaction? (First; 0·138 minute^{-1})

20. The half-life period of a gaseous substance undergoing thermal decomposition was measured for various initial pressures (p) with the following results:

p (mm)	250	300	400	450
$t_{\frac{1}{2}}$ (min)	136	112·5	85	75·5

Calculate the order of the reaction. (Second)

21. The kinetics of decomposition of N_2O_5 in CCl_4 solution is studied by measuring the evolved oxygen. If 24 mL of the gas was evolved in one hour while 35 mL of the gas was evolved when no more oxygen was coming out, calculate the fraction of N_2O_5 decomposed in one hour. (0·686)

22. The following rate data were obtained at 30°C for the decomposition of N_2O_5 in CCl_4 solution:

$[N_2O_5]$ (mole/litre)	$d[N_2O_5]/dt$ (mole/litre/hour)
0·34	0·10
0·68	0·20
1·36	0·40

Calculate the order of the reaction and the rate constant at 30°C. (First; 0·29 h^{-1})

23. From the following data calculate the order with respect to each reactant A, B and C:

[A] (mole/L)	[B] (mole/L)	[C] (mole/L)	$d[B]/dt \times 10^{-5}$ (mole/L/s)
0·010	0·005	0·010	5·0
0·015	0·005	0·010	5·0
0·010	0·010	0·010	2·5
0·010	0·005	0·020	14·1

(0; −1; 3/2)

24. For a given reaction $A + B \rightarrow P$, the orders w.r.t. A and B are 1 and 2 respectively. Fill in the blanks from the following data:

Rate ($M\ s^{-1}$)	[A]	[B]
0·10	1·0 M	0·20 M
...	2·0 M	0·20 M
...	2·0 M	0·40 M

[Hint: See Example 30**]**

($R_2 = 0{\cdot}20,\ R_3 = 0{\cdot}80$)

25. The reaction $A + B \rightarrow C + D$; $\Delta H = 25$ kJ/mole should have an activation energy

(a) −25 kJ/mole (b) < +25 kJ/mole

(c) > + 25 kJ/mole

(d) either answer (b) or (c) depending upon experiment (c)

[Hint: See Example 37**]**

26. The half-life period for the reaction, $N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2$ is 2·4 hours at 30°C. What time would be required to reduce 5×10^{10} molecules of N_2O_5 to 10^8 molecules?

(21·5 hours)

27. One mole of a gas A and two moles of a gas B are introduced into one vessel and 2 moles of A and 1 mole of B into a second vessel having the same capacity. The temperature is the same in both vessels. Will the rate of reaction between A and B in these vessels differ if it is expressed by the equation

(i) rate = k [A] [B] and (ii) rate = $k\,[A]^2\,[B]$? [(i) No (ii) Yes]

28. How many times will the rate of the reaction $2A + B \rightarrow A_2B$ change if the concentration of the substance A is tripled and that of the substance B is halved?

(Increases 4·5 times)

29. What is the temperature coefficient of the reaction if the rate grows 15·6 times when the temperature is increased by 30 K? (2·5)

[Hint: See solved example 35**]**

30. The temperature coefficient of the rate of a reaction is 2·3. How many times will the rate of the reaction increase if the temperature is raised by 25 K? (8·02 times)

31. In a second order reaction when the concentration of both the reactants are equal, the reaction is 20% completed in 500 seconds. How long will it take the reaction to go to 60% completion? (3000 s)

[Hint: Use Equation 6**]**

32. For the reaction $A + B \rightarrow C$, the following data were obtained: In the first experiment when the initial concentration of both A and B is 0·1 M, the observed initial rate of formations of C is 1×10^{-4} mole per minute. In the second experiment, when the initial concentrations of A and B are 0·1 M and 0·3 M respectively, the initial rate is 9×10^{-4} mole per minute. In the third experiment with the initial concentration of both A and B, 0·3 M, the initial rate is $2{\cdot}7 \times 10^{-3}$ mole per minute. Write the rate law and calculate the rate constant for the reaction.

[Rate $= 0{\cdot}1 \times [A]^1 [B]^2$]

[Hint: Calculate m and n in rate $= k\,[A]^m\,[B]^n$; (See solved example 14)]

33. For the reaction $A \rightarrow B + C$ the following data were obtained:

t (s)	0	900	1800
[A]	50·8	19·7	7·62

Prove that the reaction is of first order. (k_1 is found to be constant)

34. Nitrosyl chloride, NOCl decomposes to NO and Cl_2.

$$2NOCl(g) \rightarrow 2NO(g) + Cl_2(g)$$

From the following data, determine the rate law, the rate constant and the overall order for this reaction.

[NOCl]:	0·10	0·20	0·30ii
Rate (mol/L/s)	8×10^{-10}	$3{\cdot}2 \times 10^{-9}$	$7{\cdot}2 \times 10^{-9}$

(Rate $= k[NOCl]^2$, $k = 8 \times 10^{-8}$ L/mol/s, two)

35. What is the half-life for the decomposition of NOCl when [NOCl] = 0·15 M? Given that for $2NOCl \rightarrow 2NO + Cl_2$: $-\dfrac{d[NOCl]}{dt} = (8{\cdot}0 \times 10^{-8}\ \text{L/mol/s})\ [NOCl]^2$

($8{\cdot}34 \times 10^7$s)

36. The rate constant for the first order decomposition of N_2O_5 dissolved in chloroform at 45°C is $3{\cdot}1 \times 10^{-4}\text{min}^{-1}$.

$$2N_2O_5 \rightarrow 4NO_2 + O_2$$

(a) What is the rate of decomposition of N_2O_5 when $[N_2O_5] = 0{\cdot}40$ M?

(b) What are the rates of formation of NO_2 and of O_2 when $[N_2O_5] = 0{\cdot}40$ M?

(c) What is the rate of this reaction.

[(a) $2{\cdot}48 \times 10^{-4}$ mole/L/min (b) $4{\cdot}96 \times 10^{-4}$ and $1{\cdot}24 \times 10^{-4}$ mol/L/min (c) $1{\cdot}24 \times 10^{-4}$ mol/L/min]

[Hint: First-order reaction is of the type: $2A \rightarrow$ Products]

37. For the reaction: $SO_2CL_2(g) \rightarrow SO_2(g) + Cl_2(g)$, it is found that a plot of $\ln[SO_2Cl_2]$ versus time is linear, and that in 240 seconds the $[SO_2Cl_2]$ decreases from 0·4 M to 0·28 M. What is the rate constant?

($1{\cdot}49 \times 10^{-3}\,s^{-1}$)

38. A certain physiologically important first-order reaction has an activation energy equal to 45·0 kJ/mol at normal body temperature (37°C). Without a catalyst, the rate constant for the reaction is $5{\cdot}0 \times 10^{-4}s^{-1}$. To be effective in the human body, where the reaction is catalysed by an enzyme, the rate constant must be at least $2.0 \times 10^{-2} s^{-1}$. If the activation energy is the only factor affected by the presence of the enzyme, by how much must the enzyme lower the activation energy of the reaction to achieve the desired rate?

(≈ 10 kJ/mol)

39. A drop (0·05 mL) of a solution contains 3.0×10^{-6} mole of H^+ ions. If the rate constant of disappearance of H^+ is 1.0×10^7 mol/L/s, how long would it take for H^+ ions in the drop to disappear?

(6.0×10^{-9}s)

40. The gas-phase decomposition of NOBr is second order in [NOBr], with $k = 0.81\ M^{-1} \cdot s^{-1}$ at 10°C. Initial concentration of NOBr in the flask at 10°C $= 4.00 \times 10^{-3}$ M. In how many seconds does it take up 1.50×10^{-3} M of this NOBr?

$$2NOBr \rightarrow 2NO + Br_2$$

(92·6 s)

[Hint: $k_2 = \frac{1}{2t}\left\{\frac{x}{a(a-x)}\right\}$]

41. The reaction, $A \rightarrow C + D$ was found to be second order in A. The rate constant for the reaction was determined to be 2·42 L/mol/s. If the initial concentration is 0·5 mole/L, what is the value of $t_{1/2}$.

(0·8264 s)

[Hint: $k_2 = \frac{1}{t}\left\{\frac{x}{a(a-x)}\right\}$]

42. Both Technetium-99 and Thallium-201 are used to image heart muscle in patients who may have heart problems. The half-lives are 6 hours and 73 hours respectively. What per cent of radioactivity would remain for each of the isotopes after 2 days?

(0·39%, 63%)

43. Two reactions have identical values for energy of activation. Does this ensure that they will have the same rate constant if run at the same temperature?(No, $k \propto$ A)

44. The rate of the haemoglobin (Hb)– carbon monoxide reaction,

$$4Hb + 3CO \rightarrow Hb_4(CO)_3$$

has been studied at 20°C. Concentrations are expressed in μ mole/L.

[Hb] (μ mole/L)	[CO] (μ mole/L)	Rate of disappearance of Hb (μ mole/L/s)
3·36	1·00	0·941
6·72	1·00	1·88
6·72	3·00	5·64

(a) Calculate the rate constant for the reaction

(b) Calculate the rate of the reaction at the instant when

[Hb] = 1·50 and [CO] = 0·60 μ mole/L.

((a) 7×10^{-2} L/μ mole/s (b) 6.3×10^{-2} μ mole/L/s)

[Hint: Rate of reaction $= -\frac{1}{4}\frac{d[Hb]}{dt} = k[Hb][CO]$]

45. A first order reaction is 50% complete in 30 min at 27°C and in 10 min at 47°C. Calculate the reaction rate constant at 27°C and the energy of activation of the reaction in kJ/mole.

(IIT 1988) (0·0231 min^{-1}, 43·84 kJ)

[Hint: $k(27°) = \dfrac{0.6932}{\left(t_{\frac{1}{2}}\right)_{27}}$

The reaction at 47°C is 3 times faster than that at 27°C. Use Equation 12, put $R = 8.314 \times 10^{-3}$ kJ.]

46. The decomposition of arsine (AsH_3) into arsenic and hydrogen is a first order reaction. The decomposition was studied at constant volume and at constant temperature. The pressures at different times are as follows:

t (h):	0	5·5	6·5	8
p (atm):	0·9654	1·06	1·076	1·1

Calculate the velocity constant. ($4 \times 10^{-2}\,h^{-1}$)

[Hint: For $AsH_3(g) \rightarrow As(s) + \frac{3}{2}H_2(g)$; $p_0 \propto a$ and $p_t \propto \left\{(a-x) + \frac{3x}{2}\right\}$

$\therefore\ p_t - p_0 \propto \frac{x}{2}$]

47. The rate constant of the first order reaction, that is, decomposition of ethylene oxide into CH_4 and CO, may be described by the following equation

$$\log k\,(s^{-1}) = 14.34 - \frac{1.25 \times 10^4}{T} K$$

Find (a) energy of activation, and (b) rate constant at 397°C.

[(a) 239·34 kJ (b) $4.8 \times 10^{-5}\,s^{-1}$]

[Hint: Compare the given equation with $\log k = \log A - \dfrac{E}{2.303\,RT}$]

48. For a homogeneous gaseous reaction $A \rightarrow B + C + D$ the initial pressure was p_0 while pressure after time t was p. Derive an expression for rate constant k in terms of p_0, p and t.

$\left[k = \dfrac{2.303}{t} \log \dfrac{2p_0}{3p_0 - p}\right]$

[Hint: See solved example 44]

Objective Problems

1. The rate law for the single-step reaction $2A + B \rightarrow 2C$ is given by

(a) rate = k [A] · [B] (b) rate = $k\,[A]^2 \cdot [B]$

(c) rate = k [2A] · [B] (c) rate = $k\,[A]^2 \cdot [B]^0$

2. Which of the following rate laws has an overall order of 0·5 for the reaction $A + B + C \rightarrow$ Product?

(a) $R = k[A] \cdot [B] \cdot [C]$ (b) $R = k[A]^{.5}[B]^{.5}[C]^{.5}$

(c) $R = k[A]^{1.5}[B]^{-1}[C]^0$ (d) $R = k[A][B]^0[C]^{.5}$

3. The rate law of the reaction $A + 2B \rightarrow$ Product is given by $\dfrac{d\,(\text{product})}{dt} = k[A]^2 \cdot [B]$. If A is taken in large excess, the order of the reaction will be

(a) 0 (b) 1 (c) 2 (d) 3

4. Which of the following statements is not correct?
   (a) Law of mass action and rate law expressions are same for single-step reactions.
   (b) Order of the slowest elementary reaction of a complex reaction gives the order of the complex reaction.
   (c) Both order and molecularity have normally a maximum value of 3.
   (d) Molecularity of a complex reaction $A + 2B \rightarrow C$ is 3.

5. If the volume of a closed vessel in which the equilibrium $2SO_2 + O_2 \rightleftharpoons 2SO_3$ is set in is halved, the rate of
   (a) forward reaction will remain same as that of backward reaction
   (b) forward reaction will become double that of the reverse one
   (c) forward reaction will be halved that of the reverse one
   (d) all wrong

6. The rate of the simple reaction $2NO + O_2 \rightarrow 2NO_2$, when the volume of the reaction vessel is doubled,
   (a) will grow eight times of its initial rate
   (b) reduce to one-eighth of its initial rate
   (c) will grow four times of its initial rate
   (d) reduce to one-fourth of its initial rate

7. Rate of which reactions increase with temperature?
   (a) Any
   (b) Exothermic reactions
   (c) Endothermic reactions
   (d) None

8. The specific rate constant of a first order reaction depends on the
   (a) concentration of the reactant
   (b) concentration of the product
   (c) time
   (d) temperature

9. If the rate constant k of a reaction is $1{\cdot}6 \times 10^{-3}$ (mol/L) (min^{-1}), the order of the reaction is
   (a) 0 (b) 1 (c) 2 (d) cannot be known

10. If for any reaction, the rate constant is equal to the rate of the reaction at all concentrations, the order is
   (a) 0 (b) 2 (c) 1 (d) 3

11. Which of the following procedures will lead to a change in the rate constant 'k' of a reaction?
   (a) A change in the pressure
   (b) Change in temperature
   (c) Change in the volume of the reaction vessel
   (d) An introduction of a catalyst

12. If a reaction with $t_{1/2} = 69{\cdot}3$ seconds, has a rate constant value of 10^{-2} per second, the order is

(a) 0 (b) 1 (c) 2 (d) 3

13. The specific reaction rate constant for a first order reaction is $1 \times 10^{-3}\, s^{-1}$. If the initial concentration of the reactant is 0·1 mole per litre, the rate is

(a) 10^{-4} (b) 10^{-3} (c) 10^{-2} (d) 10^{-1}

14. k for a zero order reaction is $2 \times 10^{-2}\, \text{mol} \cdot L^{-1} s^{-1}$. If the concentration of the reactant after 25 s is 0·5 M, the initial concentration must have been

(a) 0·5 M (b) 1·25 M (c) 12·5 M (d) 1·0 M

[Hint: Rate $= \dfrac{a - 0{\cdot}5}{25} = 2 \times 10^{-2}$]

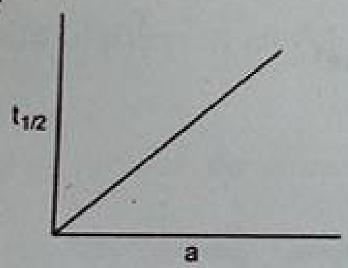
15. A first order reaction is carried out with an initial concentration of 10 moles per litre and 80% of the reactant changed into the product. Now if the same reaction is carried out with an initial concentration of 5 moles per litre, the percentage of the reactant changing to the product is

(a) 40 (b) 80

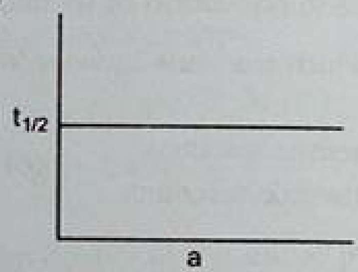
(c) 160 (d) cannot be calculated

16. Which of the following curves represents a first order reaction?

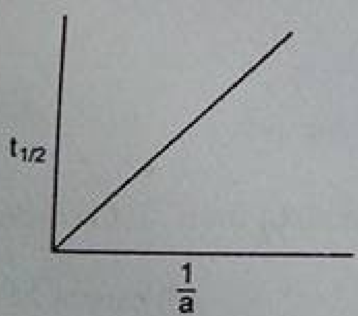
(a)



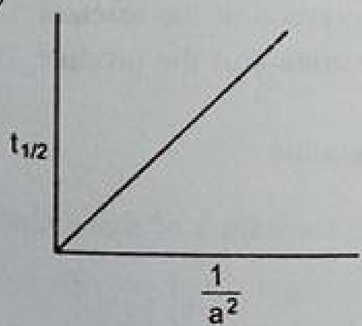
(b)



(c)



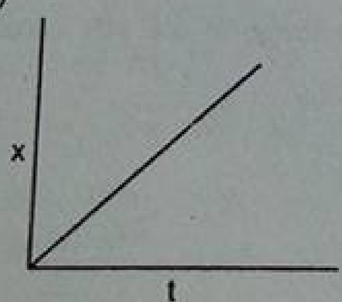
(c)



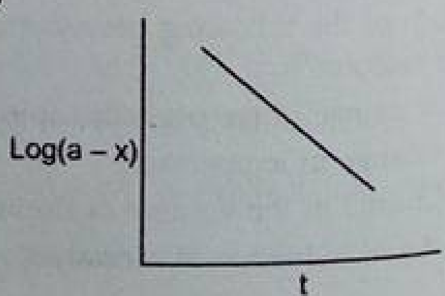
17. Which of the following curves represents a zero order reaction?

[$(a - x)$ = reactant concn.]

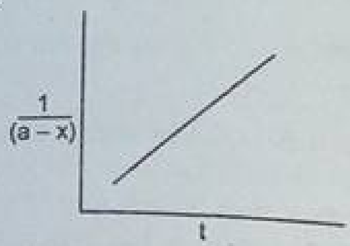
(a)



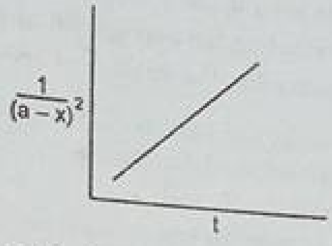
(b)



(c)



(d)



18. 75% of a first order reaction was completed in 32 min. When was 50% of the reaction completed?
(a) 24 min (b) 16 min (c) 8 min (d) 4 min

19. If doubling the initial concentration of a reactant doubles $t_{\frac{1}{2}}$ of the reaction, the order of the reaction is
(a) 3 (b) 2 (c) 1 (d) 0

20. For a given reaction the logarithm of the concentration of the reactant plotted against time gave a straight line with negative slope. The order of the reaction is
(a) 3 (b) 2 (c) 1 (d) 0

21. The concept of $t_{\frac{1}{2}}$ is useful for the reactions of
(a) zero order (b) first order (c) second order (d) all orders

22. The half-life for a given reaction was halved as the initial concentration of a reactant was doubled. The order for this component is
(a) 0 (b) 1 (c) 2 (d) 3

23. The rate constant for a second order reaction is 8×10^{-5} M^{-1} min^{-1}. How long will it take a 1 M solution to be reduced to 0·5 M in reactant?
(a) $8{\cdot}665 \times 10^3$ min (b) 8×10^{-5} min (c) $1{\cdot}25 \times 10^4$ min (d) 4×10^{-5} min

24. The rate for a first-order reaction is $0{\cdot}6932 \times 10^{-2}$ mol · L^{-1} min^{-1} and the initial concentration of the reactant is 0·1 M. $t_{\frac{1}{2}}$ is equal to
(a) $0{\cdot}6932 \times 10^{-2}$ min (b) $0{\cdot}6932 \times 10^{-3}$ min
(c) 10 min (d) 6·932 min

25. What fraction of a reactant remains after 40 min if $t_{\frac{1}{2}}$ is 20 min?
(a) 1/4 (b) 1/2 (c) 1/8 (d) 1/6

26. For a given reaction, the half-life period was found to be directly proportional to the initial concentration of the reactant. The order is
(a) 0 (b) 1 (c) 2 (d) 3

27. From different sets of data of $t_{1/2}$ at different initial concentration say 'a' for a given reaction, the product $(t_{1/2} \times a)$ is found to be constant. The order of the reaction is
(a) 0 (b) 1 (c) 2 (d) 3

28. A catalyst increases the rate of a chemical reaction by
(a) increasing the activation energy

(b) decreasing the activation energy
(c) increasing the average KE of the molecules
(d) increasing the number of active molecules

29. The energy of activation of a forward reaction is 50 kcal. The energy of activation of its backward reaction is
(a) equal to 50 kcal (b) greater than 50 kcal
(c) less than 50 kcal (d) either greater or less than 50 kcal

30. The rate constant, the activation energy and the Arrhenius parameter of a chemical reaction at 25°C are $3 \times 10^{-4}\ s^{-1}$, $104.4\ kJ\ mol^{-1}$ and $6 \times 10^{14}\ s^{-1}$ respectively. The value of the rate constant as $T \rightarrow \infty$ is
(a) $2 \times 10^{18}\ s^{-1}$ (b) $6 \times 10^{14}\ s^{-1}$ (c) ∞ (d) $3.6 \times 10^{30}\ s^{-1}$
(IIT 1996)

31. Which of the following statements is wrong about reactions?
(a) There can be only three values of molecularity, that is, 1, 2, and 3
(b) There can be only four values of order, that is, 0, 1, 2, and 3.
(c) There can be infinite number of values for order.
(d) The order involves rate while molecularity does not.

32. The temperature coefficient of a reaction is 2. The rate of this reaction, on raising the temperature by 25°, shall increase by
(a) 4 times (b) 8 times (c) 6 times (d) 5.65 times

33. The rate constant of a reaction, 2A → Products, with initial reactant concentration a mole/L, is k mole/L/min. The $t_{1/2}$ for the reaction is equal to
(a) $\frac{0.6932}{k}$ min (b) $\frac{1}{ak}$ min (c) $\frac{a}{2k}$ min (d) $\frac{a}{4k}$ min

34. The rate constant of a reaction, A → Product, with initial reactant concentration a mole/L, is k L/mole/min. The $t_{1/2}$ for the reaction is equal to
(a) $\frac{0.6932}{k}$ (b) $\frac{1}{ak}$ (c) $\frac{1}{2ak}$ (d) $\frac{a}{2k}$

35. The rate of reaction doubles when the concentration of the reactant is increased four times. The order is
(a) ½ (b) 2 (c) 1 (d) 4

36. When the concentration of a reactant, A, in a reaction: A → Products, is doubled, the rate of the reaction increases seven times, the order of the reaction is between
(a) 0 & 1 (b) 1 & 2 (c) 2 & 3 (d) 3 & 4

37. When the concentration of a reactant in a reaction, A → Products, is doubled, the increase in the rate of reaction cannot be more than
(a) 2 times (b) 4 times (c) 6 times (d) 8 times

38. For a second-order reaction of the type:

$$\underset{a-x}{\overset{a}{2A}} \rightarrow \underset{x/2}{\text{Products}},$$

the rate law is given by

$$\text{rate} = -\frac{1}{2}\frac{d(a-x)}{dt} = +\frac{d(x/2)}{dt} = k_2(a-x)^2.$$

The integrated rate law will be

(a) $k = \frac{1}{t}\left\{\frac{x}{a(a-x)}\right\}$ (b) $k = \frac{1}{2t}\left\{\frac{x}{a(a-x)}\right\}$ (c) $k = \frac{1}{t}\left\{\frac{a}{x(a-x)}\right\}$ (d) $k = \frac{1}{2t}\left\{\frac{a}{x(a-x)}\right\}$

39. 50% of a zero order reaction completes in 10 minutes. 100% of the same reaction shall complete in

(a) 5 min (b) 10 min (c) 20 min (d) ∞ time

40. The rate constant, k, of a second-order reaction, A → Products is given by

$$k = \frac{1}{t}\left\{\frac{x}{a(a-x)}\right\}$$

The ratio $t_{3/4}/t_{1/2}$ is equal to

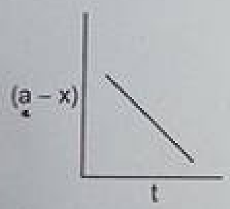
(a) 1/5 (b) 2/1 (c) 3/1 (d) 5/1

41. In which of the reactions of the following orders the molecularity and order can never be same?

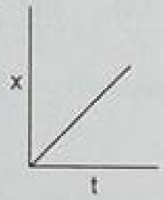
(a) Zero order (b) First order (c) Second order (d) Third order

42. Which of the following curves represent(s) a zero-order reaction?

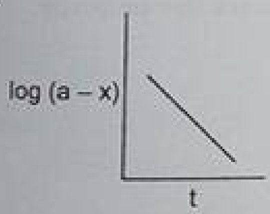
(a)



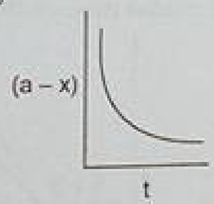
(b)



(c)



(d)



43. A plot of reactant concentration versus time for a reaction is a straight line with a negative slope giving the rate constant, and the intercept, giving the initial concentration of the reactant. The order of the reaction is

(a) 0 (b) 1 (c) 2 (d) none of these

44. Consider the chemical reaction

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

The rate of this reaction can be expressed in terms of time derivative of concentration of $N_2(g)$, $H_2(g)$ or $NH_3(g)$. Identify the correct relationship amongst the rate expressions.

(a) $\text{Rate} = -\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$

(b) $\text{Rate} = -\frac{d[N_2]}{dt} = 3\frac{d[H_2]}{dt} = 2\frac{d[NH_3]}{dt}$

(c) $\text{Rate} = \frac{d[N_2]}{dt} = \frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$

(d) Rate $= -\frac{d[N_2]}{dt} = -\frac{d[H_2]}{dt} = \frac{d[NH_3]}{dt}$ (IIT 2002)

45. If the rate constant for a reaction represented by $2HI \rightarrow H_2 + I_2$ is denoted by k then for the same reaction if represented by $HI \rightarrow \frac{1}{2}H_2 + \frac{1}{2}I_2$, the rate constant shall be equal to

(a) k (b) $2k$ (c) $k/2$ (d) $(k+2)$

46. For the chemical reaction of the type

$$2A \rightarrow \frac{1}{2}B$$

the correct relationship amongst the rate expressions is

(a) $-2\frac{d[A]}{dt} = +\frac{1}{2}\frac{d[B]}{dt}$ (b) $+2\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[R]}{dt}$

(c) $-\frac{1}{2}\frac{d[A]}{dt} = +2\frac{d[B]}{dt}$ (d) $+\frac{1}{2}\frac{d[A]}{dt} = -2\frac{d[B]}{dt}$

47. For what type of the following reactions is the law of mass action, never obeyed?

(a) Zero order (b) First order (c) Second order (d) Third order

48. If the rate law of a reaction $nA \rightarrow B$ is expressed as

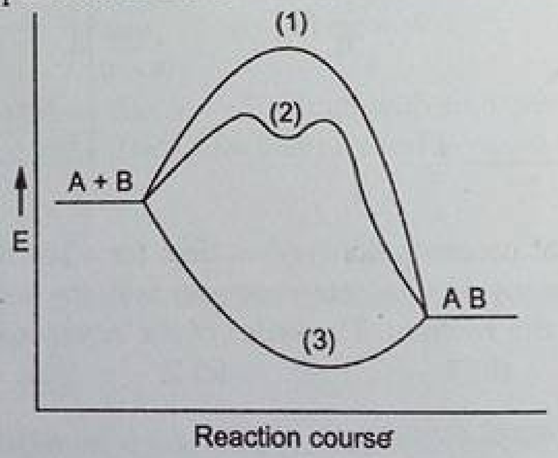
$$\underset{(mol/L/s)}{\text{Rate}} = -\frac{1}{n}\frac{d[A]}{dt} = +\frac{d[B]}{dt} = k[A]^x$$

The unit of the rate constant will be

(a) $mol^x/L^x/s$ (b) $L^x/mol^x/s$

(c) $mol^{(1-x)} \cdot L^{(x-1)} \cdot s^{-1}$ (d) $mol^{(x-1)} \cdot L^{(1-x)} \cdot s^{-1}$

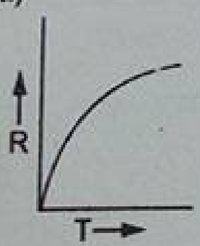
49. The exothermic reaction between substances A and B is presented in the plot below. Catalyst-induced preparation of the substance AB follows the pathway



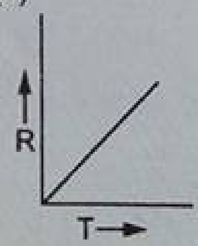
(a) 1 (b) 2 (c) 3

50. Which curve corresponds to the temperature dependence of the rate R of a simple one-step reaction?

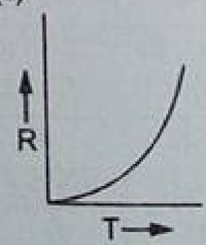
(a)



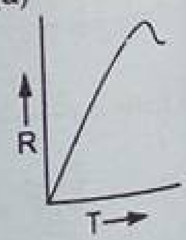
(b)



(c)



(d)



Answers

1-b, 2-c, 3-b, 4-d, 5-b, 6-b, 7-a, 8-d, 9-a, 10-a, 11-b & d, 12-b, 13-a, 14-d, 15-b, 16-b, 17-a, 18-b, 19-d, 20-c, 21-b, 22-c, 23-c, 24-c, 25-a, 26-a, 27-c, 28-b & d, 29-d, 30-b, 31-b, 32-d, 33-d, 34-b, 35-a, 36-c, 37-d, 38-b, 39-c, 40-c, 41-a, 42-a & b, 43-a, 44-a, 45-b, 46-c, 47-a, 48-c, 49-b, 50-c.

❑❑❑

CHAPTER EIGHTEEN

ELECTROMOTIVE FORCE

Electrochemical cells are of two types: 'electrolytic cells' and 'galvanic cells'. In electrolytic cells, the electrical energy is absorbed producing thereby chemical reactions. This process can also be reversed in which the chemical energy is converted to electrical energy. Any device which accomplishes this is called a galvanic cell or voltaic cell.

In an electrolytic cell electrons are fed into the cell from the external circuit. The cathode receives the electrons and becomes the negative electrode, and therefore, the anode becomes the positive electrode. Oxidation and reduction occur at the anode and cathode respectively. In a galvanic cell, oxidation occurs at the anode; the electrons so released by the anode are sent to the external circuit by it. The anode is thus regarded as the negative electrode and the cathode, where reduction occurs, thus becomes the positive electrode. Thus **the signs of cathode and anode in the electrolytic cell and in the galvanic cell are just the reverse.** Galvanic cells are of two types: chemical cell and concentration cell. In a chemical cell there is an overall cell reaction, whereas in a concentration cell, there is no overall cell reaction and the emf arises due to a concentration difference in the two half-cells. Let us consider a Daniell cell, an example of a **chemical cell** (galvanic cell)

$$\mathrm{Zn}\;\Big|\;\underset{(aq)}{\mathrm{ZnSO_4}}\;\Big\|\;\underset{(aq)}{\mathrm{CuSO_4}}\;\Big|\;\mathrm{Cu}$$

or, $\mathrm{Zn} \mid \mathrm{Zn^{2+}(aq)} \parallel \mathrm{Cu^{2+}(aq)} \mid \mathrm{Cu}$

Anode (–) (oxidation)   Cathode (+) (reduction)

The cell reactions are

$$\mathrm{Zn} \rightleftharpoons \mathrm{Zn^{2+}} + 2e; \quad \text{(Oxidation): at anode}$$

$$\mathrm{Cu^{2+}} + 2e \rightleftharpoons \mathrm{Cu}; \quad \text{(Reduction): at cathode}$$

The convention of representing such cells are:

(i) The electrode at which reduction takes place is written on the right-hand side and the electrode at which oxidation takes place is written on the left-hand side.

(ii) The single vertical line generally represents the separation of solid phase from the electrolytic solution. The double vertical lines represent the separation of two half cells having indirect electrical contact by a salt bridge. Th... junction potential which develops

Solution : The complete half-cell reaction is

$$Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O; \quad E^0 = 1{\cdot}33V$$

Given: $[Cr_2O_7^{2-}] = \frac{4{\cdot}5}{1000}$ M, $[Cr^{3+}] = \frac{15}{1000}$ M and $[H^+] = 10^{-2}$ M

$$E = E^0 - \frac{{\cdot}0591}{6} \log \frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}][H^+]^{14}}$$

$$E = 1{\cdot}33 - \frac{{\cdot}0591}{6} \log \frac{(0{\cdot}015)^2}{(0{\cdot}0045)(10^{-2})^{14}}$$

$$E = 1{\cdot}067V.$$

PROBLEMS

(Answers bracketed with questions)

[Note: See E^0 values from the table (p. 638), if not given.]

1. Calculate the reduction potentials for the following half cells:
   (i) $Ag \mid Ag^+(10^{-5}M)$; $E^0_{Ag^+, Ag} = 0{\cdot}80$ V
   (ii) $Cu \mid Cu^{2+}(0{\cdot}2\,M)$; $E^0_{Cu^{2+}, Cu} = 0{\cdot}34$ V (0·50 V, 0·32 V)

2. Construct galvanic cells from the following pairs of half cells and calculate their emf.
   (i) (Pt) H_2 (1 atm) | HCl (1 M) and Pt (Cl_2) (1 atm) | HCl (1 M)
   (ii) $Cu \mid Cu^{2+}$ (1 M) and Cl^- (1 M) | Cl_2 (1 atm) (Pt)

   Use the emf series.
   $\left\{\begin{array}{l} H_2 \mid H^+ \parallel Cl_2 \mid Cl^-; E = 1{\cdot}36\,V \\ Cu \mid Cu^{2+} \parallel Cl_2 \mid Cl^-; E = 1{\cdot}02\,V \end{array}\right\}$

3. Can F^- be oxidised to F_2 by any substance listed in the electrochemical series? (No, but it can be oxidised electrolytically)

4. A Cu rod is dipped in 0·1 M $CuSO_4$ solution. Calculate the potential of this half cell if $CuSO_4$ undergoes 90% dissociation at this dilution at 25°C. $E^0_{Cu, Cu^{2+}} = -0{\cdot}34$ V. (0·31 V)

5. If excess metallic iron is added to an N-$CuSO_4$ solution, calculate the approximate concentration of Cu^{2+} when equilibrium is established. (3×10^{-27} M)

6. Will Mg reduce $CuSO_4$? $E^0_{Mg, Mg^{2+}} = +2{\cdot}36$ V and $E^0_{Cu, Cu^{2+}} = -0{\cdot}34$ V. (Yes)

7. Calculate emf of the following cells at 25°C in which the following reactions are taking place: use E^0 values from table.
   (i) $Mg + Cl_2\,(1\,atm) \rightleftharpoons Mg^{2+}(10^{-2}M) + 2Cl^-(2 \times 10^{-2}M)$
   (ii) $Zn + Fe^{2+}(10^{-3}M) \rightleftharpoons Zn^{2+}(10^{-4}M) + Fe$ (3·879 V, 0·2595 V)

8. E^0_{cell} for $Zn\,(s) + Pb^{2+}\,(1\,M) \rightarrow Zn^{2+}\,(1\,M) + Pb\,(s)$ is + 0·66 volt. E_{cell} for the reaction

$$Zn\,(s) + Pb^{2+}\,(0{\cdot}1\,M) \rightarrow Zn^{2+}\,(0{\cdot}1\,M) + Pb\,(s) \quad \text{is}$$

(a) +0·63 volt (b) +0·66 volt (c) +0·69 volt (d) +0·72 volt (b)

9. E^0_{cell} for the reaction $Cu^{2+} + 2Cl^- \rightarrow Cu\,(s) + Cl_2\,(g)$ is − 1·02 V. This reaction
(a) can be made to produce electricity in a voltaic cell
(b) occurs whenever Cu^{2+} and Cl^- are brought together in an aqueous solution
(c) can be made to occur in an electrolytic cell
(d) can occur in an acidic solution but not in a basic solution (c)

10. E^0_{cell} for the reaction $Co\,(s) + Ni^{2+} \rightarrow Co^{2+} + Ni\,(s)$ is +0·03 volt. If cobalt metal is added to an aqueous solution having $[Ni^{2+}] = 1\,M$,
(a) the reaction will not proceed in the forward direction at all
(b) the displacement of Ni^{2+} from solution by Co will go to completion
(c) the displacement of Ni^{2+} from solution by Co will proceed to a considerable extent, but the reaction will stop before the Ni^{2+} is completely displaced
(d) only the reverse reaction will occur (c)

11. From the electrochemical series given in the text, determine the approximate value of E^0 for $X^{2+}\,(aq) + 2e \rightarrow X\,(s)$.
(a) The metal X dissolves in nitric acid but not in hydrochloric acid. It can displace Ag^+ but not Cu^{2+}.
(b) The metal X dissolves in hydrochloric acid producing H_2 but does not displace either Zn^{2+} or Fe^{2+}.
[(a) $0{\cdot}34\,V < E^0 < 0{\cdot}80\,V$
(b) $-0{\cdot}44\,V < E^0 < 0{\cdot}00\,V$]

12. The standard reduction potential of a calomel half cell is 0·28 V at 25°C. Calculate half-cell potential when 0·1 N KCl solution is used. (0·339 V)
[**Hint:** $Hg_2Cl_2\,(s) + 2e^- \rightarrow 2Hg + 2Cl^-$ (0·1 N KCl)]

13. What is the potential of a cell containing two hydrogen electrodes, the negative one in contact with 10^{-8} molar H^+ and the positive one in contact with 0·025 molar H^+? (0·379 volt)

14. Copper can reduce zinc ions if the resultant copper ions can be kept at a sufficiently low concentration by the formation of an insoluble salt. What is the maximum concentration of Cu^{2+} in solution if this reaction is to occur, when Zn^{2+} is 1 molar? (6×10^{-38} M)
[**Hint** for Cu, $Cu^{2+}\,||\,Zn^{2+}$, Zn; $E_{cell} = E_{red}\,(Zn) - E_{red}\,(Cu) = 0$]

15. A cell contains two hydrogen electrodes. The negative electrode is in contact with a solution of 10^{-6} M hydrogen ions. The emf of the cell is 0·118 V at 25°C. Calculate the concentration of hydrogen ions at the positive electrode. **(IIT 1988)** (10^{-4} M)
[**Hint : Positive electrode is cathode. See Example 26**]

16. The standard potentials, E^0 for the half-reactions are as

$$Zn = Zn^{2+} + 2e^-; \quad E^0 = 0.76\ V$$

$$Fe = Fe^{2+} + 2e^-; \quad E^0 = 0.41\ V$$

The emf for the cell reaction $Fe^{2+} + Zn \rightarrow Zn^{2+} + Fe$ is

(a) -0.35 V (b) $+0.35$ V (c) $+1.17$ V (d) -1.17 V

(IIT 1988) (b)

17. Given that

$$Fe^{3+} + e \rightleftharpoons Fe^{2+}; \quad E^0 = 0.77\ V$$

$$Fe^{2+} + 2e \rightleftharpoons Fe; \quad E^0 = -0.44\ V$$

What will be the E^0 value for the following half cell?

$$Fe^{3+} + 3e \rightleftharpoons Fe$$

(-0.04 V)

18. From the following values of E^0 drawn from the emf series, calculate standard emf and the equilibrium constant for the reaction,

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

$$E^0_{Hg_2^{2+},\ Hg} = 0.788\ V; \ E^0_{Hg^{2+},\ Hg_2^{2+}} = 0.92\ V.$$

(0.132 V; 1.72×10^2)

19. Will Fe (s) be oxidised to Fe^{2+} by reacting with 1 M HCl?

$$E^0_{Fe,\ Fe^{2+}} = +0.44\ V$$

(Yes)

20. A galvanic cell is composed of a standard Zn electrode and a chromium electrode immersed in a solution containing Cr^{3+}. At what concentration of Cr^{3+} will the emf of the cell be zero?

(0.1 M)

21. The standard electrode potential corresponding to the reduction $Cr^{3+} + e \rightarrow Cr^{2+}$ is $E^0 = -0.407$ volt. If excess Fe (s) is added to a solution in which $[Cr^{3+}] = 1$ M, what will be $[Fe^{2+}]$ when equilibrium is established at 25°C?

$$\{Fe\,(s) + 2Cr^{3+} \rightleftharpoons Fe^{2+} + 2Cr^{2+}\}$$

($[Fe^{2+}] = 0.42$ M)

22. The emf of a cell consisting of a copper and a lead electrode immersed in 1 M solution of salts of these metals is 0.47 V. Will the emf change if 0.001 M solutions are taken?

(No)

23. What is the potential of a hydrogen electrode at pH = 10? (-0.59 V)

24. We have an oxidation–reduction system:

$$[Fe(CN)_6]^{3-} + e \rightleftharpoons [Fe(CN)_6]^{4-}; \ E^0 = +0.36\ V$$

At what ratio of the concentrations of the oxidised and reduced forms will the potential of the system be 0.28 V?

(0.044)

25. Calculate the emf of the following cell at 25°C,

$$\underset{(0.1\ M)}{Fe \mid FeSO_4} \parallel \underset{(0.01\ M)}{CuSO_4 \mid Cu}$$

Given that E^0 (oxd.) of Fe and Cu are 0.44 V and -0.34 V respectively. (0.75 V)

26. Calculate the emf of the following cells, find their cell reactions using E^0 values from the table.

(i) Ag | Ag^+ (0·01 M) || Zn^{2+} (0·1 M) | Zn

(ii) Pt | Fe^{2+} (1 M), Fe^{3+} (0·1 M) || Cl^- (0·001 M) | AgCl | Ag

(iii) Zn | ZnO_2^{2-} (0·1 M), OH^- (1 M) | HgO | Hg

In each case, is the reaction as written spontaneous or not?

(i) Zn^{2+} (0·1) + 2Ag = Zn + $2Ag^+$ (0·01); − 1·473 volt

(ii) AgCl + Fe^{2+} (1·0) = Ag + Cl^- (0·001) + Fe^{3+} (0·1); − 0·313 volt

(iii) HgO + Zn + $2OH^-$ (1·0) = Hg + ZnO_2^{2-} (0·1) + H_2O; 1·343 volt

[cell (iii) is spontaneous, (i) and (ii) are not]

27. Neglecting the liquid-junction potential, calculate the emf of the following cell at 25°C.

H_2 (1 atm) | 0·5 M HCOOH || 1 M CH_3COOH | H_2 (1 atm)

The dissociation constants of HCOOH and CH_3COOH are $1{\cdot}77 \times 10^{-4}$ and $1{\cdot}8 \times 10^{-5}$ respectively. (− 0·0246 volts)

28. The emf of the cell,

(Pt) H_2 | H^+ (c = unknown) || KCl soln. | Hg_2Cl_2 | Hg is 0·4783 V.

If the electrode potential of the calomel chloride is + 0·2420 volt (reduction), calculate pH of the solution. (3·994)

29. Calculate the cell potential for the following galvanic cell:

The first electrode consists of Fe^{3+} | Fe^{2+} couple in which $[Fe^{3+}] = 1$ M and $[Fe^{2+}] = [0{\cdot}1$ M]

The second electrode consists of MnO_4^- | Mn^{2+} couple in acidic solution in which $[MnO_4^-] = 1 \times 10^{-2}$ M, $[Mn^{2+}] = 1 \times 10^{-4}$ M and $[H^+] = 1 \times 10^{-3}$ M.

($E^0_{Fe^{3+}, Fe^{2+}} = {\cdot}771$ V, $E^0_{MnO_4^-, Mn^{2+}} = 1{\cdot}51$ V)

[Hint: Cell reactions are: $Fe^{2+} = Fe^{3+} + e$ at anode

$MnO_4^- + 8H^+ + 5e = Mn^{2+} + 4H_2O$ at cathode] (0·42 V)

30. Find the equilibrium constant at 25°C for the reaction,

$$Hg_2(NO_3)_2 + 2Fe(NO_3)_2 = 2Hg + 2Fe(NO_3)_3$$

$E^0_{Hg_2^{2+}, Hg} = 0{\cdot}79$ volt; $E^0_{Fe^{3+}, Fe^{2+}} = 0{\cdot}77$ volt (4·76)

31. Calculate the potential of a silver electrode in a saturated solution of AgBr ($K_{sp} = 6 \times 10^{-13}$) containing, in addition, 0·1 mole per litre KBr. (0·14 volt)

$E^0_{Ag^+, Ag} = 0{\cdot}80$ volt

32. Calculate the potential of a cell in which hydrogen electrode is immersed in pure water, in a solution with a pH of 3·5 and in a solution with a pH of 10·7. (0·425 volt)

33. A galvanic cell is constructed of two hydrogen electrodes, one immersed in a solution with H^+ at 1 M and the other in 1 M KOH. Calculate E_{cell}. If 1 M KOH solution is replaced by 1 M NH_3, will E_{cell} be higher or lower than in 1 M KOH? (0·83 V, lower)

34. Using the electrochemical series table, explain why Cu (I) sulphate does not exist in aqueous solution.

[**Hint:** Positive E^0 value of $2Cu^+ \rightarrow Cu^{2+} + Cu$ shows that Cu (I) is not stable.]

35. For the cell,

(Pt) H_2 (1 atm) | H^+ (pH unknown) || H^+ (pH = 1) | H_2 (1 atm). The measured cell potential at 25°C is 0·16 volt. Calculate the unknown pH. (3·7)

36. Write the cell reaction and calculate the potential of the cell,

$$Cl_2 (p = 0{\cdot}9 \text{ atm}) \mid \text{NaCl solution} \mid Cl_2 (p = 0{\cdot}1 \text{ atm}).$$

Will the cell reaction be spontaneous as written? (− 0·0282 volt)

37. The emf of a galvanic cell composed of two hydrogen electrodes is 272 mV. What is the pH of the solution in which the anode is immersed if the cathode is in a solution with a pH of 3? (7·6)

38. Calculate the standard emf, standard free energy change and equilibrium constant of a cell in which the following reaction takes place at 25°C.

$$\frac{1}{2}Cu\,(s) + \frac{1}{2}Cl_2\,(g) = \frac{1}{2}Cu^{2+} + Cl^-$$

$E^0_{Cl_2,Cl^-} = +\,1{\cdot}36$ volt; $E^0_{Cu^{2+}_{,}Cu} = +\,0{\cdot}34$ volt (1·02 volt, − 98·43 kJ, 2×10^{17})

39. What must be the pressure of fluorine gas to produce a reduction potential of 2·75V in a solution that contains 0·38 M F^-? $E^0_{F_2,F^-} = 2{\cdot}87$V. ($1{\cdot}25 \times 10^{-5}$ atm)

40. Show by calculation that $E^0 = -1{\cdot}662$V for the reduction of Al^{3+} to Al(s), regardless of whether the equation for the reaction is written as

(a) $\frac{1}{3}Al^{3+} + e \rightarrow \frac{1}{3}Al(s)$; $\Delta G^\circ = 160{\cdot}4$ kJ/mole

or (b) $Al^{3+} + 3e \rightarrow Al(s)$; $\Delta G^\circ = 481{\cdot}2$ kJ/mole

41. If in a galvanic cell, say, Daniell cell, an inert platinum is used instead of a salt bridge, will the cell still produce a potential. (No)

42. Does the physical size of a galvanic cell govern the potential that it will deliver? What does the size affect? (No)

43. Consider the electrochemical cell represented by

$$Mg \mid Mg^{2+} \parallel Fe^{3+} \mid Fe^{2+}$$

If 150 mA is to be drawn from this cell for a period of 20 minutes, what is the minimum mass for the magnesium electrode? (0·0224 g)

44. Given the following E^0 values at 25°C, calculate K_{sp} for CdS.

$Cd^{2+}(aq) + 2e \rightarrow Cd(s)$; $E^0 = -0{\cdot}403V$

$CdS(s) + 2e \rightarrow Cd(s) + S^{2-}(aq)$; $E^0 = -1{\cdot}21V$

Also evaluate ΔG° at 25°C for the process

$CdS(s) \rightleftharpoons Cd^{2+}(aq) + S^{2-}(aq)$

($4{\cdot}90 \times 10^{-28}$, +155·8 kJ/mole)

45. Under standard conditions what is the maximum electrical work, in joules, that a cell employing the cell reaction

$$Cd(s) + 2H^+(aq) \rightarrow Cd^{2+}(aq) + H_2(g)$$

can accomplish if 0·780 mole of Cd is consumed?

$E^0_{Cd^{2+}, Cd} = -0{\cdot}40V$, $E^0_{H^+, H_2} = 0{\cdot}0V$

If the work comes with a negative sign, what does it indicate

(−60·2 kJ, negative sign means work is done by the cell)

46. A cell contains 0·04 M Cr^{3+} in one compartment and 1·0 M Cr^{3+} in the other with Cr electrodes in both. Which is the anode compartment? (Dilute solution side)

47. Under standard conditions for all concentrations, the following reaction is spontaneous at 25°C

$$O_2(g) + 4H^+(aq) + 4Br^-(aq) \rightarrow 2H_2O(l) + 2Br_2(l)$$

If $[H^+]$ is decreased so that the pH = 3·6, what value will E_{cell} have, and will the reaction be spontaneous at this $[H^+]$? Given:

$O_2 + 4H^+ + 4e = 2H_2O$; $E^0 = 1{\cdot}23V$

$Br_2 + 2e = 2Br^-$; $E^0 = 1{\cdot}07V$ (−0·05V; No)

48. An electrode is prepared by dipping a silver strip into a solution saturated with silver thiocyanate, AgSCN, and containing 0·10 M SCN^-. The emf of the voltaic cell constructed by connecting this electrode as the cathode to the standard hydrogen half cell as the anode is 0·45V. What is the solubility product of AgSCN?

(1×10^{-7})

49. Calculate equilibrium constant for the equilibrium,

$$2MnO_4^- + 6H^+ + 5H_2C_2O_4 \rightleftharpoons 2Mn^{2+} + 8H_2O + 10CO_2$$

Given that, $E^0_{MnO_4^-, Mn^{2+}} = 1{\cdot}51V$ and $E^0_{CO_2, C_2O_4^{2-}} = -0{\cdot}49V$ (10^{338})

Objective Problems

1. Which of the following statements is wrong about galvanic cells?
   (a) Cathode is the positive electrode.
   (b) Cathode is the negative electrode.
   (c) Electrons flow from anode to cathode in the external circuit.
   (d) Reduction occurs at cathode.

2. In a galvanic cell
   (a) chemical reaction produces electrical energy
   (b) electrical energy produces chemical reaction
   (c) reduction occurs at anode
   (d) oxidation occurs at cathode

3. In the galvanic cell $Cu \mid Cu^{2+}(1\ M) \mid\mid Ag^{+}(1\ M) \mid Ag$, the electrons will travel in the external circuit
   (a) from Ag to Cu (b) from Cu to Ag
   (c) electrons do not travel in the external circuit

4. Is 1 M H^{+} solution under hydrogen gas at 1 atm capable of oxidising Ag metal in the presence of 1 M Ag^{+}?
   (a) Yes (b) No

5. The potential of hydrogen electrode is –118 mV. The concentration of H^{+} in the solution is
   (a) 0·01 M (b) 2 M (c) 10^{-4} M (d) 1 M

6. $E°$ for the half cell $Zn^{2+} \mid Zn$ is – 0·76 V. emf of the cell
   $Zn \mid Zn^{2+}(1\ M) \mid\mid 2H^{+}(1\ M) \mid H_2(1\ atm)$ is
   (a) – 0·76 V (b) + 0·76 V (c) – 0·38 V (d) + 0·38 V

7. The standard reduction potentials at 298 K for the following half-reactions are given against each.

$$Zn^{2+}(aq) + 2e = Zn(s);\ -0.762\ V$$
$$Cr^{3+}(aq) + 3e = Cr(s);\ -0.74\ V$$
$$2H^{+} + 2e = H_2(g);\ \pm 0.0\ V$$
$$Fe^{3+}(aq) + e = Fe^{2+}(aq);\ +0.77\ V$$

   Which is the strongest reducing agent?
   (a) Zn (s) (b) Cr (s) (c) H_2 (g) (d) Fe^{3+} (aq)

8. The standard reduction potentials, E^0, for the half-reactions are as

$$Zn = Zn^{2+} + 2e;\ E^0 = +0.76\ V$$
$$Fe = Fe^{2+} + 2e;\ E^0 = +0.41\ V$$

   the emf for the cell reaction,

$$Fe^{2+} + Zn = Zn^{2+} + Fe \text{ is}$$

   (a) – 0·35 V (b) + 0·35 V (c) + 1·17 V (d) – 1·17 V
   (IIT 1988)

9. From the following E^0 values of half cells,
   (i) $A + e \rightarrow A^{-}$; $E^0 = -0.24\ V$
   (ii) $B^{-} + e \rightarrow B^{2-}$; $E^0 = +1.25\ V$
   (iii) $C^{-} + 2e \rightarrow C^{3-}$; $E^0 = -1.25\ V$
   (iv) $D + 2e \rightarrow D^{2-}$; $E^0 = +0.68\ V$
   What combination of two half cells would result in a cell with the largest potential?
   (a) (ii) and (iii) (b) (ii) and (iv) (c) (i) and (iii) (d) (i) and (iv)

10. From the following E^0 values of half cells
   (i) $A \rightarrow A^{+} + e$; $E^0 = +1.2\ V$ (ii) $B^{-} \rightarrow B + e$; $E^0 = -2.1\ V$
   (iii) $C \rightarrow C^{2+} + 2e$; $E^0 = -0.38\ V$ (iv) $D^{-2} \rightarrow D^{-} + e$; $E^0 = -0.59\ V$
   What combination of two half cells would result in a cell with the largest potential?
   (a) (i) and (iv) (b) (ii) and (iii) (c) (iii) and (iv) (d) (i) and (ii)

11. From the following E^0 values of half cells

(i) $A^{3-} \rightarrow A^{2-} + e;$ $E^0 = 1{\cdot}5$ V

(ii) $B^{+} + e \rightarrow B;$ $E^0 = -0{\cdot}5$ V

(iii) $C^{2+} + e \rightarrow C^{+};$ $E^0 = +0{\cdot}5$ V

(iv) $D \rightarrow D^{2+} + 2e;$ $E^0 = -1{\cdot}5$ V

What combination of two half cells would result in a cell with the largest potential?
(a) (i) and (iii) (b) (i) and (iv) (c) (ii) and (iv) (d) (iii) and (iv)

12. If the following half cells have the E^0 values as
$Fe^{3+} + e \rightarrow Fe^{2+}$; $E^0 = +0{\cdot}77$ V and $Fe^{2+} + 2e \rightarrow Fe$; $E^0 = -0{\cdot}44$ V; the E^0 of the half cell $Fe^{3+} + 3e \rightarrow Fe$ will be
(a) 0·33 V (b) 1·21 V (c) −0·04 V (d) 0·605 V

13. E^0 (red.) values of the half cells Mg^{2+}/Mg and Cl_2/Cl^- are respectively −2·36 V and + 1·36 V. The E^0 value of the cell $Mg \mid Mg^{2+} \parallel Cl_2 \mid Cl^-$ is
(a) 3·72 V (b) 1 V (c) 0·18 V (d) 2·64 V

14. For the cell reaction $Zn\,(s) + Mg^{2+}\,(1\,M) = Zn^{2+}\,(1\,M) + Mg$, the emf has been found to be 1·60 V. E^0 of the cell is
(a) −1·60 V (b) 1·60 V (c) 0·0 V (d) 0·16 V

15. E^0 for $F_2 + 2e = 2F^-$ is 2·8 V, E^0 for $\frac{1}{2}F_2 + e = F^-$ is
(a) 2·8 V (b) 1·4 V (c) −2·8 V (d) −1·4 V

16. $\Delta G°$ of the cell reaction $AgCl\,(s) + \frac{1}{2}H_2\,(g) = Ag\,(s) + H^+ + Cl^-$ is −21·52 kJ. $\Delta G°$ of $2AgCl\,(s) + H_2\,(g) = 2Ag\,(s) + 2H^+ + 2Cl^-$ is
(a) −21·52 kJ (b) −10·76 kJ (c) −43·04 kJ (d) 43·04 kJ

17. The value of equilibrium constant for a feasible cell reaction is
(a) < 1 (b) 0 (c) = 1 (d) > 1

18. E^0 for the reaction $Fe + Zn^{2+} = Zn + Fe^{2+}$ is −0·35 V. The given cell reaction is
(a) feasible (b) not feasible (c) in equilibrium

19. A galvanic cell is composed of two hydrogen electrodes, one of which is a standard one. In which of the following solutions should the other electrode be immersed to get maximum emf?
(a) 0·1 M HCl (b) 0·1 M CH_3COOH
(c) 0·1 M H_3PO_4 (d) 0·1 M H_2SO_4

20. $\frac{1}{2}H_2\,(g) + AgCl\,(s) = H^+\,(aq) + Cl^-\,(aq) + Ag\,(s)$ occurs in the galvanic cell:
(a) Ag/AgCl (s) | KCl (sol) | | $AgNO_3$ (sol) | Ag
(b) Pt/H_2 (g) | HCl (sol) | | $AgNO_3$ (sol) | Ag
(c) Pt/H_2 (g) | HCl (sol) | | AgCl (s) | Ag
(d) Pt/H_2 (g) | KCl (sol) | | AgCl (s) | Ag
(IIT 1985)

21. For the cell Tl | Tl^+ (0·001 M) || Cu^{2+} (0·1 M) | Cu. E_{cell} at 25°C is 0·83 V which can be increased

(a) by increasing $[Cu^{2+}]$
(b) by increasing $[Tl^+]$
(c) by decreasing $[Cu^{2+}]$
(d) by decreasing $[Tl^+]$

22. How much will the potential of Zn/Zn^{2+} change if the solution of Zn^{2+} is diluted 10 times?

(a) increase by 0·03 V
(b) decrease by 0·03 V
(c) increase by 0·059 V
(d) decrease by 0·059 V

23. The half-cell potential of a hydrogen electrode at pH = 10 will be

(a) 0·59 V (b) – 0·59 V (c) 0·059 V (d) – 0·059 V

24. How much will the potential of a hydrogen electrode change when its solution initially at pH = 0 is neutralised to pH = 7?

