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Tata McGraw-Hill's

COURSE *in*

CHEMISTRY

for IIT-JEE

2012



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Course in Chemistry for IIT-JEE 2012

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Organic and Inorganic

- Boron and its Compounds.
- Silicates and silicones.
- Oxoacids of P, S and halogens.
- Interhalogens and compounds of noble gases.
- Transition elements, coordination compounds and lanthanides.
- Important compounds such as H_2O_2, $NaHCO_3$, Na_2CO_3, $KMnO_4$ and K_2CrO_7.
- Quantitive analysis of salts.
- Isomerism including optical isomerism.
- Inductance and resonance effects on acidity and basicity of acids and bases.
- Factors affecting S_N1 and S_N2 reactions.
- Reactions involving rearrangement.
- Bromination and hydrogenation of cis- and trans-alkenes, debromination of dibromobutane.
- Characteristic reaction of aldehede, ketones and carboxylic acids derivatives.
- Reactions with Grignard reagent and those of diazonium salt.
- Carbohydrates and polymers.
- Quantitative analysis of organic compounds.

All the above topics are adequately covered in this edition, supported by plenty of practice problems.

We are hopeful that this comprehensive manual would be of great support to students preparing for the examination.

We wish the aspirants all the best in their endeavours.

THE PUBLISHERS

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A Word to the Reader

Course in Chemistry for IIT-JEE is part of Tata McGraw-Hill's series of books for IIT-JEE.

Divided into 34 chapters that covers the entire gamut of the syllabus (Physical Chemistry, Inorganic Chemistry & Organic Chemistry), each chapter begins with a revisit of the important list of definitions, formulae, theorems, etc.

This is followed by MCQs, Linked-Comprehension Type, Assertion-Reason and Matrix match type questions, all of which reflect the latest pattern of the examination.

All questions are fully solved and there is adequate coverage of more difficult concepts.

Some key features

- IUPAC recommendations and SI units used throughout.
- Straight-Objective-type questions are enlarged and classified with their solutions.
- Fully solved IIT-JEE papers of 2009 & 2010
- Practice Question Papers

What's special?

Over 3000 MCQs with one correct choice and completely solved
Around 800 MCQs with more than one correct choice and fully solved
More than 170 Linked comprehension type questions
About 370 Assertion- Reason type questions & over 120 matrix-match questions

Tips for preparation

Systematic and early preparation is often the key to success in the IIT-JEE. Attempting questions with speed is a crucial factor. Also it is important to attempt all questions within the stipulated time.

The three branches of Chemistry, viz., Physical, Inorganic and Organic are equally important. Physical Chemistry is less diverse compared to Organic and Inorganic. The applications to different problems in this are also straightforward.

Given below are some important topics of Physical, Organic and Inorganic that require special attention:

Physical:

- Bohr's theory of atomic structure, quantum numbers and orbitals.
- MO approach to diatomic molecules, concepts of hybridization/VSEPR theory.
- Van der Waals equation of state and its application to the behaviour of real gases.
- Crystal systems, packing of atoms, ionic solids, density of crystals and imperfection
- Colligative properties of non-electrolytic and electrolytic solutions.
- Electrolysis, conductance and galvanic cells.
- Rate laws, effect of catalyst and temperature on the rate of reaction.
- PH of salt solutions and solubility product.
- Le-Chatelier principle, relation between K_p and K_c.
- Thermochemical calculations and criterion of spontaneity.
- Radioactive decay.

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Chapter 1

The Concept of Atoms and Molecules

Atomic and Molecular Masses

The branch of chemistry which deals with mass relationships in chemical reactions is called stoichiometry. Before dealing with this branch, a brief review of the terms recommended by IUPAC in describing the atomic and molecular masses is in order.

Relative Atomic Mass of an Element The ratio of the average mass per atom of the natural isotopic composition of the element to 1/12th of the mass of an atom of nuclide ^{12}C is known as the relative atomic mass (formerly known as atomic weight) of the element.

Relative Molecular Mass of a Compound The ratio of the average mass per molecule of the natural isotopic composition of the compound to 1/12th mass of an atom of nuclide ^{12}C is known as relative molecular mass (formerly known as molecular weight) of the compound.

Atomic Mass Unit The quantity 1/12th mass of an atom of nuclide ^{12}C is known as the atomic mass unit. The value of atomic mass unit can be determined from the fact that 1 mol of ^{12}C has been assigned mass exactly to 0.012 kg. Hence,

$$1 \text{ amu} = \frac{(0.012 \text{ kg mol}^{-1})/(6.022 \times 10^{23} \text{ mol}^{-1})}{12} = 1.6606 \times 10^{-27} \text{ kg}$$

Atomic Mass The average mass per atom of natural isotopic composition of an element is known as atomic mass. It is given as Atomic mass = (Relative atomic mass) (atomic mass unit).

Molecular Mass The average mass per molecule of natural isotopic composition of a compound is known as molecular mass. It is given as Molecular mass = (Relative molecular mass) (atomic mass unit).

Mole of a Substance One mole (1 mol) of a substance contains as many objects (e.g. atoms, molecules, ions) as there are atoms in exactly 12 g of nuclide ^{12}C. This number is approximately equal to 6.022×10^{23}.

Amount of a Substance If a sample of a substance contians N specified entities, the amount of substance (formerly known as number of mole) is given as $n = N/N_A$, where N_A is Avogadro constant (= 6.022×10^{23} mol^{-1}). The unit of amount of substance is 'mol'.

Molar Mass The average mass per unit amount of a substance (applicable to both elements and compounds) of naturally isotopic composition is known as molar mass. Its unit is g mol^{-1} or kg mol^{-1}.

The molecular (or molar) mass of a compound is equal to the sum of atomic (or molar) masses of its constituent atoms. The atomic (or molecular) mass of an atom (or a compound) expressed in atomic mass unit and the molar mass expressed in g mol^{-1} have the same numerical value. This value is also the same as that of relative atomic (or molecular) mass of the substance.

Laws of Chemical Combination

There are three laws of chemical combination. These are as follows.

Law of Conservation of Masses (Lavoisier, 1774) The mass is conserved in a chemical reaction.

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Law of Constant Composition (Proust, 1799) All pure samples (drawn from different sources) of the same compound contain the same elements combined in the same proportion by mass.

Law of Multiple Proportion (Dalton, 1803) Two elements, A and B combine to form more than one compound, the masses of A which separately combine with a fixed mass of B (or vice versa) are in the ratio of small whole numbers.

Quantitative Information From a Chemical Equation

A balanced chemical equation provides quantitative information regarding the consumption of reactants and creation of products. The numbers which appear before the chemical symbols and which balance the equation (with the understanding that if no number appears, it is equal to unity) are called the stoichiometric coefficients (or numbers) and are proportional to the number of molecules or the amount of the constituents that change during the progress of the reaction. For a general case

$$\nu_A A + \nu_B B \rightarrow \nu_C C + \nu_D D \tag{1}$$

where ν_A, ν_B, ν_C and ν_D are the stoichiometric coefficients of the species A, B, C and D, respectively. The progress of the reaction is described in terms of a physical parameter, known as *extent of reaction* (symbol; ξ, pronounced as xi). It is expressed as

$$-\frac{\Delta n_A}{\nu_A} = -\frac{\Delta n_B}{\nu_B} = \frac{\Delta n_C}{\nu_C} = \frac{\Delta n_D}{\nu_D} = \xi \tag{2}$$

where Δns represent the changes in the amount (i.e. number of moles) of the species. The negative and positive signs represent decrease and increase in the amount of the species, respectively. The unit of ξ is mol.

Equation (2) is often interpreted as follows.

$$-\nu_A \xi \text{ of A} \equiv -\nu_B \xi \text{ of B} \equiv \nu_C \xi \text{ of C} \equiv \nu_D \xi \text{ of D} \tag{3}$$

where the sign $\equiv$ is used for the term 'equivalent to'.

Equation (3) is often used for a unit extent of reaction where $\xi = 1$ mol. In this case, we have

$$-\nu_A \text{ mol of A} \equiv -\nu_B \text{ mol of B} \equiv \nu_C \text{ mol of C} \equiv \nu_D \text{ mol of D} \tag{4}$$

In other words ν_A mol of A on reacting with ν_B mol of B gives ν_C mol of C and ν_D mol of D.

Since the amount of species is directly proportional to the number of species, Eq. (4) may also be expressed as

$$-\nu_A \text{ molecules of A} \equiv -\nu_B \text{ molecules of B} \equiv \nu_C \text{ molecules of C} \equiv \nu_D \text{ molecules of D} \tag{5}$$

indicating that ν_A molecules of A on reacting with ν_B molecules of B produces ν_C molecules of C and ν_D molecules of D.

The relative changes in the masses of species are obtained by multiplying the terms in Eq. (4) by the respective molar masses, i.e.

$$-\nu_A M_A \text{ mol of A} \equiv -\nu_B M_B \text{ mol of B} \equiv \nu_C M_C \text{ mol of C} \equiv \nu_D M_D \text{ mol of D} \tag{6}$$

Equations (4) to (6) may be illustrated by taking the example of the reaction

$$\underset{\text{Molar mass: } 331.2 \text{ g mol}^{-1}}{Pb(NO_3)_2} + \underset{166.0 \text{ g mol}^{-1}}{2KI} \rightarrow \underset{461.0 \text{ g mol}^{-1}}{PbI_2} + \underset{101.1 \text{ g mol}^{-1}}{2KNO_3}$$

Equation (4) tells that

1 mol of $Pb(NO_3)_2$ on reacting with 2 mol of KI produces 1 mol of PbI_2 and 2 mol of KNO_3.

Equation (5) tells that

1 molecule of $Pb(NO_3)_2$ on reacting with 2 molecules of KI produces 1 molecule of PbI_2 and 2 molecules of KNO_3.

Equation (6) tells that

331.2 g of $PbNO_3$ on reacting with 2×166.0 g of KI produces 461.0 g of PbI_2 and 2×101.1 g of KNO_3.

Expressing Concentration of a Substance

The different ways of expressing the concentration of a substance are as follows.