(a) Increase by 0·059 V
(b) Decrease by 0·059 V
(c) Increase by 0·41 V
(d) Decrease by 0·41 V

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

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

(IIT 1996)

26. The standard reduction potential of Cu^{2+}/Cu and Cu^{2+}/Cu^+ are 0·337 and 0·153 respectively. The standard electrode potential of Cu^+/Cu half cell is

(a) 0·184 V (b) 0·827 V (c) 0·521 V (d) 0·490 V (IIT 1997)

27. Which of the following facts about the chemical cell and concentration cell is correct?

(a) Chemical cell is an electrolytic cell whereas concentration cell is a galvanic cell.
(b) Chemical cell has an overall cell reaction whereas concentration cell has no overall reaction.
(c) Two half cells of both the chemical and concentration cells are chemically different.
(d) E_{cell} equations (Nernst equation) of both the cells have the term E^0_{cell}.

28. The temperature coefficient of a galvanie cell is $+5{\cdot}0 \times 10^{-5} VK^{-1}$. During the discharge of the cell, the cell temperature

(a) increases
(b) decreases
(c) does not change
(d) first increases and then decreases

29. Standard electrode potential data are useful for understanding the suitability of an oxidant in a redox titration. Some half-cell reactions and their standard potentials are given below:

$MnO_4^-(aq) + 8H^+(aq) + 5e \rightarrow Mn^{2+}(aq) + 4H_2O(l)$; $E^0 = 1{\cdot}51V$

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$; $E^0 = 1{\cdot}38V$

$Fe^{3+}(aq) + e \rightarrow Fe^{2+}(aq)$; $E^0 = 0{\cdot}77V$

$Cl_2(g) + 2e \rightarrow 2Cl^-(aq)$; $E^0 = 1{\cdot}40V$

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

(a) MnO_4^- can be used in aqueous HCl

(b) $Cr_2O_7^{2-}$ can be used in aqueous HCl

(c) MnO_4^- can be used in aqueous H_2SO_4

(d) $Cr_2O_7^{2-}$ can be used in aqueous H_2SO_4

(IIT 2002)

30. Using the following Latimer diagram for bromine,

$$pH = 0;\ BrO_4 \xrightarrow{1.82V} BrO_3^- \xrightarrow{1.50V} HBrO \xrightarrow{1.595V} Br_2 \xrightarrow{1.0652V} Br^-$$

the species undergoing disproportionation is

(a) BrO_4 (b) BrO_3^- (c) HBrO (d) Br_2

[**Hint:** If the potential to the left of a given chemical species is less than that to the right, the species will undergo disproportionation]

Answers

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

❑❑❑

CHAPTER NINETEEN

OXIDATION NUMBER AND BALANCING OF REDOX REACTIONS

THE OXIDATION-NUMBER CONCEPT

The oxidation number, or oxidation state, of an atom in a substance is defined as the actual charge of the atom if it exists as a monatomic ion, or a hypothetical charge assigned to the atom in the substance according to some accepted rules.

1. Electrons shared between two unlike atoms are counted to be with the more electronegative atom. Electrons between two like atoms are divided equally between the two atoms. For example, in HCl, the oxidation numbers of H and Cl atoms are +1 and −1 respectively and the oxidation numbers of H in H_2, Cl in Cl_2, etc., are all zero.

   The oxidation number of an atom in an element in its uncombined state is always zero.

3. The oxidation number of H in a compound is assigned as +1 except in metallic hydrides, where it is −1.

4. The oxidation number of O in compounds is assigned as −2 except in peroxides (H_2O_2, Na_2O_2, BaO_2, etc.), where it is −1; in OF_2, where it is +2 and in superoxide (KO_2), where it is $-\frac{1}{2}$.

5. Fluorine has an oxidation number of −1 in all of its compounds.

6. The oxidation number of halogens in halides is −1; sulphur in sulphides is −2; alkali metals, +1; alkaline earth metals, +2.

7. The algebraic sum of oxidation numbers of all atoms in a compound or ion is equal to the charge on it.

8. In coordination compounds, the ligands, for example, NH_3, CO, NO and H_2O, are neutral. Hence, their oxidation numbers are taken as zero. The oxidation numbers of CH_3, C_6H_5 are +1 and CN, OH, Cl are all −1.

The oxidation-number concept is of great utility to chemistry. In redox reactions, the oxidation number changes. The decrease in oxidation number is called reduction and increase in oxidation number, oxidation. An *oxidising agent* shows a decrease in its oxidati , and a *reducing agent* shows

PROBLEMS

Assign ON to atoms of only those elements which undergo ON change in the following redox reactions, and then balance the equations.

1. $C_2H_5OH + Cr_2O_7^{2-} + H^+ = Cr^{3+} + C_2H_4O + H_2O$
2. $Sn(OH)_3^- + Bi(OH)_3 + OH^- = Sn(OH)_6^{2-} + Bi$
3. $IO_3^- + N_2H_4 + HCl = N_2 + ICl_2^- + H_2O$
4. $NO_2 + OH^- = NO_3^- + NO_2^- + H_2O$
5. $Hg_2Cl_2 + NH_3 = Hg + HgNH_2Cl + NH_4Cl$
6. $Zn + NO_3^- + H^+ = Zn^{2+} + NH_4^+ + H_2O$
7. $I_2 + NO_3^- + H^+ = IO_3^- + NO_2 + H_2O$
8. $MnO_4^- + SO_3^{2-} + H_2O = MnO_2 + SO_4^{2-} + OH^-$

$H_2O_2 + ClO_2 + OH^- = ClO_2^- + O_2 + H_2O$

. $ClO^- + CrO_2^- + OH^- = Cl^- + CrO_4^{2-} + H_2O$

11. $I_2 + Cl_2 + H_2O = HIO_3 + HCl$
12. $Cl_2 + KOH = KOCl + KCl + H_2O$
13. $Cl_2 + KOH = KClO_3 + KCl + H_2O$
14. $H_2O_2 + I_2 = HIO_3 + H_2O$
    [**Hint:** Change in ON = 10]
15. $H_2O_2 + KMnO_4 = MnO_2 + KOH + O_2 + H_2O$
16. $HNO_2 + KMnO_4 + H_2SO_4 = HNO_3 + KMnO_4 + K_2SO_4 + H_2O$
17. $NaNO_2 + NaI + H_2SO_4 = NO + I_2 + Na_2SO_4 + H_2O$
18. $N_2H_4 + AgNO_3 + KOH = N_2 + Ag + KNO_3 + H_2O$
19. $N_2H_4 + Zn + KOH + H_2O = NH_3 + K_2[Zn(OH)_4]$
20. $Fe + N_2H_4 + H_2O = Fe(OH)_2 + NH_3$
21. $H_2S + HNO_3 = NO + S + H_2O$
22. $P + HNO_3 = HPO_3 + NO + H_2O$
23. $K_2Cr_2O_7 + HCl = KCl + CrCl_3 + H_2O + Cl_2$
24. $MnO_4^- + C_2O_4^{2-} + H^+ = CO_2 + Mn^{2+} + H_2O$
25. $Cr_2O_7^{2-} + C_2O_4^{2-} + H^+ = Cr^{3+} + CO_2 + H_2O$
26. $Cr(OH)_3 + IO_3 + OH^- = I^- + CrO_4^{2-} + H_2O$

27. $KMnO_4 + H_2S + H_2SO_4 = KHSO_4 + MnSO_4 + S + H_2O$

28. $NO_3^- + Cl^- + H^+ = NO + Cl_2 + H_2O$

29. $H_2O_2 + I^- + H^+ = I_2 + H_2O$

30. $Cr_2O_7^{2-} + NO_2^- + H^+ = Cr^{3+} + NO_3^- + H_2O$

31. $N_2O_4 + BrO_3^- + H_2O = NO_3^- + Br^- + H^+$

32. $S_2O_3^{2-} + Sb_2O_5 + H^+ + H_2O = SbO + H_2SO_3$

33. $Fe_2(SO_4)_3 + Fe = FeSO_4$

34. $Cu(NH_3)_4Cl_2 + KCN + H_2O = K_2Cu(CN)_3 + NH_3 + KCNO + NH_4Cl + KCl$

35. $Ag + KCN + H_2O + O_2 = KAg(CN)_2 + KOH$

36. $Zn + NO_3^- + H^+ = Zn^{2+} + NO_2 + H_2O$

37. $MnO_4^- + CN^- + H_2O = MnO_2 + CNO^- + OH^-$

38. $AsO_3^{3-} + IO_3^- = AsO_4^{3-} + I^-$

39. $Fe_3O_4 + MnO_4^- + H_2O = Fe_2O_3 + MnO_2 + OH^-$

40. $H_2S + Cr_2O_7^{2-} + H^+ = Cr^{3+} + S_8 + H_2O$

41. $ZnS + O_2 = ZnO + SO_2$

42. $KNO_3 + FeSO_4 + H_2SO_4 = KHSO_4 + Fe_2(SO_4)_3 + NO + H_2O$

43. $H_2S + K_2Cr_2O_7 + H_2SO_4 = KHSO_4 + Cr_2(SO_4)_3 + S + H_2O$

44. $KI + H_2SO_4 = KHSO_4 + SO_2 + I_2 + H_2O$

45. $C_2H_5OH + MnO_4^- + OH^- = C_2H_3O^- + MnO_2 + H_2O$

46. $Al + KMnO_4 + H_2SO_4 = KHSO_4 + Al_2(SO_4)_3 + MnSO_4 + H_2O$

47. $K_2Cr_2O_7 + H_2O + S = SO_2 + KOH + Cr_2O_3$

48. $MnO_2 + HCl = MnCl_2 + Cl_2 + H_2O$

49. $MnO_4^- + SO_3^{2-} + H_2O = MnO_2 + SO_4^{2-} + OH^-$

50. $Cr_2O_7^{2-} + SO_3^{2-} + H^+ = Cr^{3+} + SO_4^{2-} + H_2O$

51. $I_2 + SO_2 + H_2O = SO_4^{2-} + I^- + H^+$

52. $Sn + NO_3^- + H^+ = SnO_2 + NO_2 + H_2O$

53. $MnO_4^- + SO_2 + H_2O = Mn^{2+} + SO_4^{2-} + H^+$

54. $MnO_4^- + SO_3^{2-} + OH^- = MnO_4^{2-} + SO_4^{2-} + H_2O$

55. $ClO^- + Br^- = BrO_3^- + Cl^-$

56. $Zn + NO_3^- + H^+ = Zn^{2+} + NH_4^+ + H_2O$

57. $KMnO_4 + HCl = Cl_2 + KCl + MnCl_2 + H_2O$

58. $BaCrO_4 + KI + HCl = BaCl_2 + I_2 + KCl + CrCl_3 + H_2O$

59. $ClO_3^- + SO_2 + H^+ = ClO_2 + HSO_4^-$

60. $Mn^{2+} + S_2O_8^{2-} + H_2O = MnO_4^- + HSO_4^- + H^+$

61. $Cl_2 + IO_3^- + OH^- = Cl^- + IO_4^- + H_2O$

62. $H_2SO_3 + Cr_2O_7^{2-} + H^+ = HSO_4^- + Cr^{3+} + H_2O$

63. $ClO_2 + SbO_2^- + OH^- = ClO_2^- + Sb(OH)_6^- + H_2O$

64. $Zn + NO_3^- + OH^- = NH_3 + ZnO_2^{2-} + H_2O$

65. $AsO_3^{3-} + MnO_4^- = AsO_4^{3-} + MnO_2 + H_2O$

66. $KMnO_4 + H_2O_2 + H_2SO_4 = MnSO_4 + K_2SO_4 + O_2 + H_2O$

67. $H_2O_2 + PbS = PbSO_4 + H_2O$

68. $MnO_4^- + C_2O_4^{2-} + H^+ = Mn^{2+} + CO_2 + H_2O$

69. $Fe^{2+} + Cr_2O_7^{2-} + H^+ = Fe^{3+} + Cr^{3+} + H_2O$

70. $AsO_3^{3-} + I_2 + H_2O = AsO_4^{3-} + H^+ + I^-$

71. $S_2O_3^{2-} + I_2 = S_4O_6^{2-} + I^-$

72. $HNO_3 + I_2 = HIO_3 + NO_2 + H_2O$

73. $K_2Cr_2O_7 + H_2SO_4 + KI = I_2 + K_2SO_4 + Cr_2(SO_4)_3 + H_2O$

74. $CuO + NH_3 = Cu + N_2 + H_2O$

75. $As_2S_5 + HNO_3 = H_3AsO_4 + H_2SO_4 + NO_2 + H_2O$

76. $PbS + O_3 = PbSO_4 + O_2$

77. $Cl_2 + SeO_3^{2-} + H_2O = SeO_4^{2-} + Cl^- + H^+$

78. $Cu_3P + H^+ + Cr_2O_7^{2-} = Cu^{2+} + H_3PO_4 + Cr^{3+} + H_2O$

79. $Na_2SnO_2 + Bi(OH)_3 = Bi + Na_2SnO_3 + H_2O$

80. $H_2O + SbCl_3 = SbOCl + 2HCl$

81. $K_4Fe(CN)_6 + Ce(NO_3)_4 + KOH = Ce(OH)_3 + Fe(OH)_3 + H_2O + K_2CO_3 + KNO_3$

82. $S + OH^- = S^{2-} + S_2O_3^{2-} + H_2O$

83. $IO_4^- + I^- + H^+ = I_2 + H_2O$

84. $KMnO_4 = K_2MnO_4 + MnO_2 + O_2$
[**Hint:** $KMnO_4$ reduces to both K_2MnO_4 and MnO_2 and change in ON = 4]

85. $(NH_4)_2Cr_2O_7 = N_2 + H_2O + Cr_2O_3$

86. $MnO_4^{2-} + H^+ = MnO_4^- + MnO_2 + H_2O$

87. $H_3PO_3 = H_3PO_4 + PH_3$

88. $Zn + HNO_3 = Zn(NO_3)_2 + N_2O + H_2O$

89. $CuS + NO_3^- + H^+ = Cu^{2+} + S_8 + NO + H_2O$

90. $CuSO_4 + KI = Cu_2I_2 + I_2 + K_2SO_4$

91. $FeSO_4 = Fe_2O_3 + SO_2 + SO_3$

92. $NaOH + Cl_2 = NaCl + NaClO + H_2O$

93. $NH_3 + Hg_2Cl_2 = Hg + Hg(NH_2)Cl + HCl$
[**Hint:** Change in ON = 1]

94. $Br_2 + OH^- = BrO^- + Br^- + H_2O$

95. $As_2S_5 + HNO_3 = H_2SO_4 + NO_2 + H_3AsO_4 + H_2O$

96. $Cr_2O_7^{2-} + SO_2 + H^+ = Cr^{3+} + HSO_4^- + H_2O$

97. $HCl + WO_3 + SnCl_2 = H_2SnCl_6 + W_3O_8 + H_2O$

98. $HCl + FeCl_3 + V(OH)_4Cl = VOCl_2 + H_2O + FeCl_3$

99. $Au + KCN + H_2O + O_2 = KAu(CN)_4 + KOH$

100. $KOH + KMnO_4 = K_2MnO_4 + O_2 + H_2O$

Answers

1. $3C_2H_5OH + Cr_2O_7^{2-} + 8H^+ = 2Cr^{3+} + 3C_2H_4O + 7H_2O$

2. $Sn(OH)_3^- + 2Bi(OH)_3 + 3OH^- = 3Sn(OH)_6^{2-} + 2Bi$

3. $IO_3^- + N_2H_4 + 2HCl = N_2 + ICl_2^- + 3H_2O$

4. $2NO_2 + 2OH^- = NO_3^- + NO_2^- + H_2O$

5. $2Hg_2Cl_2 + 4NH_3 = 2Hg + 2HgNH_2Cl + 2NH_4Cl$

6. $4Zn + NO_3^- + 10H^+ = 4Zn^{2+} + NH_4^+ + 3H_2O$

7. $I_2 + 10NO_3^- + 8H^+ = 2IO_3^- + 10NO_2 + 4H_2O$

8. $2MnO_4^- + 3SO_2^{2-} + H_2O = 2MnO_2 + 3SO_4^{2-} + 2OH^-$

9. $H_2O_2 + 2ClO_2 + 2OH^- = 2ClO_2^- + O_2 + 2H_2O$

10. $3ClO^- + 2CrO_2^- + 2OH^- = 3Cl^- + 2CrO_4^{2-} + H_2O$

11. $I_2 + 5Cl_2 + 6H_2O = 2HIO_3 + 10HCl$

12. $2Cl_2 + 4KOH = 2KOCl + 2KCl + 2H_2O$

13. $3Cl_2 + 6KOH = KClO_3 + 5KCl + 3H_2O$

14. $5H_2O_2 + I_2 = 2HIO_3 + 4H_2O$

15. $3H_2O_2 + 2KMnO_4 = 2MnO_2 + 2KOH + 3O_2 + 2H_2O$

16. $5HNO_2 + 2KMnO_4 + 3H_2SO_4 = 5HNO_3 + 2KMnO_4 + K_2SO_4 + 3H_2O$

17. $2NaNO_2 + 2NaI + 2H_2SO_4 = 2NO + I_2 + 2Na_2SO_4 + 2H_2O$

18. $N_2H_4 + 4AgNO_3 + 4KOH = N_2 + 4Ag + 4KNO_3 + 4H_2O$

19. $N_2H_4 + Zn + 2KOH + 2H_2O = 2NH_3 + K_2[Zn(OH)_4]$

20. $Fe + N_2H_4 + 2H_2O = Fe(OH)_2 + 2NH_3$

21. $3H_2S + 2HNO_3 = 2NO + 3S + 4H_2O$

22. $3P + 5HNO_3 = 3HPO_3 + 5NO + H_2O$

23. $K_2Cr_2O_7 + 8HCl = 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$

24. $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ = 10CO_2 + 2Mn^{2+} + 8H_2O$

25. $Cr_2O_7^{2-} + 3C_2O_4^{2-} + 14H^+ = 2Cr^{3+} + 6CO_2 + 7H_2O$

26. $2Cr(OH)_3 + IO_3 + 4OH^- = I^- + 2CrO_4^{2-} + 5H_2O$

27. $2KMnO_4 + 5H_2S + 4H_2SO_4 = 2KHSO_4 + 2MnSO_4 + 5S + 8H_2O$

28. $2NO_3^- + 6Cl^- + 8H^+ = 2NO + 3Cl_2 + 4H_2O$

29. $H_2O_2 + 2I^- + 2H^+ = I_2 + 2H_2O$

30. $Cr_2O_7^{2-} + 3NO_2^- + 8H^+ = 2Cr^{3+} + 3NO_3^- + 4H_2O$

31. $3N_2O_4 + BrO_3^- + 3H_2O = 6NO_3^- + Br^- + 6H^+$

32. $S_2O_3^{2-} + 2Sb_2O_5 + 6H^+ + 3H_2O = 4SbO + 6H_2SO_3$

33. $Fe_2(SO_4)_3 + Fe = 3FeSO_4$

34. $2Cu(NH_3)_4Cl_2 + 7KCN + H_2O = K_2Cu(CN)_3 + 6NH_3 + KCNO + 2NH_4Cl + 2KCl$

35. $4Ag + 8KCN + 2H_2O + O_2 = 4KAg(CN)_2 + 4KOH$

36. $Zn + 2NO_3^- + 4H^+ = Zn^{2+} + 2NO_2 + 2H_2O$

37. $2MnO_4^- + 3CN^- + H_2O = 2MnO_2 + 3CNO^- + 2OH^-$

38. $3AsO_3^{3-} + IO_3^- = 3AsO_4^{3-} + I^-$

39. $6Fe_3O_4 + 2MnO_4^- + H_2O = 9Fe_2O_3 + 2MnO_2 + 2OH^-$

40. $24H_2S + 8Cr_2O_7^{2-} + 64H^+ = 16Cr^{3+} + 3S_8 + 56H_2O$

41. $2ZnS + 3O_2 = 2ZnO + 2SO_2$

42. $2KNO_3 + 6FeSO_4 + 5H_2SO_4 = 2KHSO_4 + 3Fe_2(SO_4)_3 + 2NO + 4H_2O$

43. $3H_2S + K_2Cr_2O_7 + 5H_2SO_4 = 2KHSO_4 + Cr_2(SO_4)_3 + 3S + 7H_2O$

44. $2KI + 3H_2SO_4 = 2KHSO_4 + SO_2 + I_2 + 2H_2O$

45. $3C_2H_5OH + 2MnO_4^- + OH^- = 3C_2H_3O^- + 2MnO_2 + 5H_2O$

46. $10Al + 6KMnO_4 + 27H_2SO_4 = 6KHSO_4 + 5Al_2(SO_4)_3 + 6MnSO_4 + 24H_2O$

47. $2K_2Cr_2O_7 + 2H_2O + 3S = 3SO_2 + 4KOH + 2Cr_2O_3$

48. $MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O$

49. $2MnO_4^- + 3SO_3^{2-} + H_2O = 2MnO_2 + 3SO_4^{2-} + 2OH^-$

50. $Cr_2O_7^{2-} + 3SO_3^{2-} + 8H^+ = 2Cr^{3+} + 3SO_4^{2-} + 4H_2O$

51. $I_2 + SO_2 + 2H_2O = SO_4^{2-} + 2I^- + 4H^+$

52. $Sn + 4NO_3^- + 8H^+ = SnO_2 + 4NO_2 + 4H_2O$

53. $2MnO_4^- + 5SO_2 + 2H_2O = 2Mn^{2+} + 5SO_4^{2-} + 4H^+$

54. $2MnO_4^- + SO_3^{2-} + 2OH^- = 2MnO_4^{2-} + SO_4^{2-} + H_2O$

55. $3ClO^- + Br^- = BrO_3^- + 3Cl^-$

56. $4Zn + NO_3^- + 10H^+ = 4Zn^{2+} + NH_4^+ + 3H_2O$

57. $2KMnO_4 + 16HCl = 5Cl_2 + 2KCl + 2MnCl_2 + 8H_2O$

58. $2BaCrO_4 + 6KI + 16HCl = 2BaCl_2 + 3I_2 + 6KCl + 2CrCl_3 + 8H_2O$

59. $2ClO_3^- + SO_2 + H^+ = 2ClO_2 + HSO_4^-$

60. $2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O = 2MnO_4^- + 10HSO_4^- + 6H^+$

61. $Cl_2 + IO_3^- + 2OH^- = 2Cl^- + IO_4^- + H_2O$

62. $3H_2SO_3 + Cr_2O_7^{2-} + 5H^+ = 3HSO_4^- + 2Cr^{3+} + 4H_2O$

63. $2ClO_2 + SbO_2^- + 2OH^- = 2ClO_2^- + Sb(OH)_6^- + 2H_2O$

64. $4Zn + NO_3^- + 7OH^- = NH_3 + 4ZnO_2^{2-} + 2H_2O$

65. $3AsO_3^{3-} + 2MnO_4^- = 3AsO_4^{3-} + 2MnO_2 + 2H_2O$

66. $2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 5O_2 + 8H_2O$

67. $4H_2O_2 + PbS = PbSO_4 + 4H_2O$

68. $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ = 2Mn^{2+} + 10CO_2 + 8H_2O$

69. $6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ = 6Fe^{3+} + 2Cr^{3+} + 7H_2O$

70. $AsO_3^{3-} + I_2 + H_2O = AsO_4^{3-} + 2H^+ + 2I^-$.

71. $2S_2O_3^{2-} + I_2 = S_4O_6^{2-} + 2I^-$

72. $10HNO_3 + I_2 = 2HIO_3 + 10NO_2 + 4H_2O$

73. $K_2Cr_2O_7 + 7H_2SO_4 + 6KI = 3I_2 + 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O$

74. $3CuO + 2NH_3 = 3Cu + N_2 + 3H_2O$

75. $As_2S_5 + 40HNO_3 = 2H_3AsO_4 + 5H_2SO_4 + 40NO_2 + 12H_2O$

76. $PbS + 4O_3 = PbSO_4 + 4O_2$

77. $Cl_2 + SeO_3^{2-} + H_2O = SeO_4^{2-} + 2Cl^- + 2H^+$

78. $6Cu_3P + 124H^+ + 11Cr_2O_7^{2-} = 18Cu^{2+} + 6H_3PO_4 + 22Cr^{3+} + 53H_2O$

79. $3Na_2SnO_2 + 2Bi(OH)_3 = 2Bi + 3Na_2SnO_3 + 3H_2O$

80. $H_2O + SbCl_3 = SbOCl + 2HCl$

81. $K_4Fe(CN)_6 + 61Ce(NO_3)_4 + 258KOH = 61Ce(OH)_3 + Fe(OH)_3$
$+ 36H_2O + 6K_2CO_3 + 250KNO_3$

82. $4S + 6OH^- = 2S^{2-} + S_2O_3^{2-} + 3H_2O$

83. $IO_4^- + 7I^- + 8H^+ = 4I_2 + 4H_2O$

84. $2KMnO_4 = K_2MnO_4 + MnO_2 + O_2$

85. $(NH_4)_2Cr_2O_7 = N_2 + 4H_2O + Cr_2O_3$

86. $3MnO_4^{2-} + 4H^+ = 2MnO_4^- + MnO_2 + H_2O$

87. $4H_3PO_3 = 3H_3PO_4 + PH_3$

88. $4Zn + 10HNO_3 = 4Zn(NO_3)_2 + N_2O + 5H_2O$

89. $24CuS + 16NO_3^- + 64H^+ = 24Cu^{2+} + 3S_8 + 16NO + 32H_2O$

90. $2CuSO_4 + 4KI = Cu_2I_2 + I_2 + 2K_2SO_4$

91. $2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$ [**Hint:** Change in ON = 2]

92. $12NaOH + 6Cl_2 = 10NaCl + 2NaClO + 6H_2O$

93. $NH_3 + Hg_2Cl_2 = Hg + Hg(NH_2)Cl + HCl$

94. $Br_2 + 2OH^- = BrO^- + Br^- + H_2O$

95. $As_2S_5 + 40HNO_3 = 5H_2SO_4 + 40NO_2 + 2H_3AsO_4 + 12H_2O$

96. $Cr_2O_7^{2-} + 3SO_2 + 5H^+ = 2Cr^{3+} + 3HSO_4^- + H_2O$

97. $4HCl + 3WO_3 + SnCl_2 = H_2SnCl_6 + W_3O_8 + H_2O$

98. $2HCl + FeCl_2 + V(OH)_4Cl = VOCl_2 + 3H_2O + FeCl_3$

99. $4Au + 16KCN + 6H_2O + 3O_2 = 4KAu(CN)_4 + 12KOH$

100. $4KOH + 4KMnO_4 = 4K_2MnO_4 + O_2 + H_2O$

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98. $2HCl + FeCl_2 + V(OH)_4Cl = VOCl_2 + 3H_2O + FeCl_3$

99. $4Au + 16KCN + 6H_2O + 3O_2 = 4KAu(CN)_4 + 12KOH$

100. $4KOH + 4KMnO_4 = 4K_2MnO_4 + O_2 + H_2O$

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SOLID AND LIQUID STATES

THE SOLID STATE

Solid substances are frequently classified as either crystalline or amorphous. Crystalline solids are characterised by a regular, ordered arrangement of particles. However, a small class of noncrystalline solids, known as amorphous solids, has no well-defined ordered structure. Examples are rubber, some kinds of plastics, amorphous sulphur, etc. Glass is sometimes called an amorphous solid and sometimes called an undercooled or supercooled liquid of high viscosity.

Crystalline Solid	Amorphous Solid
1. Definite and regular geometry with flat faces and sharp edges	1. No definite geometrical shape
2. It breaks up into smaller crystals of the same geometrical shape	2. Broken pieces are not generally flat
3. Sharp melting point	3. No sharp melting point
4. Anisotropic, i.e., physical properties are different in different directions	4. Isotropic, i.e., physical properties are same in all directions

Types of Crystalline Solids

	Ionic	Metallic	Covalent	Molecular
Particles occupying lattice points	Anions, cations	Metal ions in electron cloud	Atoms	Molecules (or atoms)
Binding force	Electrostatic attraction	Metallic bonds	Covalent bonds	Van der waals dipole-dipole
Properties	Hard, brittle, poor thermal and electrical conductors	Soft to very hard, good thermal and electrical conductors	Very hard, poor thermal and electrical conductors	Soft, poor thermal and electrical conductors
Examples	NaCl, $CaBr_2$, KNO_3, etc.	Li, K, Ca, Cu, Na, etc.	C (diamond), SiO_2 (quartz), etc.	H_2O, H_2, CO_2, Ar, etc.

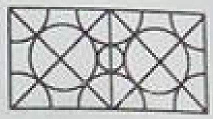
PROBLEMS

(Answers bracketed with questions)

1. Potassium metal crystallizes in a face-centred arrangement of atoms where the edge of the unit cell is 0.574 nm. What is the shortest separation of any two potassium nuclei?
[Hint: Calculate diameter of K] (0.406 nm)

2. A simple cubic lattice consists of eight identical spheres of radius R in contact, placed at the corners of a cube. What is the volume of the cubical box that will just enclose these eight spheres and what fraction of this volume is actually occupied by the spheres? ($64R^3$, 52.36%)

3. Copper has a face-centred cubic structure with a unit-cell edge length of 3.61 Å. What is the size of the largest atom which could fit into the interstices of the copper lattice without distorting it?



[Hint: Calculate the radius of the smallest circle in the figure.] (0.53 Å)

4. Calculate the packing fraction for the K unit cell. K crystallizes in a body-centred cubic unit cell. (0.68)

5. Calculate the percentage of vacant space in a Si unit cubic cell. The unit-cell content for Si is 8 and $r = \frac{\sqrt{3}\,a}{8}$. (See hint of Q. 7) (66%)

6. Calculate the packing factor for spheres occupying (a) a body-centred cubic structure, and (b) a simple cubic structure, where closest neighbours in both cases are in contact. [(a) 0.68 (b) 0.524]

7. Silicon crystallizes in a unit cell to that of diamond. Find the unit-cell content for Si. (8)
[Hint: Diamond has a face-centred cubic unit cell containing a tetrahedron of atoms.]

8. The intermetallic compound LiAg crystallizes in a cubic lattice in which both Li and Ag atoms have coordination numbers of 8. To what crystal class does the unit cell belong? (Cubic structure)

9. A compound formed by elements A and B crystallizes in the cubic structure where A atoms are at the corners of a cube and B atoms are at the face centre. Determine the simple formula of the compound. (AB_3)

10. A cubic solid is made of two elements A and B. Atoms of B are at the corners of the cube and of A, at the body centre. Determine the formula of the compound. (AB)

11. A mineral having the formula AB_2 crystallizes in the cubic close-packed lattice, with the A atoms occupying the lattice points. What are the coordination numbers of the A and B atoms? (8, 4)

12. Calculate the Avogadro constant from the following data:
Density of solid NaCl = 2.165 g/cc

Distance between centres of adjacent Na^+ and $Cl^- = 0.2819$ nm
Also, calculate the edge length of a cube containing 1 mole of NaCl and the number of ions ($Na^+ + Cl^-$) along one edge of the cube. (6.02×10^{23}, 3.0 cm, 1.064×10^8)

13. Metallic rhodium crystallizes in a face-centred cubic lattice with a unit-cell edge length of 3.803 Å. Calculate the molar volume of rhodium including the empty spaces. (8.28 cc)

14. The atomic radius of palladium is 1.375 Å. The unit cell of palladium is a face-centred cube. Calculate the density of palladium. (12.01 g/cc)

15. The unit cell of tungsten is a face-centred cube having a volume of 31.699 $Å^3$. The atom at the centre of each face just touches the atoms at the corners. Calculate the radius and atomic volume of tungsten. (1.1189 Å, 5.8676 $Å^3$)

16. Aluminium crystallizes in a face-centred cubic unit cell with an edge length of 4.094 Å. Calculate the approximate Avogadro constant. (5.83×10^{23})

17. An unknown metal is found to have a specific gravity of 10.2 at 25°C. It is found to crystallize in a body-centred cubic lattice with a unit cell edge length of 3.147 Å. Calculate the atomic weight. (95.7)

18. Zinc selenide, ZnSe, crystallizes in a face-centred cubic unit cell and has a density of 5.267 g/cc. Calculate the edge length of the unit cell. (5.667 Å)

19. A face-centred cubic solid of an element (atomic mass 60) has a cube edge of 4.0 Å. Calculate its density. (6.23 g/cc)

20. Polonium crystallizes in a simple cubic unit cell. Its atomic mass is 209 and density is 91.5 kg m^{-3}. What is the edge length of its unit cell? (1.56×10^{-7} cm)

21. A metallic element has cubic lattice. Each edge of the unit cell is 3.0 Å. The density of the metal is 8.5 g/cc. How many unit cells will be present in 50 g of the metal? (2.178×10^{23})

22. The d_{111} spacing for crystalline K is 0.3079 nm. Calculate the length of the cubic unit cell. (0.5333 nm)

23. Calculate the Miller indices of crystal planes which cut through the crystal axes at (a, b, c), $(2a, b, c)$ and $(2a, -3b, -3c)$. [(1 1 1), (1 2 2), $(3\,\bar{2}\,\bar{2})$]

24. For a primitive cubic crystal with $a = 3 \times 10^{10}$ m, what are the smallest diffraction angles θ for (a) (1 0 0) and (b) (1 1 1) planes for $\lambda = 1.50 \times 10^{-10}$ m? [(a) 15.48°, (b) 25.66°]

25. Potassium crystallizes with b.c.c. lattice and has a density of 0.856×10^3 kg m^{-3}. What is the length of the side of the unit cell, a, and what is the distance between (2 0 0), (1 1 0), and (2 2 2) planes? What is the closest distance between atoms, and what is the potassium atom radius, r? (533.3 pm; 266.7, 377.1 and 154.0 pm; 462.0, 231.0 pm)

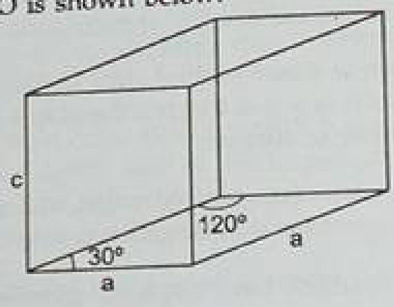
26. The ionic radii of Na^+ and Cl^- ions are 0.98×10^{-10} m and 1.81×10^{-10} m respectively. Find the coordination number of each ion. (6, 6)

27. What is the critical radius ratio for the CsCl structure? (0.732)

[Hint: See text for cubic void]

28. Calculate the fractional void volume in the c.c.p. and h.c.p. structures of hard spheres. (0.2594, 0.2594)

29. Ice crystallizes in a hexagonal lattice. At the low temperature at which the structure was determined, the lattice constants were $a = 4.53$ Å and $c = 7.41$ Å. How many H_2O molecules are contained in a unit cell? The density of ice is 0.92 g/cc at 0°C. A unit cell of H_2O is shown below: (4)



30. The surface tension of glacial acetic acid was determined using the 'bubble pressure' method in which the pressure needed to dislodge bubbles of air from the end of a capillary tube immersed in the liquid is measured. Given that the radius of the tube (r) is 1.1 mm, the depth of the tube in the liquid (h) is 3.56 cm, the pressure is 420 Pa and density (CH_3COOH) = 1.0492 g-cm^{-3}. Determine γ. (2.9×10^{-2} N m^{-1})

[Hint: Laplace equation: $\gamma = \frac{r}{2}(p - hdg)$]

31. The surface tension of toluene at 298 K is 0.0284 Nm^{-1} and its density is 0.866 g/cc. What is the largest radius of the capillary that will permit the liquid to rise 2×10^{-4} m? Assume $\theta = 0$. (3.34×10^{-4} m)

32. Calculate the capillary depression of Hg in a tube of diameter 1.0 mm. Assume that the contact angle is zero. The density of Hg is 13.6×10^3 kg m^{-3} and the surface tension of Hg is 0.460 Nm^{-1}. (1.38×10^{-2} m)

33. The time taken by a metal ball to drop through a liquid A of height h is 5.0 s, whereas that in liquid B is 7.5 s. If the densities of the metal ball, liquids A and B are 7.8×10^3, 1.5×10^3 and 4.6×10^3 kgm^{-3} respectively, calculate the viscosity of liquid A. $\eta(B) = 2.5$ cP. (3.28×10^{-2} cP)

34. A certain liquid has a viscosity of 1.0×10^4 poise and a density of 3.2 g/mL. How long will it take for a platinum ball with a 2.5-mm-radius to fall 1.0 cm through the liquid? The density of platinum is 21.4 g/cc. (40.5 s)

35. Two capillary tubes of radius 0.2 and 0.1 mm were placed into a sample of liquid H_2O_2. The difference between the heights of the liquid in the tubes is 5.50 cm. Given that density (H_2O_2) = 1.41 g cm^{-3}, determine γ. (7.61×10^{-2} N m^{-1})

36. 50 drops each of water and ether, weigh 3.64 g and 0.852 g respectively. Determine

the surface tension of ether if the surface tension of water is 72.75 dyne cm^{-1}. (17.03 dyne cm^{-1})

37. The number of drops of water, counted in falling-drop method using stalagmometer is 100, whereas the number of drops of an organic liquid is 280. Calculate the surface tension of the organic liquid if the surface tension of water is 0.07275 N m^{-1} and the densities of water and the organic liquid are 0.998×10^3 kg m^{-3} and 0.755×10^3 kg m^{-3} respectively. (0.01966 N m^{-1})

38. The viscosity of olive oil at 293 K is 0.084 N m^{-2} s and density is 1.1×10^3 kg m^{-3}. How long will it take to pass through a viscometer if water under the same conditions takes 30 seconds? ($\eta_{H_2O} = 0.00101$ N m^{-2} s, $d_{H_2O} = 0.998 \times 10^3$ kg m^{-3}) (37 min 43.7 s)

39. An organic liquid rises 1.0 cm in a capillary tube of radius r. How much will it rise if the cross-sectional area of the tube is halved? (1.414 cm)

OBJECTIVE PROBLEMS

1. Which of the following is an amorphous solid?
(a) Diamond (b) Graphite (c) Glass (d) Common salt

2. Which of the following is not a property of crystalline solids?
(a) Isotropic (b) Sharp melting point
(c) Definite geometry (d) High intermolecular forces

3. A crystal may have one or more planes of symmetry as well as one or more axes of symmetry but it has
(a) two centres of symmetry (b) no centre of symmetry
(c) one centre of symmetry (d) four centres of symmetry

4. The number of basic crystal systems is
(a) 7 (b) 8 (c) 6 (d) 4

5. The total number of elements of symmetry in a cubic crystal is
(a) 9 (b) 23 (c) 9 (d) none of these

6. The number of Bravais lattices in a cubic crystal is
(a) 3 (b) 1 (c) 4 (d) 14

7. In a sodium chloride crystal, each chloride ion is surrounded by
(a) 6 sodium ions (b) 6 chloride ions
(c) 8 sodium ions (d) 4 sodium ions

8. The structure of CsCl crystal is
(a) body-centred cubic lattice (b) face-centred cubic lattice
(c) octahedral (d) none of (a), (b) and (c)

9. The structure of NaCl crystal is
(a) body centred (b) face-centred cube
(c) octahedral (d) square plane

10. The arrangement of Cl^- ions in CsCl structure is
(a) h.c.p. (b) simple cubic (c) f.c.c. (d) b.c.c.

11. The number of atoms per unit cell in a face-centred cube is
(a) 2 (b) 3 (c) 4 (d) 14

12. The coordination number of a body-centred atom in cubic structure is
(a) 4 (b) 6 (c) 8 (d) 12

13. Close packing is maximum in the crystal which is a
(a) simple cube (b) face-centred cube
(c) body-centred cube (d) primitive cube

14. In a body-centred cubic arrangement the ion A occupies the centre while the ions of B occupy the corners of a cube. The formula of the crystal is
(a) AB (b) A_2B (c) AB_2 (d) AB_3

15. The number of atoms per unit cell in a simple cube, face-centred cube and body-centred cube are respectively
(a) 1, 4, 2 (b) 1, 2, 4 (c) 8, 14, 9 (d) 8, 4, 2

16. The radius of an ion in a body-centred cube of edge a is
(a) $\frac{a}{2}$ (b) $\frac{\sqrt{2}a}{4}$ (c) $\frac{\sqrt{3}a}{4}$ (d) a

17. The volume occupied by an atom in a simple cubic unit cell is
(a) a^3 (b) $\frac{4\pi a^3}{3}$ (c) $\frac{\pi a^3}{6}$ (d) $\frac{\sqrt{3}\pi}{8}$

18. In a body-centred cubic cell, an atom at the body centre is shared by
(a) 1 unit cell (b) 4 unit cells (c) 2 unit cells (d) 8 unit cells

19. In a face-centred cubic cell, an atom at the face centre is shared by
(a) 6 unit cells (b) 1 unit cell (c) 4 unit cells (d) 2 unit cells

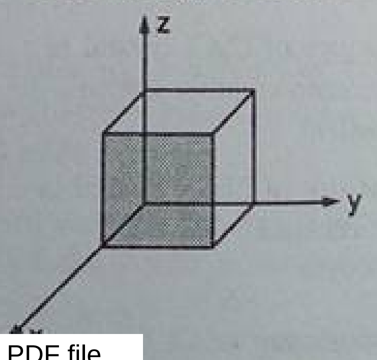
20. An atom at the corner of a simple cubic cell is shared by
(a) 2 unit cells (b) 4 unit cells (c) 8 unit cells (d) 1 unit cell

21. The atomic radius in a face-centred cubic cell is
(a) $\frac{a}{2}$ (b) $\frac{\sqrt{2}a}{4}$ (c) $\frac{\sqrt{3}a}{4}$ (d) $\frac{a}{4}$

22. The fraction of the total volume occupied by atoms in a simple cube is
(a) $\frac{\pi}{2}$ (b) $\frac{\sqrt{3}\pi}{8}$ (c) $\frac{\sqrt{2}\pi}{6}$ (d) $\frac{\pi}{6}$

23. The Miller indices of two parallel planes in a crystal are
(a) same (b) different

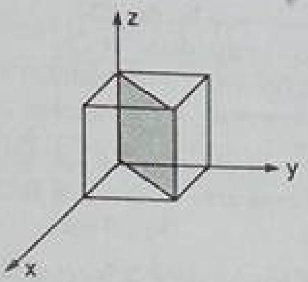
24. The Miller indices of the shaded plane shown in the figure below are
(a) (0 0 1) (b) (0 1 0)
(c) (0 1 1) (d) (1 0 0)



25. The Miller indices of the shaded plane shown in the figure below are

(a) (1 0 0) (b) $(1\,\bar{1}\,0)$

(c) (1 1 1) (d) (0 0 1)



26. Bragg's law is given by the equation

(a) $n\lambda = 2 \sin\theta$ (b) $n\lambda = 2d \sin\theta$ (c) $2d = n\lambda \sin\theta$ (d) $n\lambda = d \sin\theta$

27. A mineral having the formula AB_2 crystallizes in the c.c.p. lattice, with A atoms occupying the lattice points. The CN of A is 8 and that of B is 4. What percentage of the tetrahedral sites is occupied by B atoms?

(a) 25% (b) 50% (c) 75% (d) 100%

28. The number of octahedral sites per sphere in a c.c.p. (f.c.c.) structure is

(a) 0 (b) 1 (c) 2 (d) 4

29. The density of crystalline CsCl is 3.988 g/cc. The volume effectively occupied by a single CsCl ion pair in the crystal is (CsCl = 168.4)

(a) 7.014×10^{-23} cc (b) 2.81×10^{-22} cc (c) 6.022×10^{23} cc (d) 3.004×10^{-23} cc

30. The CsCl structure is observed in alkali halides only when the radius of the cation is sufficiently large to keep its eight nearest-neighbour anions from touching. What minimum value of r_+/r_- is needed to prevent this contact?

(a) 0.155 (b) 0.225 (c) 0.414 (d) 0.732

31. A substance A_xB_y crystallizes in an f.c.c. lattice in which atoms of 'A' occupy each corner of the cube and atoms of 'B' occupy the centres of each face of the cube. Identify the correct composition of the substance A_xB_y.

(a) AB_3 (b) A_4B_3

(c) A_3B (d) Composition cannot be specified

32. In a solid AB of NaCl structure, A atoms occupy the corners of the cubic unit cell. If all the corner atoms are removed then the formula of the unit cell will be

(a) A_4B_4 (b) B (c) A_3B_4 (d) AB

33. In a crystal AB, which of the following crystal systems will have parameters, $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90°$?

(a) Cubic (b) Orthorhombic (c) Monoclinic (d) Triclinic

34. In the NaCl crystal, which of the following facts is not true?

(a) Na^+ ions form f.c.c. lattice (b) Cl^- ions form f.c.c. lattice

(c) Na^+Cl^- units form f.c.c. structure (d) CN of each Na^+ and Cl^- is 6

35. The decreasing order of the size of the void is

(a) cubic > octahedral > tetrahedral > trigonal

(b) trigonal > tetrahedral > octahedral > cubic

(c) trigonal > octahedral > tetrahedral > cubic

(d) cubic > tetrahedral > octahedral > trigonal

36. The greater the value of r_+/r_-,
  (a) the lower will be the CN
  (b) the higher the value of CN
  (c) the higher will be the number of cations
  (d) the lower will be the number of anions

37. An organic liquid rises 2.0 cm in a capillary tube. How much will it rise if the cross-sectional area of the tube is doubled?
  (a) 2.0 cm (b) 1.0 cm (c) 4.0 cm (d) 1.4 cm

38. When the temperature is increased, surface tension of water
  (a) increases (b) decreases
  (c) remains constant (d) shows irregular behaviour

39. The units of surface tension in cgs and SI units are respectively,
  (a) dyne cm^{-1}, $N\,m^{-2}$ (b) dyne cm^{-2}, $N\,m^{-2}$
  (c) dyne cm^{-1}, $J\,m^{-2}$ (d) dyne cm^{-2}, $N\,m^{-1}$

40. The units of viscosity in cgs and SI units are respectively,
  (a) dyne $cm^{-2}\,s$, $N\,m^{-2}\,s$ (b) poise, $Pa\,s^2$
  (c) poise, $N\,m^{-2}\,s^{-1}$ (d) dyne · s, N s

41. The rise of a liquid in a capillary tube is due to
  (a) osmosis (b) surface tension (c) viscosity (d) diffusion

42. The coefficient of viscosity of a solution and its solvent are respectively η and η_0. The specific viscosity η_{sp} may be expressed as
  (a) $\frac{\eta}{\eta_0}$ (b) $\frac{\eta - \eta_0}{\eta_0}$ (c) $\frac{\eta - \eta_0}{\eta}$ (d) $\frac{\eta_0}{\eta}$

43. Which of the following properties of liquids increases with the increase in temperature?
  (a) Vapour pressure (b) Surface tension
  (c) Viscosity (d) None of these

44. The surface tension of several alcohols at 20°C is $\gamma(CH_3OH) = 22.61$ dyne-cm^{-1}, $\gamma(C_2H_5OH) = 2.275 \times 10^{-2}\,N\,m^{-1}$ and $\gamma(n-C_3H_7OH) = 23.78\,mJ\,m^{-2}$. The alcohol having the highest surface tension is
  (a) CH_3OH (b) C_2H_5OH (c) $n-C_3H_7OH$ (d) All same
  [Hint: 1 dyne = 10^{-5} N and 1 J = 1 N m]

Answers

1-c, 2-a, 3-c, 4-a, 5-b, 6-a, 7-a, 8-a, 9-b, 10-b, 11-c, 12-c, 13-b, 14-a, 15-a, 16-c, 17-c, 18-a, 19-d, 20-c, 21-b, 22-d, 23-a, 24-d, 25-b, 26-b, 27-d, 28-b, 29-a, 30-d, 31-a, 32-c, 33-b, 34-c, 35-a, 36-b, 37-d, 38-b, 39-c, 40-a, 41-b, 42-b, 43-a, 44-c

MISCELLANEOUS PROBLEMS FOR REVISION

1. A sample of a pure compound contains 2.04 grams of sodium, 2.65×10^{22} atoms of carbon and 0.132 mole of oxygen atoms. Find the empirical formula of the compound. (Na_2CO_3)

2. The total number of molecules of hydrogen and oxygen that may be obtained from a given amount of H_2O is 6000. Find the amount of H_2O. (1.195×10^{-19} g)

3. The total population of the world is now believed to be about 4.2×10^9. How many moles of people is this? If you had one sulphur atom for each person, what would be the weight of the sulphur sample? (6.9×10^{-15} mole, 2.2×10^{-13} g)

4. Does 1 g of all elements contain nucleons equal to the Avogadro constant? Explain. (Yes)

5. A solution contains 0.18 g/mL of a substance X, whose molecular weight is approximately 68000. It is found that 0.27 mL of oxygen at 760 mmHg and 30°C will combine with the amount of X contained in 1.0 mL of the solution. How many molecules of oxygen will combine with one molecule of X? (4)

6. Find the simplest formula of a solid whose cubic unit cell has an 'x' atom at each corner, a 'y' atom at each face centre, and a 'z' atom at the body centre. (xy_3z)

7. Calculate the work of an isobaric reversible expansion of three moles of an ideal gas while it is heated from 298 K to 400 K. (–2.54 kJ)
[Hint: $W = -nR(T_2 - T_1)$]

8. Calculate the work of an isothermal reversible expansion of three moles of water vapour from 5.0×10^4 to 2.0×10^4 Pa at 330 K.
[Hint: $W = -2.303\, nRT \log \frac{p_1}{p_2}$] (–7.54 kJ)

9. The heats of solution of one mole of Na and that of Na_2O in water under standard conditions are –183.79 kJ/mol and –237.94 kJ/mol respectively, water being taken in large excess in both the cases. Calculate the standard heat of formation of sodium oxide if the standard heat of formation of water is –285.84 kJ/mol. (–415.48 kJ/mol)

$$\left[\textbf{Hint:}\quad \begin{aligned} &Na + H_2O = NaOH + \tfrac{1}{2}H_2 \\ &Na_2O + H_2O = 2NaOH \end{aligned}\right]$$

10. The pressure of the water vapour of a solution containing a nonvolatile solute is 2% below that of the vapour of pure water. Calculate the molality of the solution. (1.134)

11. An aqueous solution freezes at 271.5 K. Determine its boiling point and vapour pressure at 298 K. The cryoscopic constant of water is 1.86°, its ebullioscopic

constant is 0.516° and the water vapour pressure at 298 K is 3168 Pa.

(373.42, 3124 Pa)

12. The water vapour pressure at 293 K is 2338.5 Pa, and the vapour pressure of an aqueous solution is 2295.8 Pa. Determine the osmotic pressure of this solution at 313 K if the solution density at this temperature is 1010 kg/m^3. The molecular weight of the solute is 60.

(2.56×10^6 Pa)

13. If the vapour pressure of pure liquids A and B are 300 mm and 800 mm (Hg) at 75°C, calculate the composition of the mixture such that it boils at 75°C. Find the composition of the vapour phase.