Mass Percentage The defining expression is $\text{Mass percentage of A} = \frac{\text{Mass of substance A}}{\text{Total mass of the system}} \times 100$

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Mole Fraction The defining expression is $$\text{Mole fraction of A} = \frac{\text{Amount (in mol) of substance A}}{\text{Total amount of substances in the system}}$$

In symbolic form, $x_A = n_A/n_{total}$

Molarity The defining expression is $$\text{Molarity of A} = \frac{\text{Amount (in mol) of substance A}}{\text{Volume of solution expressed in dm}^3}$$

In symbolic form, $M = n_2/V$; (V expressed in dm^3)

The unit of molarity is mol dm^{-3}. It is commonly abbreviated by the symbol M and is spelled as molar. The molarity of a substance is temperature-dependent property due to the variation of volume with temperature.

Molality The defining expression is $$\text{Molality of A} = \frac{\text{Amount (in mol) of substance A}}{\text{Mass of solvent expressed in kg}}$$

In symbolic form, $m_A = n_A/m_1$; (m_1 expressed in kg)

The unit of molality is mol kg^{-1} and is spelled as molal. The molality of a substance is independent of temperature of solution.

Conversion of Concentration Units

Representing solvent and solute in a binary solution by subscripts 1 and 2, respectively, the various conversion expressions are as follows.

Mole fraction into molarity $M = \dfrac{x_2\rho}{x_1M_1 + x_2M_2}$ *Molarity into mole fraction* $x_2 = \dfrac{MM_1}{\rho + M(M_1 - M_2)}$

Mole fraction into molality $m = \dfrac{x_2}{x_1M_1}$ *Molality into mole fraction* $x_2 = \dfrac{mM_1}{1 + mM_1}$

Molality into molarity $M = \dfrac{m\rho}{1 + mM_2}$ *Molarity into molality* $m = \dfrac{M}{\rho - MM_2}$

where M_1 and M_2 are the molar masses of solvent and solute, respectively, and ρ is the density of solution (expressed in mass per dm^3 of solution).

Concept of Equivalent

One equivalent of a substance in a reaction is defined as the amount of substance which reacts or liberates 1 mol of electrons (or H^+ or OH^- ions). In a reaction, a substance always reacts with another substance in equivalent amounts. The equivalent mass of a substance in a reaction is defined as the molar mass divided by the number of equivalents in 1 mol of the substance. The concentration of a solution may be expressed in normality(Symbol: N) which is equal to the amount of solute in equivalents dissolved in 1 dm^3 of the solution. It has the units of equivalent per dm^3 and is abbreviated by the symbol N. The number of equivalents of the substance is given as

$$\text{Amount in equivalents} = \frac{\text{Mass of solute}}{\text{Equivalent mass}}$$

The equivalent mass of a solute (and also the normality of the solution) has to be determined with reference to a reaction since the solute may react in different ways in different reactions. For example, $KMnO_4$ oxidizes a reducing agent in different manners depending upon the medium as described in the following.

Acidic medium : $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

Weakly acidic or neutral or weakly alkaline medium : $MnO_4^- + 3e^- + 4H^+ \rightarrow MnO_2 + 2H_2O$

Alkaline medium : $MnO_4^- + e^- \rightarrow MnO_4^{2-}$

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Hence,

$$\text{Equivalent mass of } KMnO_4 \text{ in acidic medium} = \frac{\text{Molar mass of } KMnO_4}{5 \text{ eq mol}^{-1}}$$

$$\text{Equivalent mass of } KMnO_4 \text{ in weakly acidic, alkaline or neutral medium} = \frac{\text{Molar mass of } KMnO_4}{3 \text{ eq mol}^{-1}}$$

Equivalent mass of $KMnO_4$ in alkaline medium = Molar mass of $KMnO_4$/eq mol^{-1}

In volumetric analysis, the expression $N_1V_1 = N_2V_2$ indicates the equality of substances being titrated in equivalents at the equivalence point.

Balancing Chemical Equation

Quite often one has to write a balanced chemical equation while dealing with the problem on stoichiometry. After writing reactants and products, the balancing can be carried out by hit and trial method. However, two systematic methods are available for balancing redox reactions. Before describing these methods, the rules governing the computation of oxidation state of an element are described in the following.

Rules to Compute Oxidation Number The oxidation number of an element is the number assigned to it by following the arbitrary rules given below.

1. A free element (regardless of whether it exists in monatomic or polyatomic form, e.g. Hg, H_2, P_4 and S_8) is assigned an oxidation number of zero.
2. A free monatomic ion is assigned an oxidation number equal to the charge it carries. For example, the oxidation numbers of Al^{3+}, S^{2-} and Cl^- are +3, −2, and −1, respectively.
3. In their compounds, the alkali and alkaline earth metals are assigned oxidation numbers of +1 and +2, respectively.
4. The oxidation number of hydrogen in its compounds is generally +1 except the ionic hydrides such as LiH, $LiAlH_4$, where its oxidation number is −1.
5. The oxidation number of fluorine in all its compounds is −1. The oxidation number of all other halogens is −1 in all compounds except those with oxygen (e.g. ClO_4^-) and halogens having a lower atomic number (e.g. ICl_3^-). The oxidation number of the latter is determined via oxygen and halogen of lower atomic number.
6. The oxidation numbers of both oxygen and sulphur in their normal oxides (e.g. Na_2O) and sulphides (e.g. CS_2) is −2. The exceptions are the peroxides (e.g. H_2O_2 and Na_2O_2), superoxides (e.g. KO_2) and the compound OF_2. Their oxidation numbers are determined by the rules 3, 4 and 5.
7. The algebraic sum of oxidation numbers of atoms in a chemical species (compound or ion) is equal to the net charge on the species.

A few examples of the computation of oxidation number of atoms N in various compounds are as follows.

If x is the oxidation number of N, we have

NH_3	$x + 3(+1) = 0$	which gives $x = -3$	HN_3	$+1 + 3(x) = 0$	which gives $x = -\frac{1}{3}$
N_2H_4	$2x + 4(+1) = 0$	which gives $x = -2$	NO_2	$x + 2(-2) = 0$	which gives $x = 4$
N_2O_4	$2x + 4(-2) = 0$	which gives $x = 4$	NO_2^-	$x + 2(-2) = -1$	which gives $x = 3$
NH_2OH	$x + 2(+1) + 1(-2) + 1 = 0$	which gives $x = -1$	NO	$x + 1(-2) = 0$	which gives $x = 2$
HNO_3	$+1 + x + 3(-2) = 0$	which gives $x = 5$	N_2O	$2x + 1(-2) = 0$	which gives $x = 1$
HCN	$+1 + 4 + x = 0$	which gives $x = -5$			

Balancing Redox Reactions via Oxidation Numbers The steps involved in this method are as follows.

1. Identify the elements in the unbalanced equation whose oxidation number are changed.
2. Balance the number of atoms of each element whose oxidation number is changed.
3. Find out the total change in oxidation number for each of oxidant and reductant and make them equal by multiplying by small coefficients.

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4. Balance the remainder of atoms by inspection and add, if necessary, H^+ (acidic medium) or OH^- (alkaline medium) or H_2O (to balance oxygen) as the case may be.

Taking the example of $Cu + H^+ + NO_3^- \rightarrow Cu^{2+} + H_2O + NO$ we have

Step 1 : $\overset{0}{Cu} + H^+ + \overset{+5}{N}O_3^- \rightarrow \overset{+2}{Cu^{2+}} + H_2O + \overset{+2}{N}O$ *Step* 2 : Not required

Step 3 : $3Cu + H^+ + 2NO_3^- \rightarrow 3Cu^{2+} + H_2O + 2NO$ (with $[1(-3) = -3] \times 2$ and $[1(+2) = +2] \times 3$)

Step 4 : $3Cu + 8H^+ + 2NO_3^- \rightarrow 3Cu^{2+} + 4H_2O + 2NO$

Balancing Redox Reaction via Ion-Electron (or Half-Equation) Method In this case, the steps involved are:

1. Write the two separate half equations involving the species oxidized along with its oxidation product and the species reduced along with its reduced product.
2. Balance the number of atoms oxidized (or reduced) on both sides of the equation.
3. Depending upon the medium (acidic or alkaline), add H^+ (two H^+ per O atom on the same side of oxygen) or OH^- (two OH^- per O atom on the opposite side of oxygen) so that the oxygen atoms in the equations are converted into water which are also included in the appropriate side of the equation.
4. Now add electrons in the right (or left) hand side of the oxidation (or reduction) reaction for balancing the charges on both sides.
5. Now multiply each resultant equation in step 4 by the smallest possible integer so as to have the same number of electrons in both oxidation and reduction reactions.
6. Add the two equations and cancel the common species appearing on both sides of the equation.

Taking again the example $Cu + H^+ + NO_3^- \rightarrow Cu^{2+} + H_2O + NO$ we have

Step 1 :	$Cu \xrightarrow{\text{oxidation}} Cu^{2+}$	$NO_3^- \xrightarrow{\text{reduction}} NO$
Step 2 :	Not required	
Step 3 :	$Cu \rightarrow Cu^{2+}$	$NO_3^- + 4H^+ \rightarrow NO + 2H_2O$
Step 4 :	$Cu \rightarrow Cu^{2+} + 2e^-$	$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$
Step 5 :	$[Cu \rightarrow Cu^{2+} + 2e^-] \times 3$	
	$[NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O)] \times 2$	
Step 6 :	$3Cu + 2NO_3^- + 8H^+ \rightarrow 3Cu^{2+} + 2NO + 4H_2O$	

Straight Objective Type

Atomic and Molar Masses

1. The atomic mass of an element is measured relative to the mass of
   (a) hydrogen atom (b) oxygen atom
   (c) carbon-12 (d) isotopic mixture of ^{12}C, ^{13}C and ^{14}C.
2. One atomic mass unit is equivalent to
   (a) 1.66×10^{-27} g (b) 1.66×10^{-27} kg (c) 1.66×10^{-27} mg (d) 1.66×10^{-27} cg
3. The numerical value of atomic mass of an element is equal to its relative atomic mass when the former is expressed in
   (a) g mol^{-1} (b) kg mol^{-1} (c) mg mol^{-1} (d) cg mol^{-1}
4. The numerical values of molecular mass and molar mass of a substance are identical when
   (a) molecular mass is expressed in grams and molar mass in atomic mass unit
   (b) both molecular mass and molar mass are expressed in atomic mass unit
   (c) molecular mass is expressed in atomic mass unit and molar mass in grams
   (d) both molecular mass and molar mass are expressed in grams

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5. The value of Avogadro constant is

(a) 6.022×10^{23} (b) 6.022×10^{23} mol^{-1}

(c) 6.022×10^{23} atoms (d) 6.022×10^{13} molecules mol^{-1}

6. The amount of electrons in one kg is

(a) 6.022×10^{23} (b) $\frac{1}{9.108} \times 10^{31}$ (c) $\frac{6.022}{9.108} \times 10^{54}$ (d) $\frac{1}{9.108 \times 6.022} \times 10^{8}$

7. Which of the following has maximum number of atoms?

(a) 24 g of C (M = 12 g mol^{-1}) (b) 23 g of Na (M = 23 g mol^{-1})

(c) 48 g of S (M = 32 g mol^{-1}) (d) 108 g of Ag (M = 108 g mol^{-1}) (2003)

8. Given that the abundances of isotopes ^{54}Fe, ^{56}Fe and ^{57}Fe are 5%, 90% and 5%, respectively, the relative atomic mass of Fe is

(a) 55.85 (b) 55.95 (c) 55.75 (d) 56.05 (2009)

9. The largest number of molecules is in

(a) 36 g of water (b) 28 g of carbon monoxide

(c) 46 g of ethyl alcohol (d) 54 g of nitrogen pentoxide (1979)

10. A gaseous mixture contains oxygen ans nitrogen in the ratio of 1: 4 by mass. The ratio of their number of molecules is

(a) 1: 4 (b) 1: 8 (c) 7: 32 (d) 3: 16 (1979)

11. Which of the following has highest mass?

(a) 20 g phosphorus (b) 5 mol of water

(c) 2 equivalent of Na_2CO_3 (d) 12×10^{24} atoms of hydrogen (1978)

12. The volume of H_2 evolved at STP when 0.9 g of Al (molar mass: 27 g mol^{-1}) is dissolved in excess of dilute H_2SO_4 is

(a) 0.58 L (b) 1.12 L (c) 2.40 L (d) 2.9 L

Concentrations

13. 40.25 g of Glauber's salt is dissolved in water to obtain 500 mL of solution of density 1077.5 g dm^{-3}. The molality of Na_2SO_4 in solution is about

(a) 0.25 mol kg^{-1} (b) 0.24 mol kg^{-1} (c) 0.26 mol kg^{-1} (d) 0.27 mol kg^{-1}

14. The mass of $NaBrO_3$ required to prepare 150 mL of 0.75 N of a solution based on the reaction $BrO_3^- + 6H^+ + 6e^- \rightarrow Br^- + 3H_2O$ is

(a) 1.42 g (b) 2.83 g (c) 3.85 g (d) 4.25 g

15. Which of the following expressions correctly represent the conversion expression of molality m of a solution in terms of mole fraction x_2 of the solute in the solution?

(a) $x_2 = mM_1/(1 - mM_1)$ (b) $x_2 = mM_1/(1 + mM_1)$ (c) $x_2 = (1 + mM_1)/mM_1$ (d) $x_2 = (1 - mM_1)/mM_1$

where M_1 is the molar mass of solvent.

16. Which of the following expressions correctly represent the conversion of molality m into molarity M of a solution?

(a) $M = m\rho/(1 + mM_2)$ (b) $M = m\rho/(1 + mM_2)$ (c) $M = (1 + m\rho)/mM_2$ (d) $M = (1 - m\rho)/mM_2$

where ρ and M_2 are the density of solution and molar mass of solute, respectively.

17. The mole fraction of ethanol in water is 0.08. Its molality will be

(a) 2.41 mol kg^{-1} (b) 4.83 mol kg^{-1} (c) 3.33 mol kg^{-1} (d) 6.41 mol kg^{-1}

18. The expression converting mole fraction of a solute into molarity of solution is

(a) $M = x_2 M_2 / (x_1 M_1 + x_2 M_2)$ (b) $M = (x_1 M_1 + x_2 M_2) / x_2 M_2$

(c) $M = x_2 \rho / (x_1 M_1 + x_2 M_2)$ (d) $M = x_1 \rho / (x_1 M_1 + x_2 M_2)$

where the various symbols have their usual meanings.

19. The expression converting molarity (M) into mole fraction x_2 of the solute in the solution is

(a) $x_2 = \frac{M M_2}{\rho + M(M_1 - M_1)}$ (b) $x_2 = \frac{M M_1}{\rho + M(M_1 - M_2)}$

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(c) $x_2 = \dfrac{M\,M_2}{\rho + M\,(M_2 - M_1)}$ (d) $x_2 = \dfrac{M\,M_1}{\rho + M\,(M_2 - M_1)}$

where the various symbols have their usual meanings.

20. The normality of 0.3 M phosphorous acid (H_3PO_3) is,
(a) 0.1 (b) 0.9 (c) 0.3 (d) 0.6

21. An aqueous solution of acetic acid has density 1.1 g mol^{-1} and molality 4.6 mol kg^{-1}. The molarity of acetic acid would be
(a) 3.2 M (b) 3.5 M (c) 3.97 M (d) 4.6 M

22. The volume of 82.5 mass percent of H_2SO_4 (density 1.6 g cm^{-3}) to prepare 200 cm^3 of 15 mass per cent of H_2SO_4 (density 1.1 g cm^{-3}) is
(a) 162 cm^3 (b) 173 cm^3 (c) 180 cm^3 (d) 193 cm^3

23. 115 ml of ethanol (density = 0.8 g ml^{-1}) on mixing with 99 mL of water gives 200 mL of solution. The numerical values molarity, molality and mole fraction of ethanol, respectively, are
(a) 10, 20.2, 0.267 (b) 20.2, 10, 0.267 (c) 10, 20.2, 0.733 (d) 20.2, 10, 0.733

Oxidation Number

24. One mole of N_2H_4 loses 10 mol of electrons to form a new compound Y. Assuming that all the nitrogen appears in the new compound, what is the oxidation state of nitrogen in Y? (There is no change in the oxidation state of hydrogen.)
(a) −1 (b) −3 (c) +3 (d) +5 (1981)

25. The oxidation number of carbon in CH_2O is
(a) −2 (b) +2 (c) 0 (d) +4 (1982)

26. The brown ring complex compound is formulated as $[Fe(H_2O)_5(NO)^+]SO_4$. The oxidation state of iron is
(a) 1 (b) 2 (c) 3 (d) 0 (1984)

27. The equivalent mass of $MnSO_4$ is half its molar mass when it is converted to
(a) Mn_2O_3 (b) MnO_2 (c) MnO_4^- (d) MnO_4^{2-} (1988)

28. The oxidation number of phosphorus in $Ba(H_2PO_2)_2$ is
(a) +3 (b) +2 (c) +1 (d) −1 (1990)

29. The oxidation states of the most electronegative element in the products of the reaction, BaO_2 with dil. H_2SO_4 are
(a) 0 and −1 (b) −1 and −2 (c) −2 and 0 (d) −2 and +1 (1992)

30. For the redox reaction $MnO_4^- + C_2O_4^{2-} + H^+ \rightarrow Mn^{2+} + CO_2 + H_2O$ the correct coefficients of the reactants for the balanced reaction are

	MnO_4^-	$C_2O_4^{2-}$	H^+		MnO_4^-	$C_2O_4^{2-}$	H^+
(a)	2	5	16	(b)	16	5	2
(c)	5	16	2	(d)	2	16	5

(1993)

31. White phosphorus reacts with caustic soda. The products are PH_3 and NaH_2PO_2. This reaction is an example of
(a) oxidation (b) reduction
(c) oxidation and reduction (d) neutralization (1980)

32. Oxidation state of oxygen atom in potassium superoxide is
(a) −1/2 (b) −1 (c) −2 (d) 0

33. The compound having the lowest oxidation state of iron is
(a) $K_4Fe(CN)_6$ (b) K_2FeO_4 (c) Fe_2O (d) $Fe(CO)_5$

34. The oxidation state of nickel in $Ni(CO)_4$ is
(a) 0 (b) +2 (c) +4 (d) −4

35. The oxidation state of nitrogen in N_3H is
(a) −1/3 (b) −1 (c) +1/2 (d) +2

36. Which of the following reactions is a redox reaction?
(a) $Cr_2O_3 + 6HCl \rightarrow 2CrCl_3 + 3H_2O$ (b) $CrO_3 + 2NaOH \rightarrow Na_2CrO_4 + H_2O$
(c) $2CrO_4^{2-} + H^+ \rightleftharpoons Cr_2O_7^{2-} + OH^-$ (d) $Cr_2O_7^{2-} + 6I^- + 14H^+ \rightleftharpoons 2Cr^{3+} + 3I_2 + 7H_2O$

37. The compound having +2 as the oxidation state of oxygen is
(a) H_2O_2 (b) CO_2 (c) F_2O (d) MnO_2

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38. The oxidation state of oxygen in O_3 is
(a) +1 and −1 (b) +2 and −2 (c) 0.5 and −0.5 (d) zero

39. The anion nitrate can be converted into ammonium ion. The equivalent mass of NO_3^- ion in this reaction would be
(a) 6.20 g eq^{-1} (b) 7.75 g eq^{-1} (c) 10.5 g eq^{-1} (d) 21.0 g eq^{-1}

40. The equivalent mass of $Na_2S_2O_3$ in its reaction with I_2 is equal to
(a) molar mass (b) molar mass/2 (c) molar mass/3 (d) molar mass/4

41. The oxidation numbers of sulphur in S_8, S_2F_2, H_2S respectively, are
(a) 0, +1 and −2 (b) +2, +1 and −2 (c) 0, +1 and +2 (d) −2, +1 and −2 (1999)

42. Amongst the following, identifies the species with an atom in +6 oxidation state
(a) MnO_4^- (b) $Cr(CN)_6^{3-}$ (c) NiF_6^{2-} (d) CrO_2Cl_2 (2000)

43. The correct order of compounds with increasing oxidation number of Ni is
(a) $Ni(CO)_4 < K_2[NiF_6] < K_2[Ni(CN)_4]$ (b) $Ni(CO)_4 < K_2[Ni(CN)_4] < K_2[NiF_6]$
(c) $K_2[Ni(CN)_4] < K_2[NiF_6] < Ni(CO)_4$ (d) $K_2[Ni(CN)_4] < Ni(CO)_4 < K_2[NiF_6]$