(0.08, 0.92; 0.0316, 0.9684)

14. For the cells

$$2\,Ag + Pt^{2+} \rightarrow 2\,Ag^+ + Pt\,;\; E^0 = 0.4\text{ V}$$

$$2\,Ag + F_2 \rightarrow 2\,Ag^+ + 2\,F^-;\; E^0 = 2.07\text{ V}$$

if the potential for the reaction $Pt \rightarrow Pt^{2+} + 2e$ is assigned as zero, determine the potential for the following electrodes.

(i) $Ag \rightarrow Ag^+ + e$

(ii) $F^- \rightarrow \frac{1}{2}F_2 + e$

(–0.4 V, –2.47 V)

15. The standard reduction potential of the $Ag^+ | Ag$ electrode at 298 K is 0.799 V. Given that for AgI, $K_{sp} = 8.7 \times 10^{-17}$, evaluate the potential of the $Ag^+ | Ag$ electrode in a saturated solution of AgI. Also, calculate the standard reduction potential of the $I^- | AgI | Ag$ electrode.

(IIT 1994)

(0.3244 V, –0.15 V)

[Hint: $[Ag^+] = \sqrt{K_{sp}\,(AgI)} = \sqrt{8.7 \times 10^{-17}}$

$$E_{Ag^+,\,Ag} = E^0_{Ag^+,\,Ag} - \frac{0.0591}{1}\log\frac{1}{[Ag^+]}$$

For standard $I^- | AgI | Ag$ electrode,

$[I^-] = 1, \quad \therefore \quad [Ag^+] = \dfrac{K_{sp}(AgI)}{1} = 8.7 \times 10^{-17}.$

The standard potential for this electrode, if the Nernst equation is used for $Ag^+ | Ag$ electrode, may be calculated considering $[Ag^+] = 8.7 \times 10^{-17}$.]

16. A blown-up balloon has a volume of 500 mL at 5°C. The balloon is distended to 7/8 of its maximum stretching capacity. Will the balloon burst at 30°C? Determine the minimum temperature above which it will burst.

(No, 44.7°C)

17. On the surface of the earth at 1 atm pressure, a balloon filled with H_2 gas occupies 500 mL. This volume is 5/6 of its maximum stretching capacity. The balloon is left in air. It starts rising. Calculate the height above which the balloon will burst if the temperature of the atmosphere remains constant and the pressure decreases 1 mm for every 100-cm rise in height.

(126.67 m)

18. A spherical balloon of radius 30 cm weighs 100 g. Find the minimum amount of hydrogen the balloon should contain just to rise from the ground. The density of air is 1.29 g/L.

(45.95 g)

19. A compound exists in the gaseous state both as a monomer (A) and a dimer (A_2). The molecular weight of the monomer is 48. In an experiment, 96 g of the compound was confined in a vessel of volume 33.6 litres and heated to 273°C. Calculate the pressure developed if the compound exists as a dimer to the extent of 50% by weight under these conditions.
(2 atm)

20. The equilibrium concentrations of HI, H_2 and I_2 were found to be 0.49, 0.08 and 0.06 mole per litre respectively, when the reaction $H_2 + I_2 \rightleftharpoons 2HI$ was initially started with some amounts of H_2 and I_2. Calculate the new equilibrium concentrations of each gas if an additional 0.3 mole per litre of HI was added.
(0.724 M, 0.113 M, 0.093 M)

21. Calculate K_c for the reaction: $A(g) + B(g) \rightleftharpoons 2C(g)$, if 1 mole of A, 1.4 moles of B and 0.50 mole of C are placed in a one-litre vessel and allowed to reach equilibrium. The equilibrium concentration of C is 0.75 mole per litre.
(0.50)

22. At 700 K, CO_2 and H_2 react to form CO and H_2O. For this process K is 0.11. A mixture of 0.45 mole of CO_2 and 0.45 mole of H_2 is heated to 700 K.
(i) Find the amount of each gas at equilibrium.
(ii) After the equilibrium is reached, another 0.34 mole of CO_2 and 0.34 mole of H_2 are added to the reaction mixture. Find the composition of the new equilibrium state.
[(i) 0.34, 0.11 (ii) 0.594, 0.196]

23. K_p for the reaction: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ is 0.66 atm at 320 K. Calculate the degree of dissociation of N_2O_4 at 320 K and 380 mm. Also calculate the partial pressures of N_2O_4 and NO_2 at equilibrium.
(0.497; 0.332 atm, 0.168 atm)

24. 100 mL of 0.6 N $CuSO_4$ solution is electrolysed between two Pt electrodes till the concentration in the residual liquid is 0.1 N when a steady current of 5.0 amp is used. How long should the current be passed to get the said change?
(965 s)

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

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

The efficiency of the reaction is 82%. What volume of ethane and CO_2 would be produced at 27°C and 740 mm of Hg if a current of 0.5 amp is passed through the solution for 420 minutes?
(1.354 L, 2.708 L)

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

$$2Cl^-(aq) + 2H_2O = 2OH^-(aq) + H_2(g) + Cl_2(g)$$

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

[Hint: See Example 15, Chapter 8]
(49 h, 1.408 M)

27. For the reaction: $2A + B_2 + C \rightarrow A_2B + BC$, the rate law expression has been

determined experimentally to be $R = k[A]^2[C]$ with

$$k = 3.0 \times 10^{-4}\ M^{-2}\ min^{-1}.$$

(i) Determine the initial rate of the reaction, started with concentrations:

$$[A] = 0.1\ M, [B_2] = 0.35\ M \text{ and } [C] = 0.25\ M.$$

(ii) Determine the rate after 0.04 mole per litre of A has reacted.

$(7.5 \times 10^{-7}\ M\ min^{-1}, 2.5 \times 10^{-7}\ M\ min^{-1})$

28. The decomposition of AB_2 to AB and B is first-order with $k = 2.8 \times 10^{-7}\ s^{-1}$ at 1000°C.

$$AB_2 \rightarrow AB + B$$

Atomic weights of A and B are 12 and 32 respectively.

(i) Find the half-life of this reaction at 1000°C.

(ii) How many days would pass before 1 g of AB_2 had decomposed to the extent that 0.60 g of AB_2 remained?

(iii) With reference to (ii), how many grams of AB would be present after this length of time?

(iv) How much of a 1-g sample of AB_2 would remain after 35 days?

(28.58 days, 20.84 days, 0.23 g, 0.43 g)

29. Nicotinic acid ($K_a = 1.4 \times 10^{-5}$) is represented by the formula HNiC. Calculate its per cent dissociation in a solution which contains 0.10 mol of nicotinic acid per 2.0 L of solution. (1.67%)

30. The solution containing dissolved CO_2 is 0.035 M. If the dissociation constants for the reactions

$$CO_2 + H_2O = H^+ + HCO_3^-$$

and

$$HCO_3^- = H^+ + CO_3^{2-}$$

are 4.16×10^{-7} and 4.84×10^{-11} respectively, calculate $[H^+]$ in the solution.

$(1.2 \times 10^{-4}\ M)$

31. Hydrozoic acid HN_3 is a weak acid which hydrolyses in water according to

$$HN_3 + H_2O = H_3O^+ + N_3^-$$

$$pK_a(HN_3) = 4.72$$

(i) Calculate $[H_3O^+]$, $[HN_3]$, $[N_3^-]$ and $[OH^-]$ in 0.1 M acid solution.

(ii) Calculate pH of the acid.

$$\begin{bmatrix} \text{(i) } 1.4 \times 10^{-3}\ M, 0.1\ M, 1.4 \times 10^{-3}\ M, 7.2 \times 10^{-12}\ M \\ \text{(ii) } 2.86 \end{bmatrix}$$

32. How many moles of NaOH can be added to one litre of a solution of 0.1 M in NH_3 and 0.1 M in NH_4Cl without changing pOH more than one unit? Assume no change in volume, $pK_b = 4.75$. (0.082 mole)

33. A 4 : 1 molar mixture of He and CH_4 is contained in a vessel at 20 bar pressure. Due to a hole in the vessel the gas mixture leaks out. What is the composition of the mixture effusing out initially? (IIT 1994) (8 : 1)

[Hint: See Example 25, Chapter 10]

34. An LPG (liquefied petroleum gas) cylinder weighs 14.8 kg when empty. When full, it weighs 29 kg and shows a pressure of 2.5 atm. In the course of use at 27°C, the weight of the full cylinder reduced to 23.2 kg. Find out the volume of the gas used up in cubic metres at the normal usage conditions, and the final pressure inside the cylinder. Assume LPG to be *n*-butane with normal boiling point of 0°C.

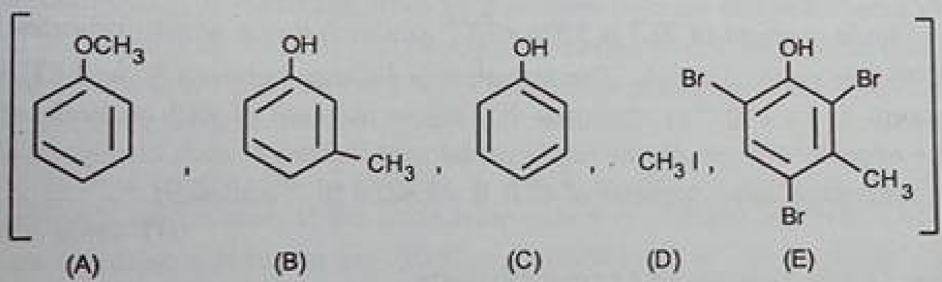
(IIT 1994) (2.463 m^3, 1.4788 atm)

[**Hint:** $1 \times V_{\text{used}}\,(27°\text{C and 1 atm}) = \frac{5800}{58} \times 0.0821 \times 300$]

35. A balloon of diameter 20 m weighs 100 kg. Calculate its payload if it is filled with He at 1.0 atm and 27°C. Density of air is 1.2 kg m^{-3}. (4249.5 kg)

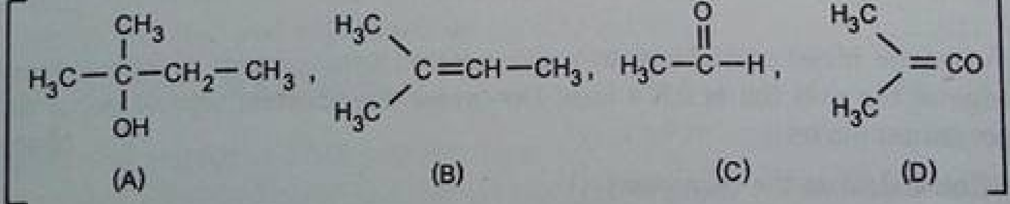
36. An organic compound containing C, H and O exists in two isomeric forms (A) and (B). An amount of 0.108 g of one of the isomers gives on combustion 0.308 g of CO_2 and 0.072 g of H_2O. (A) is insoluble in NaOH and $NaHCO_3$ while (B) is soluble in NaOH. (A) reacts with conc. HI to give compounds (C) and (D). (C) can be separated from (D) by the ethanolic $AgNO_3$ solution and (D) is soluble in NaOH. (B) reacts readily with bromine water to give compound (E) of molecular formula $C_7H_5OBr_3$.

Identify (A), (B), (C), (D) and (E). **(IIT 1991)**



37. In the Kjeldahl method the gas evolved from a 1.325-g sample of a fertilizer is passed into 50.0 mL of 0.2030 N H_2SO_4. 25.32 mL of 0.1980 N NaOH is required for the titration of the unused acid. Calculate the percentage of nitrogen in the fertilizer. (5.43%)

38. When 0.0088 g of a compound (A) was dissolved in 0.50 g of camphor, the m.p. of camphor was lowered by 8°C. Analysis of (A) gave 68.18% C and 13.16% H. Compound (A) showed the following reactions: (i) It reacted with acetyl chloride and evolved hydrogen with sodium. (ii) When reacted with HCl + $ZnCl_2$, a dense oily layer separated out immediately. Compound (A) was passed over Al_2O_3 at 350°C to give compound (B). (B) on ozonolysis followed by hydrolysis gave two neutral compounds (C) and (D), which gave a positive test with carbonyl reagents but only (C) gave a positive test with Fehling's solution and resinous substance with NaOH. Identify (A), (B), (C), and (D). K_f for camphor = 40 K mol^{-1} kg.



39. An excess of liquid mercury was added to a 10^{-3} M acidic solution of Fe^{3+}. It was found that only 4.6% of the iron remained as Fe^{3+} at equilibrium at 25°C. Calculate $E^0_{Hg_2^{2+}, Hg}$. Assume that the only reaction taking place is

$$2\,Hg + 2\,Fe^{3+} = Hg_2^{2+} + 2\,Fe^{2+}$$

Given that $\quad E^0_{Fe^{3+}, Fe^{2+}} = 0.771$ volt (0.791 V)

40. At what relative concentration of Zn^{2+} ions and Fe^{2+} ions will Zn(s) and Fe(s) have equal oxidation potential?

$$E^0_{Zn, Zn^{2+}} = 0.76\text{ V}, E^0_{Fe, Fe^{2+}} = 0.44\text{ V}$$

(7.031×10^{10})

41. The standard reduction potential for the half cell

$$NO_3^-(aq) + 2H^+(aq) + e \rightarrow NO_2(g) + H_2O$$

is 0.78 volt.

(i) Calculate the reduction potential in 8 M H^+.

(ii) What will be the reduction potential of the half cell in a neutral solution? Assume all the other species to be at unit concentration. **(IIT 1993)**

$\left[\textbf{Hint: } \text{Use } E = E^0 - \dfrac{0.0591}{1} \log \dfrac{1}{[H^+]^2}\right]$ (0.8867 V, −0.0474 V)

42. The dipole moment of KCl is 3.336×10^{-29} coulomb-metre which indicates that it is a highly polar molecule. The interatomic distance between K^+ and Cl^- in this molecule is 2.6×10^{-10} m. Calculate the dipole moment of KCl molecule if there were opposite charges of one fundamental unit located at each nucleus. Calculate the percentage ionic character of KCl. ($e = 1.602 \times 10^{-19}$ coulomb).

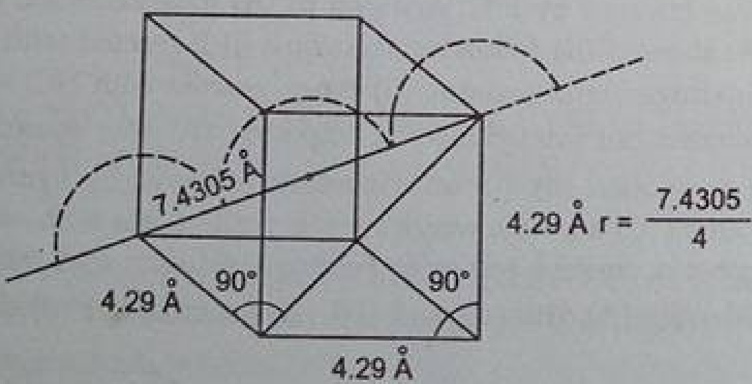
(IIT 1993) (80.09%)

[**Hint:** Dipole moment $= e \times r$ coulomb-metre,

$$\%\text{ ionic character} = \frac{3.336 \times 10^{-29}}{1.602 \times 10^{-19} \times 2.6 \times 10^{-10}} \times 100]$$

43. Sodium metal crystallizes in a body-centred cubic lattice with the cell edge $a = 4.29$ Å. What is the radius of the sodium atom? **(IIT 1994)** (1.8576 Å)

[**Hint:**



]

44. Potassium metal crystallizes in a face-centred arrangement of atoms where the edge of the unit cell is 0.574 mm. Determine the shortest separation of any two potassium nuclei. (0.406 mm)

[**Hint:** Calculate the diameter.]

45. 5.0 g of a polymer of molecular weight 50.0 kg mol^{-1} is dissolved in 1 dm^3 of water. If the density of this solution is 0.96 kg dm^{-3}, calculate the height of water that will represent this pressure. (26.52 mm)

46. The two liquids A and B have the same molecular weight and form an ideal solution. The solution has the vapour pressure 700 mm (Hg) at 80°C. The above solution is distilled without reflux till 3/4 of the solution is collected as condensate. The composition of the condensate is $x'_A = 0.75$ and that of the residue is $x_A = 0.3$. If the vapour pressure of the residue at 80°C is 600 mm (Hg), calculate x_A, P^0_A and P^0_B.

(0.635, 809.39 mm, 509.69 mm)

47. A solution containing compound X in water and a solution containing urea in water were put in a closed system. By doing this some water vapour was removed from one solution and got condensed in the other. It is found that when both the solutions were at equilibrium vapour pressure, one solution contains 2% of X and the other 5% by weight. Find the molecular weight of X. (23.26)

[**Hint:** At equilibrium, the relative lowering of vapour pressure of the two solutions is equal.]

48. The heat of Fe_2O_3 formation from simple substances is –821.32 kJ/mole at 298 K and standard pressure, and that of Al_2O_3 formation is –1675.60 kJ/mole under the same conditions. Calculate the heat of reaction of reduction of 1 mole Fe_2O_3 with metallic aluminium. (–854.28 kJ)

49. The heat of combustion of graphite at 298 K is –393.795 kJ/mole, while that of diamond's combustion at the same temperature is –395.692 kJ/mole. The specific heats for these substances are 720.83 and 505.58 J kg^{-1} K^{-1} respectively. Calculate the heat of graphite's transformation into diamond at 273 K. (1.962 kJ/mole)

[**Hint:** Use Eqn. 9a, Chapter 14)

50. Which oxidizing agent, O_2, O_3 or H_2O_2, will generate the greatest amount of energy for 1 mole of $H_2(g)$?

(i) $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$; $\Delta H = -483.6$ kJ

(ii) $3H_2(g) + O_3(g) \rightarrow 3H_2O(g)$; $\Delta H = -868.2$ kJ

(iii) $H_2(g) + H_2O_2(g) \rightarrow 2H_2O(g)$; $\Delta H = -347.3$ kJ

Which of the above given reactions will generate the greatest amount of energy on a total mass basis of reactants that may be used in rocket propulsion?

[(iii), (ii)]

51. For the reaction $[Ag(CN)_2] \rightleftharpoons Ag^+ + 2CN^-$, the equilibrium constant at 25°C is 4×10^{-19}. Calculate the silver ion concentration in a solution which was originally 0.1 molar in KCN and 0.03 molar in $AgNO_3$. **(IIT 1994)**

(**Hint:** See Example 4, Chapter 16) (7.5×10^{-18} M)

52. The Edison storage cell is represented as

$$Fe(s) \mid FeO(s) \mid KOH(aq) \mid Ni_2O_3(s) \mid Ni(s).$$

The half cell reactions are

$$Ni_2O_3(s) + H_2O(l) + 2e = 2NiO(s) + 2OH^- \quad E^0 = +0.40\ V$$

$$FeO(s) + H_2O(l) + 2e = Fe(s) + 2OH^- \quad E^0 = -0.87\ V$$

(i) What is the cell reaction?
(ii) What is the cell emf? How does it depend on the concentration of KOH?
(iii) What is the maximum amount of electrical energy that can be obtained from one mole of Ni_2O_3? (IIT 1994)

[(i) $Ni_2O_3(s) + Fe(s) \rightarrow 2NiO(s) + FeO(s)$
(ii) 1.27 V; independent of [KOH]
(iii) 245.11 kJ/mole of Ni_2O_3]

[Hint: See Example 20, Chapter 18 and for (iii) Electrical energy = nFE]

53. An aqueous solution of NaCl containing 5.85 g/L of NaCl was electrolysed by using platinum electrodes. Hydrogen and chlorine gases evolved at the cathode and anode respectively. Calculate the pH of the solution after electrolysis assuming complete electrolysis of NaCl. (13)

54. Anodic oxidation of ammonium hydrogen sulphate (NH_4HSO_4) produces ammonium persulphate.

$$NH_4HSO_4 = NH_4SO_4^- + H^+$$
$$2NH_4SO_4^- = (NH_4)_2S_2O_8 + 2e \quad \text{(at anode)}$$
$$2H^+ + 2e = H_2 \quad \text{(at cathode)}$$

$(NH_4)_2S_2O_8$ hydrolyses according to

$$(NH_4)_2S_2O_8 + 2H_2O = 2NH_4HSO_4 + H_2O_2.$$

Current efficiency in electrolytic process is 60%. Calculate the amount of current required to produce 85 g of H_2O_2 per hour if hydrolysis reaction has 100% efficiency. (223.38 amp)

55. Calculate the weight of dilute sulphuric acid solution (sp. gr. = 1) which was electrolysed to give H_2 at 300 K and 1 atm to fill a balloon of capacity 680 mL. (0.49 g)

56. The reaction $Cl_2(g) + S_2O_3^{2-} \rightarrow SO_4^{2-} + Cl^-$, is to be carried out in alkaline solution. Starting with 0.15 mole of Cl_2, 0.01 mole of $S_2O_3^{2-}$ and 0.30 mole of OH^-. How many mole of OH^- will be left in the solution after the reaction is complete? Assume that no other reaction takes place. (0.2 mole)

[Hint: $4Cl_2 + S_2O_3^{2-} + 10OH^- \rightarrow 2SO_4^{2-} + 8Cl^- + 5H_2O$]

57. 12.5 g of a sample of arsenious oxide was dissolved in water containing 7.5 g of sodium bicarbonate and the resulting solution was diluted to 250 mL. 25 mL of this solution was completely oxidized by 22.4 mL of a solution of iodine, 25 mL of which reacted with 24.5 mL of a solution of $Na_2S_2O_3 \cdot 5H_2O$ containing 27.7 g of this salt in 1 litre. Calculate the percentage of arsenious oxide in the sample.

Reactions involved are

$$As_2O_3 + 6NaHCO_3 \rightarrow 2Na_3AsO_3 + 3H_2O + 6CO_2$$

$$Na_3AsO_3 + 2I_2 + 2H_2O \rightarrow 2Na_3AsO_4 + 4HI$$

(9.74%)

58. 2.10 g of mixture of $NaHCO_3$ and $KClO_3$ requires 100 mL of 0.1 N HCl for complete reaction. Calculate the amount of residue that would be obtained on heating 2.20 g of the same mixture strongly. (1.358 g)

59. A compound was dissolved in water at 27°C. It is found that the vapour pressure lowering at 27°C is 0.72 mm. If the vapour pressure of water at 27°C is 26.74 mm, calculate the osmotic pressure of the solution. (0.028 atm)

60. The vapour pressure of water is 3167.2 Pa at 25°C. What would be the vapour pressure of a solution of sucrose (with mole fraction of sucrose = 0.1) and of a solution of levulose (with mole fraction of levulose = 0.1)?

[Hint: $p_{soln} = p_{solvent}(1 - x_{solute})$] (2850 Pa)

61. A beaker containing 0.01 mole of $C_{12}H_{22}O_{11}$ in 100 g of H_2O and a beaker containing 0.02 mole of $C_{12}H_{22}O_{11}$ in 100 g of H_2O are placed in a chamber and allowed to equilibrate. What is the concentration (mole fraction) of $C_{12}H_{22}O_{11}$ in the resulting solutions? (0.00269)

[Hint: Water vapour will be transferred from the more dilute solution to the more concentrated solution until both solutions have the same concentration.]

62. What mass of a solute ($M = 345$) is needed to decrease the vapour pressure of 100 g of H_2O at 25°C by 1 mmHg? Vapour pressure of water at 25°C is 23.756 mm. (84.2 g)

63. Azomethane, $(CH_3)_2N_2$ decomposes with a first-order rate according to the equation

$$(CH_3)_2N_2(g) \rightarrow N_2(g) + C_2H_6(g)$$

In the beginning the initial pressure was 36.2 mm and after 15 min. the total pressure was 42.4 mm. Calculate the rate constant. (1.25×10^{-2} min^{-1})

64. The rate of decomposition of a gas at a certain temperature is 5.14 and 7.25 in some units for 20% and 5% decomposition respectively. Calculate the order of the reaction. (2)

65. The order of the reaction: $A + B \rightarrow C$, is 1 with respect to each of the reactants. Find the approximate concentration of A remaining after 100 seconds if its initial concentration is 0.1 M and that of B is 6 M. Rate constant of the reaction is $5 \times 10^{-3}\ M^{-1}s^{-1}$. ($4.96 \times 10^{-3}$ M)

66. The decomposition of Cl_2O_7 at 400 K in the gas phase to Cl_2 and O_2 is a first-order reaction.

(i) After 55 seconds at 400 K, the pressure of Cl_2O_7 falls from 0.062 to 0.044 atm. Calculate the rate constant.

(ii) Calculate the pressure of Cl_2O_7 after 100 seconds of decomposition at this temperature. ($6.23 \times 10^{-3}\ s^{-1}$, 0.033 atm)

67. When a solution of formic acid was titrated with KOH solution, the pH of the

solution was 3.65 when half the acid was neutralized. Calculate $K_a(HCOOH)$.
(2.24×10^{-4})

68. Calculate $[OH^-]$ in a 1 M solution of NaOCN. $K_a(HOCN) = 3.3 \times 10^{-4}$ (5.5×10^{-6})

69. 0.1 M NH_4OH is 1% ionized. Find the extent of hydrolysis of 0.1 M NH_4Cl.
(10^{-4})

70. Calculate the change in pH of one litre of buffer solution containing 0.1 mole each of NH_3 and NH_4Cl upon addition of
(i) 0.02 mole of dissolved gaseous HCl
(ii) 0.02 mole of dissolved NaOH
Assume no change in volume, K_b for $NH_3 = 1.8 \times 10^{-5}$ (0.1761)
[**Hint:** See Example 28, Chapter 16]

71. The pH of the bloodstream is maintained by a proper balance of H_2CO_3 and $NaHCO_3$ concentrations. What volume of 5 M $NaHCO_3$ solution should be mixed with a 10 mL sample of blood which is 2 M in H_2CO_3, in order to maintain a pH of 7.4? K_a for H_2CO_3 in blood is 7.8×10^{-7}. **(IIT 1993)** (78.36 mL)
[**Hint:** mm of $NaHCO_3 = 5 \times x$
mm of $H_2CO_3 = 2 \times 10$
Apply Henderson's equation and calculate x.]

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

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

Calculate (i) how many grams of chromium will be plated out by 24000 coulombs, and (ii) how long will it take to plate out 1.5 g of chromium by using 12.5 amp current? **(IIT 1993)** (2.1554 g, 1336 s)
[**Hint:** Eq. of Cr deposited = faraday of electricity passed

$$= \frac{24000}{96500}$$

and eq. wt. of chromium $= \frac{52}{6}$]

73. In starting a car, the battery delivers roughly 50 amperes. (i) During the 5 seconds that it might take to start a car, totally how many grams of Pb and PbO_2 are consumed in the battery? (ii) If the car were run strictly from batteries, totally how many grams of Pb and PbO_2 would be consumed per mile if 50 amperes made it go at 5 mph? The cell reaction is

$$Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$$ (0.5782 g)

[**Hint:** The reaction involves 2 moles of electrons]

74. The total pressure at equilibrium of a mixture of SO_2 and O_2 in the molar ratio 2 : 1 when kept over a platinum catalyst at 723 K is 10 atm. If 60% of SO_2 is converted to SO_3, calculate K_p for the reaction:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$ ($1.35\ atm^{-1}$)

75. What would be the partial pressure of oxygen gas to get equal moles of SO_2 and SO_3?

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

Given that partial pressures of SO_2, O_2 and SO_3 are 0.662 atm, 0.101 atm and 0.331 atm respectively. (0.404 atm)

76. 8.0 moles of SO_2 and 4.0 moles of O_2 are mixed in a closed vessel. The reaction proceeds at constant temperature. By the moment equilibrium sets in, 80% of the initial amount of SO_2 enters the reaction. Determine the pressure of the gas mixture in equilibrium if the initial pressure was 2.96 atm. (2.17 atm)

77. The value of K_p for the reaction: $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ is 1.78 at 250°C. Calculate the fraction of dissociation at equilibrium when 0.40 mole of PCl_5 is vaporized in a vessel containing 0.20 mole of Cl_2 gas (i) when a constant pressure of 2 atm is maintained, and (ii) when the volume is kept constant at 4 litres. (0.247, 0.332)

78. The density of a gas at 27°C and 760 mm pressure is 3.0 g/L. If the pressure remains constant, find out the temperature at which the density will be 2.4 g/L. (102°C)

79. A volume of a gas weighing 8 g was allowed to expand at constant temperature until the pressure of the gas reduced to one-half of its former value. It was found that 500 mL of the rarefied gas weighed 1.25 g.
(i) What was the original volume of the gas?
(ii) Determine the density of the gas in g/L. (1.6 L, 5.0 g/L)

80. A certain quantity of a gas occupied 50 mL, when collected over water at 15°C and 750 mm pressure. If the dry gas occupies 45.95 mL at NTP, calculate the aqueous tension at 15°C. (13.3 mm)

81. Assume that the centre of the sun consists of gases whose average molecular weight is 2. The density and pressure of the gases are 1.3 g/mL and 1.12×10^9 atm respectively. Find the temperature. (2.1×10^7 K)

82. Calculate the equilibrium constant at 25°C for the reaction:

$$2Fe^{3+} + 2I^- = 2Fe^{2+} + I_2$$

Given that $E^0_{Fe^{3+}, Fe^{2+}} = 0.77$ V, $E^0_{I_2, I^-} = 0.536$ V (8.29×10^7)

83. If the concentrations of Fe^{2+} and Fe^{3+} are equal, what should be the concentration of Ag^+ ions to have zero voltage for a galvanic cell made up of $Ag^+ | Ag$ and $Fe^{3+} | Fe^{2+}$ electrodes. Also, calculate the equilibrium constant at 25°C for the following cell reaction: $Fe^{2+} + Ag^+ = Fe^{3+} + Ag$.
Given that $E^0_{Ag^+, Ag} = 0.799$ V, $E^0_{Fe^{3+}, Fe^{2+}} = 0.771$ V (0.33 M, 3.0)

84. For the galvanic cell

$$Ag | AgCl(s), KCl(0.2\,M) \| KBr(0.001\,M), AgBr(s) | Ag,$$

calculate the emf generated and assign correct polarity to each electrode for a spontaneous process after taking into account the cell reaction at 25°C.

$$K_{sp}(AgCl) = 1.8 \times 10^{-10}, K_{sp}(AgBr) = 3.3 \times 10^{-13}$$ (0.037 V)

[Hint: Calculate $[Ag^+]$ from K_{sp} values for both the half cells and then calculate E_{cell} for $Ag | Ag^+(c_1) | Ag^+(c_2) | Ag$.]

85. 30 mL of methanol (density 0.7980 g/mL) on mixing with 70 mL of water (density 0.9984 g/mL) at 298 K gave a solution of density 0.9575 g/mL. Calculate (i) mole fraction, (ii) molality, (iii) molarity, and (iv) f.p. of the solution. $K_f(H_2O) = 1.86$.
(0.1615, 10.7043, 7.6337, −19.91°C)

86. At 25°C the vapour pressure of methyl alcohol is 96 torr. What is the mole fraction of CH_3OH in a solution in which the (partial) vapour pressure of CH_3OH is 23 torr at 25°C? (0.24)

87. The vapour pressure of a 5% solution of a nonvolatile organic substance in water at 373 K is $0.9935 \times 10^5 \text{ N m}^{-2}$. Calculate the molecular mass of the solute ($1 \text{ atm} = 1.0132 \times 10^5 \text{ N m}^{-2}$) (0.0458 kg/mol)

88. How many grams of sugar, $C_6H_{12}O_6$, should be dissolved in 0.5 kg of water at 25°C to reduce the vapour pressure of water by 1%? (50.4 g)

89. Find the molality of a solution (containing nonvolatile solute) if its vapour pressure is 2% below the vapour pressure of pure water. (1.134 *m*)

90. Gaseous ozone is bubbled through water–ice mixture at 0°C. As the $O_3(g)$ decomposes to form $O_2(g)$, the enthalpy of reaction is absorbed by the resulting ice. Given that the heat of fusion of ice is $6.0095 \text{ kJ mol}^{-1}$, calculate the mass of ice that melts for each gram of O_3 that decomposes.

$$2O_3(g) \rightarrow 3O_2(g);\ \Delta H = -285.4 \text{ kJ}$$

(8.91 g)

91. The 'calorie' used in nutrition is actually a kilocalorie. Assume that a human requires '2500 cal' of energy each day for metabolic activity. What mass of ethanol is needed to provide this energy?

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l);\ \Delta H = -1371 \text{ kJ}$$

If the human body is considered to be a closed system, what would be the temperature increase resulting from this energy intake? Assume a mass of 75 kg and a specific heat of $4 \text{ J K}^{-1}\text{g}^{-1}$. If the body temperature is to be maintained at a constant value by the evaporation of water, what mass of water must evaporate? Assume that the heat of vaporization of water is 44 kJ mol^{-1}.

($352 \text{ g}, 35 \text{ K day}^{-1}, 4292 \text{ g}$)

92. One gram of commercial $AgNO_3$ is dissolved in 50 mL of water. It is treated with 50 mL of a KI solution. The silver iodide thus precipitated is filtered off. Excess of KI in the filtrate is titrated with (M/10) KIO_3 solution in the presence of 6 M HCl till all I^- ions are converted into ICl. It requires 50 mL of (M/10) KIO_3 solution. 20 mL of the same stock solution of KI requires 30 mL of (M/10) KIO_3 under similar conditions. Calculate the percentage of $AgNO_3$ in the sample.

(IIT 1992) (85%)

[Hint: Reaction: $KIO_3 + 2KI + 6HCl = 3ICl + 3KCl + 3H_2O$]

93. A mixture of pure $K_2Cr_2O_7$ and pure $KMnO_4$ weighing 0.561 g was treated with excess of KI in acid medium. Iodine liberated required 100 mL of 0.15 N hypo solution for exact oxidation. What is the percentage of each in the mixture? Reactions involved are

$$2KMnO_4 + 8H_2SO_4 + 10KI \rightarrow 6K_2SO_4 + 2MnSO_4 + 8H_2O + 5I_2$$
$$K_2Cr_2O_7 + 6KI + 7H_2SO_4 \rightarrow 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3I_2$$
$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$$

(39.3%, 60.7%)

94. If PCl_5 is heated to 250°C and allowed to reach equilibrium, 50% of PCl_5 is dissociated. Calculate how many moles of Cl_2 must be mixed with one mole of PCl_5 to reduce the dissociation to 40%, volume remaining constant. (0.35 mole)

95. Given that $K_c = 13.7$ at 546 K for $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$.
Calculate what pressure will develop in a 10-litre box at equilibrium at 546 K when 1 mole of PCl_5 is introduced into the empty box. (8.92 atm)

96. Under what pressure must an equimolar mixture of Cl_2 and PCl_3 be placed at 250°C in order to obtain 80% conversion of PCl_3 into PCl_5? K_p for $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$ is 1.78. (13.48 atm)

97. If the degree of dissociation of PCl_5 at a certain temperature and 1 atm is 0.2, calculate the pressure at which the substance will be half-dissociated at the same temperature. (0.125 atm)

98. In the dissociation of HI, it is found that 20% of the acid is dissociated when equilibrium is reached. Calculate the pressure equilibrium constant. (1/64)

99. 0.45 g of an organic compound (A) on ignition gives 0.905 g CO_2 and 0.185 g H_2O. 0.35 g (A) on boiling with HNO_3 and adding $AgNO_3$ solution gives 0.574 g of AgCl. The vapour density of (A) is 87.5. (A) on hydrolysis with $Ca(OH)_2$ yields (B) which on mild reduction gives an optically active compound (C). On heating (C) with I_2 and NaOH, iodoform is produced along with (D). With HCl, (D) gives a solid which is markedly more soluble in hot water than in cold. Identify (A), (B), (C) and (D).

[$C_6H_5{-}C(Cl)_2{-}CH_3$ (A), $C_6H_5{-}\overset{O}{\overset{\|}{C}}{-}CH_3$ (B), $C_6H_5CHOHCH_3$ (C), C_6H_5COONa (D)]

100. Two organic compounds containing C = 62.1%, H = 10.34%, O = 27.6% with KCN and H_2SO_4 gave compounds which on hydrolysis gave two isomeric monobasic acids with molecular mass 104. Name the compounds and also the third isomer.

[$(CH_3)_2C{=}O$ (acetone), C_2H_5CHO (propionaldehyde), $C_2H{=}CHCH_2OH$ (ally alcohol)]

101. Compound (X) of molecular formula C_5H_8O does not react appreciably with Lucas reagent at room temperature but gives a precipitate with amm. silver nitrate. With excess of MeMgBr, 0.42 g of (X) gives 224 mL of CH_4 at STP. Treatment of (X) with

H_2 in the presence of Pt catalyst followed by boiling with excess HI, gives n-pentane. Suggest the structure for (X). **(IIT 1992)**

($HC \equiv C\,CH_2\,CH_2\,CH_2\,OH$)

102. 0.037 g of an alcohol, ROH, was added to CH_3MgI and the gas evolved measured 11.2 cm^3 at STP. What is the molecular weight of ROH? On dehydration, ROH gives an alkene which on ozonolysis gives acetone as one of the products. ROH on oxidation easily gives an acid containing the same number of carbon atoms. Give structures of ROH and the acid. (C_4H_9OH, C_3H_7COOH)

103. PCl_5 dissociates into PCl_3 and Cl_2. If the total pressure of the system in equilibrium is p at a density, d, and temperature, T, show that

$$\alpha = \frac{pM}{dRT} - 1$$

where α is the degree of dissociation, M is the relative molar mass of PCl_5. If the vapour density has the value 62 when the temperature is 230°C, what is the value of p/d? (0.333 L atm g^{-1})

[**Hint:** $pV = n(1+\alpha)RT$; n is the initial no. of moles of PCl_5]

104. An unspecified quantity of an ideal gas has an initial pressure of 5 atm and temperature of 30°C. The gas is expanded at 30°C until the volume has increased by 60% of the initial value. Next, the quantity of the gas in the vessel is increased by 20% of the initial value while the volume is maintained constant. Finally the temperature is adjusted at constant volume until the gas pressure is again 5 atm. What is the final temperature? (404 K)

105. In a gaseous reaction $A \rightarrow B + C$, the pressure of A falls from 0.2 atm to 0.15 atm in one hour. Calculate the rate constant if it is a first-order reaction. What will be the pressure of A after 1.5 hours? (0.2878, 0.13 atm)

106. The decomposition of PH_3 at 950 K according to

$$4PH_3(g) \rightarrow P_4(g) + 6H_2(g)$$

is a first-order reaction. The following measurements were made on a system containing only PH_3 initially.

Time (min):	0	40	80
p (total mmHg):	100	150	166.7

Calculate the rate constant. ($2.7 \times 10^{-2}\ min^{-1}$)

107. The gas phase decomposition of dimethyl ether follows first-order kinetics:

$$CH_3-O-CH_3(g) \rightarrow CH_4(g) + H_2(g) + CO\,(g)$$

The reaction is carried out in a constant-volume container at 500°C and has a half-life of 14.5 min. Initially only dimethyl ether is present at a pressure of 0.4 atm. What is the total pressure of the system after 12 minutes? Assume ideal gas behaviour. **(IIT 1993)** (0.75 atm)

108. The standard reduction potential of the electrode $OH^- \mid H_2(Pt)$ (1 atm) is $E^0 = 0.828$ volt. Calculate K_w at 298 K if Nernst equation takes the form

$$E = E^0_{...} - 0.059 \log [OH^-]$$

[**Hint:** Compare equation $E = E^0_{H_2O,OH^-} - 0.0591 \log [OH^-]$

and $E = E^0_{H^+,H_2} - 0.0591 \log \frac{1}{[H^+]}$

$= E^0_{H^+,H_2} - 0.0591 \log \frac{[OH^-]}{K_w}$]

(1.03×10^{-14})

109. The standard reduction potential of the electrode $Cl^- \mid CuCl$ is $E^0 = 0.137$ volt. Calculate K_{sp} of CuCl at 298 K. ($E^0_{Cu^+,Cu} = 0.521$ volt). [3.19×10^{-7} $(mol/L)^2$]

[**Hint:** $CuCl + e \rightleftharpoons Cu + Cl^-$; $E^0 = 0.137$ V

$Cu^+ + e \rightleftharpoons Cu$; $E^0 = 0.521$ V

for which $E_{cell} = E^0_{cell} + 0.0591 \log K_{sp}(CuCl) = 0$]

110. Calculate the emf of the cell

$$Pb \mid \underset{\text{sat. soln.}}{PbSO_4} \mid\mid \underset{\text{sat. soln.}}{PbI_2} \mid Pb$$

at 25°C. $K_{sp}(PbSO_4) = 1.6 \times 10^{-8}$ and $K_{sp}(PbI_2) = 8 \times 10^{-9}$ (0.029 V)

111. The half-life of a substance in a first-order reaction is 100 minutes at 323.2 K and 15 minutes at 353.2 K. Calculate the temperature coefficient of the rate constant of this reaction. (1.88)

112. A metal object is to be coated with a nickel layer 0.3 mm thick. The surface area of the object is 100 cm^2. The density of nickel is 9.0 g/cm^3. How long will it take to pass a 3-amp current if the current yield is 90%? (9 h 8 min 25 s)

113. Electrolysis of a 20% potassium acetate solution at 290 K yields, among other things, ethane evolved on the anode according to the equation

$$2CH_3COO^- = C_2H_6 + 2CO_2 + 2e$$

The ratio between the molecules of ethane evolved on the anode and those of hydrogen evolved on the cathode is 0.8. Find current yield of ethane. (80%)

114. During an electrochemical experiment, 0.2773 g of Ag was transferred from one electrode to the other electrode in a coulometer. What electric charge did pass through the circuit? (248.1 C)

115. A vessel at 1000 K contains CO_2 with a pressure of 0.5 atm. Some of the CO_2 is converted to CO on addition of graphite. Calculate the value of K, if the total pressure at equilibrium is 0.8 atm. (1.8 atm)

[**Hint:** For the eqb. $\underset{(0.5-p)}{\overset{0.5\text{ atm}}{CO_2(g)}} + C(s) \rightleftharpoons \underset{2p}{2CO(g)}$

$0.5 - p + 2p = 0.8$ (given)]

116. PCl_5 was found to dissociate to the extent of 42% at 227°C and 1 atm. Find the equilibrium constant at (i) constant pressure, and (ii) constant volume. (0.214, 0.005)

117. The Deacon reaction is the oxidation of HCl by O_2:

$$HCl(g) + \frac{1}{4}O_2(g) \rightleftharpoons \frac{1}{2}Cl_2(g) + \frac{1}{2}H_2O\ (g)$$

At a pressure of 730 mm and with an initial mixture containing 8% HCl and 92% O_2, the degree of decomposition of the HCl is 0.80. What is the equilibrium partial pressure of oxygen? (660 mm)

118. What is the vapour density of PCl_5 at 250°C when dissociated to the extent of 80%? (57.9)

119. The density of a 0.33 M solution of $MgBr_2$ in water at 373 K is 1.055 g/mL. Calculate the vapour pressure of water above this solution. Assume ideal behaviour. (746.5 mm)

120. The vapour pressure of a 0.01 molal solution of a weak monobasic acid in water is 17.536 mm at 25°C. Calculate the degree of dissociation of the acid. Aqueous tension of water at 25°C is 17.54 mm. (0.266)

121. What volume of 98% sulphuric acid should be mixed with water to obtain 200 mL of 15% solution of sulphuric acid by weight? The density of water, sulphuric acid (98%) and sulphuric acid (15%) are 1 g/mL, 1.88 g/mL and 1.12 g/mL respectively. (18.2 mL)

122. What weight of the nonvolatile solute, urea $(NH_2-CO-NH_2)$ needs to be dissolved in 100 g of water in order to decrease the vapour pressure of water by 25%? What will be the molality of the solution? **(IIT 1993)**

(111.12 g, 18.52 m)

123. In an ore the only oxidizable material is Sn^{2+}. This ore is titrated with a dichromate solution containing 2.5 g of $K_2Cr_2O_7$ in 0.50 litre. A 0.40 g sample of the ore required 10.0 cm^3 of titrant to reach equivalence point. Calculate the percentage of tin in the ore.

[Hint: $3Sn^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 3Sn^{4+} + 2Cr^{3+} + 7H_2O$] (15%)

124. Upon mixing 45.0 mL of 0.25 M lead nitrate solution with 25.0 mL of 0.10 M chromic sulphate solution, precipitation of lead sulphate takes place. How many moles of lead sulphate are formed? Also calculate the molar concentrations of species left behind in the final solution. Assume that lead sulphate is completely insoluble. **(IIT 1993)**

$$\begin{pmatrix} PbSO_4 = 0.0075 \text{ mole} \\ [Pb^{2+}] = 0.05357\text{ M}, [NO_3^-] = 0.3214\text{ M} \\ [Cr^{3+}] = 0.0714\text{ M} \end{pmatrix}$$

[Hint: Apply the concept of limiting reagent]

125. During the operation of a cell with the cell reaction

$$Mn(OH)_2 + H_2O_2 \rightarrow MnO_2 + 2H_2O$$

for 45 seconds, 0.136 g of MnO_2 was produced. Calculate the average electric current produced by the cell. (6.7 amp)

126. What amount of work is needed to move an electron against a potential difference

of 1.0 volt? What amount of work is needed for 1 mole of electrons and what does this value represent?

(1.602×10^{-19} J, 96470 J $mole^{-1}$, Faraday constant)

127. The cathodic reaction of a $Zn-MnO_2$ dry cell is represented as

$$2MnO_2(s) + Zn^{2+} + 2e = Zn\,Mn_2O_4(s).$$

If there is 8.0 g MnO_2 present in the cathodic chamber, how long will the cell function to supply 4×10^{-3} ampere of current? (25.67 days)

$$\left[\text{Hint: } \frac{4 \times 10^{-3} \times t\,(s)}{96500} = \frac{8}{87};\ E_{MnO_2} = 87\right]$$

128. Calculate the total number of coulombs carried by Cl^- ions weighing 20.1 g.

(5.46×10^4 C)

129. The dissociation constant of an acid HA at 25°C is 1.34×10^{-5}. How many moles of sodium salt of this acid should be added to one litre of an aqueous solution containing 0.02 mole of this acid to obtain a buffer solution of pH 4.75? What will be the pH if 0.01 mole of HCl is dissolved in the buffer solution?

(IIT 1993) (0.015 mole)

[Hint: See Example 28, Chapter 16.]

130. An aqueous solution of a metal bromide MBr_2 (0.05 M) is saturated with H_2S. What is the minimum pH at which MS will precipitate?

$K_{sp}(MS) = 6.0 \times 10^{-21}$; concentration of saturated $H_2S = 0.1$ M;

$K_1 = 1 \times 10^{-7}$ and $K_2 = 1.3 \times 10^{-13}$ for H_2S. (IIT 1993) (0.983)

[Hint: See Example 46, Chapter 16.]

131. What change would be observed in sulphide ion concentration of 0.05 M H_2S solution if 0.1 mole of HCl is added to one litre of it? $K_a(H_2S) = 1 \times 10^{-22}$.

(1.075×10^{-8} M to 5.0×10^{-22} M)

132. The pH of 0.05 M aqueous solution of diethylamine is 12.0. Calculate its K_b.

(2.5×10^{-3})

[Hint: Hydrolysis reaction is $(C_2H_5)_2NH + H_2O = (C_2H_5)_2NH_2^+ + OH^-$]

133. Given that

(i) $\frac{1}{2}Cl_2(g) + O_2(g) \rightarrow ClO_2(g)$; $\Delta H = 102.5$ kJ

(ii) $\frac{1}{2}Cl_2(g) + \frac{3}{2}O_2(g) \rightarrow ClO_3(g)$; $\Delta H = 155$ kJ

(iii) $Cl_2(g) + \frac{7}{2}O_2(g) \rightarrow Cl_2O_7(g)$; $\Delta H = 272$ kJ

Calculate ΔH for the reaction

$$3ClO_3(g) \rightarrow Cl_2O_7(g) + ClO_2(g)$$ (–90.5 kJ)

134. Given that

(i) $Ag(s) \rightarrow Ag^+(aq) + e$ $\Delta H = 105.58$ kJ

(ii) $\frac{1}{2}Cl_2(g) + e \rightarrow Cl^-$ (aq) $\Delta H = -167.16$ kJ

(iii) $Br_2(l) + 2e \rightarrow 2Br^-(aq)$ $\Delta H = -243.10$ kJ

(iv) $AgCl(s) \rightarrow Ag^+(aq) + Cl^-(aq)$ $\Delta H = 65.49$ kJ

(v) $AgBr(s) \rightarrow Ag^+(aq) + Br^-(aq)$ $\Delta H = 84.40$ kJ

Determine which of the thermochemical equations

$$Ag(s) + \frac{1}{2}Cl_2(g) \rightarrow AgCl(s)$$

$$Ag(s) + \frac{1}{2}Br_2(l) \rightarrow AgBr(s)$$

is more exothermic. (Silver–chlorine reaction)

135. Use the following thermochemical equations to determine the average bond enthalpy for C – H bonds.

$CH_4(g) \rightarrow CH_3(g) + H(g)$; $\Delta H = 438.47$ kJ

$CH_3(g) \rightarrow CH_2(g) + H(g)$; $\Delta H = 462.65$ kJ

$CH_2(g) \rightarrow CH(g) + H(g)$; $\Delta H = 423.40$ kJ

$CH(g) \rightarrow C(g) + H(g)$; $\Delta H = 338.85$ kJ (415.84 kJ $mole^{-1}$)

[Hint: First calculate ΔH for $CH_4(g) \rightarrow C(g) + 4H(g)$]

136. Hot carbon reacts with steam to produce an equimolar mixture of CO(g) and $H_2(g)$ known as water gas. What is the energy released as water gas is used as fuel?

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g);\ \Delta H = -282.984 \text{ kJ}$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g);\ \Delta H = -241.818 \text{ kJ}$$

(– 524.802 kJ)

137. Ethanol can undergo decomposition to form two sets of products:

$$C_2H_5OH(g) \rightarrow \begin{Bmatrix} C_2H_4(g) + H_2O(g); & \Delta H = 45.54 \text{ kJ} \\ CH_3CHO(g) + H_2(g); & \Delta H = 68.91 \text{ kJ} \end{Bmatrix}$$

If the molar ratio of C_2H_4 to CH_3CHO is 8:1 in a set of product gases, determine the energy involved in the decomposition process. (48.14 kJ)

[Hint: $\Delta H = \left\{\frac{8}{9}(45.54) + \frac{1}{9}(68.91)\right\}$ kcal]

138. Given that

(i) $2ClO_2(g) + O_3(g) \rightarrow Cl_2O_7(g)$; $\Delta H = -75.7$ kJ

(ii) $O_3(g) \rightarrow O_2(g) + O(g)$; $\Delta H = 106.7$ kJ

(iii) $2ClO_3(g) + O(g) \rightarrow Cl_2O_7(g)$; $\Delta H = -287$ kJ

(iv) $O_2(g) \rightarrow 2O(g)$; $\Delta H = 498.34$ kJ

Calculate enthalpy of the reaction

$$ClO_2(g) + O(g) \rightarrow ClO_3(g)$$

(–196 kJ)

139. A solution of nitric acid of specific gravity 1.46 contains 60% nitric acid. What weight of this solution is theoretically required to dissolve 5 g of cupric oxide? (19.28 g)

140. A flash bulb used for taking photographs in poor light contains 30 mL of O_2 at

780 mm pressure at 27°C. Supposing that the metal wire flashed is pure Al which is oxidized to Al_2O_3 in the process of flashing, calculate the minimum weight of Al wire that is to be used for maximum efficiency. (0.045 g)

141. How many years would it take to spend the Avogadro constant of rupees at the rate of 10 lakh rupees per second? (1.91×10^{10} yrs)

142. To a sample of an element X (at. wt. 70) another element Y (at. wt. 120) is to be added as an impurity. The ratio of the atoms in the mixture is to be $1:10^{-7}$. How many grams of Y will be required for 35 g of X? (6.0×10^{-6} g)

143. How much calcium is there in the amount of $Ca(NO_3)_2$ that contains 20 g of nitrogen? (28.60 g)

144. At temperature T, a compound $AB_2(g)$ dissociates according to the reaction

$$2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$$

with a degree of dissociation, x, which is small compared to unity. Deduce the expression for x in terms of the equilibrium constant, K_p, and the total pressure, p.

(IIT 1994) $\left[x = \left(\frac{2K_p}{p} \right)^{1/3} \right]$

145. 8.0575×10^{-2} kg of Glauber's salt is dissolved in water to obtain 1 dm^3 of a solution of density 1077.2 kg m^{-3}. Calculate the molarity, molality and mole fraction of Na_2SO_4 in the solution. **(IIT 1994)**

[Hint: $1\ dm^3 = 1$ L, kg m^{-3} = gL^{-1}] (0.5674 M, 0.5693 *m*, 0.01)

146. The freezing point of a solution containing 0.2 g of acetic acid in 20.0 g of benzene is lowered by 0.45°C. Calculate the degree of association of acetic acid in benzene. $K_f(C_6H_6) = 5.12$ K mol^{-1} kg. (0.9453)

[Hint: Acetic acid exists as dimer in benzene.)