44. Which of the following acids has more than one oxidation state of sulphur atoms?
(a) $H_2S_2O_8$ (b) $H_2S_2O_6$ (c) $H_2S_2O_7$ (d) $H_2S_2O_5$

45. The correct order of compounds with increasing oxidation number of phosphorus is
(a) $P_4 < PH_3 < P_2O_3$ (b) $P_4 < P_2O_3 < PH_3$ (c) $P_2O_3 < P_4 < PH_3$ (d) $PH_3 < P_4 < P_2O_3$

46. The oxidation numbers of P in P_4, PH_3 and NaH_2PO_2, respectively, are
(a) 0, −3, +1 (b) 0, −3, −1 (c) 0, +3, −1 (d) 0, +3, +1

47. In the reaction $KSbO_2^- + 2KOH + 2H_2O + 2ClO_2 \rightarrow KSb(OH)_6^- + KClO_2$, the species undergone
(a) oxidation is Cl (b) oxidation is Sb (c) oxidation is O (d) reduction is Sb

48. The pair of the compounds in which both the metals are in the highest possible oxidation state is
(a) $[Fe(CN)_6]^{4-}$, $[Co(CN)_6]^{3-}$ (b) $[Co(CN)_6]^{3-}$, $Ni(CO)^4$
(c) TiO_2, MnO^2 (d) CrO_2Cl_2, MnO_4^- (2004)

Balancing Chemical Equation

49. The stoichiometric numbers of species from left to right in the chemical equation $Cu_2O + NO_3^- + H^+ \rightarrow Cu^{2+} + NO + H_2O$ when balanced respectively are
(a) 1, 1, 6, 2, 1, 3 (b) 2, 1, 8, 4, 1, 4 (c) 2, 2, 12, 4, 2, 6 (d) 3, 2, 14, 6, 2, 7

50. The stoichiometric numbers of species from left to right in the chemical equation

$$Mn^{2+} + PbO_2 + H^+ \rightarrow MnO_4^- + Pb^{2+} + H_2O$$

when balanced respectively are
(a) 1, 4, 8, 1, 4, 4 (b) 1, 3, 4, 1, 3, 2 (c) 2, 5, 4, 2, 5, 2 (d) 2, 7, 12, 2, 7, 6

51. The stoichiometric numbers of species from left to right in the chemical equation $IO_3^- + I^- + H^+ \rightarrow I_2 + H_2O$ when balanced respectively are
(a) 2, 4, 12, 3, 6 (b) 1, 3, 6, 2, 3 (c) 1, 5, 6, 3, 3 (d) 1, 1, 6, 1, 3

52. The stoichiometric numbers of species from left to right in the chemical equation $Br_2 + NaOH \rightarrow NaBr + NaBrO_3 + H_2O$ when balanced respectively are
(a) 3, 4, 3, 1, 2 (b) 1, 2, 1, 1, 2
(c) 2, 4, 3, 1, 2 (d) 3, 6, 5, 1, 3

53. The stoichiometric number of species from left to right in the chemical equation $P_4 + NaOH + H_2O \rightarrow PH_3 + NaH_2PO_2$ when balanced respectively are
(a) 1, 2, 2, 1, 2 (b) 1, 3, 3, 1, 3 (c) 2, 6, 1, 4, 4 (d) 2, 6, 6, 3, 1

Chemical Reactions

54. If 0.5 mol of $BaCl_2$ is mixed with 0.20 mol of Na_3PO_4, the maximum amount of $Ba_3(PO_4)_2$ that can be formed is
(a) 0.70 mol (b) 0.50 mol (c) 0.20 mol (d) 0.10 mol (1981)

55. A certain compound has the molecular formula X_4O_6. If 10.0 g of compound contains 6.06 g of X, the atomic mass of X is
(a) 32 amu (b) 37 amu (c) 42 amu (d) 48 amu

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56. The extent of reaction
(a) is unitless (b) has the unit of g (c) has the unit of mol (d) has the unit of mol^{-1}.

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

58. HBr and HI can reduce sulphuric acid, HCl can reduce $KMnO_4$ and HF can reduce
(a) H_2SO_4 (b) $KMnO_4$ (c) $K_2Cr_2O_7$ (d) none of these

59. A solution of sodium metal in liquid ammonia is strongly reducing agent due to the presence of
(a) sodium atoms (b) sodium hydride (c) sodium amide (d) solvated electrons

60. The reaction which proceeds in the forward direction is
(a) $Fe_2O_3 + 6HCl = 2FeCl_3 + 3H_2O$ (b) $NH_3 + H_2O + NaCl = NH_4Cl + NaOH$
(c) $SnCl_4 + Hg_2Cl_2 = SnCl_2 + 2HgCl_2$ (d) $2CuI + I_2 + 4K^+ = 2Cu^{2+} + 4KI$ (1991)

61. The masses of P_4O_6 and P_4O_{10} that will be produced by the combustion of 2.0 g of P_4 in 2.0 g of oxygen leaving no P_4 and O_2 respectively are
(a) 3.0 g, 1.0 g (b) 1.5 g, 2.5 g (c) 2.5 g, 1.5 g (d) 2.0 g, 2.0 g

62. Mixing of 50 mL of 0.25 M lead nitrate solution with 25 mL of 0.10 M chromic sulphate solution causes the precipitation of lead sulphate. The molarity of Pb^{2+} and Cr^{3+} ions in the solution respectively are
(a) 0.0667 M, 0.0667 M (b) 0.1 M, 0.2 M (c) 0.125 M, 0.05 M (d) 0.05 M, 0.125 M

63. A mixture weighing 4.08 g of BaO (molar mass of Ba = 138 g mol^{-1}) and unknown carbonate XCO_3 was heated strongly. The residue weighed 3.64 g. This was dissolved in 100 mL of 1 M HCl. The excess acid required 16 mL of 2.5 M NaOH solution for complete neutralization. The molar mass of M is about
(a) 20 g mol^{-1} (b) 30 g mol^{-1} (c) 40 g mol^{-1} (d) 50 g mol^{-1}

64. A solid mixture (5.0 g) consisting of lead nitrate and sodium nitrate was heated below 600 °C until the mass of residue was constant. If the loss in mass is 28 per cent, the masses of lead nitrate and sodium nitrate in the mixture respectively were
(a) 3.32 g, 1.68 g (b) 1.68 g, 3.32 g (c) 2.50 g, 2.50 g (d) 3.50 g, 1.50 g

65. A compound $Pb(NO_3)_2$ on strong heating loses 32.6 per cent of its mass. The molar mass of Pb is about
(a) 200 g mol^{-1} (b) 207 g mol^{-1} (c) 214 g mol^{-1} (d) 221 g mol^{-1}

66. The per cent loss in mass of $K_2Cr_2O_7$ (molar mass Cr = 52 g mol^{-1}) on heating will be about
(a) 25% (b) 16% (c) 8% (d) 4%

67. Five millilitre of 0.1 M Pb $(NO_3)_2$ is mixed with 10 mL of 0.02 M KI. The amount of PbI_2 precipitated will be about
(a) 10^{-3} mol (b) 10^{-4} mol (c) 2×10^{-4} mol (d) 4×10^{-3} mol

68. A solution containing Na_2CO_3 and $NaHCO_3$ is titrated against 0.1 M HCl solution using methyl orange indicator. At the equivalence point,
(a) both Na_2CO_3 and $NaHCO_3$ are completely neutralized
(b) only Na_2CO_3 is wholly neutralized
(c) Only $NaHCO_3$ is wholly neutralized
(d) Na_2CO_3 is neutralized upto the stage of $NaHCO_3$

69. A solution containing Na_2CO_3 and $NaHCO_3$ is titrated against 0.1 M HCl solution using phenolphthalein indicator. At the equivalence point,
(a) both Na_2CO_3 and $NaHCO_3$ are completely neutralized
(b) only Na_2CO_3 is wholly neutralized
(c) only $NaHCO_3$ is wholly neutralized
(d) Na_2CO_3 is neutralized upto the stage of $NaHCO_3$

70. A solution containing NaOH and Na_2CO_3 is titrated against 0.1 M HCl solution using phenolphthalein indicator. At the equivalence point,
(a) both NaOH and Na_2CO_3 are completely neutralized
(b) only NaOH is completely neutralized
(c) only Na_2CO_3 is completely neutralized
(d) NaOH completely and Na_2CO_3 upto the stage of $NaHCO_3$ are neutralized.

71. A solution containing NaOH and Na_2CO_3 is titrated against 0.1 M HCl solution using methyl orange indicator. At the equivalence point,

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(a) both NaOH and Na_2CO_3 are completely neutralized
(b) only NaOH is completely neutralized
(c) only Na_2CO_3 is completely neutralized
(d) NaOH completely and Na_2CO_3 upto the stage of $NaHCO_3$ are neutralized.

72. A solution containing 2.68×10^{-3} mol of A^{n+} ions requires 1.61×10^{-3} mol of MnO_4^- for the oxidation of A^{n+} to AO_3^- in acidic medium. The value of n is
(a) 1 (b) 2 (c) 3 (d) 4

73. 20 mL of an acidified solution of ferrous sulphate requires 15 mL of 0.1 M solution of $KMnO_4$ for complete oxidation. For the same solution, the volume of 0.1 M $K_2Cr_2O_7$ for complete oxidation would be
(a) 24 mL (b) 18.0 mL (c) 16.67 mL (d) 12.5 mL

74. Twenty millilitre of a solution is 0.1 M in each of Na_2CO_3 and $NaHCO_3$. It is titrated against 0.1 M HCl using phenolphthalein as the indicator. The volume of HCl used at the end point will be
(a) 10 mL (b) 20 mL (c) 30 mL (d) 60 mL

75. Twenty millitre of a solution is 0.1 M in each of Na_2CO_3 and $NaHCO_3$. It is titrated against 0.1 M HCl using methyl orange as the indicator. The volume of HCl used at the end point will be
(a) 10 mL (b) 20 mL (c) 30 mL (d) 60 mL

76. Ten millilitre of 0.01 M iodine solution is titrated against 0.01 M sodium thiosulphate solution using starch solution. The volume of sodium thiosulphate consumed upto the end point is
(a) 10 mL (b) 15 mL (c) 20 mL (d) 30 mL

77. 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 (2001)

78. The reaction, $3ClO_3^-(aq) \rightarrow ClO_3^-(aq) + 2Cl^-(aq)$, is an example of
(a) oxidation reaction (b) reduction reaction
(c) disproportionation reaction (d) decomoposition reaction (2001)

79. In the standardization of $Na_2S_2O_3$ using $K_2Cr_2O_7$ by iodometry, the equivalent mass of $K_2Cr_2O_7$ is
(a) (molar mass)/2 (b) (molar mass)/6 (c) (molar mass)/3 (d) same as molar mass

80. Which of the following is not oxidized by O_3?
(a) KI (b) $KMnO_4$ (c) K_2MnO_4 (d) $FeSO_4$

81. Consider a titration of potassium dichromate solution with acidified Mohr's salt solution using diphenylamine as indicator. The number of moles of Mohr's salt required per mole of dichromate is
(a) 3 (b) 4 (c) 5 (d) 6

82. 2.76 g of silver carbonate, on heating strongly yields a residue of
(a) 2.32 g (b) 2.48 g (c) 2.32 g (d) 2.64 g

83. One gram of $CaCO_3(s)$ and $Na_2CO_3(s)$ when heated strongly left a residue weighing 0.56 g. The mass per cent of $CaCO_3$ in the mixture is
(a) 50% (b) 60% (c) 75% (d) 80%

84. 6.0 g of C reacts completely with 12 g of O_2 producing a mixture of CO(g) and $CO_2(g)$. The mass percent of CO(g) in the gaseous mixture will be about
(a) 45% (b) 57% (c) 64% (d) 76%

85. A mixture of CO(g), $CH_4(g)$ and He gases has a volume of 20 cm^3. When exploded in the presence of excess of O_2, a net decrease of 13.0 cm^3 in volume is observed at room temperature. When the remaining mixture is passed through NaOH solution, a further decrease of 14.0 cm^3 in volume is observed. The volume percentages of CO, CH_4 and He in the original mixture, respectively, are
(a) 50, 30, 20 (b) 50, 20, 30 (c) 20, 50, 30 (d) 20, 30, 50

86. A compound $M \cdot xH_2O$ contains 45.5 mass per cent of water. If the molar mass M is 152 g mol^{-1}, the value of x will be
(a) 4 (b) 5 (c) 6 (d) 7

87. 0.5 g of fuming H_2SO_4 is diluted with water. This solution requires 22 mL of 0.5 M NaOH for complete neutralization. The mass per cent of SO_3 in the fuming H_2SO_4 is
(a) 25.1 (b) 30.2 (c) 35.2 (d) 40.1

88. 90 mL of 10 mass percent solution of KI (density: 1.132 g mL^{-1}) is mixed with 90 mL of 20 mass per cent of $Pb(NO_3)_2$ (density : 1.1 g mL, M(Pb) = 208 g mol^{-1}) The amount of PbI_2 precipitated will be
(a) 0.04 mol (b) 0.05 mol (c) 0.06 mol (d) 0.1 mol

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89. A mass of 0.355 g of the compound $M_2CO_3 \cdot xH_2O$ (molar mass of M: 23 g mol^{-1}) is dissolved in 100 mL water and titrated against 0.05 M HCl using methyl orange indicator. If the volume of HCl consumed is 100 mL, the value of x is

(a) 2 (b) 5 (c) 7 (d) 10

90. 20 mL of a solution containing 0.34 g of an impure sample of H_2O_2 reacts with 0.465 g of $KMnO_4$ (molar mass: 155 g mol^{-1}) in acidic medium. The per cent purity of H_2O_2 is about

(a) 60% (b) 70% (c) 75% (d) 80%

91. A mixture of Na_2CO_3 and NaOH in a solution requires 20 mL of 0.1M HCl solution for neutralization when phenolphthalein indicator is used. The volume consumed is 25 mL when methyl orange indicator is used. The mass per cent of Na_2CO_3 in the given mixture is about

(a) 47% (b) 57% (c) 67% (d) 75%

92. The mass of AgCl precipitated when 4.68 g of NaCl is added to a solution containing 6.8 g of $AgNO_3$ is

(a) 4.52 g (b) 5.74 g (c) 7.18 g (d) 8.2 g

Multiple Correct Choice Type

1. Which of the following statements are correct?

(a) The reaction $2H_2O_2 \rightarrow 2H_2O + O_2$ is not an example of redox reaction.

(b) The reaction $2S_2O_8^{2-} + 2H_2O \rightarrow 4SO_4^{2-} + O_2 + 2H^+$ is an example of a redox reaction.

(c) The oxidation number of an oxidant is increased in a redox reaction.

(d) The oxidation number of a reductant is increased in a redox reaction.

2. Which of the following statements are *not* correct?

(a) The increase in oxidation number of an element implies that the element has undergone oxidation.

(b) The increase in oxidation number of an element implies that the elements has undergone reduction.

(c) The oxidation number can never be a fraction. It is always a positive or negative integer.

(d) In a reaction H_2MoO_4 is changed to MoO_2^+. In this case, H_2MoO_4 acts as a reducing agent.

3. Which of the following statements are correct?

(a) The oxidation state of Mo when it undergoes transition from H_2MoO_4 to MoO_2^{2+} is increased by one.

(b) The disproportionation reaction $2Mn^{3+} + 2H_2O \rightarrow MnO_2 + Mn^{2+} + 4H^+$ is an example of a redox reaction.

(c) The equivalent mass of $KMnO_4$ in alkaline medium is molar mass divided by five.

(d) The equivalent mass of $KMnO_4$ in weakly acidic or neutral or weakly alkaline medium is molar mass divided.

4. Which of the following statements are correct?

(a) The equivalent mass of $KMnO_4$ in strongly alkaline medium is equal to its molar mass.

(b) The equivalent mass of $S_2O_3^{2-}$ in its reaction with I_2 is molar mass divided by two.

(c) A solution of cerium(IV) in sulphuric acid acts as an oxidizing reagent.

(d) The equivalent mass of $K_2Cr_2O_7$ in acidic medium is molar mass divided by five.

5. Which of the following statements are correct?

(a) Potassium bromate, $KBrO_3$, acts as a strong oxidizing agent. It accepts 6 electrons to give KBr.

(b) Potassium bromate can quantitatively convert Br^- to Br_2.

(c) Potassium iodate solution can be kept for a long time without decomposition.

(d) In 3N HCl solution, iodate can oxidize I_2 according to the reaction

$$IO_3^- + 2I_2 + 10Cl^- + 6H^+ \rightarrow 5ICl_2^- + 3H_2O$$

In this reaction, the equivalent mass of IO_3^- is molar mass divided by four.

6. Which of the following statements are correct?

(a) The equivalent mass of a substance can be calculated with out considering the reaction it undergoes.

(b) One mole of $K_4Fe(CN)_6$ produces 17 mol of total species in solution.

(c) The molar mass of N_2 is 28 g mol^{-1}. Its molecular mass will be 28 u.

(d) Hydrogen peroxide can act both as oxidizing as well reducing agent.

7. The reaction between peroxydisulphate ion ($S_2O_8^{2-}$) and chromium in acidic medium produces sulphate and dichromate ions. In this reaction (Choose only the correct ones)

(a) the oxidation state of S changes from +7 to +6.

(b) the oxidation state of Cr changes from 0 to +3.

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(c) The equivalent mass of $S_2O_8^{2-}$ would be molar mass divided by two.
(d) The equivalent mass of Cr would be molar mass divided by three.

8. In 2N HCN solution, iodate I_2 according to the reaction

$$IO_3^- + 2I_2 + 10CN^- + 6H^+ \rightarrow 5I(CN)_2^- + 3H_2O$$

In this reaction (choose only the correct ones),
(a) the oxidation state of I in IO_3^- is changed from +5 to +1.
(b) the oxidation state of I in I_2 is changed from +1 to 0.
(c) the equivalent mass of IO_3^- is molar mass divided by four.
(d) the equivalent mass of I_2 is molar mass divided by two.
(e) IO_3^- acts a a/an reducing reagent.
(f) I_2 acts as a/an oxidizing reagent.

9. Which of the following statements are correct?
(a) The oxidation number of iodine in periodic acid (H_5IO_6) is +7.
(b) Hydrazine (N_2H_4) is a reducing agent. In its reaction with I_2, nitrogen is evolved. The equivalent mass of hydrazine in this reaction is molar mass divided by two.
(c) In the reaction $IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$ the equivalent mass of IO_3^- is molar mass divided by five.
(d) The iodine produced in the reaction $IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$ is titrated against $S_2O_3^{2-}$ ions. Knowing the normality of $S_2O_3^{2-}$, normality of iodine and hence normality of IO_3^- is determined. To get the strength of IO_3^- in g L^{-1}, the equivalent mass employed for IO_3^- in g L^{-1}, would be molar mass divided by four.

10. Which of the following statements are *not* correct?
(a) IO_4^- is a strong oxidizing agent in acidic medium. In its oxidizing action, it is reduced to I_2. The equivalent mass of IO_4^- will be molar mass divided by seven.
(b) In a oxidation reaction, bromate (BrO_3^-) is converted into Br^-. The equivalent mass of BrO_3^- will be molar mass divided by five.
(c) The oxidation state of S in CNS^- is +1.
(d) In a reaction between IO_3^- and CNS^-, the latter is converted into SO_4^{2-} and HCN. The equivalent mass of CNS^- would be molar mass divided by six.

11. Which of the following statements are correct?
(a) One mole of potash alum contains a total 32 mol of the independent species.
(b) One of mole of $K_3Fe(CN)_6$ contains a total 10 mol of the independent species.
(c) 0.1 M sulphuric acid has a normality of 2 N.
(d) The oxidation number of alkali metal is always taken equal to +1.