147. Calculate the mole fraction of a benzene-toluene liquid solution that is in equilibrium with a vapour phase that contains 62 mole % C_6H_6. Vapour pressures of benzene and toluene at 25°C are 95.1 mm and 28.4 mm respectively. (0.328 for C_6H_6)

148. Calculate the electrode potential for

$$\underset{(1\ atm)}{(Pt)\ H_2} \mid H^+ (c = 0.1)$$

(–0.0591 V)

149. Calculate the emf of the cell of 25°C:

$$\underset{(1\ atm)}{(Pt)\ H_2} \mid \underset{c=0.1\ M}{CH_3COOH} \parallel \underset{c=0.01\ M}{NH_4OH} \mid \underset{(1\ atm)}{H_2\ (Pt)}$$

$K_a(CH_3COOH) = 1.8 \times 10^{-5}$ and $K_b(NH_4OH) = 1.8 \times 10^{-5}$ (0.458 V)

150. A solution contains 0.06 M of Cu^{2+} ions and Ag^+ of unknown concentration. Find the concentration of Ag^+ ions so that both the metals can be codeposited. $E^0_{Cu^{2+},Cu} = +0.337$ V and $E^0_{Ag^+,Ag} = +0.7991$ V. (3.7×10^{-9} M)

151. Calculate the ratio of the oxidized to the reduced form at half-cell potential of 0.1 volt for the half cell $Fe^{3+}, Fe^{2+} | Pt$. $E^0_{Fe^{3+}, Fe^{2+}} = 0.7591$. ($1.41 \times 10^{11}$)

152. Cadmium amalgam is prepared by electrolysis of a solution of $CdCl_2$ using Hg cathode. For how long should electrolysis be carried out in order to prepare 12% by weight of cadmium amalgam using 22.0 g of Hg as cathode and a current strength of 5 ampere? (Cd = 112) (17 min 14 s)

153. Electrolytic oxidation of H_2SO_4 gives rise to the formation of persulphuric acid, $H_2S_2O_8$.

$$2H_2SO_4 \rightarrow H_2S_2O_8 + 2H^+ + 2e$$

If 4 litres of O_2 and 11.2 litres of H_2 were produced at NTP, determine the mass of $H_2S_2O_8$ produced. (27.72 g)

[Hint: $2H_2SO_4 \rightarrow H_2S_2O_8 + H_2$

$2H_2O \rightarrow 2H_2 + O_2$

Eq. of $H_2S_2O_8$ = eq. of H_2 − eq. of O_2]

154. An alloy of Pb(II) and Tl(I) containing 70% Pb and 30% Tl by weight can be electroplated on to a cathode from a perchloric acid solution. How much time would be required to deposit 5.0 g of this alloy at a current of 1.1 amp? (Pb = 207.19, Tl = 204.37) (1 hour)

155. The tungsten used in filaments for light bulbs can be prepared from tungsten (VI) oxide by reduction with hydrogen at 1200°C

$$WO_3(s) + 3H_2(g) = W(s) + 3H_2O(g); \quad \Delta H = 114.9 \text{ kJ}$$

ΔH_f for $H_2O(g) = -241.8$ kJ mole^{-1}. Calculate ΔH_f for $WO_3(s)$. (− 840.3 kJ)

156. Water gas is produced by the action of superheated steam on red hot coke.

$$C(s) + H_2O(g) + 131.4 \text{ kcal} = \underbrace{CO(g) + H_2(g)}_{\text{water gas}}$$

ΔH_f for $H_2O(g) = -241.8$ kJ mole^{-1}. Calculate ΔH_f for CO(g). (−110.4 kJ)

157. The thermochemical equation for the dissociation of hydrogen gas into atoms may be written as:

$$H_2 \rightarrow 2H; \quad \Delta H = 436 \text{ kJ}$$

What is the ratio of the energy yield on combustion of hydrogen atoms to steam to the yield on combustion of an equal mass of hydrogen molecule to steam? Heat of formation of $H_2O(g)$ is − 241.81 kJ mole^{-1}. (2.8)

158. Calculate ΔH°_f for chloride ion from the following data.

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightarrow HCl(g); \ \Delta H^\circ_f = -92.4 \text{ kJ}$$

$$HCl(g) + xH_2O \rightarrow H^+(aq) + Cl^-(aq); \ \Delta H_{298} = -74.8 \text{ kJ}$$

$\Delta H^\circ_f[H^+(aq)] = 0.0$ kJ (−167.2 kJ)

159. The data below after the reaction of NO and Cl_2 to form NOCl at 295 K:

$[Cl_2]$	[NO]	Initial rate (mol L^{-1} s^{-1})
0.05 M	0.05 M	1×10^{-3}
0.15 M	0.05 M	3×10^{-3}
0.05 M	0.15 M	9×10^{-3}

(i) What is the order with respect to NO and Cl_2?
(ii) Write the rate expression.
(iii) Calculate the rate constant.
(iv) Determine the reaction rate when the concentrations of Cl_2 and NO are 0.2 M and 0.4 M respectively. [(i) 2, 1 (iii) 8.0 L^2 mol^{-2} s^{-1} (iv) 0.256 mol L^{-1} s^{-1}]

[**Hint:** See Example 25, Chapter 17]

160. The order of the reaction: $A + B \rightarrow C$, is one with respect to each of the reactants. Fill in the blanks in the following table.

Initial [A]	Initial [B]	Initial rate
0.2 M	0.05 M	0.1 M s^{-1}
?	0.05 M	0.4 M s^{-1}
0.4 M	?	0.8 M s^{-1}

(0.8 M, 0.2 M)

161. An unspecified quantity of an ideal gas has a volume of 30 litres at 20°C. The gas is first compressed at 20°C until the pressure has doubled and then the temperature is raised to 100°C, while the pressure is kept constant. Determine the final volume of the gas. (19.10 litres)

162. A glass tube *AD* of uniform cross section of length 100 cm sealed at both ends contains two columns of ideal gas *AB* and *CD* separated by a column of mercury of length 20 cm. When the tube is held horizontally, $AB = 20$ cm and $CD = 60$ cm. When the tube is held vertically with the end *A* up, the mercury column moves down 10 cm. What will be the length of gas column *AB* when the tube is held vertically with the end *D* up? (13.88 cm)

163. A vertical cylinder of height 100 cm contains air at a constant temperature. The top is closed by a frictionless light piston. The atmospheric pressure is equal to 75 cm of Hg. Mercury is slowly poured over the piston. Find the maximum height of the mercury column that can be put on the piston. (25 cm)

[**Hint:** Boyle's law: $75 \times 100 = p \times (100 - l)$; $p = (75 + l)$; calculate l]

164. A glass tube sealed at both ends is 100 cm long. It lies horizontally with the middle 10 cm containing Hg. The two ends of the tube containing air at 27°C and at a pressure 76 cm of Hg. The air column on one side is maintained at 0°C and on the other side at 127°C. Calculate the length of the air column on the cooler side. Neglect the changes in the volume of mercury and of the glass. (36.5 cm)

165. Mercury diffusion pumps may be used in the laboratory to produce a high vacuum. Cold traps are generally placed between the pump and the system to be evacuated. These cause the condensation of Hg vapour, and prevent mercury from diffusing back into the system. The maximum pressure of mercury that can exist in the system is the vapour pressure of mercury at the temperature of the cold trap. Calculate the number of mercury-vapour molecules per cc in a cold trap maintained at –120°C. The vapour pressure of mercury at this temperature is 10^{-6} mm. (6×10^{10})

166. Saccharin ($K_a = 2\times10^{-12}$) is a weak acid represented by the formula HSac. 4×10^{-4} mole saccharin is dissolved in 200 cm^3 aqueous solution of pH 3. Assuming no change in volume, calculate the concenration of Sac^{-1} ions in the resulting solution at equilibrium. (4.0×10^{-12})

167. K_a for butyric acid is 2.0×10^{-5}. Calculate pH and hydroxyl ion concentration of 0.2 M aqueous solution of sodium butyrate. (9.45)
[Hint: Use Equation 11 (b), Chapter 16]

168. A solution has 0.05 M Mg^{2+} and 0.05 M NH_3. Calculate the concentration of NH_4Cl required to prevent the formation of $Mg(OH)_2$ in the solution. $K_{sp}(Mg(OH)_2) = 9.0\times10^{-12}$ and $K_b(NH_3) = 1.8\times10^{-5}$. (0.067 M)

169. The solubility product of $Mg(OH)_2$ at 25°C is 3.4×10^{-11} and that of $Fe(OH)_3$ is 1.1×10^{-35}.
(i) How many grams per litre of Mg^{2+} and Fe^{3+} can remain dissolved in 100 mL of 0.1 M NH_4OH solution? $K_b(NH_4OH) = 1.01\times10^{-5}$.
(ii) How many gram per litre of Mg^{2+} and Fe^{3+} can remain in 100 mL of 0.1 M NH_4OH containing sufficient amount of NH_4Cl to make $[NH_4^+] = 2.0$ M?
[(i) 4.8×10^{-4} g/L, 2.8×10^{-26} g/L (ii) 1.14×10^{-3} g/L, 1.02×10^{-16} g/L]

170. The equilibrium constant for the following reaction:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

at 986°C is 0.63. A mixture of 1.0 mole of water vapour and 3.0 mole of CO is allowed to come to equilibrium. The equilibrium pressure is 2.0 atm.
(i) How many moles of H_2 are present at equilibrium?
(ii) Calculate the partial pressures of gases in the equilibrium mixture.
(0.68 mole; 0.34 atm, 0.34 atm, 1.16 atm, 0.16 atm)

171. 0.15 mole of CO taken in a 2.5-litre flask is maintained at 750 K along with a catalyst so that the following reaction can take place:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

Hydrogen is introduced until the total pressure of the system is 8.5 atm at equilibrium and 0.08 mole of methanol is formed. Calculate (i) K_p and K_c, and (ii) the final pressure if the same amount of CO and H_2 as before are used, but with no catalyst so that the reaction does not take place.
[(i) 4.94×10^{-2} atm^{-2}, 1.8684×10^{2} $(mol/L)^{-2}$ (ii) 12.43 atm]

172. The degree of dissociation of N_2O_4 is 0.633 under a pressure of 3 atm. What must be the pressure if dissociation is to be 80%? (0.31)

173. Calculate the energy emitted when electrons of 1.0 g of hydrogen atoms undergoes transition giving the spectral line of lowest energy in the visible region of its atomic spectrum.

$R_H = 1.1 \times 10^7 \text{ m}^{-1}$, $c = 3 \times 10^8 \text{ m s}^{-1}$, $h = 6.62 \times 10^{-34}$ Js.

(182.656 kJ)

174. What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition ($n = 4$ to $n = 2$ of He^+ spectrum)? **(IIT 1993)**

[Hint: See Example 14, Chapter 11]

($n = 2$ to $n = 1$)

175. Electromagnetic radiation of wavelength 242 nm is just sufficient to ionize sodium atom. Calculate the ionization energy of sodium atom. $c = 3 \times 10^8 \text{ m s}^{-1}$, $h = 6.626 \times 10^{-34}$ Js.

(8.203×10^{-22} kJ)

[Hint: See Example 7, Chapter 11]

176. Copper metal has a face-centred cubic structure with unit cell length equal to 0.361 nm. Picturing copper ions in contact along the face diagonal, find the apparent radius of a copper ion. (0.128 nm)

177. How many moles of electrons are involved in balancing the following redox equations?

$$H_2S + NO_3^- \rightarrow S + NO$$

and

$$Mn(OH)_2 + H_2O_2 \rightarrow MnO_2$$

(6, 2)

178. Write the half reactions and number of moles of electrons involved in the overall cell reaction for the electrochemical cell designated by

$Pt|Ag(s)|AgCl(s)|Cl^-(c = 1)|Cl_2(c = 1)|C$ (graphite)$|Pt$.

$$\left[\begin{array}{c} Ag(s) + Cl^-(aq) \rightarrow AgCl(s) + e, \\ Cl_2 + 2e \rightarrow 2Cl^-, \\ n = 2 \end{array}\right]$$

179. Given $E^0 = 0$ V for the H^+/H_2 couple and -0.8281 V for $H_2O/H_2, OH^-$ couple. Determine K_w at 25°C. (1.01×10^{-14})

180. Given $E^0 = -0.268$ V for the $PbCl_2/Pb$ couple and -0.126 V for Pb^{2+}/Pb couple. Determine K_{sp} for $PbCl_2$ at 25°C. (1.6×10^{-5})

$$\left[\textbf{Hint: } \begin{array}{l} PbCl_2 + 2e \rightarrow Pb + 2Cl^- \\ Pb \rightarrow Pb^{2+} + 2e \end{array}\right]$$

181. The vapour pressure of heptane and toluene at 50°C are 141 mm and 93 mm respectively. Find the composition of the solution (containing toluene and heptane) at which the partial pressure of toluene is equal to that of heptane. (0.602, 0.398)

182. A liquid mixture of A and B is placed in a cylinder-and-piston arrangement. The piston is slowly pulled out isothermally so that the volume of the liquid decreases and that of the vapour increases. At the instant when the quantity of the liquid still remaining is negligibly small, the mole fraction of A in the vapour is 0.4. $p_A^0 = 0.4$ atm, $p_B^0 = 1.2$ atm at the temperature in question. Calculate the total pressure at which the liquid has almost evaporated. Assume ideal behaviour. (0.667 atm)

183. Air was drawn through a solution containing 38 g of solute in 100 g of water, and then through water. The loss of weight of water was 0.0551 g and the total weight of water absorbed in sulphuric acid tube was 2.2117 g. Find the molecular weight of the dissolved substance. (267.7)

[**Hint:** Raoult's law: $\frac{\text{lowering of VP}}{\text{VP of solvent}} = \text{mole fraction of solute}$

or $$\frac{0.0551}{2.2117} = \frac{38/M}{\frac{38}{M} + \frac{100}{18}}$$]

184. Calculate the mole per cent of ammonia formed at 350°C and equilibrium pressure of 10 atm when nitrogen and hydrogen taken are in 1 : 3 molar ratio. $K_p = 7.08 \times 10^{-4}$. (9.47%)

185. A mixture of nitrogen and hydrogen in a proportion of 1 : 3 by volume was subjected to a pressure of 30 atm and a temperature of 723 K. After equilibrium was established, and cooled, the analysis indicated that the mixture contained 6% of ammonia by volume. Calculate K_p. (4.85×10^{-5} atm^{-2})

186. The equilibrium constant for the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

at 440°C is 50. How many moles of hydrogen per mole of iodine are required to convert 90% of iodine into hydrogen iodide? (1.548 moles)

187. At 21.5°C and a total pressure of 0.0787 atm, N_2O_4 is 48.3% dissociated into NO_2. Calculate K_c for the reaction: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$. At what total pressure will the per cent dissociation be 10%? (0.00396, 2.371 atm)

188. Calculate the electron affinity of chlorine from the given data:

$Na(g) = Na^+(g) + e$ $\quad \Delta H° = 499.8$ kJ

$\frac{1}{2}Cl_2(g) = Cl(g)$ $\quad \Delta H° = 120.9$ kJ

$Na(s) = Na(g)$ $\quad \Delta H° = 108.3$ kJ

$Na(s) + \frac{1}{2}Cl_2(g) = NaCl(s)$ $\quad \Delta H° = -411.3$ kJ

$Na^+(g) + Cl^-(g) = NaCl(s)$ $\quad \Delta H° = -775.4$ kJ

(−364.9 kJ mole^{-1})

189. A gas expands from a volume of 3.0 dm^3 to 5.0 dm^3 against a constant external pressure of 3.0 atm. The work done during expansion is used to heat 10 moles of water at a temperature 290 K. Calculate the final temperature of water. Specific heat of water = 4.184 J g^{-1} K^{-1}.

[**Hint:** $W = -p\,.\,\Delta V$; 1 atm = 101325 Pa, 1 dm^3 = 10^{-3} m^3] (290.807 K)

190. Determine the enthalpy of the reaction

$$C_3H_8(g) + H_2(g) \rightarrow C_2H_6(g) + CH_4(g) \text{ at } 25°C,$$

using the given heat of combustion values under standard conditions.

Compound:	$H_2(g)$	$CH_4(g)$	$C_2H_6(g)$	C (graphite)
ΔH° (kJ/mole):	−285.8	−890.0	−1560.0	−393.5

The standard heat of formation of $C_3H_8(g)$ is − 103.8 kJ/mole.

(IIT 1992)

(−55.7 kJ)

191. A cylindrical tube of length 30 cm is partitioned by a tight-fitting separator. The separator is very thin, very weakly conducting and can freely slide along the tube. Ideal gases are filled in the two parts of the vessel. In the beginning, the temperature in the parts *A* and *B* are 400 K and 100 K respectively. The separator slides to a momentary equilibrium position at which the length of the tube at part *A* is 20 cm. Find the final equilibrium position of the separator, reached after a long time.

(10 cm along part A)

[Hint: Apply $\frac{p_1V_1}{T_1}=\frac{p_2V_2}{T_2}$ for part *A* under the given two conditions and again for part *B*. Remember that at both the equilibrium positions, both sides will have the same pressure.]

192. By how many folds the temperature of a gas would increase when the rms velocity of the gas molecules in a container of fixed volume is increased from 5×10^4 cm/s to 15×10^4 cm/s?

(9 times)

193. The order of a reaction, $A+2B\rightarrow C$, is 1 and 2 with respect to A and B respectively. Fill in the blanks in the following table:

[A]	[B]	Rate
1.0 M	0.2 M	$0.1\ M\ s^{-1}$
2.0 M	0.2 M	?
2.0 M	?	$0.8\ M\ s^{-1}$

(0.4 M, $0.2\ M\ s^{-1}$)

194. The activation energy for a first-order reaction is 104.5 kJ/mole and the factor *A* in the Arrhenius equation is $5\times10^{13}\ s^{-1}$. Find the temperature at which the half-life period of the reaction is 1 minute.

(75°C)

195. The activation energy of a certain uncatalysed reaction at 300 K is 76 kJ per mole. The activation energy is lowered to 57 kJ per mole by the use of a catalyst. By what factor is the rate of the catalysed reaction increased?

(2031 times)

196. Two reactions of the same order have equal pre-exponential factors, but their activation energies differ by 24.9 kJ per mole. Calculate the ratio between the rate constants of these reactions at 27°C.

(2.2×10^{-4})

197. Two bulbs *A* and *B* of equal capacity are filled with He and SO_2 respectively at the same temperature.

(i) If the pressure in the two bulbs is the same, what will be the ratio of velocities of the molecules of the two gases?

(ii) At what temperature will the velocity of SO_2 molecules become half the velocity of He molecules at 27°C?

(iii) How will the velocities be affected if the volume of *B* becomes 4 times that of *A*?

(iv) How will the velocities be affected if half the molecules of SO_2 are removed from B?

[(i) 4 (ii) 927°C (iii) (iv)—no change]

198. A reaction mixture for the combustion of SO_2 was prepared by opening a stopcock connecting two separate chambers, one having a volume of 2.125 litres filled with SO_2 at 0.75 atm and the other having 1.5 litres volume filled with oxygen at 0.50 atm; both gases were at 80°C.

(i) What were the mole fractions of SO_2 and O_2 in the mixture, and the total pressure?

(ii) If the mixture was passed over a catalyst that promoted the formation of SO_3 and was then returned to the original two connected vessels, what were the mole fractions in the final mixture and what was the final total pressure? Assume that the conversion of SO_2 is complete to the extent of the availability of O_2.

[(i) 0.68, 0.32; 0.64 atm
(ii) 0.06, 0.94; 0.44 atm]

199. The standard electrode potential of a standard hydrogen half cell is 0 volt. If the standard state is considered when $[OH^-] = 10^{-7}$ or $[H^+] = 10^{-7}$, calculate E^0 under these conditions.

(−0.4137 V, −0.4137 V)

200. The potential for the reaction

$$O_2(g) + 4H^+ + 4e = 2H_2O(l)$$

is 1.23 V in 0.1 N acid solution. Calculate the potential of this couple in aqueous solutions having (a) pH = 10 (b) pH = 14.

[**Hint:** First calculate E^0 for the given half cell and then the potential at the given pH.]

(0.6981 V, 0.462 V)

201. Calculate the solubility product of the reaction

$$Fe(OH)_3 = Fe^{3+} + 3OH^-$$

Given that,

$$Fe(OH)_3 + 3e = Fe(s) + 3OH^- ; \quad E^0 = -0.77 \text{ V}$$

$$Fe^{3+} + 3e = Fe(s) ; \quad E^0 = -0.036 \text{ V}$$

(1.82×10^{-37})

202. Calculate the potential of the cell

Cu | Mn (s) | $MnCl_2$(0.001 M), HCl (0.01 M) | O_2(0.25 bar) | Pt | Cu.

Given that $E^0 = -1.185$ V for Mn^{2+} | Mn couple and 1.229 V for the O_2 | H_2O, H^+ couple.

(2.452 V)

203. Estimate the difference in energy between first and second Bohr orbit for a hydrogen atom. At what minimum atomic number, a transition from $n = 2$ to $n = 1$ energy level would result in the emission of X-rays with $\lambda = 3.0 \times 10^{-8}$ m? Which hydrogen-atomlike species does this atomic number correspond to? ($R = 109677 \text{ cm}^{-1}$, $c = 3 \times 10^{10} \text{ cm s}^{-1}$) (IIT 1993)

(1.63×10^{-11} erg, $Z = 2$, He^+)

[**Hint:** Apply $\Delta E = RchZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$]

204. The nucleide ratio, ^3_1H to ^1_1H in a sample of water is $8.0 \times 10^{-18}:1$. Tritium undergoes decay with a half-life period of 12.3 years. How many tritium atoms would 10.0 g of such a sample contain 40 years after the original sample is collected?

(IIT 1992) (5.62×10^5)

[Hint: Given that, $\frac{\text{mol of } T_2O \text{ molecules}}{\text{mol of } H_2O \text{ molecules}} = \frac{8 \times 10^{-18}}{1}$

$\therefore$ 10 g of sample contains $(2 \times 8 \times 10^{-18}) \times \frac{10}{18}$ mole tritium atoms]

205. A solution of Na_2CO_3 that is 2.0 M in CO_3^{2-} ions was boiled with excess of CaF_2. Very small amounts of $CaCO_3$ and F^- were formed. If the solubility product of $CaCO_3$ is x and molar solubility of CaF_2 is y, find the molar concentration of F^- in the resulting solution after equilibrium is attained.

$\left(\sqrt{\frac{8y^3}{x}}\right)$

206. The solubility product of AgCl is 1.0×10^{-10}. The equilibrium constant of the reaction

$$AgCl(s) + Br^- \rightleftharpoons AgBr(s) + Cl^-$$

is 2×10^2 and that of the reaction

$$2AgBr(s) + S^{2-} \rightleftharpoons Ag_2S(s) + 2Br^-$$

is 1.6×10^{24}. Calculate K_{sp} of Ag_2S. (1.56×10^{-49})

207. What amount of $BaSO_4$ will dissolve in 500 mL of aqueous solution? $K_{sp}(BaSO_4) = 1 \times 10^{-10}$. (0.0011 g)

208. Calculate the solubility product of Ag_2CrO_4 at 25°C if the concentration of Ag^+ ions is 1.5×10^{-4} mole/litre in a saturated solution of Ag_2CrO_4 at 25°C.

(1.69×10^{-12})

209. A sample of hard water contains 0.005 mole of $CaCl_2$ per litre. What is the minimum concentration of Na_2SO_4 which must be exceeded for removing the calcium ions from the water sample? $K_{sp}(CaSO_4) = 2.4 \times 10^{-5}$ at 25°C. (0.0048 mole/L)

210. In a 3-litre vessel the following equilibrium partial pressures are measured: $N_2 = 190$ mm, $H_2 = 317$ mm, $NH_3 = 1000$ mm. Hydrogen is removed from the vessel until the pressure of nitrogen at equilibrium is equal to 250 mm. Calculate the pressure of other substances under the new condition. $(p_{H_2} = 265.8 \text{ mm})$

211. Pure phosphine originally present at 2.5 atm and 300 K decomposes slowly according to the equation:

$$4PH_3(g) \rightleftharpoons P_4(g) + 6H_2(g)$$

What is the vapour density of phosphine if it dissociates to the extent of 40%? (13.08)

212. For equilibrium $AB(g) \rightleftharpoons A(g) + B(g)$, K_p is equal to four times the total pressure. Calculate the number of moles of B formed.

($2/\sqrt{5}$ times initial mol of AB)

213. When equimolar quantities of acetic acid and ethanol are at 25°C, 1/3 of acetic acid remains unreacted as shown by titration with standard alkali. Calculate the concentration equilibrium constant.

(4.0)

214. At room temperature the following reactions proceed nearly to completion:

$$2NO + O_2 \rightarrow 2NO_2 \rightarrow N_2O_4$$

The dimer, N_2O_4 solidifies at 262 K. A 250-mL flask and a 100-mL flask are separated by a stopcock. At 300 K the nitric oxide in the larger flask exerts a pressure of 1.053 atm and the smaller one contains oxygen at 0.789 atm. The gases are mixed by opening the stopcock and after the end of the reaction the flasks are cooled to 220 K. Neglecting the vapour pressure of the dimer, find out the pressure and composition of the gas remaining at 220 K. Assume the gases to behave ideally.

(IIT 1992)

[Hint: See Example 17, Chapter 12] (0.221 atm, NO– 0.0043 mol)

215. At 27°C, hydrogen leaks through a tiny hole in a vessel for 20 minutes. Another unknown gas at the same temperature and pressure as that of H_2 leaks through the same hole for 20 minutes. After the effusion of the gases, the mixture exerts a pressure of 6 atm. The hydrogen content of the mixture is 0.7 mole. If the volume of the container is 3 litres, what is the molecular weight of the unknown gas?

(IIT 1992) (1032)

[Hint: $\frac{r_X}{r_{H_2}} = \sqrt{\frac{2}{M}} = \frac{n_X}{n_{H_2}}; pV = (n_X + n_{H_2})RT$]

216. The emf of the cell

$Ag \mid AgCl, KCl\ (0.05\ M) \parallel AgNO_3\ (0.05\ M) \mid Ag$

is 0.788 volt. Find K_{sp} of AgCl.

(1.16×10^{-16})

[Hint: For the cell reaction: $Ag^+(0.05) = Ag^+(c)$

where c is the Ag^+ concentration in LHS half cell,

$$E_{cell} = \frac{0.0591}{1} \log \frac{0.05}{c};\ K_{sp}(AgCl) = c \times 0.05]$$

217. Calculate the solubility product of AgCl from the two half reactions and standard electrode potentials at 25°C

$Ag^+ + e \rightarrow Ag(s)$ $E^0 = 0.799$ V

$AgCl + e \rightarrow Ag(s) + Cl^-$ $E^0 = 0.222$ V

(1.66×10^{-10})

[Hint: $AgCl \rightarrow Ag^+ + Cl^-;\ E^0 = 0.222 - 0.799$

$E^0 = 0.0591 \log[Ag^+][Cl^-] = 0.0591 \log K_{sp}$]

218. Calculate emf of $Ag \mid AgCl$ electrode immersed in 1 M KCl at 25°C. $K_{sp}(AgCl) = 1.8 \times 10^{-10}$, $E^0_{Ag^+, Ag} = 0.799$ volt.

(0.223 V)

219. Determine the temperature at which the half-life for the decomposition of N_2O_5 is two hours. At 298 K, the rate constant is $3.46 \times 10^{-5}\ s^{-1}$ and $E_a = 106$ kJ mol^{-1}.

(305 K)

220. Two reactions (i) $A \rightarrow P$ (ii) $B \rightarrow P$ follow first-order kinetics. The rate of the reaction (i) is doubled when the temperature is raised from 300 K to 310 K. The half-life for this reaction at 310 K is 30 minutes. At the same temperature B decomposes twice as fast as A. If the energy of activation for the reaction (ii) is half that of reaction (i), calculate the rate constant of the reaction (ii) at 300 K.

(IIT 1992) ($3.23 \times 10^{-2}\ min^{-1}$)

[Hint:

Reactions	E_a	Rate constants	
		300 K	310 K
(i) $A \rightarrow P$	E_1	k_1	$2k_1$ (given)
(ii) $B \rightarrow P$	E_2	k_2 (?)	K_2

Given that, $2k_1 = \frac{0.6930}{30}; \frac{2k_1}{K_2} = \frac{1}{2}$ and $\frac{E_1}{E_2} = 2$]

221. A gas bulb of 1-litre capacity contains 2×10^{21} molecules of nitrogen exerting a pressure of $7.57 \times 10^3\ N\ m^{-2}$. Calculate the root-mean-square (rms) speed and the temperature of the gas molecules. If the ratio of the most probable speed to the root-mean-square speed is 0.82, calculate the most probable speed for these molecules at this temperature. **(IIT 1993)**

($494.18\ m\ s^{-1}$, 274.15 K, $405.22\ m\ s^{-1}$)

$$\left[\textbf{Hint: } \text{Use } C = \sqrt{\frac{3pV}{mn}}; V = 10^{-3}\ m^3, m = \frac{28 \times 10^{-3}}{\text{Av. const.}}\right]$$

222. A mixture of 0.5 mole of CO and 0.5 mole of CO_2 is taken in a pot and allowed to effuse out through a pinhole into another vessel which is vacuous. If a total of Z moles has effused out in time t, show that

$$M_1Z + M_2(1 - Z) = 36$$

where M_1 and M_2 are the mean molar masses of the mixture that has effused out and the mixture still remaining in the pot respectively.

223. In order to get maximum calorific output, a burner should have an optimum fuel-to-oxygen ratio which corresponds to 3 times as much oxygen as is required theoretically for complete combustion of the fuel. A burner which has been adjusted for methane as fuel (with x litre/hour of CH_4 and $6x$ litre/hour of O_2) is to be readjusted for butane, C_4H_{10}. In order to get the same calorific output, what should be the rate of supply of butane and oxygen? Assume that losses due to incomplete combustion, etc., are the same for both fuels, and that the gases behave ideally.

Heat of combustion: **(IIT 1993)**

$CH_4 = 809$ kJ/mole, $C_4H_{10} = 2878$ kJ/mole.

$$\left[\begin{array}{l}\textbf{Hint: } \text{Vol. of } C_4H_{10} \text{ required per h} = \frac{804}{2878} \text{ L} \\ \text{Vol. of } O_2 \text{ required per h} \left(\frac{804x}{2878}\right) \times \frac{13}{2} \times 3 \text{ L}\end{array}\right] \quad \left[\begin{array}{l} C_4H_{10} = 0.281x \text{ L/h} \\ O_2 = 5.481x \text{ L/h}\end{array}\right]$$

224. 0.16 g of methane was subjected to combustion at 27°C in a bomb calorimeter. The temperature of the calorimeter system (including water) was found to rise by 0.5°C. Calculate the heat of combustion of methane at (i) constant volume; (ii) constant pressure. The thermal capacity of the calorimeter system is 17.7 kJ K^{-1}. ($R = 8.31 \text{ JK}^{-1}\text{mol}^{-1}$)

$\left[\textbf{Hint: } \Delta E = \frac{17.7 \times 0.5}{0.16/16} \text{ kJ mol}^{-1}\right]$ (–885 kJ, –889.986 kJ)

225. The rates of effusion of two gases A and B under the same conditions of temperature and pressure are in the ratio $\gamma_A : \gamma_B = 2:1$. What would be the ratio of the rms speeds of molecules of A and B if $T_A : T_B = 2:1$? ($2\sqrt{2}:1$)

226. There were 201 rows of spectators sitting in a hall. A magician releases laughing gas (N_2O) from the front, and tear gas (mol. wt. 176) from the rear of the hall simultaneously. Which row of spectators from the front will have a tendency to smile and weep simultaneously? (134)

227. At what temperature does the average translational kinetic energy of a molecule in a gas become equal to the kinetic energy of an electron accelerated from rest through a potential difference of 1 volt?

$1 \text{ eV} = 1.602 \times 10^{-12}$ erg. (7.73×10^3 K)

228. The K_p value for the reaction equilibrium:

$$H_2(g) + I_2(s) \rightleftharpoons 2HI(g)$$

is 871 at 25°C. If the vapour pressure of iodine is 4×10^{-4} atm, calculate the equilibrium constant in terms of partial pressures at the same temperature. (0.3484 atm)

229. Solid NH_4HS is taken in an evacuated vessel and allowed to dissociate at a certain temperature until the total gas pressure is 0.66 atm. What would be the value of K_p for the following reaction?

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$$

What would be the partial pressure of H_2S if additional NH_3 is introduced into the equilibrium mixture at the same temperature until the partial pressure of NH_3 is 0.921 atm? (0.1089 atm)

230. Solid ammonium carbamate, NH_2COONH_4, dissociates on heating to NH_3 and CO_2:

$$NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$$

When pure carbamate is put into a closed container and allowed to come to equilibrium with the gaseous products at a constant temperature, 35°C, the total pressure is found to be 0.30 atm. Determine K_p for this reaction at 35°C.

(4.0×10^{-3} atm^3)

231. Water gas is produced by the reaction

$$C + H_2O(g) \rightarrow H_2 + CO$$

The heat required for this endothermic reaction may be supplied by adding a limited amount of air and burning some carbon to carbon dioxide. Calculate the amount of carbon to be burnt to CO_2 to provide enough heat for the water gas ($H_2 + CO$) conversion of 100 g of carbon. $\Delta H°_f$ for $CO = -110.53$ kJ, $\Delta H°_f$ for $H_2O = -241.81$ kJ and $\Delta H_{combustion}$ for $C = -393.51$ kJ. (33.4 g)

232. A first-order reaction $A \rightarrow B$, requires activation energy of 70 kJ mole^{-1}. When a 20% solution of A was kept at 25°C for 20 minutes, 25% decomposition took place. What will be the per cent decomposition in the same time in a 30% solution maintained at 40°C? Assume that activation energy remains constant in this range of temperature. **(IIT 1993)** (67.17%)

[**Hint:** First calculate k_{25}, then k_{40}. Again find out per cent decomposition at 40°C.]

233. In Arrhenius's equation for a certain reaction, the values of A and E_a are $4 \times 10^{13}\ s^{-1}$ and 98.6 kJ mole^{-1} respectively. If the reaction is of the first-order, at what temperature will its half-life period be ten minutes? (311.2 K)

234. The energy of activation of the reaction: $A + B \rightarrow C$ is 24.6 kcal/mole. If the rate of formation of C is 0.133 M min^{-1} at 40°C, what would it be at 80°C?

(11.41 M min^{-1})

235. A reaction proceeds with the energy of activation of 55.3 kcal/mole. If ΔH of the reaction is 1 kcal, what would be the energy of activation of the reverse reaction? (54.3 kcal)

236. Isopropyl alcohol and *n*-propyl alcohol, both have the same molecular formula C_3H_8O. A solution of the two, that is, 25% isopropyl alcohol by mass, has a total vapour pressure of 0.09 atm at a given temperature. A solution of the two, that is, 75% isopropyl alcohol by mass, has a total vapour pressure of 0.12 atm at the same temperature. Find the vapour pressures of the pure alcohols at this temperature. (0.135 atm, 0.075 atm)

237. The immiscible liquid system aniline–water boils at 98°C under a presssure of 760 mm. At this temperature the vapour pressure of water is 707 mm. If this system is distilled in steam, what fraction of total weight of the distillate will be aniline? (28%)

238. A current of dry air was passed through a solution containing 2.5 g of B in 100 g of solution, and through water alone. The loss of weight of solution was 1.25 g and that of water was 0.05 g. Determine the molecular weight of B. (117)

239. In nature a decay chain series starts with $^{232}_{90}Th$ and finally terminates at $^{208}_{82}Pb$. A thorium ore sample was found to contain 8×10^{-5} mL of helium at STP and 5×10^{-7} g of ^{232}Th. Find the age of the ore sample assuming the source of helium to be only the decay of ^{232}Th. Also, assume complete retention of helium within the ore. Half-life of $^{232}Th = 1.39 \times 10^{10}$ years.

[Hint: $^{232}_{90}Th \rightarrow ^{208}_{82}Pb + 6\,^{4}_{2}He + 4\,^{0}_{-1}e$]

(4.89×10^{9} years)

240. A 0.5-g sample containing MnO_2 is treated with HCl, liberating Cl_2. The Cl_2 is passed into a solution of KI and 30.0 cm^3 of 0.1 M $Na_2S_2O_3$ are required to titrate the liberated iodine. Calculate the percentage of MnO_2 in the sample. (26.10%)

241. A 2.0-g sample of a mixture containing sodium carbonate, sodium bicarbonate and sodium sulphate is gently heated till the evolution of CO_2 ceases. The volume of CO_2 at 750 mmHg pressure and at 298 K is measured to be 123.9 mL. 1.5 g of the same sample requires 150 mL of (M/10) HCl for complete neutralization. Calculate the percentage composition of the components of the mixture.

(IIT 1992) (26.5%, 42.0%, 31.5%)

242. 5.6 g of a steel sample containing sulphur impurity was burnt in oxygen. SO_2, so produced, was then oxidised to sulphate by H_2O_2 solution to which 30 mL of 0.004 M NaOH solution had been added. 22.48 mL of 0.024 M HCl was required to neutralize the base remaining after oxidation reaction. Calculate percentage of S in the given sample of steel. (0.1886%)

[Hint: $SO_2 + H_2O_2 + 2OH^- = SO_4^{2-} + 2H_2O$

mmol of S = mmol of $SO_2 = \frac{1}{2} \times \text{mmol of } OH^- = (30 \times 0.04 - 22.48 \times 0.024)$]

243. Calculate $[NH_4^+]$ (derived from NH_4Cl) to prevent $Mg(OH)_2$ from precipitating in a one-litre solution, containing 0.01 M NH_3 and 0.001 M Mg^{2+} ions.

$K_{sp}[Mg(OH)_2] = 1.2 \times 10^{-11}$, $K_b(NH_4OH) = 1.8 \times 10^{-5}$.

(1.6×10^{-3})

244. What is the maximum pH of a solution of 0.1 M in Mg^{2+} from which $Mg(OH)_2$ will not precipitate? $K_{sp}[Mg(OH)_2] = 1.2 \times 10^{-11}$. (9.04)

245. Calculate the maximum possible concentration of Ni^{2+} ions in a solution which is also 0.15 M in HCl and 0.1 M in H_2S.

$K_{sp}(NiS) = 2 \times 10^{-21}$, $K(H_2S) = 1 \times 10^{-21}$. (0.45 M)

246. Calculate the pH at which $Mg(OH)_2$ begins to precipitate from a solution containing 0.1 M Mg^{2+} ions, K_{sp} for $Mg(OH)_2 = 1 \times 10^{-11}$. (9.0)

247. A particular water sample has 131 ppm $CaSO_4$. What fraction of the water must be evaporated in a container before solid $CaSO_4$ begins to deposit?

$K_{sp}(CaSO_4) = 9.0 \times 10^{-6}$. (68%)

248. In the reaction

$$CH_3COCH_3(g) \rightarrow C_2H_4(g) + H_2(g) + CO(g)$$

the total pressure changes as follows:

Time (min):	0	6.5	13.0	19.9
Pressure (Pa):	41489.6	54386.6	65050.4	74914.6

Show that the reaction is of first-order.

249. Two reactions of the same order have equal pre-exponential factors but their activation energies differ by 41.9 kJ/mole. Calculate the ratio between the rate constants of these reactions at 600 K.

(0.0002)

250. The dissociation of a substance is a first-order reaction with an activation energy of 231 kJ/mole. At 300 K, this substance dissociates at a rate of 95% within an hour. Calculate the temperature at which the dissociation rate of the substance is 0.1% per minute.

(350 K)

251. A diazonium salt dissociates according to the equation

$$CH_3C_6H_4N_2Cl + H_2O \rightarrow CH_3C_6H_4OH + N_2 + HCl.$$

The dissociation process is a first-order reaction whose rate constants at 297.9 K and 303.2 K are 9×10^{-3} and $13 \times 10^{-3}\ \text{min}^{-1}$ respectively. Calculate the rate constant at 308.2 K and the time for 99% dissociation of the salt at 308.2 K.

($16.37 \times 10^{-3}\ \text{min}^{-1}$, 282 min)

252. A thermally insulated container initially holds N_0 molecules of an ideal monoatomic gas at an absolute temperature T_0. Molecules escape from the container through a small hole in the wall, and it can be shown that in such a process at a temperature T, the average kinetic energy of the escaping molecules is $2\,kT$. How many molecules remain in the container when the temperature has fallen to $T_0/2$?

($N_0/8$)

[**Hint:** No. of molecules at T_0 is N_0. Let at any time the temp. of the container be T and the no. of molecules present be N. Both T and N are variable. Let during the time dt, the no. of molecules escaped be dN. Then

$$\frac{3}{2}kTN - 2\,kT\,dN = \frac{3}{2}k(T - dT)(N - dN)$$

or,
$$\frac{3}{2}\int_{T_0}^{T_0/2} \frac{dT}{T} = \frac{1}{2}\int_{N_0}^{N} \frac{dN}{N} \quad \text{(neglecting } dTdN \text{ factor)}$$

or,
$$N = \frac{N_0}{8}.\ ]$$

253. K_p for the equilibrium: $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ is 1.16 atm at 1073 K. If 20 g of $CaCO_3$ was heated to 1073 K in a 10-litre vessel, find the percentage of $CaCO_3$ remaining unreacted at equilibrium.

(34.20%)

254. Solid ammonium carbamate dissociates according to the reaction

$$NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g).$$

At 298 K, the total pressure of the gases in equilibrium with the solid is 0.116 atm. Calculate K_p.

($2.31 \times 10^{-4}\ \text{atm}^3$)

255. Carbon was heated with 1.0 g of hydrogen in a 5-litre tank to 1000°C. At equilibrium 0.22 g of methane was found in the tank. Calculate the equilibrium constant for the equilibrium

$$C(s) + 2H_2(g) \rightleftharpoons CH_4(g)$$

(0.31)

256. If the reaction between steam and iron proceeds as

$$3\,Fe(s) + 4\,H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

and partial pressures of steam and hydrogen are 50 mm and 940 mm respectively at 250°C, calculate the partial pressure of steam at equilibrium when partial pressure of hydrogen is 1800 mm. (95.7 mm)

257. The equilibrium constant of the reaction $H_2 + I_2 \rightleftharpoons 2HI$ at 693 K is 50.25 (K_c). Calculate the yield of HI if 0.846×10^{-3} kg of I_2 and 0.0212×10^{-3} kg of H_2 have been placed in a vessel having a capacity of $10^{-3}\,m^3$. (0.821×10^{-3} kg)

258. At 823 K and 1.0133×10^5 Pa, the degree of dissociation of phosgene ($COCl_2$) into CO and Cl_2 is 77%. Find K_p and K_c. (1.456, 0.0215)

259. Express the equilibrium constant K_p of the reaction $H_2 + 0.5O_2 = H_2O(v)$ in terms of total pressure p and degree of dissociation α of water vapour.

$$\left[K_p = \frac{(1-\alpha)(\alpha+2)^{1/2}}{p^{1/2}\,\alpha^{3/2}}\right]$$

260. The equilibrium constant of the reaction

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

at 800 K is 4.12. A mixture of 20% CO and 80% H_2O is heated to 800 K. Determine the composition of the mixture in the state of equilibrium and the yield of hydrogen if 1 kg of water vapour is taken.

$$\begin{bmatrix} CO - 1.447\%, & H_2O - 59.858\% \\ CO_2 - 37.013\%, & H_2 - 1.68\% \end{bmatrix}$$

261. At 945°C and 1 atm, 1.7 g of H_2S occupies a volume of 5.384 litres. Calculate the degree of dissociation of hydrogen sulphide if the reaction proceeds according to the equation

$$H_2S = H_2 + 0.5\,S_2(v)$$

(0.156)

262. The degree of dissociation of N_2O_4 according to the equation $N_2O_4 \rightleftharpoons 2NO_2$ at 70°C and 1 atm is 65.6%. Calculate the apparent mol. wt. of N_2O_4 under the given conditions. (55.56)

263. A bulb contains 2 moles of H_2 at a pressure of 0.8 atm and temperature T K. 0.6 mole of O_2 is added to this bulb and the temperature of the bulb is lowered by 15 K to keep the same pressure. Calculate the volume of the bulb and its temperature T. Also, calculate the partial pressure of each gas.

($13.34\,dm^3$, 65 K; $p_{H_2} = 0.615$ atm, $p_{O_2} = 0.185$ atm)

264. The proportion of O_2, SO_2 and SO_3 present in the mixture of gases is 0.5 : 0.3 : 0.2. They are allowed through a pinhole at 27°C. Calculate the composition of the mixture leaving initially. (3.953 : 1.677 : 1.0)

265. The polymerization of ethylene to linear polyethylene is represented by the reaction

$$n\,CH_2 = CH_2 \rightarrow (-CH_2 - CH_2 -)_n$$

where n has large integral value. Given that the average enthalpies of bond dissociation for C = C and C − C at 298 K are +590 and +331 kJ mole^{-1} respectively,

calculate the enthalpy of polymerization per mole of ethylene at 298 K.
[Hint: $\Delta H = 1 \times 590 - 2 \times 331$]

(IIT 1994) (−72 kJ)

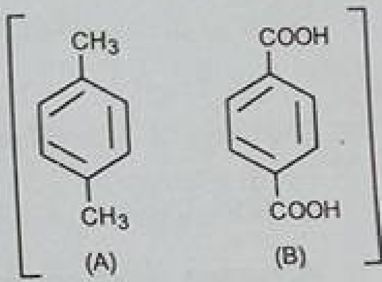
266. At 337 K the vapour pressure of ethanol is 0.526 atm and the vapour pressure of water is 0.236 atm. A solution is prepared from equimolar amounts of water and ethanol at this temperature. The vapour above the solution is removed and condensed. The condensed solution is heated to 337 K and the vapour above the solution is removed and condensed. Determine the mole fraction of the condensed solution.

(0.91, 0.09)

267. A current of dry air was bubbled through a bulb containing 26.66 g of an organic substance in 200 g of water, then through a bulb at the same temperature containing pure water, and finally through a tube containing fused calcium chloride. The loss in weight of water bulb was 0.087 g and the gain in weight of the calcium chloride tube was 2.036 g. Determine the molecular weight of the organic substance.

(56.1)

268. A hydrocarbon (A) [C − 90.56%, vapour density − 53] was subjected to vigorous oxidation to give a dibasic acid (B). 0.1 g of (B) required 24.1 mL of 0.05 N NaOH for complete neutralization. Nitration of (B) gave a single mononitro derivative. When (B) was heated strongly with soda lime, it gave benzene. Identify (A) and (B).



269. A chloro compound (A) showed the following properties:
(i) Decolorized bromine in CCl_4
(ii) Absorbed hydrogen catalytically
(iii) Gave a precipitate with amm. cuprous chloride
(iv) When vaporized, 1.49 g of (A) gave 448 mL of vapour at STP.
Identify (A).

($ClCH_2C \equiv CH$)

270. A basic, volatile nitrogen compound gave a foul-smelling gas when treated with chloroform and alcoholic potash. A 0.295-g sample of the substance dissolved in aq. HCl and treated with $NaNO_2$ solution at 0°C, liberated a colourless, odourless gas whose volume corresponded to 112 mL at STP. After the evolution of the gas was complete, the aqueous solution was distilled to give an organic liquid which did not contain nitrogen, and which on warming with an alkali and iodine, gave a yellow precipitate. Identify the original substance. Assume that it contains one N atom per molecule.

(IIT 1993) [$(CH_3)_2CHNH_2$ (isopropylamine)]

271. One mole of an organic amide (A) upon alkaline hydrolysis gives one mole of NH_3 and one mole of monobasic acid of equivalent weight 74. What is the molecular formula of (A)?

($C_2H_5CONH_2$)

272. How many grams of CaF_2 must be dissolved in 100 mL of water at 25°C to make the solution saturated? $K_{sp}(CaF_2) = 3.9 \times 10^{-11}$.

(1.66×10^{-3} g)

273. A solution which is 0.1 M in NaI and also 0.1 M in $Na_2(SO_4)$ is treated with solid $Pb(NO_3)_2$. Which compound, PbI_2 or $PbSO_4$, will precipitate first? What is the concentration of anions of the least soluble compound when the more soluble one starts precipitating?

$K_{sp}(PbI_2) = 8.7 \times 10^{-9}$, $K_{sp}(PbSO_4) = 1.8 \times 10^{-8}$ ($PbSO_4$, 0.021 M)

274. The solubility product of $Ca(OH)_2$ at 25°C is 4.42×10^{-5}. 500 mL of saturated solution of $Ca(OH)_2$ is mixed with equal volume of 0.4 M NaOH. How much $Ca(OH)_2$ in mg is precipitated? (747 mg)

275. Calculate the amount of $(NH_4)_2SO_4$ in grams which must be added to 500 mL of 0.2 M NH_3 to yield a solution with pH = 9.35. $K_b(NH_3) = 1.78 \times 10^{-5}$. (10.256 g)

276. The ClO radicals decay by second-order reaction. If the initial concentration is 2.5×10^{-5} mole dm^{-3}, calculate its (a) first half-life, (b) second half-life, and (c) concentration of ClO radical after 4 min. The rate constant of the process is $2.25 \times 10^7\ dm^3\ mol^{-1}\ s^{-1}$.

[(a) 1.778 milliseconds (b) 3.556 milliseconds (c) 7.69×10^{-6} mol dm^{-3}]

277. The data of a chemical reaction is plotted as $1/C$ vs time and the plot is a straight line. If intercept is $2 \times 10^{-3}\ mol^{-1}\ dm^3$ and slope, $2 \times 10^{-2}\ mol^{-1}\ dm^3\ s^{-1}$, calculate the half-life period of the reaction. (0.1 s)

278. A reaction is 50% complete in 10 minutes. It is allowed to proceed another 5 minutes. How much of the reaction would be complete at the end of these 15 minutes if the reaction follows zero-order kinetics? (75 %)

279. For the gaseous reaction, say, A → product, the rate is often described in terms of $d(P_A)/dt$ instead of $d[A]/dt$ or $d(n_A)/dt$. What is the relation among these three expressions?

$$\left[\frac{d(P_A)}{dt} = \frac{1}{V_{RT}}\frac{d(n_A)}{dt} = \frac{1}{RT}\frac{d[A]}{dt}\right]$$

280. A certain mass of a substance in 100 g of C_6H_6 lowers the f.p. by 1.28°C. The same mass of the substance in 100 g of water lowers the f.p. by 1.395°C. If the substance has a normal molecular weight in C_6H_6 and is completely dissociated in water, calculate the number of moles of ions produced by the dissociation of 1 mole of the substance in water. K_f for H_2O and C_6H_6 are 1.86 and 5.00 respectively. (3)

281. A solution of 3.795 g sulphur in 100 g of CS_2 (b.p. = 46.3°C) boils at 46.66°C. Determine the formula of sulphur molecule in the solution. $K_b(CS_2) = 2.42$. (S_8)

282. An aqueous solution of cane sugar (mol. wt. = 342) has an osmotic pressure of 1.5 atm at 18°C. If 100 g of this solution is cooled to –3.0°C, what mass of ice will separate out? (94.10 g)

283. An aqueous solution of mannitol in water has a vapour pressure of 17.504 mm at 20°C, at which temperature, the vapour pressure of pure water is 17.535 mm. What is the f.p. depression for this solution? $K_f(H_2O) = 1.86$. (0.183°C)

284. Potassium sulphate is a strong electrolyte which dissociates completely in aqueous solution. Urea is a nonelectrolyte substance. A 0.01 molar solution (aq) of potassium sulphate depressed the f.p. of water by 0.0558°C. What will be the depression caused by a 0.01 molar solution of urea? (0.0186°C)

285. The rate law of the reaction $H_2 + Br_2 \rightarrow 2HBr$ is

$$\frac{d[HBr]}{dt} = k\,[H_2]\,[Br_2]^{1/2}.$$

What is the order of the reaction? Is this an elementary reaction? $\left(\frac{3}{2}, \text{No}\right)$

286. Find the rate law of the reaction $2H + Ar \rightarrow H_2 + Ar$ which is elementary. $(R = k[H]^2\,[Ar])$

287. A chemical reaction is known to be of zero-order with $k = 5 \times 10^{-8}$ mole lit^{-1} s^{-1}.

(a) How long does it take for reactant concentration to decrease from 4×10^{-4} mole lit^{-1} to 2×10^{-4} mole lit^{-1}?

(b) Will the time to decrease the reactant concentration from 2×10^{-2} mol lit^{-1} to 1×10^{-2} mole lit^{-1} be the same as in (a)? $(4 \times 10^3\ \text{s, No})$

288. What is the ratio of $t_{1/2}$ to $t_{1/3}$ for a first-order reaction? (1·71)

289. Calculate the average life for a reaction undergoing a first-order reaction. $\left(\frac{1}{k}\right)$

290. Calculate K_p and K_c of the reaction: $I_2 \rightleftharpoons 2I$ when 1.513×10^{-3} mole of iodine is heated to 1073 K if its vapour occupies a volume of $249.3 \times 10^{-6}\ m^3$ at 5.81×10^4 Pa. (0.01113, 0.1264)

291. At 525 K, the equilibrium constant of the reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ is 1.78 atm (K_p). At what pressure should an equimolar mixture of Cl_2 and PCl_3 be taken for the pressure of PCl_5 to be 5×10^4 Pa at equilibrium, volume remaining constant? $(28.99 \times 10^4\ \text{Pa})$

292. The pressure dependence of the equilibrium conditions for the equation

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$$

was studied by measuring the mole fraction of NH_3 produced at various pressures for 1 : 3 mixtures of N_2 and H_2 at 500°C. K_p was found to increase with the increase in pressure. Why is K_p pressure dependent?

293. A 0.1-mole sample of NO_2 was placed in a 10-litre container and heated to 750 K. The total pressure of the equilibrium mixture as a result of the decomposition $2NO_2(g) \rightarrow 2NO(g) + O_2(g)$ was 0.827 bar. What is the value of K_p at this temperature? What amount of NO_2 must be placed in this container to obtain an equilibrium concentration of NO_2 of 0.1 mole per litre? (0.704, 1.61 mole)

294. Calculate the mass of NH_4Cl that must be completely dissolved in 1 litre of aqueous solution to attain an osmotic pressure of 5 atm at 298 K. Assume ideal behaviour. (5.46 g)

295. 10 g of a substance was dissolved in water and the solution was made up to 250 cm^3. The osmotic pressure of the soltuion was found to be 8×10^5 N m^{-2} at 288 K. Find the molecular weight of the solute. (119.72)

[Hint: 1 cc = 10^{-6} m^3]

296. A solution of crab hemocyanin, a pigmented protein extracted from crabs, was prepared by dissolving 0.75 g in 125 cc of an aqueous medium. At 4°C, an osmotic pressure rise of 2.6 mm of the solution was observed. The solution had a density of 1 g/cc. Determine the molecular weight of the protein. Solve this problem in c.g.s. units. (5.4×10^5 g/mole)

297. 4.0 g of a substance, A, dissolved in 100 g of water depressed the f.p. of water by 0.1°C, while 4.0 g of another substance, B, depressed the f.p. by 0.2°C. Which of the two substances has the higher molecular weight? (A)

298. Calculate the pressure in pascal (Pa) by a 760-mm Hg column. (101328 Pa)

299. Dibutyl phthalate is commonly used as a liquid in manometers. What pressure in N m^{-2} is equivalent to a centimetre of this liquid? The density of the liquid is 1.0465 g/cc. (102.63 N m^{-2})

300. What is the approximate mass of the atmosphere of the earth? Assume the radius of the earth to be 6370 km. (5.27×10^{18} kg)

[Hint: Surface area of the earth = $4\pi r^2$ and
atmospheric pressure = 1 atm = 101325 Pa]

301. A commercial gas cylinder contains 75 litres of helium at 15 bar (gauge pressure). Assuming ideal gas behaviour for the isothermal expansion, how many 3-litre balloons at a pressure of 1.1 bar can be filled by the gas in this cylinder? (340 balloons)

302. A diver at a depth of 45 m exhales a bubble of air that is 1 cm in radius. Assuming ideal gas behaviour, what will be the radius of this bubble as it breaks at the surface of the water? (1.8 cm)

[Hint: $p_1 = \rho gh$ + atm. pressure; p_2 = atm. pressure
Apply $p_1V_1 = p_2V_2$, calculate V_2 and then the radius]

303. 0.001 mole each of Fe^{2+} and Cd^{2+} is present in one litre of 0.02 M HCl, saturated with H_2S. Find whether each of these ions shall precipitate as sulphides. Calculate $[Cd^{2+}]$ in the solution at equilibrium.

$K_a(H_2S) = 1 \times 10^{-21}$, $K_{sp}(CdS) = 8 \times 10^{-27}$, $K_{sp}(FeS) = 3.7 \times 10^{-19}$.

(CdS precipitates, $[Cd^{2+}] = 3.86 \times 10^{-8}$ M)

304. A solution contains both Ag^+ (0.30 M) and Ba^{2+} (0.05 M).

(i) If solid Na_2SO_4 is added very slowly to this solution, which will precipitate first, Ag_2SO_4 or $BaSO_4$?

(ii) The addition of Na_2SO_4 is continued until the second cation just starts precipitating as sulphate. What is the concentration of the first cation at this point? $K_{sp}(Ag_2SO_4) = 1.2 \times 10^{-5}$, $K_{sp}(BaSO_4) = 1.5 \times 10^{-9}$.

($BaSO_4$, 1.15×10^{-5} M)

305. At a pressure of 1.0 bar, an equilibrium exists at 2000 K between 0.25 mole of $Br_2(g)$, 0.75 mole of $F_2(g)$ and 0.497 mole of $BrF_3(g)$. What will be the amounts of each gas after the pressure on the system has been increased to 2.0 bar and the equilibrium at 2000 K re-established?

$Br_2(g) + 3F_2(g) \rightarrow 2BrF_3(g)$

(0.189 mole, 0.567 mole, 0.619 mole)

306. For the equation $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$, $K_{1000} = 0.059$. Exactly 10 g of $CaCO_3$ is placed in a 10-litre container at 1000 K. After equilibrium is reached, what mass of $CaCO_3$ remains?

(9.29 g)

307. Hot copper turnings can be used as an 'oxygen getter' for inert gas supplies by slowly passing the gas over the turnings at 600 K:

$$2Cu(s) + \frac{1}{2}O_2(g) \rightleftharpoons Cu_2O(s);\ K_p = 7.5 \times 10^{10}$$

How many molecules of O_2 are left in one litre of a gas supply after equilibrium has been reached?

($2.17 \approx 2$)

308. For $O_3(g) + OH(g) \rightleftharpoons H(g) + 2O_2(g)$, $K = 0.096$ at 298 K and $K = 1.4$ at 373 K. Above what temperature will the reaction become thermodynamically spontaneous?

($T > 361$ K)

[**Hint:** For spontaneous process $K_p > 1$. Use Equation 11, Chapter 15]

309. For the reaction $A + 2B \rightarrow$ product, the reaction rate was halved as the concentration of A was doubled. What is the order of reaction with respect to A?

(−1)

310. The total pressure of the system at 279.0°C for the equation $SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$ was observed as a function of time. Find the order of the reaction.

Time (s):	204	3270	7500	8400	∞
p (mm):	325	365	415	425	594.2

(First)

311. $t_{1/2}$ for a given reaction was doubled as the initial concentration of a reactant was doubled. What is the order of the reaction for this component?

(Zero)

312. Which reaction will have the greater temperature dependence for the rate constant—one with a small value of energy of activation (E) or one with a large value of E?

(Large value of E)

$$\left[\textbf{Hint: } \frac{dk}{dt} = Ae^{-E/RT}\frac{E}{RT^2} = k\frac{E}{RT^2}\right]$$

313. The half-time of the first-order decomposition of nitramide is 2.1 hour at 15°C,

$$NH_2NO_2(aq) \rightarrow N_2O(g) + H_2O(l)$$

If 6.2 g of NH_2NO_2 is allowed to decompose, calculate

(i) the time taken for 99% decomposition, and

(ii) the volume of dry N_2O produced at this point measured at STP.

[(i) 21 hours (ii) 2.2176 litres]

314. A toy balloon originally held 1.0 g of helium gas and had a radius of 10.0 cm. During the night, 0.25 g of the gas effused from the balloon. Assuming ideal gas behaviour under these constant pressure and temperature conditions, what was the radius of the balloon the next morning? (9.0 cm)

315. Assuming ideal gas behaviour, how many atoms of Ar are contained in a typical human breath of 0.5 litre at 1.0 bar and 37°C? Air consists of 1% Ar atoms. Assuming that the argon atoms from the last breath of Plato have been distributed randomly throughout the atmosphere (5×10^{18} m^3), how long would it take to breathe one of these atoms? A typical adult breath rate is 10 min^{-1}.

(1×10^{20} $breath^{-1}$, 10 min)

316. The total pressure of a mixture of H_2 and O_2 is 1.0 bar. The mixture is allowed to react to form water, which is completely removed to leave only pure H_2 at a pressure of 0.35 bar. Assuming ideal gas behaviour, and that all pressure measurements were made under the same temperature and volume conditions, calculate the composition of the original mixture. (0.78, 0.22)

317. A mixture of He and CO_2 has a volume of 63.5 mL at 1.0 bar and 28°C. The system containing the mixture is cooled in liquid nitrogen, and the remaining gas is evacuated. The system is restored to 1.0 bar and 28°C, and the volume is 40.5 mL. Find the composition of the original mixture. (0.638, 0.362)

318. The average molar mass of the vapour above solid NH_4Cl is nearly 26.5 g $mole^{-1}$. Find the composition of the vapour. (0.5, 0.5)

319. The escape velocity is given by

$$v = \sqrt{2gr}$$

where $r = 6.37 \times 10^6$ m for the earth. At what temperature will the rms velocity of an H_2 molecule attain the escape velocity? (1.02×10^4 K)

320. An He atom at 25°C is released from the surface of the earth to travel upwards. Assuming that it undergoes no collisions with other molecules, how high will it travel before coming to rest? (9.47×10^4 m)

[Hint: Use $\frac{3}{2}kT = mgh$]

321. Addition of 0.643 g of a compound to 50 mL of benzene (density = 0.879 g/mL) lowers the f.p. from 5.51°C to 5.03°C. If K_f for benzene is 5.12, calculate the molecular weight of the compound. **(IIT 1992)** (156.06)

322. A solution of cane sugar at 27°C develops an osmotic pressure of 4.93 atm. Calculate the f.p. of this solution (molecular depression constant for 100 g of water is 18.6). (0.372°C)

323. What relative proportions of ethylene glycol $C_2H_6O_2$ and water (by weight) should be mixed to form an antifreeze solution that will not start to freeze until the temperature reaches −37°C? K_f for $H_2O = 1.86$. (1.23 : 1)

324. In a cold climate water gets frozen causing damage to the radiator of a car. Ethylene glycol is used as antifreezing agent. Calculate the amount of ethylene glycol to be added to 4 kg of water to prevent it from freezing at $-6°C$. K_f for H_2O is $1.85\ K\ mol^{-1}\ kg$.

(804.3 g)

325. From the following data for the reaction between A and B:

[A], $mol\ L^{-1}$	[B], $mol\ L^{-1}$	Initial rate, $mol\ L^{-1}\ s^{-1}$, at	
		300 K	320 K
2.5×10^{-4}	3.0×10^{-5}	5.0×10^{-4}	2.0×10^{-3}
5.0×10^{-4}	6.0×10^{-5}	4.0×10^{-3}	—
1.0×10^{-3}	6.0×10^{-5}	1.6×10^{-2}	—

Calculate
(i) the order of the reaction with respect to A and with respect to B,
(ii) the rate constant at 300 K,
(iii) the energy of activation, and
(iv) the pre-exponential factor. **(IIT 1994)**

[(i) 2, 1 (ii) 2.67×10^8 (iii) 55.3 kJ (iv) 1.145×10^{18}]

326. Show that in case of a first-order reaction, the time required for 93.75% of the reaction to take place is four times that required for half of the reaction.

327. What will be the initial rate of reaction if its rate constant is $10^{-3}\ min^{-1}$ and the concentration of the reactant is $0.2\ mol\ dm^{-3}$? How much of the reactant will be converted into products in 200 minutes? ($2.0 \times 10^{-4}\ mol\ dm^{-3}\ min^{-1}$, 18%)

328. In a first-order reaction $A \rightarrow P$, if it takes 20 minutes to bring about decomposition of 30% of the initial substance, calculate the time to decompose (i) 60% of it, and (ii) all of it. (51.3 min, infinite)

329. What is the pH of a 1.0×10^{-8} M solution of NaOH? (7.021)

330. What is the pH of a 0.1 M solution of Na_2SO_4? For H_2SO_4, $K_{a_2} = 1 \times 10^{-2}$. (7.51)

331. A 50-mL aliquot of 0.01 M solution of HCOOH was titrated with 0.1 M NaOH. Predict the pH of the solution
(a) at the beginning of the reaction,
(b) at the half-equivalence point,
(c) at the equivalence point, and
(d) after 10 mL of the base has been added.
$K_a(HCOOH) = 1.772 \times 10^{-4}$ (2.88, 3.75, 7.86, 11.92)

332. The equilibrium constant of the reaction: $2D_2O = D_3O^+ + OD^-$ (D is deuterium) is 1.35×10^{-15} at 25°C. Calculate pD of the heavy water at 25°C. (7.435)

333. How much water should be added to 10 g of acetic acid to give a hydrogen-ion concentration equal to 1×10^{-3} M? $K_a(CH_3COOH) = 1.8 \times 10^{-5}$. (3.0 litres)

334. For the equilibrium: $NH_4HS(s) = NH_3(g) + H_2S(g)$; $K_p = 0.05\ atm^2$ at 20°C. If

0.06 mole of solid NH_4HS is placed in a 2.40-litre flask at 20°C, calculate the percentage of the solid decomposed under equilibrium. (37.18%)

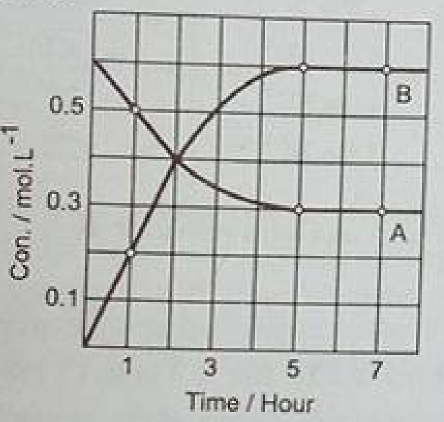
335. The progress of the reaction $A \rightleftharpoons nB$, with time is presented in the figure. Determine

(i) the value of n

(ii) the equilibrium constant K

(iii) the initial rate of conversion of A **(IIT 1994)** (2, 1.2, 0.1)

[**Hint:**



At equilibrium:

Rate (forward) = Rate (backward)

$$\frac{0.6-0.3}{5} = \frac{0.6}{5} \times \frac{1}{n}$$

For the eqb.: $A \rightleftharpoons 2B$, $K = \frac{0.6^2}{0.3}$.

Initial rate = change in concentration of A in the 1st hour]

336. Calculate the per cent dissociation of $H_2S(g)$ if 0.1 mole of H_2S is kept in a 0.4-litre vessel at 1000 K. For the reaction

$$2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g),$$

the value of K_c is 1.0×10^{-6}. (2%)

337. Find the amount of time expressed in units of $t_{1/2}$ at which $A/A_0 = 0.125$.

[**Hint:** $N = 2^{-n} N_0$; $n \equiv$ no. of $t_{1/2}$] (3)

338. A radioisotope has a half-life of 900 seconds. Calculate the fraction of the original isotope which will remain behind after four half-life periods. (1/16)

339. What is the minimum half-life of an isotope needed so that not more than 0.1% of the nuclei undergo decay during a 3-hour laboratory period? (88 days)

340. Isotopes of oxygen with mass number less than 16 undergo β^+ emission. Assuming an equimolar mixture of ^{14}O and ^{15}O, find the ratio of the nuclides at the end of one hour. $t_{1/2}$ for $^{14}O = 71$ s, $t_{1/2}$ for $^{15}O = 124$ s. At what time will the ratio of ^{14}O nuclei to ^{15}O nuclei be equal to 0.25? (3.02×10^{-7}, 332 s)

341. What volume of concentrated HCl solution ($d = 1.18$) containing 36% HCl by weight is required to produce 6.55 litres of a solution with pH 1.85? (7.88 mL)

342. An ammonia solution is 9.9% ammonia by mass and has a density of 0.99 g/mL. Calculate the pH of the solution. $K_b(NH_4OH) = 1.7 \times 10^{-5}$. (12.0)

343. How much (volume) of 0.001 M HCl (aq) should be added to 10 mL of 0.001 M NaOH to change its pH by one unit? (8.18 mL)

344. A current of 1 amp is passed through one litre of 1.0 M HCl solution for one day.

Find the pH of the solution after electrolysis. Assume no change in volume.

(0.98)

345. In how many litres of water, 10 g of CH_3COOH should be dissolved to give $[H^+] = 10^{-3}$? $K_a(CH_3COOH) = 1.8 \times 10^{-5}$?

(3.0 litres)

346. Find the pH of 0.4833% HCl (aq) solution.

(0.824)

347. Calculate the pH at the equivalence point when a solution of 0.1 M CH_3COOH is titrated with a solution of 0.1 M NaOH.
$K_a(CH_3COOH) = 1.8 \times 10^{-5}$.

(8.66)

348. The coolant usually contains a solution of antifreeze prepared by mixing equal volumes of ethylene glycol, $C_2H_4(OH)_2$ and water. The density of ethylene glycol is 1.113 g/mL. Calculate the f.p. of the mixture.
K_f for H_2O is 1.86.

(– 33.4°C)

349. A 7.64-g sample of the salt MF_x (at. wt. of M = 96) is dissolved in 100 g of water and the f.p. of the solution is found to be 268.69 K. Find the formula of the salt, assuming ideal behaviour. $K_f(H_2O) = 1.8$

(MF_5)

350. The f.p. of nitrobenzene is 3°C. When 1.2 g of chloroform (mol. wt. = 120) is dissolved in 100 g of nitrobenzene, the f.p. of the solution is 2.3°C. When 0.6 g of acetic acid is dissolved in 100 g of nitrobenzene, the f.p. of the solution is 2.64°C. Calculate the molecular weight of acetic acid. What conclusion can be drawn from it?

(116.6, dimer)

351. By dissolving 0.517 g of nitrogen sulphide in 18.25 g of chloroform, the b.p. raised by 0.6°C. Nirogen sulphide contains 30.5% S. Find the molecular weight and molecular formula of nitrogen sulphide.

(184, N_2S_4)

352. Consider the equilibrium: $LiCl \cdot 3NH_3(s) \rightleftharpoons LiCl \cdot NH_3(s) + 2NH_3(g)$ with $K_p = 9$ atm^2 at 40°C. A 5-litre flask contains 0.1 mole of $LiCl \cdot NH_3$. How many moles of NH_3 should be added to the flask at this temperature to drive the backward reaction practically to completion?

(0.7837)

353. Given that

$$S + S^{2-} \rightleftharpoons S_2^{2-} \quad \ldots \quad K_1 = 1.7$$

$$S + S_2^{2-} \rightleftharpoons S_3^{2-} \quad \ldots \quad K_2 = 3.1$$

Calculate the equilibrium constant for

$$2S + S^{2-} \rightleftharpoons S_3^{2-}$$

(5.27)

354. For the equilibrium: $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$, $K_c = 6.45 \times 10^5$.
(i) At what O_2 concentration is the NO_2 concentration equal to the NO concentration?
(ii) At what O_2 concentration is the NO_2 concentration 100 times the NO concentration?

(1.55×10^{-6}, 1.55×10^{-2})

355. For the gas reaction: $3H_2 + N_2 = 2NH_3$, the partial pressures of H_2 and N_2 are 0.4

and 0.8 atm respectively. The total pressure of the entire system is 2.8 atm. What will be the value of K_p if all the concentrations are given in terms of atmosphere? (50)

356. What is the value of K_a such that K_a for an acid is equal to K_b for its conjugate base at 25°C? (1×10^{-7})

357. A solution contains 0.1 M H_2S and 0.3 M HCl. Calculate the concentration of S^{2-} and HS^- ions in the solution. For H_2S, $K_{a_1} = 1 \times 10^{-7}$, $K_{a_2} = 1.3 \times 10^{-13}$.
$(3.34 \times 10^{-8}$ M, 1.447×10^{-20} M)

358. Calculate the molarity of an aqueous solution of ammonia of pH 9.3. K_b for ammonia is 1.8×10^{-5} and $K_w = 1 \times 10^{-14}$. $(1.95 \times 10^{-5}$ M)

359. 0.98% (by wt.) H_2SO_4 is 96% ionized. Find its pH. (0.71)

360. What volume of N/20 CH_3COONa should be mixed to 250 mL N/10 CH_3COOH to get a solution of pH = 5. $K_a(CH_3COOH) = 1.8 \times 10^{-5}$ (900 mL)

361. Calculate pH of the following mixtures:
(i) 0.4 litre of 0.1 M NaOH and 0.2 litre of 0.05 M C_2H_5COOH
(ii) 0.2 litre of 0.1 M NaOH and 0.4 litre of 0.1 M C_2H_5COOH
(iii) 0.4 litre of 0.1 M NaOH and 0.4 litre of 0.1 M C_2H_5COOH
$K_a(C_2H_5COOH) = 5.6 \times 10^{-6}$, $K_w = 1 \times 10^{-14}$ (12.67, 5.25, 7.97)

362. COF_2 gas passed over a catalyst at 1000°C comes to equilibrium:

$$2\,COF_2(g) \rightleftharpoons CO_2(g) + CF_4(g)$$

Analysis of the equilibrium mixture (after quick cooling to freeze the equilibrium) shows that 500 mL of equilibrium mixture (NTP) contains 300 mL (NTP) of COF_2 and CO_2. Taking the total pressure to be 10 atm, calculate K_p. (4.0)

[**Hint:** At eqb.: $2COF_2 \rightleftharpoons CO_2 + CF_4$; 100 mL, 200 mL, 200 mL]

363. When 0.5 mole of H_2 and 0.5 mole of I_2 react in a 10-litre evacuated vessel at 450°C, HI is formed. K_c for $H_2 + I_2 \rightleftharpoons 2HI$ is 50.
(i) Calculate K_p.
(ii) Calculate moles of I_2 which are in excess. (50, 0.11 mole)

364. The value of K_c for $2HF(g) = H_2(g) + F_2(g)$ is 1.0×10^{-3} at a particular temperature. At a certain time, the concentrations of HF, H_2 and F_2 were found to be 0.5, 1×10^{-3} and 4×10^{-3} mole/litre respectively. Is the reaction at equilibrium? If not, what would be the direction to attain equilibrium? (No, towards right)

365. Find out the number of waves made by a Bohr electron in one complete revolution in its third orbit. **(IIT 1994)** (3)

$$\left[\textbf{Hint: } \frac{nh}{2\pi} = mvr;\ \frac{2\pi r}{h/mv} = \frac{2\pi r}{\lambda} = n\right]$$

366. The composition of a sample of wustite is $Fe_{0.93}O_{1.00}$. What percentage of iron is present in the form of Fe (III)? **(IIT 1994)** (15.05%)

[Hint: Let the moles of Fe in FeO and Fe_2O_3 be n_1 and n_2 respectively. Thus,

$$\frac{\text{moles of Fe}}{\text{moles of O}} = \frac{n_1 + n_2}{n_1 + \frac{3n_2}{2}} = 0.93]$$

367. A is a binary compound of a univalent metal. 1.422 g of A reacts completely with 0.321 g of sulphur in an evacuated and sealed tube to give 1.743 g of a white crystalline solid B, that forms a hydrated salt C, with $Al_2(SO_4)_3$. Identify A, B and C. **(IIT 1994)** (KO_2, K_2SO_4, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$)

368. A 1.345-g sample of a compound of barium and oxygen was dissolved in hydrochloric acid to give a solution of barium ion, which was then precipitated with an excess of potassium chromate to give 2.012 g of barium chromate, $BaCrO_4$. What is the formula of the compound? (BaO_2)

369. Haemoglobin is the oxygen-carrying molecule of red blood cells, consisting of a protein and a nonprotein substance. The nonprotein substance is called haeme. A sample of haeme weighing 35.2 mg contains 3.19 mg of iron. If a haeme molecule contains one atom of iron, what is the molecular weight of haeme? (616 amu)

370. The wavenumber of the first line in the Balmer series of hydrogen is 15200 cm^{-1}. What is the wavenumber of the first line in the Balmer series of Be^{3+}? (2.43×10^5 cm^{-1})

[Hint: $\left(\frac{1}{\lambda}\right)_{Be^{3+}} = z^2\left(\frac{1}{\lambda}\right)_H$]

371. Sufficient NaCN was added to 0.015 M $AgNO_3$ to give a solution that was initially 0.1 M in CN^-. What is the concentration of Ag+ in this solution after $Ag(CN)_2^-$ forms? The formation constant K_f for the complex ion $Ag(CN)_2^-$ is 5.6×10^{18}.

$$Ag^+ + 2CN^- \rightleftharpoons Ag(CN)_2^-$$ (5.5×10^{-19} M)

372. In an Arrhenius's equation, $k = Ae^{-E/RT}$, A may be termed as the rate constant at ...... **(IIT 1997)** (infinite temp.)

373. When Fe (s) is dissolved in aqueous acid in a closed vessel, the work done is ...... **(IIT 1997)** (zero)

374. A liquid which is permanently supercooled is frequently called a ...... **(IIT 1997)** (glass)

375. Enthalpy is an ...... property. **(IIT 1997)** (extensive)

376. A quantity of 0.25 M NaOH is added to a solution containing 0.15 mole of acetic acid. The final volume of the solution is 375 mL and the pH of the solution is 4.45.

(a) What is the molar concentration of sodium acetate?

(b) How many mL of NaOH were added to the original solution?

(c) What was the original concentration of the acetic acid?

[(a) 0.048 M (b) 1.9×10^2 mL (c) 0.81 M]

377. What are the concentration and percentage of Ag^+ ion remaining after Ag_2CrO_4 precipitates when 25 mL of 0.10 M $AgNO_3$ is added to 25 mL of 0.10 M K_2CrO_4? K_{sp} (Ag_2CrO_4) = 1.1×10^{-12}. (6.6×10^{-6} M, 0.013%)

378. The pH of a white-vinegar solution is 2.45. This vinegar is an aqueous solution of acetic acid with a density of 1.09 g/mL. What is the mass percentage of acetic acid in the solution? (4.1%)

379. A chemist needs a buffer with pH 4.35. How many mL of pure acetic acid (density = 1.049 g/mL) must be added to 465 mL of 0.0941 M NaOH solution to obtain such a buffer? (9.1 mL)

380. Calculate the pH of a solution which has a hydronium-ion concentration of 6×10^{-8} M. (7.22)

381. Calculate the per cent error in the hydronium-ion concentration made by neglecting the ionisation of water in a 1×10^{-6} M NaOH solution. (1%)

382. Calculate $[CH_3COOH]/[CH_3COO^-]$ in a buffer solution whose pH is 7.0. Explain how it is possible to have any acid in a neutral solution.
(5.6×10^{-3}, possible when some base is present)

383. Calculate the molar solubility of AgCl in 1.0 M NH_3. K_{sp} (AgCl) = 1.8×10^{-10}, K_f ($Ag(NH_3)_2^+$) = 1.7×10^7. (0.050 M)

384. An acid solution of a $KReO_4$ sample containing 26·83 mg of combined rhenium was reduced by passage through a column of granulated zinc. The effluent solution, including the washings from the column, was then titrated with 0.1 N $KMnO_4$. 11.45 mL of standard permanganate was required for the reoxidation of all the rhenium to the perrhenate ion, ReO_4^-. Assuming that Re was the only element reduced, what is the oxidation state to which Re was reduced by the zinc column? (Re = 186.2) (−1 oxd. state)

385. A diver quickly ascends to the surface of the water from a depth of 4.08 m without exhaling out the air in her lungs. By what factor would the volume of her lungs increase by the time she reaches the surface? Assume constant temperature and ideal gas behaviour. The density of sea water is 1.03 g/cc and g = 980.67 cm s^{-2}. (1.4 times)

386. The density of dry air at 1 atm and 34.4°C is 1.15 g/L. Calculate the composition of air (% by weight) assuming only N_2 and O_2 to be present and ideal gas behaviour. (N_2 72.4%)

[Hint: First calculate mol. wt. of air by using $p = \frac{dRT}{M}$.]

387. At what pH will 1×10^{-3} M solution of an indicator with $K_b = 1 \times 10^{-10}$ change colour? (4)

[Hint: The indicator changes colour when the conjugates are of equal concentration.]

388. Which has greater molarity in water, AgCl or $Mg(OH)_2$? Can the relative solubilities be predicted on the basis of the values of K_{sp} alone? [Mg(OH)2, No]

389. An electrochemical cell is made by placing a zinc electrode in 1.0 litre of 0.2 M $ZnSO_4$ solution and a copper electrode in 1.0 litre of 0.015 M $CuCl_2$ solution.

(a) What is the initial voltage of this cell when it is properly constructed?

(b) Calculate the final concentration of Cu^{2+} in this cell if it is allowed to produce an average current of 1 amp for 225 seconds. Given that $E^0_{cell} = 1.1$ V.

[(a) 1.07 V (b) 0.014 M]

390. Dinitrogen pentoxide, N_2O_5, undergoes first-order decomposition in chloroform solvent to yield NO_2 and O_2. The rate constant at 45°C is 6.2×10^{-4} min^{-1}. Could the volume of O_2 obtained from the reaction of 1 mole of N_2O_5 at 45°C and 780 mmHg after 20 hours, be calculated? (Insufficient information)

391. What would you expect to be the general temperature and pressure conditions for an optimum yield of nitric oxide, NO, by the oxidation of ammonia?

$4NH_3 (g) + 5O_2 (g) \rightleftharpoons 4NO (g) + 6H_2O (g)$; $\Delta H < 0$

(Low temperature and low pressure)

392. At 850°C and 1-atm pressure, a gaseous mixture of CO and CO_2 in equilibrium with solid carbon is 90.55% CO by mass.

$$C (s) + CO_2 (g) \rightleftharpoons 2CO (g)$$

Calculate K_c for this reaction at 850°C. (0.153)

393. The following equilibrium exists in a closed system at 25°C:

$$NH_4HS (s) \rightleftharpoons NH_3 (g) + H_2S (g)$$

(a) When a sample of pure NH_4HS (s) is placed in an evacuated vessel and allowed to reach equilibrium at 25°C, the total pressure is 0.66 atm. Find the value of K_p.

(b) To this system, sufficient H_2S (g) is injected until the pressure of H_2S is three times that of the ammonia at equilibrium. What are the partial pressures of NH_3 and H_2S?

(c) In a different experiment, 0.75 atm of NH_3 and 0.5 atm of H_2S are introduced into a 1-litre vessel at 25°C. How many moles of NH_4HS are present when equilibrium is established? [(a) 0.1089 (b) 0.19, 0.57 (c) 0.5672 g]

394. Equal volumes of 1.0 M Na_2CO_3 and 1.0 M HCl are mixed. Calculate $[CO_3^{2-}]$ at equilibrium. K_1 and K_2 for H_2CO_3 are 4.5×10^{-7} and 4.7×10^{-11} respectively.

(5×10^{-3} M)

[Hint: Solution is 0.50 M $NaHCO_3$ (plus 0.5 M NaCl). Now see Example 71, Chapter 16.]

395. Calculate pH of a 0.1 M Na_2HPO_4 solution. K_1, K_2 and K_3 for H_3PO_4 are 7.1×10^{-3}, 6.3×10^{-8} and 4.5×10^{-13} respectively. Which approximation is necessary for the calculation? (10.10)

[Hint: As K_3 for H_3PO_4 is very low compared to K_1, assume no acidic ionisation. Consider only the equilibrium,

$HPO_4^{2-} + H_2O \rightleftharpoons H_2PO_4^- + OH^-$]

96. A tenfold increase in pressure on the reaction,

$$N_2 (g) + 3H_2 (g) \rightleftharpoons 2NH_3 (g)$$

at equilibrium results in ...... in K_p. **(IIT 1996)** (No change)

397. The reaction

$$Sb_2S_3\,(s) + 3H_2\,(g) \rightleftharpoons 2Sb\,(s) + 3H_2S\,(g)$$

was studied by analysing the equilibrium mixture for the amount of H_2S produced. A vessel whose volume was 2.5 litre was filled with 0.01 mole of Sb_2S_3 and 0.01 mole of H_2S. After the mixture came to equilibrium in the closed vessel at 440°C, the gaseous mixture was removed and the H_2S was dissolved in water. Sufficient Pb^{2+} ions were added to react completely with the H_2S to precipitate PbS. If 1.029 g of PbS was obtained, what is the value of K_c at 440°C? (0.430)

398. An aqueous solution containing 288 g of a nonvolatile compound having composition $C_nH_{2n}O_n$ in 90 g of water boils at 101.24°C at 1-atm pressure. What is the molecular formula of the compound? K_b = 0.512°C/*m*. ($C_{44}H_{88}O_{44}$)

399. Although AgCl is insoluble in water, it readily dissolves upon the addition of ammonia

$$AgCl\,(s) + 2NH_3\,(aq) \rightleftharpoons Ag(NH_3)_2^+\,(aq) + Cl^-\,(aq)$$

(a) What is the equilibrium constant for this dissolving process?

(b) Ammonia is added to a solution containing excess AgCl (s). The final volume is 1 litre and the resulting equilibrium concentration of NH_3 is 0.80 M. Calculate the number of moles of AgCl dissolved, the molar concentration of $Ag(NH_3)_2^+$ and the number of moles of NH_3 added to the original solution.

K_{sp} (AgCl) = 1.8×10^{-10} and $K_f\,[Ag(NH_3)_2^+] = 1.7 \times 10^7$.

[(a) 3.1×10^{-3} (b) 0.045 mole, 0.045 mole, 0.89 mole]

400. From the dissociation constants K_a and K_b for an acid and its conjugate base, show that $K_a \cdot K_b = K_w$.

[Hint: See text, Chapter 16.]

401. The tallest trees known are the redwoods in California. Assuming the height of a redwood to be 105 m, estimate the osmotic pressure required to push water up from the roots to the treetop. (1.029×10^6 Pa)

402. A sample of impure cuprite, Cu_2O, contains 66.6% copper. Calculate the percentage of pure Cu_2O in the sample. (75%)

403. How much Ag^+ would remain in solution after mixing equal volumes of 0.08 M $AgNO_3$ and 0.08 M HOCN? K_a (HOCN) = 3.3×10^{-4}. K_{sp} (AgOCN) = 2.3×10^{-7}. (5×10^{-3} M)

[Hint: See Example 66, Chapter 16.]

404. The following equilibrium was studied by analysing the equilibrium mixture for the amount of HCl produced.

$$LaCl_3\,(s) + H_2O\,(g) \rightleftharpoons LaOCl\,(s) + 2HCl\,(g)$$

A vessel whose volume was 1.25 litre was filled with 0.0125 mole of lanthanum (III) chloride and 0.025 mole of water. After the mixture came to equilibrium in a closed vessel at 619°C, the gaseous mixture was removed and dissolved in more water. Sufficient silver (I) ion was added to precipitate the chloride ions completely as silver chloride. If 3.59 g of AgCl was obtained, what is the value of K_c at 619°C? (0.04)

405. A solution is 0.10 M Co^{2+} and 0.10 M Hg^{2+}. Calculate the range of pH in which only one of the metal sulphides precipitates when the solution is saturated in H_2S. K_{sp} (CoS) = 4×10^{-21} and K_{sp} (HgS) = 1.6×10^{-52}. (pH less than 0.8)

406. A standard electrochemical cell is made by dipping an Ag electrode into a 1.0 M Ag^+ solution and a Cd electrode into a 1.0 M Cd^{2+} solution.

(a) What is the spontaneous chemical reaction and what is the maximum potential produced by the cell?

(b) What would be the effect on the potential of this cell if Na_2S were added to the Cd^{2+} half cell and CdS were precipitated? Why?

(c) What would be the effect on the potential of the cell if the size of the silver electrode was doubled?

See E^0 values from the table if required.

[(a) $Cd(s) + 2Ag^+ = 2Ag(s) + Cd^{2+}$; 1.20 V
(b) It would increase (c) No effect]

407. A sample of impure ore contains 42.34% Zn. Calculate the percentage of pure ZnS in the sample. (67.10%)

408. A peroxidase enzyme isolated from human red blood cells was found to contain 0.29% selenium. What is the minimum molecular weight of the enzyme? (Se = 78.96) (2.7×10^4)

409. In an experiment to measure the charge on an electron, the following values of charge were found on oil droplets: -1.6×10^{-19}, -2.4×10^{-19}, -4.0×10^{-19} (in coulomb). What values of electronic charge would be indicated by these results?
[**Hint:** Find the largest common factor.] $(-0.8 \times 10^{-19}$ C)

410. A diatomic molecule has a dipole moment of 1.2 D. If its bond distance is 1.0 Å, what fraction of an electronic charge, e, exists on each atom? (1 D = 10^{-18} esu cm and $e = 4.8 \times 10^{-10}$ esu) (25%)

411. How many grams of Cu will be replaced from 2 litres of 1.5 M $CuSO_4$ solution by 40 g of Al? (141 g)

412. At the top of a mountain a thermometer reads 0°C and a barometer reads 710 mmHg. At the bottom of the mountain the temperature is 30°C and the pressure is 760 mmHg. Compare the density of the air at the top with that at the bottom. (1.04 : 1)

413. What is the pH of a 0.50 M aqueous NaCN solution? pK_b of CN^- is 4.70. **(IIT 1996)** (11.5)

414. In the reaction $I^- + I_2 \longrightarrow I_3^-$, the lewis acid is ...... **(IIT 1997)** (I_2)

415. A monoatomic ion has a charge of +2. The nucleus of the ion has a mass number of 62. The number of neutrons in the nucleus is 1.21 times that of protons. How many electrons are in the ion? What is the atomic number of the element? (26, 28)

416. Potassium superoxide, KO_2, is used in rebreathing gas masks to generate oxygen.

$$4KO_2\,(s) + 2H_2O\,(l) \longrightarrow 4KOH\,(s) + 3O_2\,(g)$$

If a reaction vessel contains 0.15 mole of KO_2 and 0.10 mole of H_2O, what is the limiting reactant? How many moles of oxygen can be produced?

(KO_2, 0.1125 mole)

417. A 0.288 g sample of an unknown monoprotic organic acid is dissolved in water and titrated with a 0.115 M sodium hydroxide solution. After the addition of 17.54 mL of base, a pH of 4.92 is recorded. The equivalence point is reached when a total of 33.83 mL of NaOH is added.

(a) What is the molar mass of the organic acid?

(b) What is the K_a value for the acid? The K_a value could have been determined very easily if a pH measurement had been made after the addition of 16.92 mL of NaOH. Why?

[(a) 74, (b) 1.3×10^{-5}]

418. How many grams of NaCl can be added to 785 mL of 0.0015 M $AgNO_3$ before a precipitate forms? K_{sp} (AgCl) = 1.8×10^{-10}.

(5.5×10^{-6} g)

419. Metallic Ba has a body-centred cubic structure (all atoms at the lattice points) and a density of 3.51 g/cc. Assume Ba atoms to be spheres. The spheres in a body-centred array occupy 68.0% of the total space. Find the atomic radius of Ba.

(3.14×10^{-8} cm)

420. In a reaction:

$$2ClO_2\,(aq) + 2I^-\,(aq) \longrightarrow 2ClO_2^-\,(aq) + I_2\,(aq)$$

the order of the reaction with respect to ClO_2 was determined by starting with a large excess of I^-, so that its concentration was essentially constant. Then

$$\text{Rate} = k\,[ClO_2]^m\,[I^-]^n = k'\,[ClO_2]^m$$

where $k' = k\,[I^-]^n$. Determine the order of the reaction and also k' from the following data:

Time (s)	$[ClO_2]$ (mol/L)
0.00	4.77×10^{-4}
1.00	4.31×10^{-4}
2.00	3.91×10^{-4}
3.00	3.53×10^{-4}

(First, 0.101 s^{-1})

421. A 0.1 M solution of an acid (density = 1.01 g/cc) is 4.5% ionised. Calculate the f.p. of the solution. The molecular weight of the acid is 300. $K_f = 1.86$. (–0.199°C)

422. How much heat is required to change 10 g of ice at 0°C to steam at 100°C?

$$\left[\begin{aligned} \Delta H\,(\text{total}) &= \Delta H_{\text{fusion}} + \Delta H_{\text{heating}} + \Delta H_{\text{vap.}} \\ &= 10(80 + 1 \times 100 + 540)\ \text{cal} \end{aligned}\right]$$

423. After 11.2 g of carbon reacts with oxygen originally occupying 21.2 litres at 18°C and 750 mmHg, the cooled gases are passed through 3 litres of 2.50 M NaOH solution. Determine the concentration of NaOH remaining in solution which is not converted to Na_2CO_3.

(1.95 M)

[**Note:** CO does not react with NaOH under these conditions.]

424. From the kinetic theory of gases, predict the effect on the pressure of a gas inside a cubic box of side l by reducing the size so that each side measures $l/2$.

(8 times increase)

425. The equilibrium equations and K_a values for three reaction systems are given below:

$$H_2C_2O_4 + H_2O \rightleftharpoons H_3O^+ + HC_2O_4^-; \quad K_a = 5.6 \times 10^{-2}$$
$$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-; \quad K_a = 6.9 \times 10^{-3}$$
$$HCOOH + H_2O \rightleftharpoons H_3O^+ + HCOO^-; \quad K_a = 1.7 \times 10^{-4}$$

(a) Which conjugate pair would be best for preparing a buffer with a pH of 2.88?

(b) How would you prepare 50 mL of a buffer with a pH of 2.88 assuming that you had available 0.1 M solution of each pair?

[(a) H_3PO_4 and $H_2PO_4^-$ (b) 8 mL H_3PO_4 and 42 mL $H_2PO_4^-$]

426. Tartaric acid is a weak diprotic acid with $K_1 = 1 \times 10^{-3}$ and $K_2 = 4.6 \times 10^{-5}$.

(a) Letting the symbol H_2A represent tartaric acid, write the chemical equations that represent K_1 and K_2. Write the chemical equation that represents $K_1 \times K_2$.

(b) Qualitatively describe the relative concentrations of H_2A, HA^-, A^{2-} and H_3O^+ in a solution that is about 0.5 M in tartaric acid.

(c) Calculate the pH of a 0.025 M tartaric acid solution and the equilibrium concentration of H_2A.

(d) What is the A^{2-} concentration?

[(a) $H_2A + H_2O \rightleftharpoons H_3O^+ + HA^-$
$HA^- + H_2O \rightleftharpoons H_3O^+ + A^{2-}$
$H_2A + 2H_2O \rightleftharpoons 2H_3O^+ + A^{2-}$
(b) $[H_2A] >> [H_3O^+] = [HA^-] >> [A^{2-}]$
(c) pH = 2.34; $[H_2A]$ = 0.0205 M
(d) 4.6×10^{-5} M]

427. Tritium, ^3_1H, is a radioactive nucleus of hydrogen. It is used in luminous watch dials. Tritium decays by beta emission with a half-life of 12.3 years. What is the decay constant (in s^{-1})? What is the activity (in Ci) of a sample containing 2.5 µg of tritium? The atomic mass of tritium is 3.02 amu. (1.79×10^{-9} /s, 0.024 Ci)

428. The equilibrium equations and K_a values for three reaction systems are given below.

$$NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3; \quad K_a = 5.6 \times 10^{-2}$$
$$H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^-; \quad K_a = 4.3 \times 10^{-7}$$
$$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-}; \quad K_a = 6.2 \times 10^{-8}$$

(a) Which conjugate pair would be the best for preparing a buffer with a pH of 6.96? Why?

(b) How would you prepare 100 mL of a buffer with a pH of 6.96 assuming that you had available 0.10 M solutions of each pair?

[(a) H_2CO_3 and HCO_3^- (b) H_2CO_3 – 20·4 mL, HCO_3^- – 79·6 mL]

429. How many grams of silver could be plated out on a serving tray by electrolysis of a solution containing silver in +1 oxidation state for a period of 8.0 hours at a

current of 8.46 amp? What is the area of the tray if the thickness of the silver plating is 0.00254 cm? Density of silver is 10.5 g/cm^3.

(IIT 1997) (271.65 g, 1.02×10^4 cm^2)

430. Assuming that 50% of the heat is useful, how many kg of water at 15°C can be heated to 95°C by burning 200 litres of methane at NTP? $\Delta H_{combustion}$ (CH_4) = 211 kcal/mole, sp. heat of water = 1 kcal/kg K.

(11.8 kg)

431. The rate of reaction:

$$CH_3C(S)NH_2\,(aq) + H_2O \longrightarrow H_2S\,(aq) + CH_3C(O)NH_2\,(aq)$$

is given by the rate law:

$$\text{Rate} = k[H_3O^+]\,[CH_3C(S)NH_2]$$

Consider 1 litre of solution that is 0.20 M in $CH_3C(S)NH_2$ and 0.15 M in HCl at 25°C.

(a) For each of the following changes, state whether the rate of reaction increases, decreases or remains the same.

(i) A 4 g sample of NaOH is added to the solution

(ii) 500 mL of water is added to the solution

(iii) The 0.15 M HCl solution is replaced by a 0.15 M acetic acid solution.

(b) State whether the value of k will increase, decrease or remain the same.

(i) A catalyst is added to the solution

(ii) The reaction is carried out at 15°C instead of 25°C

[(a) (i), (ii) and (iii) decreases (b) (i) increases (ii) decreases]

432. What per cent of a sample of nitrogen must be allowed to escape if its temperature, pressure and volume are to be changed from 220°C, 3 atm and 1.65 litre to 110°C, 0.7 atm and 1 litre respectively?

(81.8%)

433. The vapour pressure of water at 20°C is 17.5 mmHg. Calculate mass of water per litre of air at 20°C and 45% relative humidity.

(7.8 mg)

[**Hint:** Relative humidity is the ratio of the partial pressure of water in air at a given temperature to the vapour pressure of water at that temperature.]

434. A gas is composed of 30.4% N and 69.6% O. Its density is 11.1 g/L at –20°C and 2.5 atm. What are the empirical and molecular formula of the gas? (NO_2, N_2O_4)

435. The active ingredients of an antacid tablet contained only magnesium hydroxide and aluminium hydroxide. Complete neutralisation of the sample of the active ingredients required 48.5 mL of 0.187 M hydrochloric acid. The chloride salts from the neutralisation were obtained by evaporation of the filtrate from the titration; they weighed 0.42 g. What was the percentage by mass of magnesium hydroxide in the active ingredients of the antacid tablet?

(61.7%)

436. In a reaction:

$$CH_3COOCH_3\,(aq) + OH^-\,(aq) \rightarrow CH_3COO^-\,(aq) + CH_3OH\,(aq)$$

The overall order of the reaction was determined by starting with methyl acetate and hydroxide ion at the same concentrations, so

$$[CH_3COOCH_3] = [OH^-] = x$$

Then rate = $k\,[CH_3COOCH_3]^m\,[OH^-]^n = kx^{m+n}$

Determine the overall order and the value of rate constant, k, from the following data:

Time (min)	$[CH_3COOCH_3]$ (mole/litre)
0.00	0.01
3.00	0.0074
4.00	0.00683
5.00	0.00634

(Second, 11.61 L mol^{-1} s^{-1})

437. A sample of natural gas is 85.2% methane, CH_4, and 14.8% ethane, C_2H_6, by mass. What is the density of this mixture at 18°C and 748 mmHg? (0.71 g/L)

438. If the rms speed of the NH_3 molecule is found to be 0.51 km/s, what is the temperature? (–95°C)

439. The disintegration of ^{239}Pu is accompanied by the loss of 5.24 MeV/dis. The half-life of ^{239}Pu is 24400 years. Calculate the energy released per day from 1 g sample of ^{239}Pu in MeV. (1.03×10^{15} MeV/d)

440. Calculate the effective neutron capture radius of a nucleus having a cross section of 1.0 barn. (5.6×10^{-13} cm)

[**Hint:** 1 barn = 10^{-24} cm^2 and area of circle = πr^2]

441. New industrial plants for acetic acid react liquid methanol with carbon monoxide in the presence of a catalyst.

$$CH_3OH + CO \rightarrow CH_3COOH$$

In the experiment, 15 g of methanol and 10 g of carbon monoxide were placed in a reaction vessel. What is the theoretical yield of acetic acid? If the actual yield is 19.1 g, what is the percentage yield? (21.4 g, 89.1%)

442. A 1.0-mg sample of technetium-99 has an activity of 1.7×10^{-5} Ci decaying by β-emission. What is the decay constant for $^{99}_{43}Tc$? (1.0×10^{-13} /s)

443. The nuclide ^{227}Ac undergoes β emission (98.6%) or α emission (1.4%) with a half-life of 21.6 years. Determine λ(α) and λ(β). (4.5×10^{-4} yr^{-1}, 0.0317 yr^{-1})

444. Crystals of AgBr can be removed from black-and-white photographic film by reacting the AgBr with sodium thiosulphate.

$$AgBr\,(s) + 2S_2O_3^{2-}\,(aq) \rightleftharpoons [Ag(S_2O_3)_2]^{3-}\,(aq) + Br^-\,(aq)$$

(a) What is the equilibrium constant for this dissolving process?
(b) In order to dissolve 2.5 g of AgBr in a 1-litre solution, how many moles of $Na_2S_2O_3$ must be added? K_{sp} (AgBr) = 5×10^{-13}, $K_f\,[Ag(S_2O_3)_2]^{3-} = 2.9 \times 10^{13}$ [(a) 14.5 (b) 0.03 mole]

445. One of the hazards of nuclear explosion is the generation of ^{90}Sr and its subsequent incorporation in bones. The nuclide has a half-life of 28.1 years. Suppose one microgram was absorbed by a newborn child, how much ^{90}Sr will remain in his bones after 20 years? **(IIT 1995)** (0.061 μg)

446. A 0.239 g sample of unknown organic base is dissolved in water and titrated with a 0.135 M HCl solution. After the addition of 18.35 mL of acid, a pH of 10.73 is recorded. The equivalence point is reached when a total of 39.24 mL of HCl is added. The base and acid combine in a 1 : 1 ratio.

(a) What is the molar mass of the organic base?

(b) What is the K_b value for the base? The K_b value could have been determined very easily if a pH measurement had been made after the addition of 19.62 mL of HCl. Why? [(a) 45.12 (b) 4.72×10^{-4}]

447. A solution is 1.5×10^{-4} M Zn^{2+} and 0.20 M HSO_4^-. The solution also contains Na_2SO_4. What should be the minimum molarity of Na_2SO_4 to prevent precipitation of ZnS when the solution is saturated with H_2S (0.1 M H_2S)? K_{sp} (ZnS) = 1.1×10^{-21}. (0.18 M)

448. A 0.50-g mixture of Cu_2O and CuO contains 0.425 g of Cu. What is the mass of CuO in the mixture? (0.21 g)

449. An alloy of iron (54.7%), nickel (45.0%) and manganese (0.3%) has a density of 8.17 g/cc. How many iron atoms are there in a block of alloy measuring 10.0 cm × 20.0 cm × 15.0 cm? (1.45×10^{26})

450. (a) Calculate the equilibrium constant for the following reaction at 25°C.

$$Sn\,(s) + Pb^{2+}\,(aq) \rightarrow Sn^{2+}\,(aq) + Pb\,(s)$$

The standard emf of the corresponding voltaic cell is 0.01 V.

(b) If an excess of tin metal is added to 1.0 M Pb^{2+}, what is the concentration of Pb^{2+} at equilibrium? [(a) 2.2 (b) 0.3 M]

451. (a) Calculate the equilibrium constant for the following reaction at 25°C.

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

The standard emf of the corresponding voltaic cell is 0.03 V.

(b) When equal volumes of 1.0 M solutions of Ag^+ and Fe^{2+} are mixed, what is the equilibrium concentration of Fe^{2+}? [(a) 7.11 (b) 0.31 V]

452. The thermochemical equation for the dissociation of hydrogen gas into atoms may be written as

$$H_2 \rightarrow 2H\ ; \quad \Delta H = 436 \text{ kJ}$$

What is the ratio of the energy yield on combustion of hydrogen atoms to steam to the yield on combustion of an equal mass of hydrogen molecules to steam? $\Delta H_{combustion}$ for $H_2 = -241.81$ kJ. (2.80)

453. A mixture of N_2 and Ne contains equal moles of each gas and has a total mass of 10.0 g. What is the density of this gas mixture at 500 K and 10 atm? (5.88 g/L)

454. Calculate the hydronium-ion concentration and the sulphide ion concentration of a 0.1 M H_2S solution, $K_1 = 1 \times 10^{-7}$ and $K_2 = 1 \times 10^{-14}$ (1×10^{-4}, 1×10^{-14})

[**Hint:** $[H^+]$ is mainly due to the first step of ionisation while $[S^{2-}]$ is due to the second step of ionisation.]

455. Calculate $[SO_4^{2-}]$ in 0.15 M H_2SO_4 solution if the first step of ionisation is complete and the second step $K_2 = 1.02 \times 10^{-2}$. (8.9×10^{-3})

456. What is the limiting value of the time required for the radioactive daughter to reach its maximum activity as the value of $t_{1/2}$ (parent)/ $t_{1/2}$ (daughter) increases? (∞)

457. Under standard conditions for all concentrations, the following reaction is spontaneous at 25°C.

$$O_2(g) + 4H^+(aq) + 4Br^-(aq) = 2H_2O(l) + 2Br_2(l)$$

If $[H^+]$ is decreased so that the pH = 3.6, what value will E_{cell} have, and will the reaction be spontaneous at this $[H^+]$? (–0.05 V, No)

458. An electrode is prepared by dipping an Ag strip into a solution saturated with silver thiocyanate, AgSCN, and containing 0.10 M SCN^-. The emf of the voltaic cell constructed by connecting this electrode as the cathode to the standard hydrogen half cell as the anode is 0.45 V. What is K_{sp} of AgSCN? (1×10^{-7})

459. An ideal gas with density of 3.0 g/L has pressure of 675 mmHg at 25°C. What is the rms speed of the molecules of this gas? $(3.0 \times 10^2$ m/s)

460. Determine the emf of the following cell:

$$Pb \mid PbSO_4(s), SO_4^{2-}(1.0\,M) \parallel H^+(1.0\,M) \mid H_2(1.0\,atm) \mid Pt$$

The anode is essentially a lead electrode, $Pb \mid Pb^{2+}$ (aq). However, the anode solution is saturated with $PbSO_4$, so that Pb^{2+} ion concentration is determined by the solubility product of $PbSO_4$ $(=1.7 \times 10^{-8})$. See E^0 values from the table if required. (0.36 V)

461. Under standard conditions for all concentrations, the following reaction is spontaneous at 25°C.

$$O_2(g) + 4H^+(aq) + 4Br^-(aq) \rightarrow 2H_2O(l) + 2Br_2(l);\ E^0 = 0.17\ V$$

If $[H^+]$ is adjusted by adding a buffer of 0.10 M NaOCN and 0.10 M HOCN $(K_a = 3.5 \times 10^{-4})$, what value will E_{cell} have, and will the reaction be spontaneous at this $[H^+]$? (–0.042 V, No)

462. How many moles of NH_3 must be added to 1 litre of 0.75 M $AgNO_3$ in order to reduce the Ag^+ concentration to 5×10^{-8} M? $K_d[Ag(NH_3)_2^+] = 1 \times 10^{-8}$ (1.9 mole)

463. What fraction of a mole of iron metal will be produced by passage of 4 amp of current through 1 litre of 0.1 M Fe^{3+} solution for 1 hour? (0.025 mole)

464. Metallic Mg has a hexagonal close-packed structure and a density of 1.74 g/cc. Assume Mg atoms to be spheres with radius r. Because Mg has a close-packed structure, 74.1% of the space is occupied by atoms. Calculate the volume of each atom and then find the atomic radius r. $(1.72 \times 10^{-23}$ cc, 1.6×10^{-10} m)

465. A solution is 0.10 M in Na_2SO_4. When 50 mL of 0.1 M $Ba(NO_3)_2$ is added to 50 mL of this solution, what fraction of the sulphate ion is not precipitated? $K_{sp}(BaSO_4) = 1.1 \times 10^{-10}$. (2.1×10^{-4})

466. A metallic element crystallises into a lattice containing a sequence of layers

ABABAB.... Any packing of spheres leaves out voids in the lattice. What percentage by volume of this lattice is empty space? **(IIT 1996)** (25.94%)

[**Hint:** The empty space in h.c.p. or c.c.p. arrangement is same as for f.c.c. See Chapter 19.]

467. A sample of $^{14}CO_2$ was to be mixed with ordinary CO_2 for biological tracer experiment. In order that 10 cc (NTP) of the diluted gas should have 10^4 disintegrations per minute, how many microcuries of radioactive carbon are needed to prepare 60 litres of the diluted gas? (27 μCi)

468. Which state of the triply ionised beryllium, Be^{3+}, has the same radius as that of the ground state of hydrogen atom? (Second)

469. At what temperature would the average translational kinetic energy of gaseous hydrogen molecules equal the energy required to dissociate the molecules into atoms, i.e., 104 kcal per mole? (34900 K)

470. Calculate the pH of a 0.005 M Na_2S solution. K_1 and K_2 for H_2S are 1×10^{-7} and 1×10^{-14} respectively. (11.70)

[**Hint:** The first step of hydrolysis, i.e., $S^{2-} + H_2O \rightleftharpoons HS^- + OH^-$ is predominant and hence K_2 value is used in the calculations.]

471. A voltaic cell whose cell reaction is

$$2Fe^{3+}(aq) + Zn(s) = 2Fe^{2+}(aq) + Zn^{2+}(aq)$$

has an e.m.f. of 0.72 V. What is the maximum electrical work that can be obtained from the cell per mole of Fe (II) ion? (69 kJ)

472. The dipole moment of HBr is 2.6×10^{-30} C m, and the interatomic spacing is 1.41 Å. What is the per cent ionic character of HBr? (11.5%)

473. How much AgBr would dissolve in 1 litre of 0.40 M NH_3? K_{sp} (AgBr) = 5×10^{-13} K_d $[Ag(NH_3)_2^+] = 1 \times 10^{-8}$. ($2.83 \times 10^{-3}$ M)

474. An electron beam can undergo diffraction by crystals. Through what potential should a beam of electrons be accelerated so that its wavelength becomes equal to 1.54 Å? See values of m_e and h from the table. **(IIT 1997)** (63.5 V)

[**Hint:** See Example 28, Chapter 11.]