12. In the reaction $6OCl^- + 2NH_3 \rightarrow 6Cl_2 + N_2 + 6OH^-$, the species undergone
(a) oxidation is N (b) reduction is N (c) oxidation is Cl (d) reduction is Cl

13. Which of the following concentrations are correct for 13 mass percent of sulphuric acid (dendity : 1.09 g mL^{-1})?
(a) 1.443 M (b) 1.625 M (c) 1.625 mol kg^{-1} (d) 1.525 mol kg^{-1}

14. 1.8 g of Mg in burnt in a closed vessel which contains 0.8 g of oxygen. Which of the following facts are correct for the resultant system?
(a) Amount of MgO formed is 0.05 mol
(b) Mass of Mg left in excess is 0.8 g
(c) Amount of oxygen left is zero.
(d) Volume of 0.25 M H_2SO_4 to dissolve the formed MgO is 200 mL

Linked Comprehension Type

1. 250 mL of a solution contains 0.42 g of oxalic acid. This solution is used in determining molarity of sodium hydroxide solution which, in turn, is used to determine the molarity of sulphuric acid solution. This acid solution is furthur used in determining the masses of Na_2CO_3 and $NaHCO_3$ present in a solution. Based on these experiments, answer correctly the following three questions.
(i) In determining the molarity of sodium hydroxide solution, 9.6 mL of this solution required 10 mL of oxalic acid solution to locate end point with the help of phenolphthalein indicator. For sulphuric acid

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solution, 9.0 mL of NaOH solution is used in neutralizing 10 mL of sulphuric acis solution while using phenolphthalein indicator. The molarity of sulphuric acid solution is

(a) 0.01 M (b) 0.0125 M (c) 0.02 M (d) 0.025 M

(ii) 10.0 mL of the solution containing Na_2CO_3 and $NaHCO_3$ requires 4.0 mL of sulphuric acid with phenolphthalein indicator. The mass of Na_2CO_3 present per litre of the solution is

(a) 1.06 g L^{-1} (b) 2.12 g L^{-1} (c) 2.52 g L^{-} (d) 3.18 g L^{-1}

(iii) 10.0 mL of the solution containing Na_2CO_3 and $NaHCO_3$ requires 14.0 mL of suphuric acid with methyl orange indicator. The mass of $NaHCO_3$ present per litre of the solution is

(a) 0.63 g L^{-1} (b) 1.06 g L^{-} (c) 1.26 g L^{-1} (d) 2.52 g L^{-1}

2. 250 mL of a solution contains 0.63 g of oxalic acid. This solution is used in determining molarity of sodium hydroxide solution, which, in turn, is used to determine the molarity of sulphuric acid solution. This acid solution is furthur used in determining the masses of Na_2CO_3 and NaOH present in a solution. Based on these experiments, answer correctly the following three questions.

(i) In determining the molarity of sodium hydroxide solution, 9.6 mL of this solution required 10 mL of oxalic acid solution to locate end point with the help of phenolphthalein indicator. For sulphuric acid solution, 8.4 mL of NaOH solution is used in neutralizing 10 mL of sulphuric acid solution while using phenolphthalein indicator. The mass of sulphuric acid present per litre of the solution is

(a) 1.51 g (b) 1.72 g (c) 1.92 g (d) 2.21 g

(ii) 10.0 mL of the solution containing Na_2CO_3 and NaOH requires 12.0 mL of sulphuric acid with phenolphthalein indicator and 16.0 mL with methyl orange indicator. The mass of Na_2CO_3 present per litre of the solution is

(a) 1.48 g (b) 1.88 g (c) 2.28 g (d) 2.68 g

(iii) From the part (ii), the mass of NaOH present per litre of the solution is

(a) 0.56 g (b) 0.92 g (c) 1.12 g (d) 1.52 g

3. 250 mL of a solution contains 0.63 g of oxalic acid. This solution is used to determine molarities of NaOH solution and $KMnO_4$ solution. These solutions, in turn, are used separately to determine the masses of oxalic acid and sodium oxalate present together in a solution. Based on these experiments, answer correctly the following three questions

(i) In determining the molarty of sodium hydroxide solution, 9.6 mL of this solution is used to locate the end point for 10 mL of oxalic acid solution with phenolphthalein indicator. For $KMnO_4$ solution, 9.8 mL of $KMnO_4$ solution is used to locate the end point for acidified 10 mL of oxalic acid. The molarities of NaOH and $KMnO_4$ solutions, respectively, are

(a) M/24, M/24.5 (b) M/24, M/122.5 (c) M/24.5, M/24 (d) M/122.5, M/24

(ii) 10.0 mL of the solution containing oxalic acid and sodium oxalate together requires 8.5 mL of sodium hydroxide to get end point with phenolphthalein indicator. The mass of oxalic acid present per litre of the solution is

(a) 2.23 g (b) 1.58 g (c) 2.58 g (d) 3.2 g

(iii) 10.0 mL of the acidified solution containing oxalic acid and sodium oxalate required 20.7 mL of $KMnO_4$ solution. The mass of sodium oxalate present per litre of the given solution is

(a) 2.86 g (b) 3.08 g (c) 3.58 g (d) 4.18 g

4. 10 mL of a given hydrogen peroxide sample (density 1.2 g/mL) is titrated with M/50 solution of $KMnO_4$ in acidic medium. The volume of $KMnO_4$ solution used is found to be 28.4 mL. Based on this information, answer the following three questions.

(i) The molatity of H_2O_2 in the given hydrogen peroxide sample is

(a) 0.284 M (b) 0.142 M (c) 0.426 M (d) 0.071 M

(ii) The molality of H_2O_2 in the given hydrogen peroxide sample is

(a) 0.119 mol kg^{-1} (b) 0.238 mol kg^{-1} (c) 0.056 mol kg^{-1} (d) 0.36 mol kg^{-1}

(iii) The volume strength at STP of the given hydrogen peroxide sample is

(a) 2.59 (b) 2.09 (c) 1.59 (d) 0.99

Assertion Reason Type

Below are given a STATEMENT (S) in the left hand column and an EXPLANATION (E) in the right hand column. Ascertain the relationship between S and E and select the correct code among a, b, c and d which are, defined below.

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Code

(a) Both S and E are true, and E is the correct explanation of S.
(b) Both S and E are true but E is not the correct explanation of S.
(c) S is true but E is false.
(d) S is false but E is true

STATEMENT(S)	EXPLANATION(E)
1. In the titration of Na_2CO_3 with HCl using methyl orange indicator, the volume of acid required at the equivalence point is twice that of the acid required using phenolphthalein as the indicator.	Two moles of HCl are required for the complete neutralization of one mole of Na_2CO_3.
2. In the titration of Na_2CO_3 with HCl using methyl orange indicator, the equivalent mass of Na_2CO_3 is the molar mass divided by 2.	Two moles of HCl are required for the complete neutralization of one mole of Na_2CO_3.
3. In the titration of Na_2CO_3 with HCl using phenolphthalein indicator, the equivalent mass of Na_2CO_3 is the molar mass divided by 2.	Two moles of HCl are required for the complete neutralization of one mole of Na_2CO_3.
4. The equivalent mass of $KMnO_4$ in a redox reaction depends on the medium whether it is acidic, basic or neutral.	The oxidation reaction of MnO_4^- is $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$. This reaction occurs irrespective of the nature of medium
5. The $Cr_2O_7^{2-}$ is reduced to CrO_4^{2-} when the medium is made alkaline.	The oxidation states of Cr in $Cr_2O_7^{2-}$ and CrO_4^{2-} are identical.
6. The atomic mass of an element expressed in amu (atomic mass unit) and its molar mass expressed in g mol^{-1} have the same numerical value.	The numerical value of product of amu in SI unit Avogadro constant is equal to 1
7. The density of a substance expressed in g cm^{-3} kg dm^{-3} have the same numerical value.	The numerical value of density is same because 1 kg = 10^3 g and 1 cm = 10^{-1} dm.
8. The atomic mass of most elements have non-integral values.	The atomic mass of an element is the mass of protons and neutrons contained in its nucleus.
9. Amount of a substance is defined as $n = N/N_A$ where N is the number specified entities of the substance and N_A is Avogadro constant.	The amount of a substance may be expressed in various ways such as parts per million and grams.
10. If the amount x of A in the reaction $2A \rightarrow B$ is converted into B, then the extent of reaction is x.	The extent of reaction is defined as $\Delta n_A/\nu_A$ where Δn_A is the amount of substance undergone a change and ν_A is its stoichiometric number.
11. The extent of reaction has the unit of 'mol'.	The unit of amount of substance is 'mol'.
12. Molarity of a solution is a temperature dependent physical property.	Volume of a solution changes with change in temperature.
13. In the volumetric analysis, molarity of unknown solution may be determined by using the molarity expression $M_1V_1 = M_2V_2$.	The molarity expression $M_1V_1 = M_2V_2$ cannot be written like the normality expression $N_1V_1 = N_2V_2$.
14. 1 mol (5 Fe^{2+} ions) ≡ 5 mol of Fe^{2+} ions.	A grouping of five Fe^{2+} ions together as a single unit decreases the amount of Fe^{2+} ion to one fifth of the original amount.
15. Mole fraction of a constituent in a solution is an intensive quantity.	Mole fraction of a constituent is independant of the volume of the solution.

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Matrix Match Type

1. Column I lists some of the concentration terms and Column II includes some of their characteristics. Match each entry of Column I with those listed in Column II.

Column I	**Column II**
(a) Molarity	(p) eq dm^{-3}
(b) Molality	(q) mol dm^{-3}
(c) Mole fraction	(r) unit less
(d) Normality	(s) mol kg^{-1}
	(t) Temperature dependent
	(u) Temperature independent

2. Column I lists equivalent masses and Column II lists some of the typical titrations. Match each entry of Column I with those given in Column II.

Column I	**Column II**
(a) Molar mass/ (5 eq mol^{-1})	(p) $KMnO_4$ in Fe^{2+} versus MnO_4^- titration in alkaline medium
(b) Molar mass/ (2 eq mol^{-1})	(q) $KMnO_4$ in oxalic acid vesus MnO_4^- titration in acidic medium
(c) Molar mass/ (6 eq mol^{-1})	(r) $Na_2S_2O_3$ in I_2 versus $S_2O_3^{2-}$ titration
(d) Molar mass/ (1 eq mol^{-1})	(s) $K_2Cr_2O_7$ in Fe^{2+} versus $Cr_2O_7^{2-}$ titration
	(t) Oxalic acid in oxalic acid versus MnO_4^- titration in acidic medium.