475. Calculate the wavenumber for the shortest wavelength transition in the Balmer series of atomic hydrogen. **(IIT 1996)** ($27419\ cm^{-1}$)

476. What is the solubility of CaF_2 in a buffer solution containing 0.45 M HCOOH and 0.20 M HCOONa? K_{sp} (CaF_2) = 3.4×10^{-11}, K (HF) = 6.8×10^{-4}, K (HCOOH) = 1.7×10^{-4}. (2.75×10^{-4} M)

[**Hint:** $2[Ca^{2+}] = [F^-] + [HF]$]

477. What is the solubility of MgF_2 in a buffer solution containing 0.45 M CH_3COOH and 0.20 M CH_3COONa? K_{sp} (MgF_2) = 6.5×10^{-9}, K (HF) = 6.8×10^{-4}, K (CH_3COOH) = 1.7×10^{-5}. (1.22×10^{-3} M)

478. The reaction

$$LaCl_3(s) + H_2O(g) \rightleftharpoons LaClO(s) + 2HCl(g)$$

is taking place in a closed container at a constant temperature. After the equilibrium is reached, more water vapour is added and the reaction shifted to a new equilibrium state at which the concentration of water vapour is found to be doubled. Calculate the factor by which the concentration of HCl is increased at the second equilibrium state. ($\sqrt{2}$)

479. ^{227}Ac has a half-life of 22 years with respect to radioactive decay. The decay follows two parallel paths, one leading to ^{227}Th and the other to ^{223}Fr. The percentage yields of these two daughter nuclides are 2.0 and 98.0 respectively. What are the decay constants (λ) for each of the separate paths?

(IIT 1996) ($6.302 \times 10^{-4}\ yr^{-1}$, $3.088 \times 10^{-2}\ yr^{-1}$)

[**Hint:** See Example 66, Chapter 11.]

480. A space capsule is filled with neon gas at 1 atm and 290 K. The gas effuses through a pinhole into outer space at such a rate that the pressure drops by 0.3 mm/second. If the capsule were filled with 30% He, 20% O_2 and 50% N_2 (mole %) at a total pressure of 1 atm and a temperature of 290 K, calculate the rate of pressure drop. (0.29 mm/s)

[**Hint:** Use Equation 10, Chapter 12.]

481. Find the equivalent weight of Br_2 in each of the following reactions:

(a) $Br_2 + 2e = 2Br^-$ or $5Br_2 + 10\,e = 10Br^-$

(b) $Br_2 + 12OH^- = 2BrO_3^- + 6H_2O + 10\,e$

(c) $6Br_2 + 12OH^- = 10Br^- + 2BrO_3^- + 6H_2O$

Equation (c) is the sum of equations (a) and (b).

What is the relationship between the answer to (c) and the answers to (a) and (b)? [(a) 80.0 (b) 16 (c) 96]

(Br = 80.0)

[**Note:** The equivalent weight of Br_2 in the overall reaction is the sum of that of the two half-reactions (for a species which disproportionates).]

482. Find the equivalent weight of $KMnO_4$ in the reaction:

$$Mn^{2+} + MnO_4^- + H_2O \longrightarrow MnO_2 + H^+ \text{ (unbalanced)}$$

What mass in g of $MnSO_4$ is oxidised by 1.25 g of $KMnO_4$? (52.7, 1.79 g)

[**Hint:** Eq. of $MnSO_4$ = Eq. of $KMnO_4$.]

483. A sample of radioactive material has an apparently constant activity of 2000 dis/min. By chemical means, the material is separated into two fractions, one of which has an initial activity of 1000 dis/min. The other fraction decays with a 24-hour half-life. Estimate the total activity in both samples 48 hours after the separation. Explain your estimate. (2000)

[**Hint:** The total activity when the samples are separated will be the same as the total activity when they are mixed, i.e., the mixing makes no difference to the activity.]

484. The time required for 10% completion of a first-order reaction at 298 K is equal to that required for its 25% completion at 308 K. If the pre-exponential factor for the reaction is $3.56 \times 10^9\ s^{-1}$, calculate its rate constant at 318 K and also the energy of activation. **(IIT 1997)** (18.67 kcal, $6.352 \times 10^{-4}\ s^{-1}$)

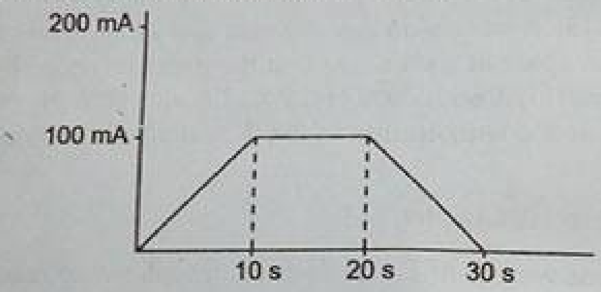
[Hint: $k_2/k_1 = \frac{2.303}{t}\log\frac{4}{3}/\frac{2.303}{t}\log\frac{10}{9}$; now use eqn. (12), Chapter 17 to calculate E and then Arrhenius's equation to calculate k (318 K).]

485. For a gaseous reaction 2B → A, the equilibrium constant K_p is...... to/than K_c.
(IIT 1997) (less)

486. When an aqueous solution of sodium fluoride is electrolysed, the gas liberated at the anode is ......
(IIT 1997) (O_2)

487. When 10 mL of ethanol of density 0.7893 g/L is mixed with 20 mL of water of density 0.9971 g/L at 25°C, the final solution has a density of 0.9571 g/L. Calculate the percentage change in total volume on mixing.
(3.05%)

488. In a Cu-voltameter, mass deposited in 30 seconds is m gram. If the time-current graph is as shown in the figure, calculate the electrochemical equivalent of Cu.



$[\frac{m}{2}]$

489. A litre of CO_2 at 15°C and 1-atm pressure dissolves in 1 litre of water at the same temperature when the pressure of CO_2 is 1 atm. Calculate the molal concentration of CO_2 in a solution over which the partial pressure of CO_2 is 150 mmHg.
(0.0083 m)

[Hint: $m_{CO_2} \propto p_{CO_2}$]

490. The voltage of the cell,

$$Pb (s) | PbSO_4 (s) | NaHSO_4 (0.6 M) || Pb^{2+} (2.5 \times 10^{-5}) | Pb (s)$$

is 0.061 V. Calculate $K_2 = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]}$.

Given $PbSO_4 (s) + 2e = Pb (s) + SO_4^{2-}$; $E^0 = -0.356$ V

$Pb^{2+} + 2e = Pb (s)$; $E^0 = -0.126$ V

(9.7×10^{-3})

491. 0.75 g of solid benzoic acid was placed in a 0.5-litre pressurised reaction vessel filled with O_2 at 10-atm pressure and 25°C. To the extent of availability of O_2, the acid burned to give CO_2 and H_2O. What were the final mole fractions of CO_2 and H_2O vapour in the resulting gas mixture brought to the initial temperature? The vapour pressure of water at 25°C is 23.8 torr. Neglect the volume occupied by nonaqueous substances and the solubility of CO_2 in H_2O.
(CO_2 0.213, H_2O 0.0033)

[Hint: Benzoic acid is the limiting reactant.]

492. A silent electric discharge was passed through 100 mL of air when 95 mL of ozonised air was formed. The ozonised air took 48.7 seconds to diffuse through a very small hole. If 100 mL of air diffused through the same hole under the identical conditions, it took 50 seconds. Find the molecular weight of ozone assuming air to contain 79% N_2 and 21% O_2.

[Hint: Composition of 95 mL of ozonised air is N_2 79 mL, O_3 10 mL and O_2 6 mL.] (48)

493. An element forms two oxides, the per cent composition in them A : O = $x : y$ in the first oxide and $y : x$ in the second oxide. If the equivalent weight of A in the first oxide is 10.33, what is the equivalent weight of A in the second oxide? (6.19)

494. For the nonequilibrium process A + B → Products, the rate is first-order w.r.t. A and second-order w.r.t. B. If one mole each of A and B were introduced into a 1-litre vessel, and the initial rate were 1×10^{-2} mol/litre s, calculate the rate when half the reactants have been turned into products. (1.2×10^{-3} mol/L s)

495. A solution of the two liquids A and B obeys Raoult's law. At a certain temperature, it is found that when the total pressure above the given solution is 400 mmHg, the mole fraction of A is 0.45 and that in the liquid is 0.65, what are vapour pressures of the two liquids? (277 mm, 629 mm)

496. A certain fertiliser is advertised to contain 12% K_2O. What percentage of the fertiliser is potassium? (9.96%)

497. How many grams of excess reactant will remain after the reaction of 12.5 g of CaO and 75.0 g of $HClO_4$? (30.4 g)

498. Calculate the number of moles of NaOH required to remove the SO_2 from 10 metric tons of atmosphere if the SO_2 is 0.1% by mass. 1 metric ton = 1.0×10^6 g.

$$2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O$$ (312 mole)

499. How many sandwiches, each containing 1 slice of cheese and 2 slices of bread, can you make with 30 slices of bread and 20 slices of cheese? Which is in the limiting quantity? (15, bread)

500. In certain areas where coal is cheap, artificial gas is produced for household use by the 'water gas' reaction

$$C(s) + H_2O(g) \xrightarrow{600°C} H_2(g) + CO(g)$$

Assuming that coke is 100% carbon, calculate the maximum heat obtainable at 298 K from the combustion of 1.0 kg of coke and compare this value to the maximum heat obtainable at 298 K from burning the water gas produced from 1.0 kg of coke.

Heat of combustion of C, H_2 and CO are –94.1, –68.4 and –68.0 kcal/mole respectively. (More energy is obtainable from the water gas, 11366 kcal)

501. Calculate the concentration of all the ions in solution if 1 mole of HCl and 2 moles of NaCl are dissolved in sufficient water to make 6 litres of a single solution. (0.17 M H^+, 0.50 M Cl^-, 0.33 M Na^+)

502. Calculate the final concentration of all ions in solution after 2 litres of 1.3 M $Ba(OH)_2$ is treated with 3 litres of 2.0 M HCl. (0.16 M H^+, 0.52 M Ba^{2+}, 1.2 M Cl^-)

503. What is the meaning of a positive sign for (a) a cell potential, and (b) a half-cell potential? [(a) The reaction can proceed as written. (b) Nothing]

504. A solution of silver benzoate has a pH of 8.63. K_a (C_6H_5COOH) = 6.5×10^{-5}. Calculate the value of K_{sp} for silver benzoate. (1.4×10^{-3})

[**Hint:** Use pH = $\frac{1}{2}(pK_w + pK_a + \log C)$.]

505. The rate constant for the first-order decomposition of a certain reaction is described by the equation

$$\log k\,(s^{-1}) = 14.34 - \frac{1.25 \times 10^4\,K}{T}$$

(i) What is the energy of activation for this reaction?

(ii) At what temperature will its half-life period be 256 minutes?

(IIT 1997) (239.34 kJ mole^{-1}, 669K)

[**Hint:** See Example 51, Chapter 17.]

506. A compound of vanadium has a magnetic moment of 1.73 BM. Work out the electronic configuration of the vanadium ion in the compound. (V = 23)

(IIT 1997) [$\mu = \sqrt{n(n+2)}$ BM, for μ = 1.73 BM, n = 1, V^{4+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$]

507. The decomposition of N_2O into N_2 and O in the presence of gaseous argon follows second-order kinetics, with

$$k = (5.0 \times 10^{11}\ L\ mol^{-1}\ s^{-1})\, e^{-29000k/T}$$

What is the energy of activation of this reaction? (241 kJ/mol)

[**Hint:** Compare the given equation with Arrhenius's equation.]

508. K_p for the reaction

$$N_2O_4\,(g) = 2NO_2\,(g)$$

is 0.66 at 46°C. Calculate the per cent dissociation of N_2O_4 at 46°C and a total pressure of 380 mm. What are the partial pressures of N_2O_4 and NO_2 at equilibrium? (0.168 atm, 0.332 atm)

509. An excess of liquid mercury is added to an acidified solution of 1×10^{-3} M Fe^{3+}. It is found that 5% of Fe^{3+} remains at equilibrium at 25°C. Calculate $E^0_{Hg_2^{2+},\,Hg}$, assuming that the only reaction that occurs is

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

Given $E^0_{Fe^{3+},\,Fe^{2+}}$ = 0.77 V. **(IIT 1995)** (0.792 V)

[**Hint:** See Example 28, Chapter 18.]

510. Calculate the pH of an aqueous solution of 1.0 M ammonium formate assuming complete dissociation. pK_a of formic acid = 3.8 and pK_b of ammonia = 4.8.

(IIT 1995) (6.5)

511. At 380°C, the half-life period for the first-order decomposition of H_2O_2 is 360 minutes. The energy of activation of the reaction is 200 kJ mol^{-1}. Calculate the time required for 75% decomposition at 450°C. **(IIT 1995)** (20.34 min)

512. $^{224}_{88}Ra$ having $t_{1/2}$ = 3.64d emits an α particle to form $^{220}_{86}Rn$, which has $t_{1/2}$ = 54.5 s. Given that the molar volume of radon under these condtions is

35.2 dm^3, what volume of radon is in secular equilibrium with 1 g of radium?
(2.72×10^{-8} m^3)

513. Find the ratio of the mass needed to generate 1 μCi of $^{226}_{88}Ra$ ($t_{1/2}$ = 1622 yr) to that for 1 μCi of $^{222}_{86}Rn$ ($t_{1/2}$ = 3.825 d). (1.58×10^5)

514. The composition of the equilibrium mixture $Cl_2 \rightleftharpoons 2Cl$, which is attained at 1200°C, is determined by measuring the rate of effusion through a pinhole. It is observed that at 1.80 mmHg pressure, the mixture effuses 1.16 times as fast as krypton effuses under the same conditions. Calculate the fraction of chlorine molecules dissociated into atoms. (At. wt. of Kr = 84) **(IIT 1995)** (0.14)

(See Example 33, Chapter 12.)

515. A 5-cc solution of H_2O_2 liberates 0.508 g of iodine from an acidified KI solution. Calculate the strength of H_2O_2 solution in terms of volume strength at STP.
(IIT 1995) (0.8 V)

[**Hint:** See examples 25 and 29, Chapter 7.]

516. A 20-cc mixture of CO, CH_4 and He gases is exploded by an electric discharge at room temperature with excess of oxygen. The volume contraction is found to be 13 cc. A further contraction of 14 cc occurs when the residual gas is treated with KOH solution. Find out the composition of the gaseous mixture in terms of volume percentage. **(IIT 1995)** (50% 20%, 30%)

[**Hint:** See Example 19, Chapter 3.]

517. What is the pH of a 0.50 M aqueous NaCN solution? pK_b of CN^- is 4.70.
(IIT 1996) (11.5)

518. A unit cell of sodium chloride has four formula units. The edge length of the unit cell is 0.564 nm. What is the density of sodium chloride?
(IIT 1997) (2.16×10^3 kg m^{-3})

[**Hint:** See Example 9, Chapter 20.]

519. Electrolysis of a solution of $MnSO_4$ in aqueous sulphuric acid is a method for the preparation of MnO_2 as per the reaction

$$Mn^{2+}(aq) + 2H_2O \longrightarrow MnO_2(s) + 2H^+(aq) + H_2(g)$$

Passing a current of 27 A for 24 hours gives one kg of MnO_2. What is the value of current efficiency? Write the reactions taking place at the cathode and at the anode. **(IIT 1997)** (95.09%)

520. How many equivalents are there in 98 g of H_2SO_4 in the following reaction?

$$8H^+ + H_2SO_4 + 4Zn \longrightarrow H_2S + 4Zn^{2+} + 4H_2O$$

Also, find out the equivalent weight of H_2SO_4 in this reaction. (8 eq., 12.25)

521. What is the molarity of 4N H_2SO_4 in the following reaction? (0.5 M)

$$8H^+ + H_2SO_4 + 8e^- \longrightarrow H_2S + 4H_2$$

522. Show that the ratio $t_{\frac{1}{2}}/t_{\frac{3}{4}}$ for an *n*th-order reaction is a function of *n* alone.

523. An aqueous solution contains 10% ammonia by mass and has a density of 0.99 g/cc.

Calculate the hydroxyl and hydrogen-ion concentration in this solution. $K_a(NH_4^+) = 5 \times 10^{-10}$ M. $(1.08 \times 10^{-2}, 9.28 \times 10^{-13}$ M)

524. 0.15 mole of pyridinium chloride has been added into 500 cc of 0.2 M pyridine solution. Calculate the pH and hydroxyl-ion concentration in this resulting solution assuming no change in volume. K_b for pyridine $= 1.5 \times 10^{-9}$ M. (5, 10^{-9} M)

525. Calculate the amount of ice that will separate out on cooling a solution containing 50 g of ethylene glycol in 200 g water to –9.3°C. K_f for water = 1.86 K · mol^{-1}. kg (38.71 g)

[Hint: See Example 41, Chapter 13.]

526. Calculate the equilibrium constant for the reaction

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

Given $E^0_{Ce^{4+}/Ce^{3+}} = 1.44$ V; $E^0_{Fe^{3+}/Fe^{2+}} = 0.68$ V. **(IIT 1997)** (7.6×10^{12})

[Hint: See Example 12, Chapter 18.]

527. Chromium metal crystallizes with a body-centred cubic lattice. The length of the unit-cell edge is found to be 287 pm. Calculate the atomic radius. What would be the density of chromium in g/cm^3? **(IIT 1997)**

[Hint: See Example 8, Chapter 20.] (124.27 pm, 7.32 g/cm^3)

528. Anhydrous $AlCl_3$ is covalent. From the data given below, predict whether it would remain covalent or become ionic in aqueous solution. (Ionization energy for Al = 5137 kJ mole^{-1}; $\Delta H_{hydration}$ for Al^{3+} = –4665 kJ mole^{-1}; $\Delta H_{hydration}$ for Cl^- = –381 kJ mole^{-1}). **(IIT 1997)**

[Hint: Total energy evolved due to hydration = –4665 – 3(–381) = –5808 kJ/mole. As this released energy is greater than ionization energy (5137 kJ/mole) of Al, $AlCl_3$ can be ionic in aqueous solution.]

529. Write a balanced equation for the reaction of ^{14}N with α particle.

$({}^{14}_{7}N + {}^{4}_{2}He \longrightarrow {}^{17}_{8}O + {}^{1}_{1}H)$

530. Isotopes of oxygen with mass number less than 16 undergo β^+ emission. Assuming an equimolar mixture of ^{14}O and ^{15}O, find the ratio of the nuclides at the end of one hour. Given that $t_{1/2}(^{14}O) = 71$ s and $t_{1/2}(^{15}O) = 124$ s. At what time will the above said ratio be equal to 0.25? $(3.29 \times 10^{-7}$, 332 s)

[Hint: Use Equation 25, Chapter 11.]

531. What is the minimum half-life of an isotope needed so that not more than 0.1% of the nuclei undergo decay during a 3.0-hour laboratory period? (88 days)

532. Calculate the percentage of hydrolysis in 0.003 M aqueous solution of NaOCN. K_a for HOCN $= 3.33 \times 10^{-4}$ M. (0.01%)

[Hint: $OCN^- + H_2O \rightleftharpoons HOCN + OH^-$]

533. A sample of ^{238}U (half-life $= 4.5 \times 10^9$ yr) ore is found to contain 23.8 g of ^{238}U and 20.6 g of ^{206}Pb. Calculate the age of the ore. $(4.489 \times 10^9$ years)

[Hint: See Example 48, Chapter 11.]

534. An aqueous solution of aniline of concentration 0.24 M is prepared. What concentration of sodium hydroxide is needed in this solution so that anilinium ion concentration remains at 1×10^{-8} M? K_a for $C_6H_5NH_3^+ = 2.4 \times 10^{-5}$ M. $(1 \times 10^{-2}$ M)

535. 20% of N_2O_4 molecules are dissociated in a sample of gas at 27°C and 760 torr. Calculate the density of the equilibrium mixture. (3.12 g/L)

536. The average molar mass of the vapour above solid NH_4Cl is nearly 26.75 g mole^{-1}. What is the composition (by wt.) of this vapour? (NH_3 31.8%, HCl 68.2%)

537. When 12 g of carbon reacted with oxygen to form CO and CO_2 at 25°C and constant pressure, 75 kcal of heat was liberated and no carbon remained. Calculate the mass of oxygen which reacted. Given,

$$C + O_2 \longrightarrow CO_2 \; ; \quad \Delta H = -94.05 \text{ kcal/mole}$$

$$C + \tfrac{1}{2}O_2 \longrightarrow CO \; ; \quad \Delta H = -26.41 \text{ kcal/mole}$$

(27.5 g)

538. A proposed mechanism for the catalysed decomposition of aqueous H_2O_2 is

$$H_2O_2 + I^- \xrightarrow{k_1} H_2O + IO^-$$

$$H_2O_2 + IO^- \xrightarrow{k_2} H_2O + O_2 + I^-$$

where $k_2 >> k_1$. Derive the rate law for the reaction. $\left(-\dfrac{d[H_2O_2]}{dt} = k_1 [H_2O_2][I^-]\right)$

539. Prepare a reaction-coordinate diagram for the reaction

$$2H_2O_2 \longrightarrow 2H_2O_2 + O_2 \; ; \quad \Delta H = -191.78 \text{ kJ}$$

in which energy of activation for uncatalysed and catalysed reactions are 75.3 kJ mole^{-1} and 56.6 kJ mole^{-1} respectively at 298 K.

(a) What is the ratio of the rate constant for the forward catalysed reaction to that for the forward uncatalysed reaction?

(b) By what factor will the rate constant for the reverse catalysed reaction increase compared to that for the reverse uncatalysed reaction?

(c) Hence prove that the catalyst increases both the forward and reverse reactions by the same factor. [(a) 1970 (b) 1970]

540. A weak base BOH was titrated against a strong acid. The pH at one-fourth equivalence point was 9.24. Enough strong base was now added (6 m.e.) to completely convert the salt. The total volume was 50 mL. Find the pH at this point. (11.2)

[**Hint:** $(14 - 9.24) = pK_b + \log \dfrac{(1/4)}{(3/4)}$; cal K_b

6 m.e. of the strong base, added, is used to convert the salt to the weak base. Thus before the addition of the strong base, m.e. of the salt and the base were 6 and 18 respectively. As 6 m.e. of the strong base shall combine with the same number of m.e. of the salt to produce 6 m.e. of BOH, total m.e. of BOH = 6 + 18 = 24 and thus molarity $= \dfrac{24}{50}$ M. Now using K_b value, calculate the pH.]

541. An aqueous solution containing 0.10 g $KClO_3$ (formula weight = 214.0) was treated with an excess of KI solution. The solution was acidified with HCl. The liberated I_2 consumed 45.0 mL of thiosulphate solution to decolourise the blue starch-iodine complex. Calculate the molarity of the sodium thiosulphate solution.

(IIT 1998) (0.062 M)

[**Hint:** $KIO_3 + 5\ KI = 3K_2O + 3I_2$]

542. Calculate the equilibrium constant for the reaction $2Fe^{3+} + 3I^- \rightleftharpoons 2Fe^{2+} + I_3^-$. The standard reduction potentials in acidic-medium conditions are 0.77 and 0.54 V respectively for Fe^{3+}/Fe^{2+} and I_3^-/I^- couples. **(IIT 1998)** (6.07×10^7)

[**Hint:** Apply Equation 2, Chapter 18, $n = 2$]

543. From the following data, calculate the enthalpy change for the combustion of cyclopropane at 298 K. The enthalpy of formation of CO_2(g), H_2O(l) and propene (g) are –393.5, –285.8 and 20.42 kJ mol^{-1} respectively. The enthalpy of isomerisation of cyclopropane to propene is –33.0 kJ mol^{-1}. **(IIT 1998)** (–2091.32 kJ)

544. The degree of dissociation is 0.4 at 400 K and 1 atm for the gaseous reaction

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2.$$

Assuming ideal behaviour of all the gases, calculate the density of equilibrium mixture at 400 K and 1 atm. **(IIT 1998)** (4.535 g/L)

[**Hint:** Apply $p = \dfrac{dRT}{M_{mix}}$]

545. Given: $Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3$, $K_c = 6.2 \times 10^{-8}$ and K_{sp} of $AgCl = 1.8 \times 10^{-10}$ at 298 K. Calculate the concentration of the complex in 1.0 M aqueous ammonia.

(IIT 1998) (0.054 M)

[**Hint:** Let the concentration of the complex, $[Ag(NH_3)_2]Cl$, be x mole per litre in 1 M NH_3 and concentration of Ag^+ be y mole/litre

$$Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3;\ K_c = 6.2 \times 10^{-8}$$

At eqb.: $x \quad y \quad 2y + 1 \approx 1$

$$AgCl \rightleftharpoons Ag^+ + Cl^-;\ K_{sp} = 1.8 \times 10^{-10}$$

At eqb.: $y \quad x$

546. A solution of a nonvolatile solute in water freezes at –0.30°C. The vapour pressure of pure water at 298 K is 23.51 mmHg and K_f for water is 1.86 degree/molal. Calculate the vapour pressure of this solution at 298 K. **(IIT 1998)** (23.44 mm)

547. For the reaction, $N_2O_5(g) \rightleftharpoons 2NO_2(g) + 0.5\ O_2(g)$, calculate the mole fraction of $N_2O_5(g)$ decomposed at a constant volume and temperature, if the initial pressure is 600 mmHg and the pressure at any time is 960 mmHg. Assume ideal gas behaviour.

(IIT 1998) (0.25)

[**Hint:** If 'p' mm of N_2O_5 decomposes then $600 - p + 2p + \frac{p}{2} = 960$]

548. Find the solubility product of a saturated solution of Ag_2CrO_4 in water at 298 K if the emf of the cell

$$Ag \mid Ag^+ \text{ (satd. } Ag_2CrO_4 \text{ soln.)} \mid\mid Ag^+(0.1\ M) \mid Ag$$

is 0.164 V at 298 K.

(IIT 1998) (2.44×10^{-12})

549. What will be the resultant pH when 200 mL of an aqueous solution of

HCl(pH = 2.0) is mixed with 300 mL of an aqueous solution of NaOH (pH = 12)?

(IIT 1998) (11.3)

550. The rate constant of a reaction is $1.5 \times 10^7 \ s^{-1}$ at 50°C and $4.5 \times 10^7 \ s^{-1}$ at 100°C. Evaluate the Arrhenius parameters A and E_a.

(IIT 1998) (2.19×10^4 J/mol, $5.4 \times 10^{10} \ s^{-1}$)

[**Hint:** Apply Arrhenius's equation.]

551. How many millilitres of 0.5 M H_2SO_4 are needed to dissolve 0.5 g of copper (II) carbonate?

(IIT 1999) (8.09 mL)

552. Nitrobenzene is formed as the major product along with a minor product in the reaction of benzene with a hot mixture of HNO_3 and H_2SO_4. The minor product consists of C: 42.86%, H: 2.40%, N: 16.67% and O: 38.07%. (i) Calculate the empirical formula of the minor product, (ii) when 5.5 g of the minor product is dissolved in 45 g of benzene, the b.p. of the solution is 1.84°C higher than that of pure benzene. Calculate the molecular weight of the minor product and determine its molecular and structural formula. $K_b(C_6H_6) = 2.53$ K kg mol^{-1}.

(IIT 1999) ($C_3H_2NO_2$, 168, *m*-dinitrobenzene)

553. A plant virus is found to consist of uniform cylindrical particles of 150 Å in diameter and 5000 Å long. The specific volume of the virus is 0.75 cm^3/g. If the virus is considered to be a single particle, find its molecular weight.

(IIT 1999) (7.0939×10^7)

[**Hints:** Mol wt. = Mass of 1 molecule × Av. constant.]

554. When 3.06 g of solid NH_4HS is introduced into a two-litre evacuated flask at 27°C, 30% of the solid decomposes into gaseous NH_3 and H_2S (i) Calculate K_c and K_p for the reaction at 27°C. (ii) What would happen to the equilibrium when more solid NH_4HS is introduced into the flask?

(IIT 1999) [(i) 8.1×10^{-5} mole/L, 0.049 atm^{-2}, (ii) No effect]

555. One mole of nitrogen gas at 0.8 atm takes 38 s to diffuse through a pinhole, whereas one mole of an unknown compound of xenon with fluorine at 1.6 atm takes 57 s to diffuse through the same hole. Calculate the molecular formula of the compound. (Xe = 131, F = 19)

(IIT 1999) (XeF_6)

556. The pressure exerted by 12 g of an ideal gas at temperature t°C in a vessel of volume V litre is one atm. When the temperature is increased by 10 degrees at the same volume, the pressure increases by 10%. Calculate the temperature t and volume V. (Mol wt. of the gas = 120)

(IIT 1999) (100 K, 0.821 L)

[**Hint:** Apply $pV = nRT$ twice]

557. A cell, $Ag \mid Ag^+ \mid\mid Cu^{2+} \mid Cu$, initially contains 1 M Ag^+ and 1 M Cu^{2+} ions. Calculate the change in the cell potential after the passage of 9.65 A of current for 1 h.

(IIT 1999) (0.1355 V)

[**Hint:** See examples 31 and 32, Chapter 18.]

558. The solubility of $Pb(OH)_2$ in water is 6.7×10^{-6} M. Calculate the solubility of $Pb(OH)_2$ in a buffer solution of pH = 8.

(IIT 1999) (1.2×10^{-3} M)

559. Estimate the average S-F bond energy in SF_6. The standard heat of formation values of $SF_6(g)$, S(g) and F(g) are: –1100, 275 and 80 kJ mol^{-1} respectively.
(IIT 1999) (309.6 kJ mol^{-1})

560. The rate constant for an isomerisation reaction $A \rightarrow B$ is 4.5×10^{-3} min^{-1}. If the initial concentration of A is 1 M, calculate the rate after 1 h.
[Hint: See Example 3, Chapter 17.] **(IIT 1999)** (3.43×10^{-3} M/min)

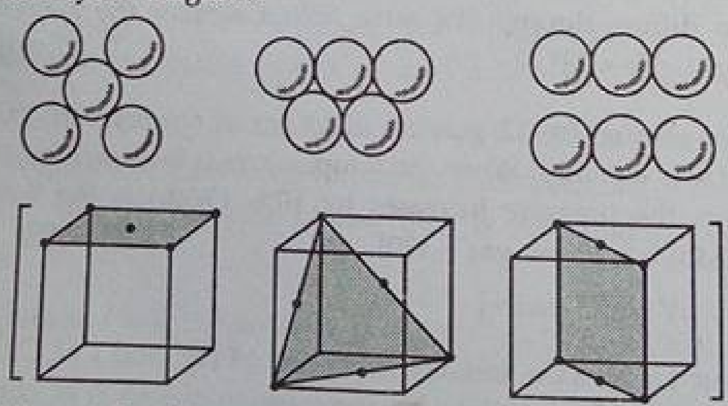
561. A metal cystallises into two cubic phases, f.c.c and b.c.c. whose unit-cell lengths are 3.5 and 3.0 Å. Calculate the ratio of densities of f.c.c. and b.c.c.
[Hint: Apply Equation (1), Chapter 20.] **(IIT 1999)** (1.259)

562. $^{238}_{92}U$ is radioactive and it emits α and β particles to form $^{206}_{82}Pb$. Calculate the number of α and β particles emitted in this conversion. An ore of $^{238}_{92}U$ is found to contain $^{238}_{92}U$ and $^{206}_{82}Pb$ in the weight ratio of 1 : 0.1. The half-life period $^{238}_{92}U$ is 4.5×10^9 years. Calculate the age of the ore. **(IIT 2000)** (8, 6, 7.098×10^8 years)
[Hint: See Example 36 and 40, Chapter 11.]

563. The average concentration of SO_2 in the atmosphere over a city on a certain day is 10 ppm, when the average temperature is 298 K. Given that the solubility of SO_2 in water at 298 K is 1.3653 mole lit^{-1} and the pK_a of H_2SO_3 is 1.92, estimate the pH of rain on that day. **(IIIT 2000)** (0.913)
[Hint: $[SO_2] = [H_2SO_3] = 1.3653$ M, $H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$; $K_a = 1.2 \times 10^{-2}$]

564. Calculate the pressure exerted by one mole of CO_2 gas at 273 K if the van der Waals constant $a = 3.593$ dm^6 atm mol^{-2}. Assume that the volume occupied by CO_2 molecules is negligible. **(IIT 2000)** (0.9922 atm)
[Hint: Apply $\left(p + \frac{a}{V^2}\right)V = RT$; $V = 22.4$ dm^3 (suppose)]

565. The figures given below show the location of atoms in three crystallographic planes in an f.c.c. lattice. Draw the unit cell for the corresponding structure and identify these planes in your diagram. **(IIT 2000)**



[Hint: The atom at the face centre in f.c.c. touches the 4 corner atoms on that face but the corner atoms do not touch each other. The atoms at the centre of the faces at right angles touch each other.]

566. A hydrogenation reaction is carried out at 500 K. If the same reaction is carried out in the presence of a catalyst at the same rate, the temperature required is 400 K.

Calculate the activation energy of the reaction if the catalyst lowers the activation barrier by 20 kJ mol^{-1}.

(IIT 2000) (100 kJ mol^{-1})

[Hint: From Arrhenius's equation, under the given condition, we have,

$$-\frac{E}{RT_1} = -\frac{E-20}{RT_2}$$]

567. Copper sulphate solution (250 mL) was electrolysed using a platinum anode and copper cathode. A constant current of 2 mA was passed for 16 minutes. It was found that after electrolysis the absorbance of the solution was reduced to 50% of its original value. Calculate the concentration of copper sulphate in the solution to begin with.

(7.958×10^{-5} M) (IIT 2000)

[Hint: Initial mole of $CuSO_4$ per 250 mL

$= 2 \times$ mol of $CuSO_4$ lost

$= 2 \times$ mol of Cu deposited]

568. Calculate the energy required to excite 1 litre of H_2 gas at 1 atm and 298 K to the first excited state of atomic hydrogen. The energy for the dissociation of H–H bonds is 436 kJ mol^{-1}. Rydberg constant for H = 109679 cm^{-1}, $h = 6.626 \times 10^{-34}$ Js and $C = 3 \times 10^8$ m s^{-1}.

(IIT 2000) (98.19 kJ)

[Hint: Mole of H $= 2 \times$ mole $H_2 = 2 \times \frac{pV}{RT}$

Energy to excite 1 H atom $= h\nu = \frac{hc}{\lambda} = hcR\left(\frac{1}{n_1} - \frac{1}{n_2}\right)$.

Total energy = energy to break H–H bonds + energy to excite H atom]

569. A sample of argon gas at 1-atm pressure and 27°C expands reversibly and adiabatically from 1.25 dm^3 to 2.50 dm^3. Calculate the enthalpy change in this process. $C_{V,m}$ for argon is 12.48 JK^{-1} mol^{-1}.

(IIT 2000) (–117.6 J)

[Hint: $T_1 = 300$ K, cal. T_2 using $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{R/C_V}$ then

$\Delta H = nC_p(T_2 - T_1) = n(C_V + R)(T_2 - T_1)$]

570. To 500 cm^3 of water, 3×10^{-3} kg of acetic acid is added. If 23% of acetic acid is dissociated, what will be the depression in freezing point? K_f and density of water are 1.86 K kg^{-1} mol^{-1} and 0.997 g cm^{-3} respectively.

(IIT 2000) (0.228 K)

571. Show that the reaction $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$ at 300 K is spontaneous and exothermic, when the standard entropy change is –0.094 kJ mol^{-1} K^{-1}. The standard Gibbs free energies of formation for CO_2 and CO are –394.4 and –137.2 kJ mol^{-1} respectively.

(IIT 2000) [$\Delta G^0 = -257.2$ kJ (spontaneous), $\Delta H^0 = -285.4$ kJ (exothermic)]

[Hint: $\Delta G^0 = \Delta H^0 - T\Delta S^0$]

572. The following electrochemical cell has been set up.

$Pt(1) \mid Fe^{3+}, Fe^{2+}(a=1) \mid\mid Ce^{4+}, Ce^{3+}(a=1) \mid Pt(2)$

$E°(Fe^{3+}/Fe^{2+}) = 0.77\ V, E°(Ce^{4+}/Ce^{3+}) = 1.61\ V$
If an ammeter is connected between the two platinum electrodes, predict the direction of flow of current. Will the current increase or decrease with time?
(IIT 2000) (Right to left, decrease)

573. Diborane is a potential rocket fuel which undergoes combustion according to the reaction,

$$B_2H_6(g) + 3O_2(g) \rightarrow B_2O_3(s) + 3H_2O(g).$$

From the following data, calculate the enthalpy change for the combustion of diborane.

(i) $2B(s) + \frac{3}{2}O_2(g) \rightarrow B_2O_3(s); \Delta H = -1273\ kJ\ mol^{-1}$

(ii) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l); \Delta H = -286\ kJ\ mol^{-1}$

(iii) $H_2O(l) \rightarrow H_2O(g); \Delta H = 44\ kJ\ mol^{-1}$

(iv) $2B(s) + 3H_2(g) \rightarrow B_2H_6(g); \Delta H = 36\ kJ\ mol^{-1}$ **(IIT 2000)** ($-2035\ kJ\ mol^{-1}$)

[Hint: Apply inspection method: (i) + 3 (ii) + 3 (iii) − (iv)]

574. The following solutions were mixed: 500 mL of 0.01 M $AgNO_3$ and 500 mL of a solution that was both 0.01 M in NaCl and 0.01 M in NaBr. Calculate $[Ag^+]$, $[Cl^-]$ and $[Br^-]$ in the equilibrium solution.
$K_{sp}(AgCl) = 1.0 \times 10^{-10}, K_{sp}(AgBr) = 5 \times 10^{-13}$ (2.0×10^{-8} M, 0.005 M, 2.5×10^{-5} M)

575. 1.1 g $CH_3(CH_2)_nCOOH$ was burnt in excess of air and the resultant gases ($CO_2 + H_2O$) were passed through a solution of NaOH. The resulting solution is divided into two equal parts. One part required 75 m.e. of HCl for neutralisation using phenolphthalein as indicator. The other part required 100 m.e. of HCl using methyl orange as indicator. Find *n*. (2)

576. The Mn_3O_4 formed on strong heating of a sample of $MnSO_4.4H_2O$ was dissolved in 100 cm^3 of 0.1 N $FeSO_4$ containing dilute H_2SO_4. The resulting solution reacted completely with 50 cm^3 of $KMnO_4$ solution. 25 cm^3 of this $KMnO_4$ solution required 30 cm^3 of 0.1 N $FeSO_4$ solution for complete reaction. Calculate the amount of $MnSO_4.4H_2O$ in the sample. (1.338 g)

[Hint: See Example 55, Chapter 7.]

577. Determine the number of moles of AgI which may be dissolved in 1.0 litre of 1.0 M CN^- solution. K_{sp} for AgI and K_f for $[Ag(CN)_2]^-$ are $1.2 \times 10^{-17}\ M^2$ and $7.1 \times 10^{19}\ M^{-2}$ respectively. (0.49 mole)

[Hint: $AgI \rightleftharpoons Ag^+ + I^-; K_{sp} = 1.2 \times 10^{-17}$

$Ag^+ + 2CN^- \rightleftharpoons Ag(CN)_2^-; K_f = 7.1 \times 10^{19}$

$\therefore\quad AgI + 2CN^- \rightleftharpoons Ag(CN)_2^- + I^-; K = K_{sp} \cdot K_f$

$(1-2x) \qquad x \qquad x$ (x-solubility of AgI)]

578. x g of a nonelectrolytic compound (molar mass = 200) are dissolved in 1.0 L of 0.05 M NaCl aqueous solution. The osmotic pressure of this solution is found to be 4.92 atm at 27°C. Calculate the value of x. Assume complete dissociation of NaCl and ideal behaviour of this solution. (19.9 g)

[**Hint:** $OP = \left(\frac{x}{200} + 2 \times 0.05\right) \times 0.0821 \times 300$]

579. 0.16 g of N_2H_4 are dissolved in water and the total volume made upto 500 mL. Calculate the percentage of N_2H_4 that has reacted with water in this solution. $K_b(N_2H_4) = 4.0 \times 10^{-6}$ M. (2%)

[**Hint:** $N_2H_4 + H_2O \rightarrow N_2H_5OH \rightleftharpoons N_2H_5^+ + OH^-$]

580. Determine the value of ΔE and ΔH for the reversible isothermal evaporation of 90.0 g of water at 100°C. Assume that water vapour behaves as an ideal gas and heat of evaporation of water is 540 cal g^{-1}. (44.87 kcal, 48.6 kcal)

581. 12.0 g of an impure sample of arsenious oxide was dissolved in water containing 7.5 g of sodium bicarbonate and the resulting solution was diluted to 250 mL. 25 mL of this solution was completely oxidised by 22.4 mL of a solution of iodine. 25 mL of this iodine solution reacted with same volume of a solution containing 24.8 g of $Na_2S_2O_3 \cdot 5H_2O$ in one litre. Calculate the percentage of arsenious oxide in the sample. (As = 75) (9.24%)

582. Two buffers, (X) and (Y) of pH 4.0 and 6.0 respectively, are prepared from acid HA and the salt NaA. Both the buffers are 0.50 M in HA. What would be the pH of the solution obtained by mixing equal volumes of the two buffers? $K_a(HA) = 1.0 \times 10^{-5}$. (5.70)

[**Hint:** Calculate [salt] in X and Y using Henderson equation. Find $[salt]_{mix}$ and again apply the same equation]

583. Calculate the value of $\log K_p$ for the reaction: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at 25°C. The standard enthalpy of formation of $NH_3(g)$ is –46 kJ and standard entropies of N_2, H_2 and NH_3 gases are 191, 130, 192 $JK^{-1}\ mol^{-1}$ respectively. (5.845)

[**Hint:** Apply $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ and $\Delta G^\circ = -2.303RT \log K_p$]

584. Determine the concentration of NH_3 solution, one litre of which can dissolve 0.10 mole AgCl. K_{sp} of AgCl and K_f of $Ag(NH_3)_2^+$ are $1.0 \times 10^{-10}\ M^2$ and $1.6 \times 10^7\ M^{-2}$ respectively. (2.7 M)

[**Hint:** 0.1 M Ag^+ combines with 0.2 M NH_3 to produce 0.1 M complex which then dissociates.

$AgCl \rightleftharpoons Ag^+ + Cl^-$; $K_{sp} = 1.0 \times 10^{-10}$

0.1 $\quad x \quad$ 0.1 M

$Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3$; $K_d = \frac{1}{1.6 \times 10^7}$

$(0.1 - x) \approx 0.1 \quad x \quad (2x + y) \approx y$

Total $[NH_3] = y + 0.2$].

585. At 817°C, K_p for the reaction between $CO_2(g)$ and excess hot graphite(s) is 10 atm

(a) What are equilibrium concentrations of the gases at 817°C and a total pressure of 5 atm.

(b) At what total pressure, the gas contains 5% CO_2 by volume?

[(a) 0.0167, 0.041 mole/L
(b) 0.554 atm]

586. 1.4 g of acetone dissolved in 100 g of benzene gave a solution which freezes at 277.12 K. Pure benzene freezes at 278.4 K. 2.8 g of a solid (A) dissolved in 100 g of benzene gave a solution which froze at 277.76 K. Calculate the molecular weight of (A). (232)

587. The rate law of the reaction is given as $2A + B \rightarrow \text{product}$

$$\text{Rate} = k[A]^2[B]$$

$[A]_{\text{Initial}}$	$[B]_{\text{Initial}}$	$t_{1/2}(s)$
3.0×10^{-4} M	4.0×10^{-5} M	60
3.0×10^{-4} M	6.0×10^{-5} M	x

Find x. (60 s)

[**Hint:** In a reaction with more than one reactant, $t_{1/2}$ of the limiting reactant is $t_{1/2}$ of the reaction.]

588. A 0.025-g sample of a compound that is composed of B and H, has a molecular mass of about 28 amu and burns spontaneously when exposed to air, producing 0.063 g of B_2O_3. Find the molecular formula of the compound. (B_2H_6)

589. Excited hydrogen atoms with very large radii have been detected. How large is an H atom with an electron characterised by a quantum number of 106? How many times larger is that than the radius of an H atom in its ground state?

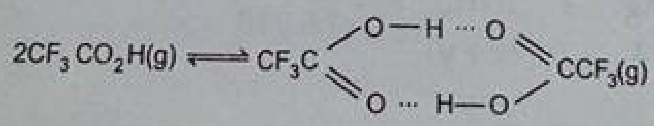
[11236 times larger (106^2)]

590. One molecule of haemoglobin will combine with four molecules of oxygen. If 1.0 g of haemoglobin combines with 1.53 mL of O_2 at body temperature (37°C) and a pressure of 743 torr, what is the molar mass of haemoglobin? (6.8×10^4 g mol^{-1})

591. What is the half-life for the decomposition of NOCl when the concentration of NOCl is 0.15 M? The rate constant for the reaction is 8.0×10^{-8} L mol^{-1} s^{-1}. (8.3×10^7 s)

592. If both the functional groups of salicylic acid, HOC_6H_4COOH, ionise in water, with $K_a = 1 \times 10^{-3}$ for the –COOH group and 4.2×10^{-13} for the –OH group, calculate pH of the saturated solution of the acid (solubility = 1.8 g/L)? (2.45)

593. The density of trifluoroacetic acid vapour was determined at 117°C and 470 mm and found to be 2.784 g/L. Calculate K_c for (17.09)



594. The following equilibria exist simultaneously in a vessel.

$$2NO_2(g) \rightleftharpoons N_2O_4(g);\ K_{p_1} = 6.8 \text{ atm}^{-1}$$

and $$NO(g) + NO_2(g) \rightleftharpoons N_2O_3(g);\ K_{p_2} \text{ (say)}$$

If initially only NO and NO_2 are present in 1 : 2 mole ratio and total pressure at equilibrium is 5.05 atm and the partial pressure of N_2O_4 is 1.7 atm, calculate the equilibrium partial pressure of NO and K_{P_2}. (1.05 atm, 3.43 atm^{-1})

[Hint: See Example 51, Chapter 15]

595. In a reaction of the type

$$A(s) + 2B(g) \rightleftharpoons C(g) + D(g),$$

the equilibrium concentrations of A, B, C and D are 1, 2, 5 and 6 mol/litre respectively. Argon is then introduced at equilibrium at constant volume. Calculate the concentrations of A, B, C and D at the new equilibrium position.

(Eqb. concs. do not change)

596. The rate law of the reaction given below is given as $2A + B \rightarrow$ product

Rate = $k[A]^2[B]$

$[A]_{Initial}$	$[B]_{Initial}$	$t_{1/2}$ (s)
5.0×10^{-6} M	3.0×10^{-4} M	400
10.0×10^{-6} M	3.0×10^{-4} M	x

(200 s)

Find x.

[Hint: In a reaction with more than one reactant, $t_{1/2}$ of the limiting reactant gives the $t_{1/2}$ of the reaction.]

597. (a) Nitric acid is prepared from ammonia in a three-step process.

(i) $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$ (fast)

(ii) $2NO + O_2 \rightarrow 2NO_2$ (slow)

(iii) $3NO_2 + H_2O \rightarrow 2HNO_3 + NO$ (fast)

Calculate how much HNO_3 can be produced from 10^5 kg of ammonia assuming 100% efficiency in each of the reactions.

(b) If equation (ii) is second-order in NO and first-order in O_2, calculate the rate of formation of HNO_3 when oxygen concentration is 0.50 M and the nitric oxide concentration is 0.75 M. $k = 5.8 \times 10^2$ L^6 mol^{-2} s^{-1}.

[(a) 2.47×10^5 kg (b) 1.63×10^{-6}]

598. The reaction of WCl_6 with Al at about 400°C gives black crystals of a compound that contains only tungsten and chlorine. A sample of this compound, when reduced with hydrogen gives 0.2232 g of tungsten metal and hydrogen chloride, which is absorbed in water. Titration of the hydrochloric acid thus produced required 46.2 mL of 0.1051-M NaOH to reach the end point. What is the empirical formula of the black tungsten chloride? (WCl_4)

599. When an electron in an excited molybdenum atom falls from L to K shell, an X-ray is emitted. These X-rays are diffracted at an angle of 7.75° by planes with a separation of 2.64 Å. What is the difference in energy in joules between the K shell and the L shell in Mo assuming a first-order diffraction? (2.79×10^{-15} J)

600. A bottle of milk stored at 300 K sours in 36 hours. When stored in a refrigerator at 275 K it sours in 360 hours. Calculate the energy of activation of the reaction involved in the souring process. (63.18 kJ/mol)

601. The rate constant for the first-order decomposition at 45°C of N_2O_5, dissolved in chloroform, is $6.2 \times 10^{-4}\ min^{-1}$. $2N_2O_5 \rightarrow 4NO_2 + O_2$

(a) What is the rate of decomposition when $[N_2O_5] = 0.40$ M?

(b) What are the rates of formation of NO_2 and of O_2 when $[N_2O_5] = 0.40$ M?

[(a) 2.5×10^{-4} (b) 5×10^{-4}, 1.2×10^{-4}]

602. A balloon weighing 50 kg has a radius of 10 m. What will be its payload if it is filled with He at 1 atm and 25°C. Density of air = 1.22 kg m^{-3}. Also calculate its payload if H_2 is filled in place of He. (4372.8 kg, 4715.4 kg)

[**Hint:** $pV = \frac{w}{M}RT$; w – wt. of He in g

$$\frac{\text{Wt. of balloon} + w'}{\text{Volume of balloon}} = \text{density of air}$$

w'–wt. of He for the balloon to just lift from the ground.

Payload $= (w' - w)$]

603. Calculate the coefficient of viscosity of CO_2 at 300 K on the basis of kinetic theory of gases. Molecular diameter for $CO_2 = 3.64 \times 10^{-10}$ m. (2.37×10^{-4} poise)

604. Show that the excluded volume is four times the actual volume of a molecule.

[**Hint:** Excluded volume per two molecules $= \frac{4}{3}\pi(2r)^3$]

605. A gas dimerizes to a small extent as

$$2A(g) = A_2(g)$$

Show that to a first approximation

$$\frac{pV}{RT} = 1 - \frac{K_c}{V}.$$

606. A vessel contains three gases A, B and C in the equilibrium

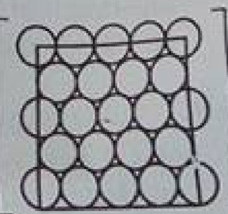
$$A \rightleftharpoons 2B + C$$

At equilibrium, the concentration of A was 3 M and that of B was 4 M. On doubling the volume of the vessel, the new equilibrium concentration of B was 3 M. Calculate K_c and the initial equilibrium concentration of C. (28.5, 5.4)

607. The average velocity of the molecules of a gas is 400 m/s. Calculate its rms velocity at the same temperature. (434.26 m/s)

608. The wavelength of high energy transition of H-atoms is 91.2 nm. Calculate the corresponding wavelength of He atoms. (22.8 nm)

609. You are given marbles of diameter 10 mm. They are to be placed such that their centres lie in a square bound by four lines, each of length 40 mm. What will be the arrangements of marbles in a plane so that maximum number of marbles can be placed inside the area? Draw the diagram and derive expressions for the number of molecules per unit area.

[]

610. 1 g of charcoal adsorbs 100 mL of 0.5 M CH_3COOH to form a monolayer, and thereby the molarity of CH_3COOH reduces to 0.49. Calculate the surface area of the charcoal adsorbed by each molecule of acetic acid. Surface area of charcoal $= 3.01 \times 10^2\ m^2/g$.

($5 \times 10^{-19}\ m^2/\text{molecule}$)

[**Hint:** No. of molecules of CH_3COOH adsorbed $= 0.001 \times$ Av. constant]

611. Two students use the same stock solution of $ZnSO_4$ and a solution of $CuSO_4$. The emf of one cell is 0.03 V higher than the other. The concentration of $CuSO_4$ in the cell with higher emf value is 0.5 M. Find out the concentration of $CuSO_4$ in the other cell $\left(\frac{2.303\,RT}{F} = 0.06\right)$.

(0.05 M)

612. Match the following if the molecular weights of X, Y and Z are the same.

	Boiling point	K_b
X	100	0.68
Y	27	0.53
Z	253	0.98

(Same as given)

613. The C_V value of He is always $3R/2$ but the C_V value of H_2 is $3R/2$ at low temperatures and $5R/2$ at moderate temperatures and more than $5R/2$ at higher temperatures. Explain.

[Rotational and vibrational degrees of freedom for diatomic molecules contribute towards C_V at high temperature.]

614. At 298 K, the inversion of sucrose proceeds with constant half-life of 500 min at pH = 5 and with half-life of 50 min at pH = 4 for any concentration of sucrose. If the rate law for the reaction is given by

$$-\frac{d\,[\text{sucrose}]}{dt} = k\,[\text{sucrose}]^x\,[H^+]^y$$

(1, 1)

find x and y.

615. Calculate the equilibrium pressure for the conversion of graphite to diamond at 25°C. The densities of graphite and diamond may be taken to be 2.25 and 3.51 g/cc respectively, independent of pressure. The change in ΔG with pressure is $-2900\ J\ mol^{-1}$

(1.52×10^9 Pa)

[**Hint:** $\Delta G = -S\Delta T + V\Delta p$; $\int_1^2 d\,\Delta G = \int_{p_1}^{p_2} \Delta V\, dp$, $p_2 = \frac{\Delta G_2 - \Delta G_1}{\Delta V} + p_1$]

616. For the given reaction: $A + B \rightarrow$ products, the following data were given.

Initial concentration (mol/L) [A]	Initial concentration (mol/L) [B]	Initial rate ($mol\ L^{-1}\ s^{-1}$)
0.1	0.1	0.05
0.2	0.1	0.1
0.1	0.2	0.05

(a) Write the rate equation.

(b) Calculate the rate constant.