3. Column I includes some of the concentration terms and their defining/ equivalent expressions are listed in Column II. In the expressions, the symbols stand for the various physical fquantities as described in the following

x_1 Mole fraction of solvent
x_2 Mole fraction of solute
M_1 Molar mass of solvent
M_2 Molar mass of solute
ρ density of solution
m Molality of solute in solution
M Molarity of solute in solution

Match each entry in Column I with those given in Column II.

Column I	**Column II**
(a) x_1	(p) $x_2\rho/(x_1M_1 + x_2M_2)$
(b) x_2	(q) x_2/x_1M_1
(c) M	(r) $mM_1/(1 + mM_1)$
(d) m	(s) $MM_1/\{\rho + M(M_1 - M_2)\}$
	(t) $mr/(1 + mM_2)$
	(u) $M/(r - MM_2)$
	(v) $1/(1 + mM_1)$

ANSWERS

Straight Objective Type

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

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71. (a)	**72.** (b)	**73.** (d)	**74.** (b)	**75.** (d)	**76.** (c)	**77.** (a)
78. (c)	**79.** (b)	**80.** (b)	**81.** (d)	**82.** (a)	**83.** (c)	**84.** (c)
85. (b)	**86.** (d)	**87.** (c)	**88.** (b)	**89.** (a)	**90.** (c)	**91.** (a)

Multiple Correct Choice Type

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

Linked Comprehension Type

1. (i) (b) (ii) (a) (iii) (c)
2. (i) (b) (ii) (a) (iii) (c)
3. (i) (b) (ii) (a) (iii) (d)
4. (i) (b) (ii) (a) (iii) (c)

Assertion Reason Type

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

Matrix Match Type

1. (a) – (q), (t);	(b) – (s), (u);	(c) – (r), (u);	(d) – (p), (t)
2. (a) – (q);	(b) – (t);	(c) – (s);	(d) – (p), (r)
3. (a) – (v);	(b) – (r), (s);	(c) – (p), (t);	(d) – (q), (u)

Hints and Solutions

Straight Objective Type

Atomic and Molar Masses

1. The atomic mass of an element is measured relative to the atomic mass of carbon-12.

2. One atomic mass unit $= \dfrac{(1/12)\text{th of mass of } {}^{12}C}{\text{Avogadro constant}} = \dfrac{(1/12)\left(12\text{g mol}^{-1}\right)}{6.023\times10^{23}\text{mol}^{-1}} = 1.66\times10^{-24}\text{g} = 1.66\times10^{-27}\text{ kg}$

6. Mass of a single electron $= 9.108\times10^{-28}$ g; Number of electrons in 1 kg $= \dfrac{10^3\text{g}}{9.108\times10^{-2}\text{g}}$

Amount of electrons in 1 kg $= \dfrac{10^3\text{g}}{(9.108\times10^{-28}\text{g})\,(6.022\times10^{23}\text{mol}^{-1})} = \dfrac{10^8}{9.108\times6.022}\text{ mol}$

7. Amount of C $= \dfrac{24\text{g}}{12\text{g mol}^{-1}} = 2$ mol Amount of Na $= \dfrac{23\text{g}}{23\text{g mol}^{-1}} = 1$ mol

Amount of S $= \dfrac{48\text{g}}{32\text{g mol}^{-1}} = 1.5$ mol Amount of Ag $= \dfrac{108\text{g}}{108\text{g mol}^{-1}} = 1$ mol

Larger the amount of substance, larger the number of molecules.

8. Relative atomic mass Fe is $(0.05\times54 + 0.9\times56 + 0.05\times57) = 55.95$

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9. Amount of water, $\frac{M}{M} = \frac{36\text{ g}}{18\text{ g mol}^{-1}} = 2\text{ mol}$; Amount of carbon monoxide $= \frac{28\text{ g}}{28\text{ g mol}^{-1}} = 1\text{ mol}$

Amount of ethyl alcohol $= \frac{46\text{ g}}{46\text{ g mol}^{-1}} = 1\text{ mol}$; Amount of nitrogen pentoxide $= \frac{54\text{ g}}{108\text{ g mol}^{-1}} = 0.5\text{ mol}$

Larger the amount of substance, larger the number of molecules.

11. Mass of water = (5 mol) (18g mol^{-1}) = 90 g; Mass of Na_2CO_3 = (2 eq) (53 g eq^{-1}) = 106 g

Mass of hydrogen $= \left(\frac{12\times10^{24}}{6.022\times10^{23}\text{ mol}^{-1}}\right)(2\text{ g mol}^{-1}) = 40\text{ g}$

12. The reaction is $2Al + 3H_2SO_4 \rightarrow Al_2(SO_4) + 3H_2$

Amount of Al $= \left(\frac{0.9\text{g}}{27\text{g mol}^{-1}}\right) = \frac{1}{30}\text{ mol}$; Amount of H_2 evolved $= \left(\frac{3}{2}\right)\left(\frac{1}{30}\text{ mol}\right) = \frac{1}{20}\text{ mol}$

Volume of H_2 evolved $= \left(\frac{1}{20}\text{ mol}\right)$ (22.4 L mol^{-1}) = 1.12 L

13. Molar mass of Glauber's salt, $Na_2SO_4 \cdot 10H_2O$ = 322 g mol^{-1}

Molar mass of Na_2SO_4 = 142 g mol^{-1}

Mass of Na_2SO_4 in solution = (40.25 g) $\left(\frac{142\text{ g mol}^{-1}}{322\text{ g mol}^{-1}}\right) = 17.75\text{ g}$

Mass of solution = (500 mL) (1.0775 g mol^{-1}) = 538.75 g

Mass of water = (538.75 – 17.75) g = 521 g

Amount of $Na_2SO_4 = \frac{17.55\text{ g}}{142\text{ g mol}^{-1}} = 0.125\text{ mol}$

Molality of $Na_2SO_4 = \frac{0.125\text{ mol}}{0.521\text{ kg}} = 0.24\text{ mol kg}^{-1}$

14. Amount of $NaBrO_3$ in the solution = (0.75 eq dm^{-3}) (0.150 dm^3) = 0.1125 eq

Mass of $NaBrO_3$ required = (0.1125 eq) (151 / 6) g eq^{-1} = 2.83 g

15. Since $m = n_2$ / (1 kg of solvent), we have n_1 = 1 kg / M_1

$$x_2 = \frac{n_2}{n_1 + n_2} = \frac{n_2}{(1\text{ kg} / M_1) + n_2} = \frac{(n_2/\text{kg})}{(1/M_1) + n_2/\text{kg}} = \frac{m M_1}{1 + m M_1}$$

16. Since $m = n_2$/(1 kg of solvent), we have $n_1 = 1\text{ kg}/M_1$

The molarity of solution is $M = \frac{n_2}{V} = \frac{n_2}{(1\text{ kg} + n_2 M_2)/\rho} = \frac{(n_2/1\text{ kg})\rho}{1 + (n_2/1\text{ kg}) M_2} = \frac{m\rho}{1 + m M_2}$

17. We have $n_2 = 0.08$ mol, $n_1 = 0.92$ mol; $m = \frac{0.08\text{ mol}}{(0.92\text{ mol})(0.018\text{ kg mol}^{-1})} = 4.83\text{ mol kg}^{-1}$

18. We have $x_2 = \frac{n_2}{n_1 + n_2}$

Mass of solution = $n_1M_1 + n_2M_2$; Volume of solution, $V = (n_1M_1 + n_2M_2)/\rho$

Hence, $M = \frac{n_2}{V} = \frac{n_2}{(n_1M_2 + n_2 M_2)/\rho} = \frac{n_2\,\rho}{n_1M_2 + n_2 M_2} = \frac{x_2}{x_1M_2 + x_2 M_2}$

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20. Phosphorous acid is a dibasic acid. Hence 0.3 M will be 0.6 N.

21. Let m_1 = 1000 g. Then n_2 = 4.6 mol; $m_2 = n_2 M_2$ = (4.6 mol) (60 g mol^{-1}) = 276 g
Mass of solution = 1000 g + 276 g = 1276 g; Volume of solution = m/ρ = (1276g)/(1.1g mL^{-1}) = 1160 mL
$M_1 = n_2/V$ = (4.6 mol)/(1.16 L) = 3.97 M

22. Mass of 200 cm^3 of 15 mass percent of H_2SO_4; $m = \rho V$ = (1.1g cm^{-3})(200 cm^3) = 220 g

Mass of H_2SO_4 in this solution = $\left(\frac{15}{100} \times 220\text{g}\right)$ = 33g; Mass of water in this solution = 220g – 33g = 187g

Mass of 82.5% H_2SO_4 containing 33 g H_2SO_4; $M = \frac{100}{82.5} \times 33$ g = 40 g

Mass of water in this solution = 40 g – 33 g = 7 g; Volume of water in this solution = 7 cm^3
Thus 7 cm^3 of 84 % H_2SO_4 should be diluted to get 200 cm^3 of 15% H_2SO_4. The volume of water required with be 200 cm^3 – 7 cm^3 = 193 cm^3.

23. Mass of ethanol, $m_2 = V_2\rho$ = (115 mL) (0.8 g mL^{-1}) = 92.0 g

Amount of ethanol, $n_2 = \frac{m_2}{M_2} = \frac{92.0\text{g}}{46\text{ g mol}^{-1}}$ = 2.0 mol; Mass of water, m_1 = 99 g (since ρ = 1 g mL^{-1})

Amount of water, $n_1 = \frac{m_1}{M_1} = \frac{99\text{g}}{18\text{g mol}^{-1}}$ = 5.5 mol

Molality of ethanol, $m = \frac{n_2}{m_1} = \frac{2.0\text{ mol}}{(99\times10^{-3}\text{ kg})}$ = 20.2 mol kg^{-1}

Molarity of ethanol, $M = \frac{n_2}{V} = \frac{2.0\text{ mol}}{(200\times10^{-3}\text{ L})}$ = 10 mol L^{-1}

Mass fraction of ethanol, $x_2 = \frac{n_2}{n_1+n_2} = \frac{2}{2+5.5}$ = 0.267

Oxidation Number

24. $(2\overset{-4}{N})$ in $N_2H_4 \xrightarrow{-10e^-} (2\overset{+6}{N})$ in Y. Oxidation state of N in Y is +3

25. We have x + 2(+1) + (–2) = 0. This gives x = 0.

26. The oxidation state of iron in $[Fe(H_2O)_5(NO)^+]^{2+}$ is +1.

27. The oxidation states of Mn^{2+} are $\overset{+2}{Mn}SO_4$; $\overset{+3}{Mn}_2O_3$; $\overset{+4}{Mn}O_2$; $\overset{+7}{Mn}O_4^-$; $\overset{+6}{Mn}O_4^{2-}$
When $MnSO_4$ is changed to MnO_2, the change in oxidation state is +2. Hence, equivalent mass of $MnSO_4$ will be half of its molar mass.