(Rate $= k[A][B]^0$, $k = 0.5\ s^{-1}$)

[**Hint:** See Example 27, Chapter 17]

617. 100 mL of a liquid is contained in an isolated container at a pressure of 1 bar. The pressure is steeply increased to 100 bar. The volume of the liquid is decreased by 1 mL at this constant pressure. Find ΔH and ΔU. $(0, 10^{-2}\ \text{kJ})$

[Hint: $\Delta H = \Delta E + p\Delta V$, $(E \equiv U)$

$\Delta H = 0, \Delta E = -p\Delta V$

$1\ \text{atm} \cdot \text{mL} = 10^{-4}\ \text{kJ}$]

618. The crystal AB (rock-salt structure) has molecular weight $6.023y$ amu, where y is an arbitrary number in amu. If the minimum distance between the cation and anion is $y^{1/3}$ nm and the observed density is $20\ \text{kg/m}^3$, find (a) density in kg/m^3, and (b) type of defect. $(5\ \text{kg/m}^3$, metal excess)

[Hint: $\rho = \dfrac{zM}{NV}$; $z = 4, V = (2\,y^{1/3} \times 10^{-9})^3\ \text{m}^3$

$M = 6.023\,y \times 10^{-3}\ \text{kg/mol}$

Observed density $(20\ \text{kg/m}^3)$ is greater than calculated density.]

619. (a) The Schrödinger equation for the hydrogen atom is

$$\psi_{2S} = \frac{1}{4(2\pi)^{1/2}}\left(\frac{1}{a_0}\right)^{3/2}\left(2 - \frac{r}{a_0}\right)e^{-r/2a_0}$$

where a_0 is Bohr's radius. If the radial node in 2 s is at r then find r in terms of a_0.

(b) A baseball having a mass of 100 g moves with velocity 100 m/s. Find out the value of the wavelength of the baseball.

(c) ${}^{234}_{92}X \xrightarrow[-6\beta]{-7\alpha} Y$. Find out the atomic number and mass number of Y and identify it. [(a) $2a_0$ (b) 6.626×10^{-25} m (c) ${}^{206}_{84}\text{Po}$]

[Hint: (a) $\psi^2 = 0$ at node $\therefore \left(2 - \dfrac{r}{a_0}\right)$ has to be zero.

(b) Apply $\lambda = \dfrac{h}{mv}$.]

620. (a) In the following equilibrium

$$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$$

When 5 mole of each are taken, the temperature is kept at 298 K. The total pressure was found to be 20 bar. Given: $\Delta G_f^0(N_2O_4) = 100$ kJ and $\Delta G_f^0(NO_2) = 50$ kJ,

(i) find ΔG of the reaction, and

(ii) the direction of the reaction in which the equilibrium shifts.

(b) A graph is plotted for a real gas which follows van der Waals equation with pV_m taken on the y-axis and p on the x-axis. Find the intercept and the slope of the line. V_m is the molar volume.

((a) +56.03 L atm, reverse
(b) RT and $-\dfrac{a}{RT}$)

[**Hint:** (a) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ ... initial(1 bar ≈ 1 atm)
10 bar   10 bar

Reaction quotient $(Q) = \frac{10^2}{10} = 10$ bar

$\Delta G^0 = 2 \times 50 - 100 = 0$

Apply $\Delta G = \Delta G^0 + 2.303\,RT \log Q$.

(b) To determine the intercept and the slope, the pressure has to be very low tending to zero and in such a condition, the volume would be sufficiently large, and b in van der Waals equation could be neglected.

$$\left(p + \frac{a}{V^2}\right)V = RT$$

$$pV = -\frac{a}{RT} \cdot p + RT$$]

621. (a) 1.22 g C_6H_5COOH is added to two solvents.

(i) In 100 g CH_3COCH_3 : $\Delta T_b = 0.17$, $K_b = 1.7$ kg K mol^{-1}

(ii) In 100 g C_6H_6 : $\Delta T_b = 0.13$, $K_b = 2.6$ kg K mol^{-1}

Find out the molecular weight of C_6H_5COOH in both the solvents and interpret the result.

(b) If 0.1 M HA is titrated with 0.1 M NaOH, calculate the pH at the end point. $K_a(HA) = 5 \times 10^{-6}$ and $\alpha << 1$.

((a) (i) 122 (ii) 244, C_6H_5COOH dimerises in C_6H_6
(b) 9)

[**Hint:** (a) Apply $\Delta T_b = K_b \cdot m$ in both cases.

(b) Apply $pH = \frac{1}{2}\{pK_w + pK_a + \log a\}$, $a = \frac{0.1}{2}$ M]

622. Find the equilibrium constant for the reaction

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

given that, $E^0_{Cu^{2+}, Cu^+} = 0.15$ V

$E^0_{In^{2+}, In^+} = -0.4$ V

$E^0_{In^{3+}, In^+} = -0.42$ V (10^{10})

[**Hint:** Example 11, Chapter 18]

623. Fill in the blanks.

(a) ${}^{235}_{92}U + {}^{1}_{0}n \rightarrow {}^{137}_{52}A + {}^{97}_{40}B + \ldots$ [(a) $2\,{}^{1}_{0}n$ (b) ${}^{82}_{36}Kr$]

(b) ${}^{82}_{34}Se \rightarrow 2\,{}^{0}_{-1}e + \ldots$

624. Calculate the amount of calcium oxide required when it reacts with 852 g of P_4O_{10}.   (1008 g)

[**Hint:** $CaO + P_4O_{10} \rightarrow Ca_3(PO_4)_2$
Apply POAC for Ca and P atoms.]

625. An element crystallizes in f.c.c. lattice having edge length 400 pm. Calculate the maximum diameter of the atom which can be placed in the interstitial site without distorting the structure.   (117.1 pm)

[Hint: See pg. 711 and Eqn. 4 on pg. 706.

$r = 0.414\,R$ and $R = \frac{\sqrt{2}a}{4}$]

626. 20% surface sites have adsorbed N_2. On heating, N_2 gas evolved from sites and was collected at 0.001 atm and 298 K in a container of volume 2.46 cm^3. The density of surface sites is $6.023 \times 10^{14}/cm^2$. Density of surface area is 1000 cm^2. Find out the number of surface sites occupied per molecule of N_2. (2)

[Hint: No. of surface sites per molecule of N_2

$$= \frac{\text{no. of surface sites used to adsorb } N_2 \text{ on a surface area of } 1000\ cm^2}{\text{total no. of adsorbed molecules}}]$$

627. For the reaction: $2X\,(g) \rightarrow 3Y\,(g) + 2Z\,(g)$

Time (min)	0	100	200
p_x (mm Hg)	800	400	200

Assuming ideal gas condition, calculate
(a) order of the reaction
(b) rate constant
(c) time taken for 75% completion of reaction
(d) total pressure when $p_X = 700$ mm

((a) 1, (b) $3.46 \times 10^{-3}\ min^{-1}$ (c) 200 min (d) 950 mm)

[Hint: (a) $\because t_{1/2}$ is constant, order is one. (b) $k = \frac{0.6932}{2t_{1/2}}$

(b) Time for 75% completion of the reaction $= 2t_{1/2}$

(c) $\underset{(800-p)\text{mm}}{\overset{800\text{ mm}}{2X}} \rightarrow \underset{\frac{3p}{2}\text{mm}}{3Y} + \underset{p\text{ mm}}{2Z}$; $800 - p = 700$]

628. (a) Calculate the velocity of electrons in the first Bohr orbit of hydrogen atom. $r = a_0 = 0.53 \times 10^{-10}$ m.
(b) Find the de Broglie wavelength of the electron in the first orbit.
(c) Find the orbital angular momentum of the 2p orbital in terms of $h/2\pi$ units.

((a) 2.18×10^6 m/s (b) 3.3×10^{-10} m (c) $\sqrt{2}\,\frac{h}{2\pi}$)

[Hint: (a) $mvr = \frac{nh}{2\pi}$; $n = 1$

(b) $\lambda = \frac{h}{mv}$

(c) For 2p, $l = 1$; $L = \sqrt{l(l+1)} \cdot \frac{h}{2\pi}$ (pg. 247)]

629. (a) Calculate ΔG^0 for the following reaction.

$$Ag^+\,(aq) + Cl^-\,(aq) \rightarrow AgCl\,(s)$$

Given: $\Delta G_f^0\,(AgCl) = -109$ kJ/mol

$$\Delta G_f^0(Cl^-) = -129 \text{ kJ/mol}$$
$$\Delta G_f^0(Ag^+) = 77 \text{ kJ/mol}$$

Represent the above reaction in the form of a cell. Also calculate E^0 of the cell and find $\log K_{sp}$ of AgCl.

(b) 6.539×10^{-2} g of metallic Zn (65.39 amu) was added to 100 mL of saturated solution of AgCl. Calculate $\log([Zn^{2+}]/[Ag^+]^2)$.

Given: $Ag^+ + e = Ag;\ E^0 = 0.80$ V

$Zn^{2+} + 2e = Zn;\ E^0 = -0.76$ V

Also find how many moles of Ag will be formed.

((a) $Ag \mid Ag^+(aq), AgCl(s), Cl^-(aq) \mid Cl_2(g)$, 0.59 V, −10
(b) 52.79, 10^{-6} mol)

[**Hint:** (a) For $Ag^+ + Cl^- = AgCl;\ \Delta G^0 = -109 - (-129 + 77)$

$\Delta G^0 = -nFE^0$ and $\Delta G^0 = -2.303\, RT \log K$

Calculate K and then apply $K_{sp}(AgCl) = \dfrac{1}{K}$

(b) $2Ag^+ + Zn = 2Ag + Zn^{2+};\ E^0_{cell} = 0.80 - (-0.76) = 1.56$ V

Apply $E^0_{cell} = \dfrac{0.0591}{2}\log([Zn^{2+}]/[Ag^+]^2)$

Again, $K_{sp}(AgCl) = [Ag^+][Cl^-] = S^2$

$S = \sqrt{10^{-10}} = 10^{-5}$ mol/L

$\therefore$ mol of Ag^+ per 100 mL $= 10^{-6}$

and mol of $Zn = \dfrac{6.539 \times 10^{-2}}{65.39} = 10^{-3}$

As Ag^+ is the limiting reactant and the cell reaction is feasible in the forward direction, mole of Ag formed $= 10^{-6}$.]

630. The electrode potential of the half-cell $Ag \mid AgCl \mid Cl^-$ (1 M) is 0.22 V. What should be the electrode potential $(E_{Ag^+,Ag})$ of the same half-cell if represented as $Ag \mid Ag^+, AgCl, Cl^-$ (1 M)? (same)

□□□

MISCELLANEOUS OBJECTIVE QUESTIONS

1. The degree of dissociation of 100 mL of pure water at 25°C is
   (a) 1.8×10^{-16} (b) 1×10^{-14} (c) 1.8×10^{-9} (d) 1.0
2. The pH of 10^{-8} M NaOH aqueous solution at 25°C is
   (a) 7.02 (b) 7.0 (c) 6.89 (d) 6.0
3. The effect of temperature on the equilibrium constant is given by
   (a) $\log K_{p_2} - \log K_{p_1} = \frac{H}{2.303\,R} \cdot \frac{(T_2 - T_1)}{T_1 T_2}$
   (b) $\log k_2 - \log k_1 = \frac{E}{2.303\,R} \cdot \frac{(T_2 - T_1)}{T_1 T_2}$
   (c) $\log K_{p_2} - \log K_{p_1} = \frac{\Delta H}{2.303} \cdot \frac{(T_2 - T_1)}{T_1 T_2}$
   (d) none of these
4. The rate constant of a first-order reaction of the type $2A \rightarrow P$ is $1.5 \times 10^{-4}\ s^{-1}$. The half-life period of the reaction is
   (a) 2.31×10^3 s (b) 4.62×10^3 s (c) 9.24×10^3 s (d) 1.5×10^{-4} s
5. For the following reaction:
   Initial concentration: 10 mol/L 2 mol/L
   $2A + B \rightarrow$ product
   $t_{1/2}$ of the overall reaction is the time when
   (a) half of A changes to product
   (b) half of B changes to product
   (c) half of each of A and B changes to product
   (d) 6 moles of A and B changes to product
6. From the following half cells a galvanic cell is made,
   $A^{2+} + 2e = A \quad \ldots \quad E_1^0 = 0.8$ V
   $B = B^{3+} + 3e \quad \cdots \quad E_2^0 = -0.3$ V
   E^0 cell is
   (a) $E_1^0 - E_2^0$ (b) $E_1^0 + E_2^0$ (c) $3E_1^0 - 2E_2^0$ (d) $3E_1^0 + 2E_2^0$
7. An inert gas is added to the following equilibrium,
   $A(s) + 2B(g) \rightleftharpoons 3C(g)$
   at constant pressure. The equilibrium
   (a) is not affected (b) shifts to right
   (c) shifts to left (d) may shift right and left both
8. The rate of the process: $Cu \rightarrow Ni + {}_{+1}^{0}e$
   (a) changes with the change in pressure

(b) changes with the change in temperature
(c) changes with the change in pressure and temperature
(d) is independent of pressure and temperature

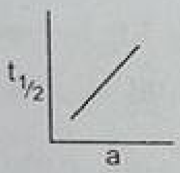
9. In a successive radioactive disintegration

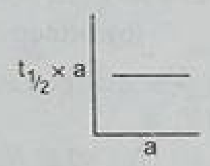
$$\underset{N_1}{A} \xrightarrow{\lambda_1} \underset{N_2}{B} \xrightarrow{\lambda_2} C \quad \text{... no. of nuclides after time } t.$$

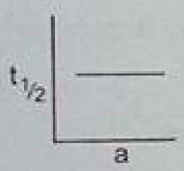
in which the parent has a longer but not much longer half-life than the daughter. Which of the following expressions is correct?

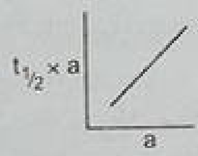
(a) $\frac{N_1}{N_2} = \frac{\lambda_2}{\lambda_1}$ (b) $\frac{N_1}{N_2} = \frac{\lambda_2 - \lambda_1}{\lambda_1}$ (c) $\frac{N_1}{N_2} = \frac{\lambda_1}{\lambda_2}$ (d) $\frac{N_1}{N_2} = \frac{\lambda_2 - \lambda_1}{\lambda_2}$

10. Which of the following curves represents a second-order reaction? ('a' is the concentration of the reactant)

(a)


(b)


(c)


(d)


11. For the equilibrium:

0.5 M	0	0	... Initial concentration
$PCl_5(g)$ $\rightleftharpoons$	$PCl_3(g)$ +	$Cl_2(g)$	
0.3 M	0.2 M	0.2 M	... Equilibrium concentration

the degree of dissociation of PCl_5 is

(a) 0.2 (b) 0.01 (c) 0.1 (d) 0.4

12. The degree of hydrolysis of a salt of weak acid and strong base is ≈ 0.5. The equation to be used to calculate the accurate value of the degree of hydrolysis (h) is

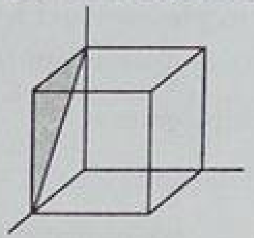
(a) $h = \sqrt{\frac{K_w}{K_a \cdot K_b}}$ (b) $h = \sqrt{\frac{K_w}{K_a \cdot C}}$

(c) $h = \sqrt{\frac{K_w}{K_b \cdot C}}$ (d) none of these

13. For $CuSO_4 \cdot 5H_2O$, which is the correct mole relationship?

(a) $9 \times$ mole of Cu = mole of O
(b) $5 \times$ mole of Cu = mole of O
(c) $9 \times$ mole of Cu = mole of O_2
(d) Mole of Cu = $5 \times$ mole of O

14. The shaded plane in the simple cubic crystal is designated by



(a) (101) (b) (100) (c) (111) (d) (010)

15. If a reaction is represented by

$2A + 3B \rightarrow$ product

(a) the order of the reaction w.r.t. A and B may be 2 and 3 respectively
(b) the molecularity may be 5
(c) both order and molecularity are same
(d) the choices (a), (b) and (c) are wrong

16. The crystal with $a \neq b \neq c; \alpha = \beta = \gamma = 90°$ is

(a) cubic (b) orthorhombic (c) tetragonal (d) hexagonal

17. The reduction potential of $Cu^{2+}|Cu$ at pH = 14, if $K_{sp}(Cu(OH)_2) = 1 \times 10^{-19}$ and $E^0_{Cu^{2+}, Cu} = +0.34$ V, is

(a) −0.22 V (b) +0.22 V (c) 0.059 V (d) −0.059 V

18. What is the thermodynamic condition for the feasibility of a process?

(a) $(\Delta S)_{sys} > 0$ (b) $(\Delta G)_{sys} > 0$
(c) $(\Delta S)_{sys} + (\Delta S)_{surr} > 0$ (d) $(\Delta G)_{sys} + (\Delta G)_{surr} < 0$

19. If m_0 is the initial mass of the nuclei, the mass of undecayed radioactive isotope at the end of the nth half-life is

(a) $2^n m_0$ (b) $2^{-n} m_0$ (c) $n^{-2} m_0$ (d) $n^2 m_0$

20. Dry air is bubbled successively through (i) a solution, (ii) its solvent, and (iii) through $CaCl_2$. The lowering of vapour pressure of the solvent due to the addition of solute is equal to

(a) $p^0 \times \dfrac{\text{loss in wt. of solvent}}{\text{gain in wt. of } CaCl_2}$ (b) $\dfrac{\text{loss in wt. of solvent}}{\text{gain in wt. of } CaCl_2}$

(c) $\dfrac{\text{loss in wt. of solution}}{\text{gain in wt. of } CaCl_2}$ (d) $\dfrac{\text{loss in wt. of solute}}{\text{gain in wt. of } CaCl_2}$

21. The number of 2-fold axis of symmetry in a cubic crystal is

(a) 10 (b) 13 (c) 23 (d) 9

22. The nuclide lying below the stability belt in n-p graph does not disintegrate by

(a) α-emission (b) ${}^{0}_{-1}\beta$-emission
(c) ${}^{0}_{+1}\beta$-emission (d) K-electron capture

23. The osmotic pressure of glucose solution (400 mm), on dilution, decreased to 100 mm. The extent of dilution is

(a) two times (b) four times (c) one-fourth times (d) eight times

24. The molal depression constant for water is 1.86. The depression constant for 100 g of H_2O is

(a) 1.86 (b) 18.6 (c) 0.186 (d) 186

25. Urea is added to 2 litres of water to such an extent that $\Delta T_b / K_b$ becomes equal to 1/100. The weight of urea added is
(a) 0.6 g (b) 6.0 g (c) 12 g (d) 1.2 g

26. The equilibrium partial pressure of N_2, H_2 and NH_3 are 4, 4 and 8 atm respectively. The value of K_p for the Haber's process in atm^{-1} is
(a) 1/4 (b) 1/2 (c) 4 (d) 2

27. 5 moles of a gas occupy 100 litres at NTP. The compressibility factor of the gas is
(a) < 1 (b) > 1 (c) 1 (d) 0

28. A gas absorbs 400 J of heat and expands by 2×10^{-2} m^3 against a constant pressure 1×10^5 Pa. The internal energy of the gas is
(a) 200 J (b) –200 J
(c) 600 J (d) cannot be calculated

29. 4 g of He is expanded from 1 litre to 10 litres isothermally. The change in entropy is
(a) 19.15 J/K (b) 76.6 J/K (c) –19.15 J/K (d) –76.6 J/K

30. 1.5 moles of electrons are passed through 1 litre of 1 M Fe^{3+} solution. The number of moles of Fe produced is
(a) 0.25 (b) 0.50 (c) 1.0 (d) 1.5

31. In which case, a reaction is impossible at any temperature?
(a) $\Delta H > 0, \Delta S > 0$ (b) $\Delta S > 0, \Delta S < 0$
(c) $\Delta S < 0, \Delta S < 0$ (d) In all cases

32. The molecular weight of NaCl (degree of diss. $= x$) determined by the osmotic pressure method, is found to be different from its actual molecular weight (M). Which of the following relationships is correct?
(a) Obs. mol. wt. $= (1 + x) M$ (b) $M = (1 + x) \times$ obs. mol. wt.
(c) Obs. mol. wt. $= x \times M$ (d) $M = x \times$ obs. mol. wt.

33. Which of the following equations gives the combined form of the first and second laws of thermodynamics?
(a) $q = \Delta E - w$ (b) $\Delta E = T\Delta S - p\Delta V$
(c) $\Delta S = \frac{q}{T}$ (d) $\Delta H = \Delta E + \Delta n_g RT$

34. For a real gas at a given temperature, which of the following facts is not correct?
(a) pV may increase with the increase in pressure
(b) pV may decrease with the increase in pressure
(c) pV will not change with the change in pressure
(d) p/V will increase with the increase in pressure

35. The heat capacity of air is 20 J/K/mol. The amount of heat, required to heat the room through 1°, assuming the amount of air in the room to be 29 kg, is
(a) 20 kJ (b) –20 J (c) 200 J (d) –200 kJ

36. The molarity of 4 N H_2SO_4 in the following reaction is
$$8H^+ + H_2SO_4 + 8e^- \rightarrow H_2S + 4H_2O$$
(a) 2 M (b) 8 M (c) 32 M (d) 0.5 M

37. Phenol associates in benzene to produce double molecules. To what degree phenol associates if van't Hoff factor is 0.54?
(a) 0.54 (b) 0.92 (c) 0.98 (d) 0.46

38. A mixture of He(4) and Ne(20) in a 5-litre flask at 300 K and 1 atm weighs 4 g. The mole % of He is
(a) 2 (b) 0.02 (c) 20 (d) 4

39. The pH of the solution when 0.2 mole of HCl is added to one litre of a solution containing 0.1 M CH_3COOH and 0.1 M CH_3COO^- is
(a) 0.7 (b) 4.57 (c) 3.8 (d) 1.0

40. 100 mL of an O_2-O_3 mixture was passed through turpentine, and 20 mL was reduced. If 100 mL of such a mixture is heated, the increase in volume will be
(a) 110 mL (b) 10 mL (c) 90 mL (d) 100 mL

41. Which of the relationships is wrong?
(a) rms speed $\propto \sqrt{p}$ (b) Diffusion rate $\propto p$
(c) Diffusion rate $\propto T$ (d) rms speed $\propto \sqrt{T}$

42. The heats evolved and absorbed when 100 g each of $CuSO_4$ and $CuSO_4 \cdot 5H_2O$ are dissolved in water are 41.7 and 4.7 kJ/mole respectively. The heat of hydration of $CuSO_4$ is (in kJ/mole)
(a) –66.59 (b) +11.72 (c) –78.2 (d) +78.2

43. The energy of the second Bohr orbit of the hydrogen atom is –3.41 eV. The energy of the third Bohr orbit of the He^+ ion will be
(a) –30.69 eV (b) –13.64 eV (c) –7.67 eV (d) –6.06 eV

44. It requires 40 mL of 0.5 M Ce^{4+} to titrate 10 mL of 1.0 M Sn^{2+} to Sn^{4+}. The oxidation state of Ce in the reduction product is
(a) +2 (b) +3 (c) +6 (d) none

45. From the following reaction sequences

$$2A = B + C$$
$$5B + D = 2E + F$$
$$E + G = 4H + J$$

calculate moles of H produced by 10 moles of A
(a) 20 (b) 10 (c) 5 (d) 8

46. If T_1 and T_2 are the temperatures of the heat source and sink respectively, the efficiency of a heat engine may be expressed as
(a) $\frac{T_2 - T_1}{T_2}$ (b) $\frac{T_1}{T_2}$ (c) $\frac{T_1 - T_2}{T_1}$ (d) $\frac{T_2}{T_1}$

47. Which of the following, when mixed, will give a solution with pH greater than 7?
(a) 0.1 M HCl + 0.2 M NaCl
(b) 100 mL of 0.2 M H_2SO_4 + 100 mL of 0.3 M NaOH
(c) 100 mL of 0.1 M $C_2H_4O_2$ + 100 mL of 0.1 M KOH
(d) 100 mL of 0.1 M HCl + 100 mL of 0.1 M $NaC_2H_3O_2$

48. In the reaction:

$$\overset{3}{A} + \overset{2}{2B} + + \overset{1}{3C} \longrightarrow D \quad \text{... initial no. of moles}$$

the limiting reactant may be

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

49. An element forms two oxides, the weight-ratio composition in them is $A:O = x:y$ in the first oxide and $y:x$ in the second oxide. If the equivalent weight of A in the first oxide is 10.33, the equivalent weight of A in the second oxide is

(a) 6.2 (b) 10.33 (c) x/y (d) y/x

50. For the cell: $A \mid A^{m+} \mid\mid B^{n+} \mid B$; $E_{cell} = -1.1$ V

(a) right electrode is cathode

(b) the cell shall not operate

(c) left electrode is cathode

(d) electrons flow from left to right in the external circuit

51. Which of the following concepts is (are) wrong?

(a) If for, $A \rightarrow B$ $\Delta H = +q$ cal

then for, $B \rightarrow A$ $\Delta H = -q$ cal

(b) If for, $A \rightleftharpoons B$ eqb. constant $= K$

then for, $B \rightleftharpoons A$ eqb. constant $= \frac{1}{K}$

(c) If for, $A \rightarrow B$ rate constant $= k$

then for, $B \rightarrow A$ rate constant $\neq k$

(d) If for, $A \rightarrow B$ energy of activation $= E$

then for, $B \rightarrow A$ energy of activation $= -E$

52. The wrong statement is

(a) heat of neutralisation is always negative

(b) resonance energy is always negative

(c) heat of atomisation is always positive

(d) heat of combustion is always negative

53. Choose the correct answers for a given amount of hydrogen.

(a) Mole of H_2 = mole of H (b) Eq. of H_2 = eq. of H

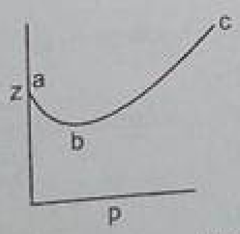
(c) Mole of H_2 = eq. of H_2 (d) Mole of H = eq. of H

54. 5 moles of H_2SO_4 contain

(a) 5 eq. of H (b) 5 moles of S

(c) 20 eq. of O (d) 10 eq. each of H, S and O

55. In the figure representing variation of the compressibility factor Z of a real gas with pressure



(a) ab shows that the gas is more compressible than an ideal gas

(b) *bc* shows that the gas is less compressible than an ideal gas

(c) *ab* may be explained by $p\bar{V} = RT - \frac{a}{\bar{V}}$

(d) *bc* may be explained by $p\bar{V} = RT + pb$

56. Which of the following galvanic cells has no liquid-junction potential?

(a) $Zn - Hg \mid ZnSO_4$ solution $\mid Zn - Hg$
(C_1) (C_2)

(b) $Cu \mid CuSO_4$ solution $\vdots$ $CuSO_4$ solution $\mid Cu$
(C_1) (C_2)

(c) $Ag \mid AgCl \mid HCl$ solution $\vdots$ HCl solution $\mid AgCl \mid Ag$
(C_1) (C_2)

(d) $Zn \mid ZnSO_4$ solution $\mid\mid ZnSO_4$ solution $\mid Zn$
(C_1) (C_2)

57. In the Nernst equation, we substitute

$$\frac{2.303RT}{F} = 0.0591$$

where,

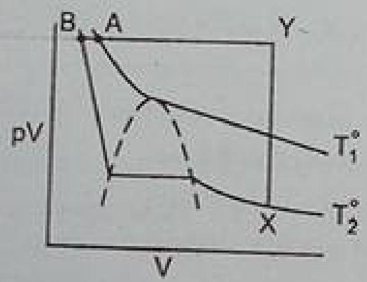
(a) $R = 8.314$ J, $T = 273$ K and $F = 96500$ C

(b) $R = 0.0821$ L. atm, $T = 298$ K and $F = 96500$ C

(c) $R = 8.314$ J, $T = 298$ K and $F = 96500$ C

(d) $R = 2.0$ cal, $T = 298$ K and $F = 1$ C

58. A gas at $T_2°$ is condensed to liquid following the path XYAB. The liquid appears at the point



(a) Y at $T_2°$ (b) A at $T_2°$ (c) B at $T_1°$ (d) A at $T_1°$

59. For the electrode process,

$$H^+ + e = \frac{1}{2}H_2;\ E_{H^+, H_2} = x \text{ volt}$$

then for $2H^+ + 2e = H_2;\ E_{2H^+, H_2}$ is equal to

(a) x volt (b) $2x$ volt (c) $\frac{x}{2}$ volt (d) 0 volt

60. For the cell:

$Cu(10\ g) \mid CuSO_4$ solution $\mid\mid ZnSO_4$ solution $\mid Zn(10\ g)$, $E_{cell} = E$ V
(C_1) (C_2)

E_{cell} for the cell: $Cu(20\ g) \mid CuSO_4$ solution $\mid\mid ZnSO_4$ solution $\mid Zn(20\ g)$, is
(C_1) (C_2)

(a) E volt (b) $2E$ volt (c) $\frac{E}{2}$ volt (d) 1.1 volt

61. In an electrolysis process, 10 electrons could deposit x kg of a univalent metal M. The atomic weight of M is (N is Avogadro constant.)
(a) $x \times N$ (b) $x \times N \times 10^3$ (c) $x \times N \times 10^2$ (d) $x \times 10^3$

62. If a gas gets half compressed, compared to an ideal gas, the compressibility factor Z is equal to
(a) 1 (b) 2 (c) ½ (d) none of these

63. The temperature at which the second virial coefficient of a real gas is zero is called
(a) critical temperature (b) eutectic point
(c) boiling point (d) Boyle temperature

64. A gaseous mixture of 2 moles of A, 3 moles of B, 5 moles of C and 10 moles of D is contained in a vessel. Assuming that the gases are ideal and the partial pressure of C is 1.5 atm, the total pressure is
(a) 3 atm (b) 6 atm (c) 9 atm (d) 15 atm

65. The maximum efficiency of a steam engine operating between 100°C and 25°C is
(a) 20% (b) 22.2% (c) 25% (d) 30%

66. The entropy change accompanying the evaporation of 1 mole of water at 100°C, assuming that the latent heat of vaporisation of water is 540 cal g^{-1}, in cal/K/mole is
(a) 20 (b) 25 (c) 26.06 (d) 30

67. The compressibility factor of a van der Waals gas at the critical point is equal to
(a) 0 (b) 1 (c) 0.375 (d) any value

68. The equivalent volume of CO_2 in the following reaction is

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$$

(a) 22.4 litres (b) 11.2 litres (c) 5.6 litres (d) 22 litres

69. The equivalent volume of CO_2 in the following reaction is

$$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$$

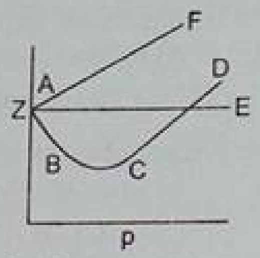
(a) 22.4 litres (b) 11.2 litres (c) 5.6 litres (d) 44 litres

70. One coulomb is the charge of
(a) 1 mole of electrons (b) $\frac{1}{96500}$ mole of electrons
(c) 96500 moles of electrons (d) none of these

71. For a zero-order reaction, with the initial reactant concentration a, the time for completion of the reaction is
(a) k/a (b) a/k (c) $2k/a$ (d) $a/2k$

72. Which statement(s) about the behaviour of a real gas is (are) wrong?
(a) A gas exerts more pressure compared to an ideal gas
(b) A gas can be compressed more compared to an ideal gas
(c) A gas with high value of van der Waals constant, a, is highly liquefiable
(d) H_2 and He are less compressible compared to an ideal gas at ordinary temperature

The figure shows the effect of pressure on the compressibility factor, Z, of a gas.



The wrong conclusion(s) is (are),

(a) the curves AE and BC can be explained by $pV = RT$

(b) the curves AF and CD can be explained by $pV = RT + Pb$

(c) the curve AB can be explained by $pV = RT - \frac{a}{V}$

(d) all the three curves AF, AE and AD show the real gas behaviour

74. Equivalent weights of CO_2 in the following reactions

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$$

and
$$NaHCO_3 + HCl = NaCl + H_2O + CO_2$$

are respectively,

(a) 22 & 44 (b) 44 & 22 (c) 44 & 44 (d) 22 & 22

75. According to Faraday's laws of electrolysis, the discharge of one electrochemical equivalent of ions should involve

(a) 1 mole of electrons (b) 96500 moles of electrons

(c) $\frac{1}{96500}$ mole of electrons (d) none of these

76. In which of the following cases a gas is more compressible than the ideal gas?

(a) $p\overline{V} > RT$ (b) $p\overline{V} = RT$ (c) $p\overline{V} < RT$

77. In the electrolysis of aq. $CuSO_4$ solution with Pt electrodes, using 1 F of electricity, which of the following processes shall occur?

(a) 1 eq. of Cu is deposited at the cathode

(b) 1 eq. of O_2 is liberated at the anode

(c) 1 eq. of OH^- is discharged at the anode

(d) 1 eq. of H_2SO_4 is produced

78. On electrolysis of 500 mL of an aqueous solution of NaCl, NaOH is produced, the normality of which is found to be N/2. The number of faradays used is

(a) 0.25 (b) 250 (c) 500 (d) 1000

79. 10% of a reactant decomposes in 1 hour, 20% in 2 hours and 30% in 3 hours. The order of the reaction is

(a) 0 (b) 1 (c) 2 (d) 3

80. One way of writing the equation of state for real gases is

$$p\overline{V} = RT\left[1 + \frac{B}{\overline{V}} + \dots\right]$$

The constant B is equal to

(a) $\left(a - \frac{b}{RT}\right)$ (b) $\left(a + \frac{b}{RT}\right)$ (c) $\left(b + \frac{a}{RT}\right)$ (d) $\left(b - \frac{a}{RT}\right)$

[**Hint:** Example 66, Chapter 12]

81. Equal number of moles of A and B are allowed to react with each other till it reaches equilibrium.

$$2A + B \rightleftharpoons C + D$$

The value of K_c for this equilibrium can never be

(a) >1 (b) <1 (c) $=1$ (d) ∞

82. In $Ca(OH)_2$, solution (aqueous), the molar concentration of OH^- is found to be x, the solubility of $Ca(OH)_2$ in moles/litre is

(a) $2x$ (b) x (c) $x/2$ (d) $4x$

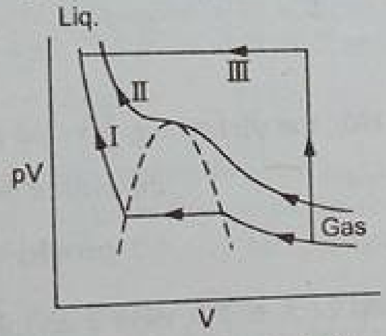
83. For a reaction of the order of 0.5, when the concentration of the reactant is doubled, the rate

(a) doubles
(b) increases four times
(c) decreases four times
(d) increases $\sqrt{2}$ times

84. In the decomposition of H_2O_2 at a given temperature T, the energy of activation decreases from E_1 to E_2 by the use of a catalyst. How many times does the rate of the catalysed reaction increase?

(a) $(E_1 - E_2)$ (b) $\frac{E_2}{E_1}$ (c) $\frac{E_1 - E_2}{R}$ (d) $e^{(E_1 - E_2)/RT}$

85. A gas can be condensed to liquid through the paths I, II and III, as shown in the figure. The path(s) through which the gas changes to liquid abruptly is (are)



(a) I & II (b) II & III (c) I & III (d) II

86. The volume of 1 mole of a gas at NTP is 20 litres.

(a) The gas is ideal.
(b) The gas deviates from ideal behaviour.
(c) The compressibility factor, $Z>1$.
(d) $Z<1$.

87. 10 mL of a solution containing Na_2CO_3 and $NaHCO_3$ is titrated by HCl using phenolphthalein and then methyl orange (added after first end point). The first and second end points were found after adding 10 mL and 15 mL of N/10 HCl respectively. The ratio of m.e. of Na_2CO_3 and $NaHCO_3$ in the solution is

(a) 2/1 (b) 1/2 (c) 5/1 (d) 1/5

88. The initial concentrations of X and Y were 2 and 4 moles/litre respectively for the following equilibrium

$$X + 2Y \rightleftharpoons Z.$$

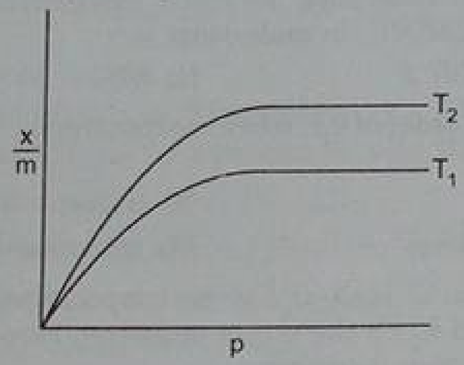
Which of the following relationships among equilibrium concentrations of X, Y and Z is (are) not feasible?

(a) $[X]=[Z]$ (b) $[X]<[Y]$ (c) $[X]>[Y]$ (d) $[Y]>=<[Z]$

89. For an ideal gas

(a) $\left(\frac{\partial V}{\partial T}\right)_p = 0$ (b) $\left(\frac{\partial p}{\partial T}\right)_V = 0$ (c) $\left(\frac{\partial E}{\partial V}\right)_T = 0$ (d) $\left(\frac{\partial E}{\partial T}\right)_V = 0$

90. x g of a gas is absorbed per m grams of a solid. A plot x/m vs pressure p at two different temperatures T_1 and T_2 shows



What we conclude is

(a) $\frac{x}{m} \propto p^n$, where $n = 0$ at low pressure

(b) $\frac{x}{m} \propto p^n$, where $n = 1$ at high pressure

(c) $T_1 > T_2$

(d) $T_2 > T_1$

91. In the above problem (90), the plot of $\log \frac{x}{m}$ vs $\log p$ should be a straight line

(a) with a negative slope (b) with a positive slope

(c) passing through origin (d) parallel to $\frac{x}{m}$-axis

92. The initial concentrations of A and B were 2 and 4 moles/litre respectively for the following equilibrium.

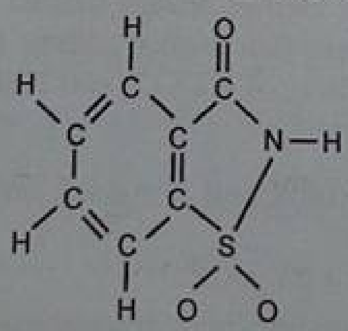
$$A + 2B \rightleftharpoons C$$

If at equilibrium, [B] = [C], [C] must be equal to

(a) 2 moles/litre (b) $\frac{8}{3}$ moles/litre

(c) $\frac{4}{3}$ moles/litre (d) none of these

93. The number of molecules of the sweetener saccharin, which can be prepared



from 30 C-atoms, 25 H-atoms, 12 O-atoms, 8 S-atoms and 14 N-atoms is

(a) 7 (b) 5 (c) 8 (d) 4

94. The equilibrium partial pressures of A, B and C are 1, 2 and 4 atm respectively in the equilibrium

$$A + B \rightleftharpoons C$$

The value of the reaction quotient just after reducing the volume of the container to half is

(a) 1 (b) 2 (c) 4 (d) none of these

95. For a system at equilibrium the system acquires a state of

(a) maximum entropy (b) minimum entropy
(c) zero entropy (d) optimum entropy

96. 14 g of an element X combines with 16 g of oxygen. The element X could have an at. wt. of

(a) 14 and its oxide the formula X_2O
(b) 7 and its oxide the formula X_2O
(c) 7 and its oxide the formula XO
(d) 14 and its oxide the formula XO_2

97. 2 volumes of a diatomic gas of an element combine with 5 volumes of O_2 to give 2 volumes of its oxide. The equivalent weight of the element is 2.8, the atomic weight of the element is

(a) 32 (b) 14 (c) 35.5 (d) 1

98. The vapour density of a volatile chloride of a metal is 55.5. When 40 g of the metal is dissolved in the acid, 22.4 litres of H_2 is liberated at NTP. The valency of the metal is

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

99. 0.09 g of a trivalent metal (M) combines with 56 mL of O_2 at NTP. The vapour density of its chloride is 133.5. The molecular formula of the chloride is

(a) MCl_2 (b) M_2Cl_4 (c) MCl_3 (d) M_2Cl_6

100. 6.0 g of a solid is heated, the residue left behind weighs 2 g and 1120 cc of a gas measured at 0°C and 1 atm is evolved. The molecular weight of the gas is

(a) 80 (b) 40 (c) 20 (d) 60

101. A compound is found to contain 5.47% nitrogen by weight. The minimum value which can be assigned to its molecular weight is

(a) 256 (b) 100 (c) 130 (d) 65

102. One volume of a diatomic gas (mol. wt. = 28) combines with three volumes of another diatomic gas (mol. wt. = 2) and forms 2 volumes of a gaseous compound. The molecular weight of the gas is

(a) 16 (b) 17 (c) 30 (d) 32

103. 2000 mL of air on ozonisation formed 1915 mL of ozonised air. The volume of ozone formed is

(a) 85 mL (b) $\frac{2}{3} \times 85$ mL (c) 49.5 mL (d) 170 mL

104. The volume of oxygen needed for complete combustion of 20 cc of a gaseous hydrocarbon C_xH_y is

(a) 20 cc (b) $\left(x + \frac{y}{4}\right)$ cc (c) $20\left(x + \frac{y}{4}\right)$ cc (d) $\frac{1}{2}\left(x + \frac{y}{4}\right)$ cc

105. At high temperature, S_4N_4 decomposes into sulphur vapour and nitrogen. If 1 mL of S_4N_4 is decomposed and 2.5 mL of mixture are obtained, the formula of sulphur vapour is

(a) S_2 (b) S_4 (c) S_6 (d) S_8

106. The approximate atomic weight of an element is 26.89. If its equivalent weight is 8.9, the exact atomic weight of the element would be

(a) 26.89 (b) 8.9 (c) 26.70 (d) 17.8

107. The oxide of an element possesses the formula M_2O_3. If the equivalent weight of the metal is 9, the molecular weight of the oxide will be

(a) 54 (b) 102 (c) 120 (d) 200

108. A container contains a certain gas of mass m at high pressure. A little amount of the gas has been allowed to escape from the container and after some time, the pressure of the gas becomes half and its absolute temperature two-third. The mass of the gas escaped is

(a) $\frac{2m}{3}$ (b) $\frac{m}{2}$ (c) $\frac{m}{4}$ (d) $\frac{m}{6}$

109. Two vessels A and B contain the same gas. If the pressure, volume and absolute temperature of the gas in A are two times as compared to that in B, and if the mass of the gas in B is x grams, the mass of the gas in A will be

(a) $4x$ g (b) $\frac{x}{2}$ g (c) $2x$ g (d) x g

110. The vapour density of undecomposed N_2O_4 is 46. When heated, the vapour density decreases to 24.5 due to its dissociation to NO_2. The per cent dissociation of N_2O_4 at the final temperature is

(a) 88 (b) 60 (c) 40 (d) 70

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

(a) −3.4 eV (b) −4.2 eV (c) −6.8 eV (d) +6.8 eV

(IIT 1998)

112. Which of the following statement(s) is (are) correct?

(a) The coordination number of each type of ion in CsCl crystal is 8.
(b) The metal that crystallises in b.c.c. structure has a coordination number of 12.
(c) A unit cell of an ionic crystal shares some of its ions with other unit cells.
(d) The length of the unit cell in NaCl is 552 pm.
($r_{Na^+} = 95$ pm, $r_{Cl^-} = 181$ pm) **(IIT 1998)**

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

(a) Y > Z > X (b) X > Y > Z
(c) Z > Y > X (d) Z > X > Y **(IIT 1998)**

114. Decrease in atomic number is observed during

(a) α-emission (b) β-emission
(c) positron emission (d) electron capture **(IIT 1998)**

115. For a first-order reaction
(a) the degree of dissociation $= (1 - e^{-kt})$
(b) a plot of reciprocal of concentration of the reactant vs time gives a straight line
(c) the time taken for the completion of 75% reaction is thrice the $t_{1/2}$ of the reaction
(d) the pre-exponential factor in the Arrhenius's equation has the dimension of time, T^{-1} **(IIT 1998)**

116. According to Graham's law at a given temperature the ratio of the rates of diffusion r_A/r_B of gases A and B is given by
(a) $\left(\frac{p_A}{p_B}\right)\left(\frac{M_A}{M_B}\right)^{1/2}$
(b) $\left(\frac{M_A}{M_B}\right)\left(\frac{p_A}{p_B}\right)^{1/2}$
(c) $\left(\frac{p_A}{p_B}\right)\left(\frac{M_B}{M_A}\right)^{1/2}$
(d) $\left(\frac{M_A}{M_B}\right)\left(\frac{p_B}{p_A}\right)^{1/2}$ **(IIT 1998)**

117. 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 can be increased by
(a) adding a suitable catalyst
(b) adding an inert gas
(c) decreasing the volume of the container
(d) increasing the amount of CO(g) **(IIT 1998)**

118. Which of the following statement(s) is (are) 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 increases with temperature.
(d) When a solution of a weak monoprotic acid is titrated against a strong base, at half-neutralisation point, $pH = 1/2\, pK_a$. **(IIT 1998)**

119. The number of neutrons accompanying the formation of $^{139}_{54}Xe$ and $^{94}_{38}Sr$ from the absorption of a slow neutron by $^{235}_{92}U$, followed by nuclear fission, is
(a) 0 (b) 2 (c) 1 (d) 3 **(IIT 1999)**

120. A gas will approach ideal behaviour at
(a) low temperature and low pressure
(b) low temperature and high pressure
(c) high temperature and low pressure
(d) high temperature and high pressure **(IIT 1999)**

121. The normality of 0.3 M phosphorus acid (H_3PO_3) is
(a) 0.1 (b) 0.9 (c) 0.3 (d) 0.6 **(IIT 1999)**

122. The coordination number of a metal crystallising in a hexagonal close-packed structure is
(a) 12 (b) 4 (c) 8 (d) 6

123. A gas X at 1 atm is bubbled through a solution containing a mixture of 1 M Y^- and 1 M Z^- at 25°C. If the reduction potential of $Z > Y > X$, then
(a) Y will oxidise X and not Z
(b) Y will oxidise Z and not X
(c) Y will oxidise both X and Z
(d) Y will reduce both X and Z **(IIT 1999)**

124. The pH of a 0.1 M solution of the following salts increases in the water,
(a) $NaCl < NH_4Cl < NaCN < HCl$
(b) $HCl < NH_4Cl < NaCl < NaCN$
(c) $NaCN < NH_4Cl < NaCl < HCl$
(d) $HCl < NaCl < NaCN < NH_4Cl$ **(IIT 1999)**

125. 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 **(IIT 1999)**

126. One mole of calcium phosphide on reaction with excess water gives
(a) one mole of phosphine
(b) two moles of phosphoric acid
(c) two moles of phosphine
(d) one mole of phosphorus pentoxide **(IIT 1999)**

127. The oxidation numbers of S in S_8, S_2F_2 and H_2S respectively are
(a) 0, +1 & −2 (b) +2, +1 & −2 (c) 0, +1 & +2 (d) −2, +1 & −2

128. Which of the following statement(s) is (are) correct?
(a) A plot of log K_p vs $\frac{1}{T}$ is linear.
(b) A plot of log [X] vs time is linear for a first-order reaction, $X \rightarrow p$.
(c) A plot of log p vs $\frac{1}{T}$ is linear at constant volume.
(d) A plot of p vs $\frac{1}{V}$ is linear at constant temperature.

129. In depression-of-freezing-point experiment, it is found that the
(a) vapour pressure of the solution is less than that of pure solvent
(b) vapour pressure of the solution is more than that of pure solvent
(c) only solute molecules solidify at the freezing point
(d) only solvent molecules solidify at the freezing point **(IIT 1999)**

130. A buffer solution can 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

131. The ΔH_f° for $CO_2(g)$, $CO(g)$ and $H_2O(g)$ are −393.5, −110.5 and −241.8 kJ mol^{-1} respectively. The standard enthalpy change (in kJ) for the reaction,

$$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g), \text{ is}$$

(a) 524.1 (b) 41.2 (c) −262.5 (d) −41.2 **(IIT 2000)**

132. The rate constant for the reaction $2N_2O_5 \rightarrow 4NO_2 + O_2$ is $3.0 \times 10^{-5}\ s^{-1}$. If the rate is 2.40×10^{-5} mol lit^{-1} s^{-1} then the concentration of N_2O_5 (in mol L^{-1}) is

(a) 1.4 (b) 1.2 (c) 0.04 (d) 0.8 **(IIT 2000)**

133. For the electrochemical cell, $M | M^+ || X^- | X$, $E^0(M^+/M) = 0.44$ V and $E^0(X/X^-) = 0.33$ V. From this data, one can deduce that

(a) $M + X \rightarrow M^+ + X^-$ is the spontaneous reaction

(b) $M^+ + X^- \rightarrow M + X$ is the spontaneous reaction

(c) $E_{cell} = 0.77$ V

(d) $E_{cell} = -0.77$ V

(IIT 2000)

134. For the reversible reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at 500°C, the value of K_p is 1.44×10^{-5} when partial pressure is measured in atm. The corresponding value of K_c, with concentration in mol L^{-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) $1.44 \times 10^{-5}/(0.082 \times 773)^{-2}$

(IIT 2000)

135. The rms velocity of hydrogen is $\sqrt{7}$ times the rms velocity of nitrogen. If T is the temperature of the gas,

(a) $T(H_2) = T(N_2)$ (b) $T(H_2) > T(N_2)$

(c) $T(H_2) < T(N_2)$ (d) $T(H_2) = \sqrt{7}\,T(N_2)$ **(IIT 2000)**

136. The compressibility of a gas is less than unity at STP. Therefore,

(a) $V_m > 22.4$ L (b) $V_m < 22.4$ L (c) $V_m = 22.4$ L (d) $V_m = 44.8$ L

(IIT 2000)

137. At 100°C and 1 atm, if the density of liquid water is 1.0 g cm^{-3} and that of water vapour is 0.0006 g cm^{-3}, the volume occupied by water molecules in 1 litre of steam at that temperature is

(a) 6 cm^3 (b) 60 cm^3 (c) 0.6 cm^3 (d) 0.06 cm^3

(IIT 2000)

138. The number of nodal planes in a p_x orbital is

(a) 1 (b) 2 (c) 3 (d) 0 **(IIT 2000)**

139. 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

140. Which of the following mixtures will have pH equal to 2.0 if the normalities of HCl and NaOH are 0.1 N?

(a) 50 mL HCl + 50 mL NaOH (b) 55 mL HCl + 45 mL NaOH

(c) 75 mL HCl + 25 mL NaOH (d) 60 mL HCl + 140 mL NaOH

141. The equilibrium constant depends only on temperature because

(a) the energy of activation of forward reaction is different from that of the backward reaction

(b) for a certain change in temperature, the rate of the forward reaction and that of the backward reaction do not change by the same amount

(c) rate constants of the forward and the backward reactions change to different extents
(d) every reaction is caused by heating

142. K_p and K_c are related by $K_p = K_c(RT)^{\Delta n}$. Under what practical condition/s, $K_p = K_c$?

(a) $RT = 1$ (b) $T = 12K$ (c) $\Delta n = 0$ (d) $R \propto \frac{1}{T}$

143. The equilibrium constant shall not depend on temperature if (E-energy of activation)

(a) $E_f = E_b$ (b) $E_f > E_b$ (c) $E_b > E_f$ (d) $(\Delta H)_{reaction} = 0$

144. The pK_a of an indicator is 4. Its pH range is

(a) 1–3 (b) 3–5 (c) 5–8 (d) 8–12

145. The heat of fusion is 334.7 J g^{-1}. The entropy change in J K^{-1} kg^{-1} in melting of 1 g of ice at 0°C is

(a) 1.226 (b) 0.293 (c) 293 (d) 1226

146. Which statement is not correct about internal energy?

(a) Internal energy is the sum of kinetic energy and potential energy of the particles making up the system.
(b) Internal energy of the system can be measured.
(c) Internal energy is a state function.
(d) ΔE is the heat of reaction at constant volume.

147. At what temperature does an aqueous solution containing 3×10^{23} molecules of a nonelectrolyte substance in 250 g of water freeze? ($K_f = 1.86$).

(a) 269.28 K (b) 271.14 K (c) 271 K (d) 276.72 K

148. A plot between time and the amount of reactant consumed is found to be a straight line passing through origin for a reaction. The order of the reaction is

(a) 0 (b) 1 (c) 2 (d) 3

149. The unit of rate constant is the same as that of the rate of the reaction of order

(a) 0 (b) 1 (c) 2 (d) 3

150. The time required to decompose half of the reactant for an nth-order reaction is inversely proportional to (a is the initial concentration)

(a) a^n (b) a^{n-2} (c) a^{n-1} (d) a^{n+1}

151. For a chemical change $A \rightarrow B$, it is found that the rate doubles when the concentration of A is increased 4 times. The order in A is

(a) 2 (b) 1 (c) 0 (d) $\frac{1}{2}$

152. A metallic element exists as a cubic lattice. Each edge of the unit cell is 2.88 Å and the density of the metal is 7.2 g cm^{-3}. The number of unit cells in 100 g of the metal is

(a) 5.82×10^{23} (b) 6.023×10^{23} (c) 8.52×10^{23} (d) none of these

153. The vapour pressure of a solvent decreased by 10 mmHg when a nonvolatile solute was added to the solvent. The mole fraction of the solute in the solution is 0.2. What would be the mole fraction of the solvent if the decrease in the vapour pressure is to be 20 mmHg?

(a) 0.8 (b) 0.6 (c) 0.4 (d) 0.2

154. Schottky defect in crystals is observed when
(a) an ion leaves its normal site and occupies an interstitial site
(b) unequal number of cations and anions are missing from the lattice
(c) density of the crystal is increased
(d) equal number of cations and anions are missing from the lattice

155. The face diagonal length of f.c.c. cubic cell is 508 pm. If the radius of the cation is 110 pm, the radius of the anion is
(a) 288 pm (b) 398 pm (c) 144 pm (d) 618 pm

156. Haemoglobin contains 0.334% of Fe by weight. The molecular weight of haemoglobin is approximately 67200. The number of Fe atoms present in one molecule of haemoglobin is
(a) 1 (b) 6 (c) 4 (d) 2

157. Given that

$$C + O_2 = CO_2;\quad \Delta H = -x \text{ kJ}$$
$$2CO + O_2 = 2CO_2;\quad \Delta H = -y \text{ kJ}$$

The enthalpy of formation of CO will be
(a) $(y - 2x)$ (b) $(2x - y)/2$ (c) $(y - 2x)/2$ (d) $(2x - y)$

158. E^0 for some half reactions are given below:

$$Sn^{4+} + 2e = Sn^{2+} \quad ; E^0 = 0.15 \text{ V}$$
$$2Hg^{2+} + 2e = Hg_2^{2+} \quad ; E^0 = 0.92 \text{ V}$$
$$PbO_2 + 4H^+ + 2e = Pb^{2+} + 2H_2O \quad ; E^0 = 1.45 \text{ V}$$

Based on the given data which statement is correct?
(a) Sn^{4+} is a stronger oxidising agent than Pb^{4+}.
(b) Sn^{2+} is a stronger reducing agent than Hg_2^{2+}.
(c) Hg^{2+} is a stronger oxidising agent than Pb^{4+}.
(d) Pb^{2+} is a stronger reducing agent than Sn^{2+}.

159. An element (atomic mass = 100 g/mole) having b.c.c. structure has unit cell edge 4.00 Å. The density in g/cc of the element is
(a) 10.376 (b) 5.188 (c) 7.289 (d) 2.144

160. Solid ammonium carbamate dissociates as follows:

$$NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$$

At equilibrium, total pressure is found to be 0.3 atm at a given temperature. The value of K_p is
(a) 0.3 atm^3 (b) 0.108 atm^3
(c) 4.0×10^{-3} atm^3 (d) 0.158 atm

161. The dimensions of pressure are the same as that of
(a) force per unit volume (b) energy per unit volume
(c) force (d) energy
[**Hint:** Force – kg m s^{-2}, energy – kg m^2s^{-2}, pressure – kg $m^{-1}s^{-2}$]

162. The number of atoms in 100 g of an f.c.c. crystal, with density 10 g/cc and cell edge equal to 100 pm, is equal to

(a) 3×10^{25} (b) 4×10^{25} (c) 1×10^{25} (d) 2×10^{25}

[**Hint:** No. of atoms per g $= \frac{N}{M}$: Apply Equation 1, Chapter 20]

163. Consider the following reactions occurring in an automobile

$$C_8H_{18}(g) + \frac{25}{2}O_2(g) \rightarrow 8CO_2(g) + 9H_2O(g)$$

The sign of $\Delta H, \Delta S$ and ΔG would be respectively,

(a) +, −, + (b) −, +, − (c) −, +, + (d) +, +, −

164. 8 moles of SO_2 and 4 moles of O_2 are mixed in a closed vessel. The reaction proceeds at constant temperature. By the moment when equilibrium sets in, 80% of the initial amount of SO_2 enters into the reaction. The equilibrium pressure would be

(a) 2.17 atm (b) 8 atm
(c) 12 atm (d) cannot be calculated

165. For the adsorption of a gas on a solid, the plot of log $\frac{x}{m}$ vs log p(x-axis) is linear with slope equal to

(a) k (b) log K (c) n (d) $\frac{1}{n}$

166. Select the rate law corresponding to the data for the following reaction.

$$A + B \rightarrow C$$

$[A]_{Initial}$	$[B]_{Initial}$	Initial Rate
0.012	0.035	0.10
0.024	0.070	0.80
0.024	0.035	0.10
0.012	0.070	0.80

(a) Rate $= k[B]^3$ (b) Rate $= k[B]^4$
(c) Rate $= k[A][B]^3$ (d) Rate $= k[A]^2[B]^2$

167. Under what conditions will a pure sample of an ideal gas not only exhibit a pressure of 2 atm but also a concentration of 2 mole/litre?

(a) at STP (b) when $V = 22.4$ L
(c) at 12 K (d) impossible under any condition

168. At NTP, 0.5 mole of H_2 and 1.0 mole of He gas

(a) have equal kinetic energy (b) have equal molecular velocity
(c) occupy equal volume (d) have equal diffusion rate

169. In which of the following solvents will AgBr have the highest solubility?

(a) 10^{-3} M HBr (b) 10^{-3} M NaBr
(c) 10^{-3} M NH_4OH (d) pure water

170. Based on the following thermochemical equation:

$$H_2O(g) + C(s) = CO(g) + H_2(g) \quad ; \Delta H = 131 \text{ kJ}$$

$$CO(g) + \frac{1}{2}O_2(g) = CO_2(g) \quad ; \Delta H = -282 \text{ kJ}$$

$$H_2(g) + \frac{1}{2}O_2(g) = H_2O(g) \quad ; \Delta H = -242 \text{ kJ}$$

$C(s) + O_2(g) = CO_2(g)$; $\Delta H = -x$ kJ

The value of x will be

(a) 393 kJ (b) −393 kJ (c) 655 kJ (d) −655 kJ

171. The equivalent mass of NO_3^- in the following reaction is

$$NO_3^- \rightarrow NH_4^+$$

(a) 7.75 (b) 31 (c) 62 (d) 15

172. The molarity of 0.56 L of water vapour at STP is

(a) 0.089 M (b) 0.045 M (c) 0.45 M (d) 0.22 M

173. If the compressibility factor, Z, of a gas increases with the increase in pressure (usually at very high pressure),

(a) $\frac{a}{V^2}$ is negligible in comparison to p

(b) b is negligible in comparison to V

(c) both are negligible

(d) none of them is negligible

174. For an acid, it is always true that lower the

(a) pH value, higher the acid strength

(b) molarity, higher the acid strength

(c) K_a value, higher the acid strength

(d) pK_a value, higher the acid strength

175. The hydrogen-ion concentration in weak acid HA of dissociation constant K_a and concentration C is nearly equal to

(a) $\sqrt{\frac{K_a}{C}}$ (b) $\frac{C}{K_a}$ (c) $K_a \cdot C$ (d) $\sqrt{K_a \cdot C}$

176. For pure water at an unknown temperature, the pH should always be equal to

(a) 7 (b) >7 (c) <7 (d) any of them

177. A first-order reaction is carried out with an initial concentration of 10 mol/L and 80% of the reactant changed into the product. Now if the same reaction is carried out with an initial concentration of 5 mol/L, the percentage of the reactant changing to the product will be

(a) 40 (b) 80 (c) 160 (d) 20

178. The buffering action of an acidic buffer is maximum when its pH is equal to

(a) 5 (b) 7 (c) 1 (d) pK_a

179. van der Waals equation: $\left(p + \frac{a}{4V^2}\right)\left(V - \frac{b}{2}\right) = \frac{RT}{2}$ is valid for

(a) 1 mole of an ideal or real gas (b) 2 moles of an ideal or real gas

(c) $\frac{1}{2}$ mole of an ideal or real gas (d) $\frac{1}{2}$ mole of real gas only

180. When an ideal gas filled in a closed vessel is heated through 1°C, its pressure increases by 0.4%, the initial temperature of the gas was

(a) 250 K (b) 2500 K (c) 250°C (d) 25°C

181. Which of the following relations is correct for the mole fraction of the solute (x)? (m and M are the molality of the solution and molar mass of the solvent respectively.)

(a) $x=\frac{mM}{1000+mM}$ (b) $x=\frac{mM}{1000-mM}$

(c) $x=\frac{1+mM}{mM}$ (d) $x=\frac{1-mM}{mM}$

182. The correct statement(s) of Charles's law is (are),

(a) pressure remaining constant, all gases expand (or contract) by the same fraction of its volume at 0°C for 1° rise (or fall) in temperature.

(b) The volume of a given amount of any gas at constant pressure increases linearly with temperature at any scale, i.e., °C or K.

(c) In the plot V vs T at constant pressure, a straight line of positive slope is obtained. This line passes through the origin only if the temperature is in the Kelvin scale.

(d) For any number of gases of the same volume and at the same temperature, the slopes of the above plot (c) would be same for all these gas samples.

183. The volume of 0.1 M HCl required to neutralise completely 2 g of an equimolar mixture of Na_2CO_3 and $NaHCO_3$ is

(a) 318.76 mL (b) 325 mL (c) 215 mL (d) 225 mL

184. The diameter of molecule B is half that of molecule A. The ratio of mean free path (λ_A/λ_B) will be

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

185. Which of the following is not a state function?

(a) $(q+w)$ (b) $\frac{q}{T}$ (c) $(E+pV)$ (d) $\frac{q}{w}$

186. Two moles of an ideal monoatomic gas are allowed to expand adiabatically and reversibly from 300 K to 200 K. The work done by the system is ($C_V = 12.5$ J K^{-1} mol^{-1})

(a) +2.5 kJ (b) −2.5 kJ (c) +6.25 kJ (d) −50 kJ

187. The work required to raise a mass of 0.5 kg through a height of 1 m is

(a) 4.9 J (b) 49 J (c) 490 J (d) 4900 J

188. Entropy change for an adiabatic reversible process is

(a) positive (b) zero (c) negative (d) infinite

189. Three engines A, B and C take steam at 130°C and reject it at 20°C, 40°C and 50°C respectively. The most efficient engine would be

(a) A (b) B (c) C (d) all same

190. One mole of an ideal gas is expanded isothermally from 1 dm^3 to 10 dm^3 at 300 K. ΔG will be equal to

(a) 5.744 kJ (b) 57.44 J (c) 574.4 J (d) −5744 J

191. Which of the following relations gives the mathematical expression for the combined first and second law of thermodynamics?

(a) $\Delta G = V\Delta p - S\Delta T$ (b) $\Delta A = -p\Delta V - S\Delta T$

(c) $\Delta E = T\Delta S - p\Delta V$ (d) $\Delta H = T\Delta S + V\Delta p$

192. For the expression: $dG = Vdp - SdT$, which of the following is correct?

(a) $\left(\frac{\partial G}{\partial T}\right)_p = V$ (b) $\left(\frac{\partial G}{\partial p}\right)_T = V$

(c) $\left(\frac{\partial G}{\partial T}\right)_S = V$ (d) $\left(\frac{\partial G}{\partial p}\right)_T = -S$

193. Which of the following will increase with the increase in temperature?

(a) Surface tension (b) Viscosity

(c) Molality (d) Vapour pressure

194. One mole of an ideal gas expands reversibly and isothermally at 300 K from 5 dm^3 to 50 dm^3. The work done by the gas for the process is equal to

(a) −1.382 kcal (b) +1.382 kcal (c) −1381.8 kcal (d) +1382 kcal

195. The equilibrium constant for the reaction

$$A + B \rightleftharpoons C + D$$

is 10. $\Delta G°$ for the reaction at 300 K is

(a) −0.6 kcal (b) −116 kcal (c) −691 kcal (d) −1.382 kcal

196. For the reaction

$$3Br_2 + 6OH^- = 5Br^- + BrO_3^- + 3H_2O$$

Equivalent weight of Br_2 (mol. wt. M) is

(a) $\frac{M}{2}$ (b) $\frac{M}{10}$ (c) $\left(\frac{M}{2} + \frac{M}{10}\right)$ (d) $\frac{M}{6}$

[**Hint:** As Br_2 disproportionates (simultaneous oxidation and reduction) its equivalent weight is the sum of equivalent weights of the two half reactions.]

Note: Some other reactions of this type are given below. If the molecular weight of the underlined substance is M, the equivalent weights of the underlined substances are as follows:

$\underline{3I_2} + 6OH^- = 5I^- + IO_3^- + 3H_2O$; eq. wt. $= \left(\frac{M}{2} + \frac{M}{10}\right)$

$\underline{P_4} + 3OH^- + 3H_2O = 3H_2PO_2^- + PH_3$; eq. wt. $= \left(\frac{M}{4} + \frac{M}{12}\right)$

$\underline{3KClO_3} + 3H_2SO_4 = 3KHSO_4 + HClO_4 + 2ClO_2 + H_2O$;

eq. wt. $= \left(M + \frac{M}{2}\right)$

197. The equivalent weight of Cu_2S (mol. wt. $= M$) in the following reaction is

$$Cu_2S + MnO_4^- = Cu^{2+} + SO_2 + Mn^{2+}$$

(a) $\frac{M}{2}$ (b) $\frac{M}{6}$ (c) $\frac{M}{8}$ (d) $\frac{M}{4}$

[**Hint:** Both Cu and S in Cu_2S undergo oxidation.]

Note: Some other reactions of this type are given below. The equivalent weight of the underlined substances (mol wt. = M) are as follows:

$\underline{Cu_2S} + 4SO_4^{2-} + 2H^+ = 2Cu^{2+} + 5SO_3^{2-} + H_2O$; eq. wt. $= \frac{M}{8}$

$\underline{As_2S_3} + 7NaClO_3 + 12NaOH = 2Na_3AsO_4 + 7NaClO + 3Na_2SO_4$;

eq. wt. $= \frac{M}{28}$

198. The equivalent weight of HNO_3 (mol. wt. = 63) in the following reaction is

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O$$

(a) $\frac{4 \times 63}{3}$ (b) $\frac{63}{5}$ (c) $\frac{63}{3}$ (d) $\frac{63}{8}$

[**Hint:** Out of 8 N atoms in HNO_3, only 2 N atoms undergo reduction to NO. Further, 6 moles of electrons are involved with 8 moles of HNO_3. $E = M + \frac{M}{3} = \frac{8}{6}M; M = 63$]

199. The equivalent weight of H_2SO_4 in the following reaction is

$$Na_2Cr_2O_7 + 3SO_2 + H_2SO_4 = 3Na_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

(a) 98 (b) $\frac{98}{6}$ (c) $\frac{98}{2}$ (d) $\frac{98}{8}$

[**Hint:** 6 moles of electrons are involved with 1 mole of H_2SO_4 in this redox reaction.]

200. The largest diagonal in a cubic crystal of edge length a is

(a) $\sqrt{3a}$ (b) $\sqrt{2}a$ (c) $\sqrt{3}a$ (d) $\sqrt{2a}$

201. The decreasing order of density of different crystals is

(a) f.c.c > b.c.c > simple cube (b) b.c.c. > f.c.c. > simple cube

(c) simple cube > f.c.c. > b.c.c. (d) h.c.p. > f.c.c. > simple cube

202. The empty space left between the spheres in close-packed structure is called voids. The decreasing order of the size of voids is

(a) cubic > octahedral > tetrahedral > trigonal

(b) octahedral > tetrahedral > trigonal > cubic

(c) tetrahedral > trigonal > cubic > octahedral

(d) trigonal > cubic > octahedral > tetrahedral

203. One unit cell of NaCl contains

(a) 1 Na^+ and 6 Cl^- (b) 6 Na^+ and 1 Cl^-

(c) 4 Na^+ and 4 Cl^- (d) 6 Na^+ and 6 Cl^-

204. In a close-packed structure, if r is the radius of the spherical void and R is the radius of the spheres forming voids, the critical r/R value for the tetrahedral void is equal to

(a) 0.155 (b) 0.225 (c) 0.414 (d) 0.732

205. A reaction $A + B \rightarrow D + E$ takes place as

$$A + B \xrightarrow{k_1} 2C$$

$$C + B \xrightarrow{k_2} 2D$$

$$C + A \xrightarrow{k_3} 2E$$

The rate of disappearance of C is given by

(a) $-\frac{d[C]}{dt} = k_2[B][C] + k_3[A][C] - k_1[A][B]$

(b) $-\frac{d[C]}{dt} = k_2[B][C] + k_3[A][C]$

(c) $-\frac{d[C]}{dt} = k_2[D] + k_3[E] - k_1[C]$

(d) $-\frac{d[C]}{dt} = k_2 \cdot k_3[D][E]$

206. In the NaCl crystal, the coordination number of each ion is 6. How can the CN change to 8?

(a) By increasing temperature
(b) By keeping it for some time
(c) By increasing pressure
(d) CN does not change by any way

[**Note:** In CsCl : 8 : 8 CN changes to 6 : 6 on increasing temperature]

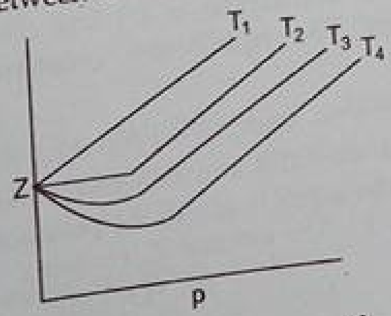
207. The pK_a for acetyl salicylic acid (aspirin) is 3.5. The pH of gastric juice in the human stomach is about 2–3 and the pH in the small intestine is about 8. Aspirin will be

(a) un-ionised in the small intestine and in the stomach
(b) completely ionised in the small intestine and in the stomach
(c) ionised in the stomach and almost un-ionised in the small intestine
(d) ionised in the small intestine and almost un-ionised in the stomach

208. The degree of dissociation of an electrolyte does not depend on

(a) nature of electrolyte (b) catalyst
(c) dilution (d) temperature

209. From the given plot between Z and p for a real gas, the correct relation is



(a) $T_1 = \frac{2a}{Rb}$ (b) $T_2 = \frac{a}{Rb}$ (c) $T_3 = \frac{a}{Rb}$ (d) $T_4 = \frac{2a}{Rb}$

210. The van der Waals equation for 1 mole of gas is

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

where,

(a) p and V are ideal pressure and ideal volume respectively

(b) $(V-b)$ is the real volume

(c) $\left(p+\frac{a}{V^2}\right)$ is the ideal pressure

(d) $\left(p+\frac{a}{V^2}\right)$ is the real pressure

211. A mixture of H_2 and O_2 taken in a bulb in 2 : 1 mole ratio is allowed to diffuse through a fine hole. The composition of the gases (mole ratio) coming out initially is 8 : 1. The composition of the gases after some time may be

(a) 8 : 1 (b) 9 : 1 (c) 7 : 1 (d) 4 : 1

212. For a dilute solution,
lowering of vapour pressure ∝ mole fraction of the solute
or, lowering of vapour pressure = $K \times$ mole fraction of the solute, where K is

(a) a constant for the solute (b) a constant for the solvent
(c) a constant for the solution (d) vapour pressure of the solvent

213. For ideal binary solution,

$$p = x_A \cdot p_A^0 + x_B \cdot p_B^0$$

This equation reflects

(a) Boyle's law (b) Charles's law
(c) Dalton's law of partial pressure (d) none of these

214. Dry air is passed through a solution and then through its solvent and finally through $CaCl_2$. The ratio of weight loss in the solvent to the weight gain in $CaCl_2$ gives

(a) relative lowering of vapour pressure
(b) lowering of vapour pressure
(c) mole fraction of the solute
(d) mole fraction of the solvent

215. The relative lowering of vapour pressure of an aqueous solution of urea is 0.018. If K_b for H_2O is 0.54° m^{-1}, the elevation in boiling point will be

(a) 0.54°C (b) 0.18°C (c) 0.54 K (d) 0.18 K

216. 1 mole of A is allowed to decompose in a 1-litre container. 0.4 mole of B was produced at equilibrium. The equilibrium constant K_c for the equilibrium $A(g) \rightleftharpoons 2B(g) + C(g)$, is

(a) 0.04 (b) 0.053 (c) 0.08 (d) 0.106

217. V_1 mL of SO_2, filled in a tube at 1 atm between a movable frinctionless piston and a porous plug. The tube is left in air till the piston stops moving. The volume V_1 is found to increase to V_2. The volume V_2 contains

(a) air only (b) SO_2 only
(c) both air and SO_2 (d) neither air nor SO_2

218. The equilibrium: $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, may be shifted to the right if

(a) an inert gas is added at constant volume
(b) an inert gas is added at constant pressure
(c) pressure is increased
(d) PCl_3 and Cl_2 are added

219. Two flasks A and B of equal volume containing 1 mole and 2 moles of O_3

respectively, are heated to the same temperature. When the reaction $2O_3 = 3O_2$ practically stops, then both the flasks shall have

(a) the same ratio: $[O_2]/[O_3]$
(b) the same ratio: $[O_2]^{3/2}/[O_3]$
(c) only O_2
(d) the same time to reach equilibrium

220. For a 0.1 M aqueous solution of a weak acid, HA ($K_a = 10^{-9}$), the pH is approximately equal to

(a) 9 (b) 3 (c) 11 (d) 10

221. If 720 litres of a gas were collected over water at 25°C and 720 mm then the volume of the dry gas at the same temperature and pressure is (aq. tension of water at 25°C = 23.8 mm)

(a) 696.2 litres (b) 360 litres (c) 743.8 litres (d) 1440 litres

222. Which of the following values of heat of formation indicates that the product is the least stable?

(a) –94 kcal (b) –231.6 kcal (c) +21.4 kcal (d) +64.8 kcal

223. In a first-order reaction of the type: $A(g) \rightarrow 2B(g)$, the initial and final pressures are p_1 and p respectively. The rate constant can be expressed by

(a) $k = \frac{1}{t} \ln \frac{p_1}{2p_1 - p}$
(b) $k = \frac{1}{t} \ln \frac{p_1}{p_1 - p}$
(c) $k = \frac{1}{t} \ln \frac{p_1}{p - p_1}$
(d) $k = \frac{1}{t} \ln \frac{p_1}{p}$

224. The pH of a 0.1 M solution of a weak acid HA is found to be 2 at a temperature *T*. The osmotic pressure of the acid solution would be equal to

(a) 0.11 *RT* (b) 0.22 *RT* (c) 2 *RT* (d) *RT*

225. For a first-order reaction of the type

$$nA \rightarrow \text{product}$$

where initial concentration of A is '*a*' moles/litre. The correct expression for the rate constant or half-life is

(a) $k = \frac{2.303}{nt} \log \frac{a}{(a-x)}$
(b) $k = \frac{2.303}{t} \log \frac{a}{a-x}$
(c) $t_{1/2} = \frac{0.6932}{k}$
(d) $t_{1/2} = \frac{0.6932}{nk}$

226. Which of the following give(s) the strength of the acid or base?

(a) pH (b) Normality
(c) Degree of dissociation (d) Dissociation constant

227. Choose the correct statement about the equilibrium

$$A(s) + 2B(g) \rightleftharpoons C(g) + D(g)$$

(a) change in temp. changes both the state of eqb. and the eqb. constant
(b) change in pressure changes both the state of eqb. and the eqb. constant
(c) change in temperature changes eqb. constant but not the state of eqb.
(d) change in pressure does not affect either eqb. constant or state of eqb.

228. Choose the wrong statement(s).

(a) If the eqb. constant changes, the state of eqb. has to change.
(b) If the state of eqb. changes, the eqb. constant has to change.

(c) The acid with a lower pK_a value has higher acid strength than the acid with a higher value of pK_a.
(d) Two acids of the same pH are always of equal acid strength

229. x and y moles/litre of A and B respectively were allowed to react $A + 2B \rightleftharpoons \frac{1}{2}C$. At equilibrium, the concentrations of A, B and C were found to be 4, 2 and 2 moles/litre respectively. x and y are
(a) 6 & 4 (b) 8 & 10 (c) 6 & 10 (d) 8 & 4

230. 116 g of A_3B_4 has 1.5 moles of A. Molecular weight of A_3B_4 is
(a) 164 (b) 232
(c) 77 (d) cannot be calculated

231. 0.8 g of silver salt of a dibasic organic acid on ignition yielded 0.54 g of metallic silver. Molecular weight of the acid is (Ag = 108)
(a) 106 (b) 108 (c) 320 (d) 85
[**Hint:** See Example 12, Chapter 5]

232. 0.80 g of chloroplatinate of a monoacid organic base on ignition gave 0.25 g of Pt. The molecular weight of the base is (Pt = 195)
(a) 624 (b) 214 (c) 107 (d) 312
[**Hint:** See Example 14, Chapter 5]

233. One volume of a gaseous organic compound of C, H and N on combustion produced 2 volumes of CO_2, 3.5 volumes of H_2O vapour and 0.5 volume of N_2 under identical conditions of temperature and pressure. The molecular formula of the compound is
(a) C_2H_7N (b) $C_4H_{14}N_2$ (c) $C_2H_7N_2$ (d) $C_4H_{14}N_4$

234. In a gravimetric determination of phosphorus, 0.248 g of an organic compound was strongly heated in a Carius tube with concentrated HNO_3. Phosphoric acid so produced was precipitated as $MgNH_4PO_4$ which on ignition yielded 0.444 g of $Mg_2P_2O_7$. The percentage of phosphorus in the compound is
(a) 2.5 (b) 5.0 (c) 7.5 (d) 50

235. The empirical formula of a substance whose composition includes H, C, O and N in the mass ratio 1 : 3 : 4 : 7 is
(a) $HC_3O_4N_7$ (b) H_4CON_2 (c) $HC_4O_4N_2$ (d) none of these

236. 500 cc of a hydrocarbon gas burnt in excess of oxygen yielded 2500 cc of CO_2 and 3 litres of H_2O vapour, measured under identical conditions of temperature and pressure. The formula of the hydrocarbon is
(a) C_5H_{12} (b) C_5H_{10} (c) C_4H_{10} (d) none of these

237. The minimum weight of H_2 filled in a balloon of weight w_1 kg to just lift it from the ground is w_2 kg. If w_3 kg of H_2 is filled into this balloon, the payload of the balloon will be (the volume of the balloon is supposed to be same with w_2 or w_3 kg of H_2)
(a) $w_2 - w_3$ (b) $(w_2 - w_3 - w_1)$ (c) $(w_3 - w_2)$ (d) $(w_3 - w_2 - w_1)$

238. The degree of dissociation (α) can be calculated using the formula,

$$\alpha = \frac{dt - d_0}{(n-1)d_0}$$

This formula is applicable at
(a) constant volume and constant temperature
(b) constant volume and variable temperature
(c) constant pressure and constant temperature
(d) all the above conditions

239. For a reaction a graph plotted between $\log\left(\frac{dx}{dt}\right)$ and $\log(a-x)$ along y and x axes respectively shows a straight line with a positive slope of 45°. The order of the reaction is
(a) 0 (b) 1 (c) 2 (d) 3

240. The pH of an aqueous solution of HCl is 2. Its osmotic pressure at a temperature T would be equal to
(a) 0.01 RT (b) 0.02 RT (c) RT (d) 2 RT

241. The K_p value for a homogeneous gaseous reaction is found to vary with the change in pressure. The correct conclusion is
(a) the gases behave ideally
(b) the gases deviate from ideal behaviour
(c) the gases in a reaction do not behave ideally
(d) K_p variation with pressure is a consequence of experimental error

242. For a first-order reaction, $A \xrightarrow{k} B$, the degree of dissociation is equal to
(a) e^{-kt} (b) $1-e^{-kt}$ (c) e^{kt} (d) $1+e^{-kt}$

[Hint: For $\underset{(1-x)}{\overset{1\,M}{A}} \longrightarrow \underset{x}{B}$ integrate $\frac{dx}{dt}=k(1-x)$]

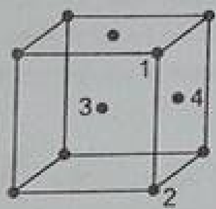
243. 1 mole of N_2 and 3 moles of H_2 filled in a one-litre bulb were allowed to react. When the reaction attained equilibrium, two-thirds of N_2 converted to NH_3 ($N_2+3H_2 \rightleftharpoons 2NH_3$). If a hole is then made in the bulb, the mole ratio of the gases N_2, H_2 and NH_3 effusing out initially would be respectively.
(a) $1:3:4$ (b) $\sqrt{28}:\sqrt{2}:\sqrt{17}$
(c) $\frac{1}{\sqrt{28}}:\frac{1}{\sqrt{2}}:\frac{1}{\sqrt{17}}$ (d) $\frac{1}{\sqrt{28}}:\frac{3}{\sqrt{2}}:\frac{4}{\sqrt{17}}$

244. In the above problem (243) what would be to the state of equilibrium during the course of effusion?
(a) Remains same (b) Shifts right
(c) Shifts left (d) First shifts right and then left

245. The reaction $A+2B \rightarrow$ product, is first order in A and second order in B. If $t_{1/2}$ w.r.t. A is same as the $t_{1/2}$ of the reaction,
(a) $[A]_{Initial} > [B]_{Initial}$ (b) $[A]_{Initial} = [B]_{Initial}$
(c) A is the limiting reactant (d) B is the limiting reactant

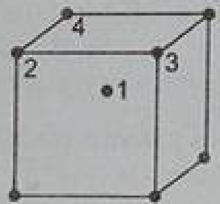
246. For which of the following reactions, the degree of dissociation cannot be calculated applying the formula: $\alpha=\frac{dt-d_0}{(n-1)d_0}$
(a) $PCl_5 \rightleftharpoons PCl_3+Cl_2$ (b) $2NH_3 \rightleftharpoons N_2+3H_2$
(c) $2HI \rightleftharpoons H_2+I_2$ (d) $2KClO_3 \rightleftharpoons 2KCl+3O_2$

247. In an f.c.c. unit cell, atoms are numbered as shown below. The atoms not touching each other are



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

248. In a b.c.c. unit cell, atoms are numbered as shown below. The atoms touching each other are



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

249. The coordination number of h.c.p. or c.c.p. structure is 12, that is, one atom touches 12 other atoms. The 12 atoms lie as

(a) 8 atoms are on the same plane, 2 above and 2 below the plane
(b) 6 atoms are on the same plane, 3 above and 3 below the plane
(c) 4 atoms are on the same plane, 4 above and 4 below the plane
(d) 2 atoms are on the same plane, 5 above and 5 below the plane

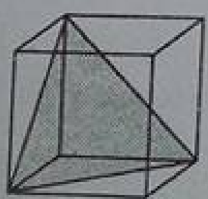
250. In a simple cubic crystal, the corner atom touches

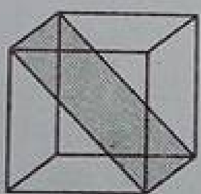
(a) 3 other atoms (b) 4 other atoms
(c) 6 other atoms (d) 8 other atoms

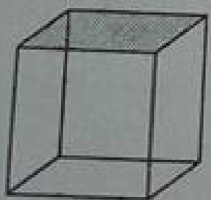
251. In a simple cubic crystal, each atom is shared by

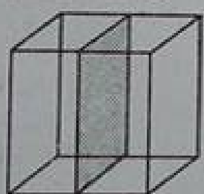
(a) 2 unit cells (b) 4 unit cells (c) 6 unit cells (d) 8 unit cells

252. In an f.c.c. crystal, which of the following shaded planes contains the following arrangement of atoms?

(a)


(b)


(c)


(d)


253. In which of the following aqueous solutions, the degree of dissociation of water is maximum?

(a) NH_4Cl solution
(b) CH_3COONa solution
(c) CH_3COONH_4 solution
(d) Same in all

254. When a drop of a concentrated HCl solution is added to one litre of pure water at 25°C, the pH drops from 7 to about 4. When the second drop of the same HCl solution is added, the pH further drops to about
(a) 3.7
(b) 2
(c) 1
(d) 0

255. The quantum numbers $+\frac{1}{2}$ and $-\frac{1}{2}$ for the electron spin represent
(a) rotation of the electron in clockwise and anticlockwise directions respectively
(b) rotation of the electron in anticlockwise and clockwise directions respectively
(c) magnetic moment of the electron pointing up and down respectively
(d) two quantum mechanical spin states which have no classical analogue

(IIT 2001)

256. Which one of the following statements is false?
(a) Work is a state function.
(b) Temperature is a state function.
(c) Change in the state is completely defined when the initial and final states are specified.
(d) Work appears at the boundary of the system. (IIT 2001)

257. In thermodynamics, a process is called reversible when
(a) surroundings and system change into each other
(b) there is no boundary between system and surroundings
(c) the surroundings are always in equilibrium with the system
(d) the system changes into the surroundings spontaneously (IIT 2001)

258. In a solid 'AB' having the NaCl structure, A atoms occupy the corners of the cubic unit cell. If all the face-centred atoms along one of the axes are removed then the resultant stoichiometry of the solid is
(a) AB_2
(b) A_2B
(c) A_4B_3
(d) A_3B_4 (IIT 2001)

259. An aqueous solution of 6.3 g oxalic acid dihydrate is made up to 250 mL. The volume of 0.1 N NaOH required to completely neutralize 10 mL of this solution is
(a) 40 mL
(b) 20 mL
(c) 10 mL
(d) 4 mL (IIT 2001)

260. In the standardization of $Na_2S_2O_3$ using $K_2Cr_2O_7$ by iodometry, the equivalent weight of $K_2Cr_2O_7$ is
(a) (molecular weight)/2
(b) (molecular weight)/6
(c) (molecular weight)/3
(d) same as molecular weight (IIT 2001)

261. If 'I' is the intensity of absorbed light and 'C' is the concentration of AB for the photochemical process $AB + h\nu \rightarrow AB^*$, the rate of formation of AB^* is directly proportional to
(a) C
(b) I
(c) I^2
(d) C.I (IIT 2001)

262. The correct order of equivalent conductance at infinite dilution of LiCl, NaCl and KCl is
(a) LiCl > NaCl > KCl
(b) KCl > NaCl > LiCl
(c) NaCl > KCl > LiCl
(d) LiCl > KCl > NaCl (IIT 2001)

263. At constant temperature, the equilibrium constant (K_p) for the decomposition reaction $N_2O_4 \rightleftharpoons 2NO_2$ is expressed by $K_p = (4x^2p)/(1-x^2)$, where p = pressure, x = extent of decomposition. Which one of the following statements is true?
(a) K_p increases with increase of p.
(b) K_p increases with increase of x.
(c) K_p increases with decrease of x.
(d) K_p remains constant with change in p and x. **(IIT 2001)**

264. The root-mean-square velocity of an ideal gas at constant pressure varies with density (d) as
(a) d^2 (b) d (c) $\sqrt{d}$ (d) $\frac{1}{\sqrt{d}}$ **(IIT 2001)**

265. The wavelength associated with a golf ball weighing 200 g and moving at a speed of 5 m/h is of the order (Planck constant, $h = 6.626 \times 10^{-34}$ J s)
(a) 10^{-10} m (b) 10^{-20} m (c) 10^{-30} m (d) 10^{-40} m **(IIT 2001)**

266. The set with correct order of acidity is
(a) $HClO < HClO_2 < HClO_3 < HClO_4$
(b) $HClO_4 < HClO_3 < HClO_2 < HClO$
(c) $HClO < HClO_4 < HClO_3 < HClO_2$
(d) $HClO_4 < HClO_2 < HClO_3 < HClO$ **(IIT 2001)**

267. The reaction $3ClO^-_{(aq)} \rightarrow ClO^-_{3(aq)} + 2Cl^-_{(aq)}$ is an example of
(a) oxidation reaction (b) reduction reaction
(c) disproportionation (d) decomposition reaction **(IIT 2001)**

268. Saturated solution of KNO_3 is used to make 'salt-bridge' because
(a) velocity of K^+ is greater than that of NO_3^-
(b) velocity of NO_3^- is greater than that of K^+
(c) velocities of both K^+ and NO_3^- are nearly the same
(d) KNO_3 is highly soluble in water **(IIT 2001)**

269. For a sparingly soluble salt A_pB_q, the relationship of its solubility product (L_s) with its solubility (S) is
(a) $L_s = S^{p+q} \cdot p^p \cdot q^q$ (b) $L_s = S^{p+q} \cdot p^q \cdot q^p$
(c) $L_s = S^{pq} \cdot p^p \cdot q^q$ (d) $L_s = S^{pq} \cdot (pq)^{p+q}$ **(IIT 2001)**

The questions below (270 to 279) consist of an *'assertion'* in column 1 and the *'reason'* in column 2. Use the following key to choose the appropriate answer.

(a) If both the *assertion* and *reason* are correct, and the *reason* is the correct explanation of the *assertion*.
(b) If both the *assertion* and *reason* are correct but the *reason* is not the correct explanation of the *assertion*.
(c) If *assertion* is correct but *reason* is incorrect.
(d) If *assertion* is incorrect but *reason* is correct.

Assertion (column 1)	Reason (column 2)
270. The pressure of a fixed amount of an ideal gas is proportional to its temperature.	Frequency of collisions and their impact both increase in proportion to the square root of temperature. (IIT 2001)
271. The heat absorbed during the isothermal expansion of an ideal gas against vacuum is zero.	The volume occupied by the molecules of an ideal gas is zero. (IIT 2001)
272. In any ionic solid [MX] with Schottky defects, the number of positive and negative ions are same.	Equal number of cation and anion vacancies are present. (IIT 2001)
273. When H_2S is passed into an aqueous solution of Zn^{2+} in the presence of NH_4OH, ZnS gets precipited.	Common-ion effect supresses the dissociation of weak electrolytes.
274. The time for completion of a first-order reaction is infinite.	The time for completion of any definite fraction of the reaction is constant for first-order reaction.
275. The addition of an inert gas at constant volume may affect the state of equilibrium: $PCl_5(g) = PCl_3(g) + Cl_2(g)$	The addition of inert gas at constant volume increases both the number of molecules and pressure to the same extent.
276. $Fe^{3+} + e = Fe^{2+}$; $E° = +0.77$ V $Fe^{2+} + 2e = Fe$; $E° = -0.44$ V ∴ $Fe^{3+} + 3e = Fe$; $E° = -0.04$ V	$E°$ is an extensive property
277. van der Waals equation describes the behaviour of real gases.	The kinetic theory postulates of negligible volume of gaseous molecules and intermolecular forces of attraction do not stand correct at high pressure and low temperature.
278. The nuclide $^{30}_{13}Al$ is less stable than $^{40}_{20}Ca$.	Nuclides having odd number of protons and neutrons are generally unstable. (IIT 1998)
279. The value of van der Waals constant 'a' is larger for ammonia than for nitrogen.	Hydrogen bonding is present in ammonia. (IIT 1998)

280. For which of the following types of reactions does $t_{1/2}$ go on decreasing with the progress of the reaction?
(a) Zero order (b) First order (c) Second order (d) Third order

281. When a reacton progresses, which of the following facts is not true?
(a) $t_{1/2}$ remains constant throughout in first-order reactions
(b) $t_{1/2}$ goes on decreasing in zero-order reactions.
(c) $t_{1/2}$ goes on decreasing in first-order reactions.
(d) $t_{1/2}$ goes on increasing in second-order reactions.

282. A hypothetical reaction $A_2 + B_2 \rightarrow 2AB$ follows the following mechanism.
$A_2 \rightarrow A + A$ (fast)

$$A + B_2 \rightarrow AB + B \quad \text{(slow)}$$
$$A + B \rightarrow AB \quad \text{(fast)}$$

The order of the overall reaction is

(a) 0 (b) 1 (c) 2 (d) 3/2

283. The internal energy change when a system goes from the state A to B is 40kJ/mol. If the system goes from A to B by a reversible path and returns to the state A by an irreversible path, what would be the net change in internal energy?

(a) > 40 kJ (b) < 40 kJ (c) Zero (d) 40 kJ

284. If at 298 K the bond energies of C–H, C–C, C=C and H–H bonds are respectively 414, 347, 615 and 435 kJ mol^{-1}, the value of enthalpy change for the reaction given below at 298 K will be

$$H_2C{=}CH_2\,(g) + H_2\,(g) \rightarrow H_3C{-}CH_3\,(g)$$

(a) –250 KJ (b) +125 KJ (c) –125 KJ (d) +250 kJ

285. One mole of the complex compound $Co(NH_3)_5Cl_3$, gives 3 moles of ions on dissolution in water. One mole of the same complex reacts with two moles of $AgNO_3$ solution to yield two moles of AgCl (s). The structure of the complex is

(a) $[Co(NH_3)_3Cl_3] \cdot 2NH_3$ (b) $[Co(NH_3)_4Cl_2]Cl \cdot NH_3$

(c) $[Co(NH_3)_4Cl]Cl_2 \cdot NH_3$ (d) $[Co(NH_3)_5Cl]Cl_2$

286. How many unit cells are present in a cube-shaped ideal crystal of NaCl of mass 1.00 g?

(a) 5.14×10^{21} (b) 1.28×10^{21} (c) 1.71×10^{21} (d) 2.57×10^{21}

287. In an irreversible process taking place at constant temperature and constant pressure and in which only p–V work is being done, the change in Gibbs free energy (dG) and the change in entropy (dS), satisfy the criteria

(a) $(dS)_{V,E} > 0, (dG)_{T,p} < 0$ (b) $(dS)_{V,E} = 0, (dG)_{T,p} = 0$

(c) $(dS)_{V,E} = 0, (dG)_{T,p} > 0$ (d) $(dS)_{V,E} < 0, (dG)_{T,p} < 0$

288. What volume of hydrogen gas at 273 K and 1 atm pressure will be consumed in obtaining 21.6 g of elemental boron (atomic mass = 10.8) from the reduction of BCl_3 by hydrogen?

(a) 67.2 L (b) 44.8 L (c) 22.4 L (d) 89.6 L

289. Standard reduction electrode potentials of three metals A, B and C are respectively + 0.5 V, –3.0 V and –1.2 V. The reducing powers of these metals are

(a) A > B > C (b) C > B > A (c) A > C > B (d) B > C > A

290. If liquids A and B form an ideal solution,

(a) the entropy of mixing is zero

(b) the free energy of mixing is zero

(c) the free energy as well as the entropy of mixing are each zero

(d) the enthalpy of mixing is zero

291. The rate law from a reaction between the substances A and B is given by

$$\text{rate} = k\,[A]^n\,[B]^m$$

On doubling the concentration of A and halving the concentration of B, the ratio of the new rate to the earlier rate of the reaction will be as

(a) $(m+n)$ (b) $(n-m)$ (c) $2^{(n-m)}$ (d) $\frac{1}{2^{(m+n)}}$

292. The effect of a tenfold pressure increase on the equilibrium composition of the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \text{is}$$

(a) 100-fold increase in K_x
(b) 10-fold increase in K_x
(c) no change in K_x
(d) 10-fold decrease in K_x

293. The addition of one of the reactants in a reaction at equilibrium

(a) always shifts the equilibrium towards product at constant volume but not always at constant pressure
(b) always shifts the equilibrium towards product at constant pressure but not always at constant volume
(c) always shifts the equilibrium towards product either at constant pressure or at constant volume
(d) does not shift the equilibrium either at constant pressure or at constant volume

294. A crystal of formula AB_3 has A ions at the cube corners and B ions at the edge centres. The coordination numbers of A and B are respectively

(a) 6 and 2 (b) 2 and 6 (c) 6 and 6 (d) 8 and 8

295. The rate of a first-order reaction is 1.5×10^{-2} mol L^{-1} at 0.5 M concentration of the reactant. The half-life of the reaction is

(a) 0.383 min (b) 23.1 min (c) 8.73 min (d) 7.53 min

296. The standard emf of a galvanic cell involving cell reaction with $n = 2$ is found to be 0.295 V at 25°C. The equilibrium constant of the reaction would be

(a) 2.0×10^{11} (b) 4.0×10^{12} (c) 1.0×10^{2} (d) 1.0×10^{10}

297. The rapid change of pH near the stoichiometric point of an acid–base titration is the basis of indicator detection. The pH of the solution is related to ratio of the concentration of the conjugate acid (HIn) and base (In^-) forms of the indicator by the expression

(a) $\log \frac{[In^-]}{[HIn]} = pK_{In} - pH$
(b) $\log \frac{[HIn]}{[In]} = pK_{In} - pH$
(c) $\log \frac{[HIn]}{[In^-]} = pH - pK_{In}$
(d) $\log \frac{[In^-]}{[HIn]} = pH - pK_{In}$

298. The frequency of radiation emitted when the electron falls from $n = 4$ to $n = 1$ in a hydrogen atom will be (given ionization energy of H $= 2.18 \times 10^{-18}$ J atom^{-1} and $h = 6.625 \times 10^{-34}$ J s

(a) $1.54 \times 10^{15}\ s^{-1}$ (b) $1.03 \times 10^{15}\ s^{-1}$ (c) $3.08 \times 10^{15}\ s^{-1}$ (d) $2.00 \times 10^{15}\ s^{-1}$

[Hint: $\Delta E = h\nu = E_1\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$]

299. The work done during the expansion of a gas from a volume of 4 dm^3 to 6 dm^3 against a constant external pressure of 3 atm is (1 L atm = 101.32 J)

(a) –6 J (b) –608 J (c) +304 J (d) –304 (J)

300. The emf of the cell,

$$Zn \mid Zn^{2+}(a = 0.1\ M) \parallel Fe^{2+}(a = 0.01\ M) \mid Fe$$

is 0.2905 V. The equilibrium constant of the cell reaction is

(a) $10^{0.32/0.0591}$ (b) $10^{0.32/0.0295}$ (c) $10^{0.26/0.0295}$ (d) $e^{0.32/0.295}$

301. HX is a weak acid ($K_a = 10^{-5}$). It forms a salt NaX (0.1 M) on reacting with caustic soda. The degree of hydrolysis of NaX is

(a) 0.01% (b) 0.0001% (c) 0.1% (d) 0.5%

302. Spontaneous adsorption of a gas on solid surface is an exothermic process because

(a) ΔH increases for system (b) ΔS increases for gas

(c) ΔS decreases for gas (b) ΔG increases for gas

303. For a monoatomic gas, kinetic energy is equal to E, its relation with rms velocity is

(a) $C = \sqrt{\frac{2E}{M}}$ (b) $C = \sqrt{\frac{3E}{2M}}$ (c) $C = \sqrt{\frac{E}{2M}}$ (d) $C = \sqrt{\frac{E}{3M}}$

304. The pair of compounds having metals in their highest oxidation state is

(a) MnO_2, $FeCl_3$ (b) $[MnO_4]^-$, CrO_2Cl_2

(c) $[Fe(CN)_6]^{3-}$, $[Co(CN)_3]$ (d) $[NiCl_4]^{2-}$, $[CoCl_4]^-$

305. The spin magnetic moment of the compound $Hg[Co(SCN)_4]$ is

(a) $\sqrt{3}$ (b) $\sqrt{15}$ (c) $\sqrt{24}$ (d) $\sqrt{8}$

[Hint: $\mu = \sqrt{n(n+2)}$ BM]

306. Which hydrogenlike species will have the same radius as that of the Bohr orbit of the hydrogen atom?

(a) $n = 2$, Li^{2+} (b) $n = 2$, Be^{3+} (c) $n = 2$, He^+ (d) $n = 3$, Li^{2+}

[Hint: $r = \frac{n^2h^2}{4\pi^2 m z e^2}$]

307. 0.004 M Na_2SO_4 is isotonic with 0.01 M glucose. Degree of dissociation of Na_2SO_4 is

(a) 75% (b) 50% (c) 25% (d) 85%

[Hint: $(1 + 2\alpha)0.004 = 0.01$]

308. $\Delta H_{vap} = 30$ kJ/mol and $\Delta S_{vap} = 75\ J\ mol^{-1}\ K^{-1}$. Find the temperature of the vapour at 1 atm.

(a) 400 K (b) 350 K (c) 298 K (d) 250 K

[Hint: See pg. 414: $T = \frac{\Delta H}{\Delta S}$]

309. 2 mol of an ideal gas expands isothermally and reversibly from 1 litre to 10 litres at 300 K. What is the enthalpy change?

(a) 4.98 kJ (b) 11.47 kJ (c) −11.47 kJ (d) 0 kJ

310. (A) follows a first-order reaction: (A) → Product, and the concentration of A changes from 0.1 M to 0.025 M in 40 minutes. Find the rate of reaction of A when the concentration of A is 0.01 M.

(a) $3.47 \times 10^{-4}\ M\ min^{-1}$ (b) $3.47 \times 10^{-5}\ M\ min^{-1}$

(c) $1.73 \times 10^{-4}\ M\ min^{-1}$ (d) $1.73 \times 10^{-5}\ M\ min^{-1}$

311. When I^- is oxidised by MnO_4^- in an alkaline medium, I^- converts into
(a) IO_3^- (b) I_2 (c) IO_4^- (d) IO^-

312. Which of the following will not be oxidised by O_3?
(a) KI (b) $FeSO_4$ (c) $KMnO_4$ (d) K_2MnO_4
[**Hint:** In $KMnO_4$, Mn is in maximum possible oxidation state.]

313. Which of the following f.c.c. structures contains cations in alternate voids?
(a) NaCl (b) ZnS (c) Na_2O (d) CaF_2
[**Hint:** See pg. 710]

314. The elevation in boiling point when 13.44 g of freshly prepared $CuCl_2$ are added to one kilogram of water is ($K_b = 0.52$ kg K mol^{-1}, mol. wt of $CuCl_2 = 134.4$)
(a) 0.05 (b) 0.1 (c) 0.156 (d) 0.21

315. The half-cell reactions of rusting of iron are

$$2H^+ + \frac{1}{2}O_2 + 2e \rightarrow H_2O; \quad E^0 = +1.23 \text{ V}$$

$$Fe^{2+} + 2e \rightarrow Fe; \quad E^0 = -0.44 \text{ V}$$

ΔG^0 (in kJ) for the reaction is
(a) –76 (b) –322 (c) –122 (d) –176
[**Hint:** $Fe + 2H^+ + \frac{1}{2}O_2 \rightarrow Fe^{2+} + H_2O$; $E^0_{cell} = 1.67$ V]

316. The number of radial nodes in 3s and 2p respectively are
(a) 2 and 0 (b) 1 and 2 (c) 0 and 2 (d) 2 and 1
[**Hint:** See pg. 247, Chapter 11]

317. 0.1 mole of $CH_3 \cdot NH_2$ ($K_b = 5 \times 10^{-4}$) is added to 0.08 mole of HCl and the solution is diluted to one litre. The resulting $[H^+]$ is
(a) 1.6×10^{-11} (b) 8×10^{-11} (c) 5×10^{-5} (d) 8×10^{-2}
[**Hint:** The resulting solution is a buffer solution.]

318. If He and CH_4 are allowed to diffuse out of the container under similar conditions of temperature and pressure then the ratio of the rate of diffusion of He to CH_4 is
(a) 2.0 (b) 1.0 (c) 0.5 (d) 4.0

319. Which of the following is correct for lyophilic sols?
(a) They are irreversible.
(b) They are formed by inorganic substances.
(c) They are readily coagulated by addition of electrolytes.
(d) They are self-stabilized.

320. Which of the following statements is incorrect about the order of a reaction?
(a) The order of a reaction is determined experimentally.
(b) It is the sum of the powers of concentration terms in the rate law expression.
(c) It does not necessarily depend on stoichiometric coefficients.
(d) The order of a reaction can not have a fractional value.

321. One mole of a monoatomic ideal gas expands adiabatically at initial temperature T against a constant external pressure of 1 atm from one litre to two litres. Find out the final temperature. ($R = 0.0821$ L atm K^{-1} mol^{-1})

(a) T (b) $\frac{T}{(2)^{5/3-1}}$ (c) $T - \frac{2}{3 \times 0.0821}$ (d) $T + \frac{2}{3 \times 0.0821}$

[Hint: In adiabatic expansion, $q = 0$

$\therefore \ \Delta E = q + w = w = -p_{ext} (V_2 - V_1)$

Also $\Delta E = n\, C_V (T_2 - T_1)$ (Eqn. 6, Chapter 14)

Answers

1-c, 2-a, 3-d, 4-a, 5-b, 6-b, 7-b, 8-d, 9-b, 10-b, 11-d, 12-d, 13-a, 14-d, 15-d, 16-b, 17-a, 18-c, 19-b, 20-a, 21-a, 22-b, 23-b, 24-b, 25-d, 26-b, 27-a, 28-d, 29-a, 30-a, 31-b, 32-b, 33-b, 34-c, 35-a, 36-d, 37-b, 38-a, 39-d, 40-b, 41-a, 42-c, 43-d, 44-b, 45-d, 46-c, 47-c, 48-c, 49-a, 50-c, 51-d, 52-d, 53-b & d, 54-b & d, 55-All correct, 56-a & d, 57-c, 58-d, 59-a, 60-a, 61-c, 62-b, 63-d, 64-b, 65-a, 66-c, 67-c, 68-b, 69-a, 70-b, 71-b, 72-a & b, 73-d, 74-a, 75-c, 76-c, 77-All correct, 78-a, 79-a, 80-d, 81-c & d, 82-c, 83-d, 84-d, 85-b & d, 86-b & d, 87-a, 88-c, 89-c, 90-c, 91-b, 92-c, 93-d, 94-a, 95-a, 96-b, 97-b, 98-b, 99-d, 100-a, 101-a, 102-b, 103-d, 104-c, 105-d, 106-c, 107-b, 108-c, 109-c, 110-a, 111-a, 112-a & c, 113-a, 114-a, c & d, 115-a & d, 116-c, 117-d, 118-c, 119-d, 120-c, 121-d, 122-a, 123-a, 124-b, 125-a, 126-c, 127-a, 128-a, b & d, 129-a & d, 130-a, b & c, 131-b, 132-d, 133-b, 134-d, 135-c, 136-b, 137-c, 138-a, 139-d, 140-b, 141-a, b & c, 142-c, 143-a & d, 144-b, 145-d, 146-b, 147-a, 148-a, 149-a, 150-c, 151-d, 152-a, 153-b, 154-d, 155-c, 156-c, 157-c, 158-d, 159-b, 160-c & d, 161-b, 162-b, 163-b, 164-a, 165-c, 166-a, 167-c, 168-d, 169-c, 170-a, 171-a, 172-b, 173-a, 174-d, 175-d, 176-d, 177-b, 178-d, 179-c, 180-a, 181-a, 182-All correct, 183-a, 184-b, 185-d, 186-b, 187-a, 188-b, 189-a, 190-d, 191-c, 192-b, 193-d, 194-a, 195-d, 196-c, 197-c, 198-a, 199-b, 200-c, 201-a, 202-a, 203-c, 204-b, 205-a, 206-c, 207-d, 208-b, 209-b, 210-c, 211-c & d, 212-b & d, 213-c, 214-a & c, 215-a & c, 216-a, 217-a, 218-b, 219-b, 220-a, 221-a, 222-b, 223-a, 224-a, 225-a & d, 226-c & d, 227-a & d, 228-b & d, 229-b, 230-b, 231-a, 232-c, 233-a, 234-d, 235-b, 236-a, 237-a, 238-c, 239-b, 240-b, 241-b, 242-b, 243-d, 244-c, 245-c, 246-c, 247-b, 248-a & d, 249-b, 250-c, 251-d, 252-a, 253-c, 254-a 255-d, 256-a, 257-c, 258-d, 259-a, 260-b, 261-b, 262-b, 263-d, 264-d, 265-c, 266-a, 267-c, 268-c, 269-a, 270-a, 271-b, 272-a, 273-b, 274-a, 275-d, 276-c, 277-a, 278-a, 279-a, 280-a, 281-c, 282-d, 283-c, 284-c, 285-d, 286-d, 287-a, 288-a, 289-d, 290-d, 291-c, 292-a, 293-a, 294-a, 295-b, 296-d, 297-b, 298-c, 299-b, 300-b, 301-a, 302-c, 303-a, 304-b, 305-b, 306-b, 307-a, 308-a, 309-d, 310-a, 311-a, 312-c, 313-b, 314-c, 315-b, 316-a, 317-b, 318-a, 319-d, 320-d, 321-c.

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This book is indispensable for science students at the +2 (intermediate) level, especially for those who are preparing for the entrance examinations of engineering and medical colleges. This book highlights the importance of the concept of mole in solving problems quickly and easily. Some of the key features of the book are:

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