28. For the species $H_2PO_2^-$, we have $2(+1) + x + 2(-2) = -1 \Rightarrow x = +1$

29. The reaction is $BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2$
The oxidation states of most electronegative atom in the products (which is oxygen) are –2 and –1.

30. The balanced equation can be obtained as follows.

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O] \times 2$$
$$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-] \times 5$$
$$\overline{2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O}$$

31. Oxidation and reduction reactions take place simultaneously.

32. Potassium superoxide is KO_2. The oxidation state of oxygen is –1/2.

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33. The oxidation states of Fe are $\overset{+2}{K_4Fe}(CN)_6$; $K_2\overset{+6}{Fe}O_4$; $\overset{+1}{Fe_2}O$; $\overset{0}{Fe}(CO)_5$

34. The oxidation state of Ni is zero as the CO ligand is a neutral species.

35. The oxidation of N in N_3H may be computed from the expression $3x + 1 = 0$. This gives $x = -1/3$.

36. Only in the reaction d, oxidation states of Cr and I change. In the other reactions, no change in oxidation state of any of the species occurs.

37. The oxidation states of oxygen are $H_2\overset{-1}{O_2}$; $\overset{-2}{CO_2}$; $\overset{+2}{F_2O}$; $Mn\overset{-2}{O_2}$

38. The oxidation state of oxygen in O_3 is zero.

39. We have $\overset{+5}{N}O_3^- \rightarrow \overset{-3}{N}H_4^+$. The change in oxidation state is –8. The equivalent mass of NO_3^- would be molar mass/8, i.e., 62 g mol^{-1}/8 eq mol^{-1} = 7.75 g eq^{-1}.

40. The reactions are

$$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$$
$$I_2 + 2e^- \rightarrow 2I^-$$
$$\overline{2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-}$$

For 2 mol of $Na_2S_2O_3$, 2 mol of electrons are involved. Hence, its equivalent mass will be equal to molar mass.

41. The oxidation numbers are $\overset{0}{S_8}$; $\overset{+1}{S_2}F_2$; $H_2\overset{-2}{S}$

42. The oxidation states are $\overset{+7}{Mn}O_4^-$; $\overset{+3}{Cr}(CN)_6^{3-}$; $\overset{+4}{Ni}F_6^{2-}$; $\overset{+6}{Cr}O_2Cl_2$

43. The oxidation number of Ni are as follows. $\overset{0}{Ni}(CO)_4$; $K_2(\overset{+IV}{NiF_6})$; $K_2[\overset{+II}{Ni}(CN)_4]$

44. The structure of $H_2S_2O_5$ is $HO-\overset{O}{\overset{\|}{S}}-S-OH$. The oxidation states of S are +V and +III.

45. The oxidation number of phosphorus in PH_3, P_4 and P_2O_3 are –3, 0 and +3, respectively.

47. Oxidation implies increase in oxidation number. The oxidation number of Sb in $KSbO_2^-$ and $KSb(OH)_6^-$ are +2 and +4, respectively.

48. The oxidation states are as follows. (a) +2, +3 (b) +3, 0 (c) +4, +4 (d) +6, +7

49. The balanced chemical equation is $3Cu_2O + 2NO_3^- + 14H^+ \rightarrow 6\ Cu^{2+} + 2NO + 7H_2O$
Not only atoms but also the charges should be balanced on both sides of a balanced chemical equation.

50. The balanced chemical equation is $2Mn^{2+} + 5PbO_2 + 4H^+ \rightarrow 2MnO_4^- + 5Pb^{2+} + 2H_2O$

51. The balanced chemical equation is $IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$

52. The balanced chemical equation is $3Br_2 + 6NaOH \rightarrow 5NaBr + NaBrO_3 + 3H_2O$

53. The balanced chemical equation is $P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$

Chemical Reactions

54. The reaction is $3BaCl_2 + 2Na_3PO_4 \longrightarrow Ba_3(PO_4)_2 + 6NaCl$. Hence

3 mol $BaCl_2 \equiv$ 2 mol Na_3PO_4 and thus 0.5 mol $BaCl_2 \equiv$ (2/3) (0.5 mol Na_3PO_4) $\equiv$ 0.33 mol Na_3PO_4

2 mol $Na_3PO_4 \equiv$ 3 mol $BaCl_2$ and thus 0.2 mol $Na_3PO_4 \equiv$ (3/2) (0.2 mol $BaCl_2$) $\equiv$ 0.1 mol $BaCl_2$

Obviously, Na_3PO_4 is the limiting reagent. Hence

2 mol $Na_3PO_4 \equiv$ 1 mol $Ba_3(PO_4)_2$ and thus 0.2 mol $Na_3PO_4 \equiv$ 0.1 mol $Ba_3(PO_4)_2$

55. If M is the atomic mass of X, we have $\dfrac{4M}{4M + 96\ \text{amu}} = \dfrac{6.06}{10}$

Solving for M, we get $M = 36.9$ amu

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56. The unit of extent of reaction is mol.

57. The reactions are

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \;] \times 2$$
$$SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e^-] \times 5$$
$$2MnO_4^- + 5SO_3^{2-} + 6H^+ \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$$

$$2 \text{ mol } MnO_4^- \equiv 5 \text{ mol } S_2O_3^{2-} \quad \text{and hence} \quad (2/5) \text{ mol } MnO_4^- \equiv 1 \text{ mol } S_2O_3^{2-}$$

58. F^- is most stable species amongst Cl^-, Br^- and I^-. It does not reduce none of the three species H_2SO_4, $KMnO_4$ and $K_2Cr_2O_7$.

59. Sodium in liquid ammonia is strongly reducing agent due to the presence of solvated electrons.

60. The reactions b to d have tendencies to proceed from right side to left side. The reaction a proceeds in the forward direction.

61. The reactions are $\underset{n_1}{P_4} + \underset{3n_1}{3O_2} \rightarrow \underset{n_1}{P_4O_6}$ and $\underset{n_2}{P_4} + \underset{5n_2}{5O_2} \rightarrow \underset{n_2}{P_4O_{10}}$

Given: $n_1 + n_2 = \dfrac{2\text{ g}}{124\text{ g mol}^{-1}} = \dfrac{1}{62}$ mol and $3n_1 + 5n_2 = \dfrac{2\text{ g}}{124\text{ g mol}^{-1}} = \dfrac{1}{16}$ mol

Solving for n_1 and n_2, we get $n_1 = 0.009$ mol and $n_2 = 0.007$ mol

$m_1 = (0.009 \text{ mol})\ (124 + 96) \text{ g mol}^{-1} \simeq 1.98$ g and $m_2 = (0.007 \text{ mol})\ (124 + 160) \text{ g mol}^{-1} = 1.99$ g.

62. The reaction is $3Pb(NO_3)_2 + Cr_2(SO_4)_3 \rightarrow 3PbSO_4 + 2Cr(NO_3)_3$

Amount of $Pb(NO_3)_2 = (0.25 \text{ mol dm}^{-3})\ (0.05 \text{ dm}^3) = 0.0125$ mol

Amount of $Cr_2(SO_4)_3 = (0.10 \text{ mol dm}^{-3})\ (0.025 \text{ dm}^3) = 0.0025$ mol

Here, $Cr_2(SO_4)_3$ acts as a limiting reagent.

$$\text{Molarity of } Pb^{2+} \text{ ions} = \frac{(0.0125 - 3 \times 0.0025)\text{ mol}}{0.075\text{ dm}^3} = 0.066 \text{ mol dm}^{-3}$$

$$\text{Molarity of } Cr^{3+} \text{ ions} = \frac{2 \times 0.0025\text{ mol}}{0.075\text{ dm}^3} = 0.066 \text{ mol dm}^{-3}$$

63. Loss in mass on heating is due to the reaction $XCO_3 \rightarrow XO + CO_2$. Hence

$$\text{Amount of } XCO_3 = \text{Amount of } XO = \text{Amount of } CO_2 = \frac{4.08\text{ g} - 3.64\text{ g}}{44\text{ g mol}^{-1}} = 0.01 \text{ mol}$$

The dissolution of BaO and XO consumes HCl due to the processes

$$BaO + 2HCl \rightarrow BaCl_2 + H_2O \quad \text{and} \quad XO + 2HCl \rightarrow XCl_2 + H_2O$$

Amount of excess acid = Amount of NaOH consumed = (2.5 M) (0.016 L) = 0.04 mol

Amount of HCl used in the dissolution processes = (1.0 M) (0.1 L) − 0.04 mol = 0.06 mol

Hence $n_1(BaO) + n_2(XO) = 0.06 \text{ mol} / 2 = 0.03$ mol

Amount of BaO in the mixture is $n_1(BaO) = 0.03 \text{ mol} - 0.01 \text{ mol} = 0.02$ mol

Hence $(0.02 \text{ mol})\ (M_{BaO}) + (0.01 \text{ mol})\ M_{XCO_3} = 4.08$ g

that is, $(0.02 \text{ mol})\ (154 \text{ g mol}^{-1}) + (0.01 \text{ mol})\ (M_X + 60 \text{ g mol}^{-1}) = 4.08$ g

This gives $M_X = 40 \text{ g mol}^{-1}$

64. Heating of the mixture results into the reactions:

$$2Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2 \quad \text{and} \quad 2NaNO_3 \rightarrow 2NaNO_2 + O_2$$

We have $M(Pb(NO_3)_2) = 331 \text{ g mol}^{-1}$ $\qquad$ $M(NaNO_3) = 85 \text{ g mol}^{-1}$

$M(PbO) = 223 \text{ g mol}^{-1}$ $\qquad$ $M(NaNO_2) = 69 \text{ g mol}^{-1}$

If x is the mass of $Pb(NO_3)_2$, then $\dfrac{223}{331}x + \dfrac{69}{85}(5.0\text{ g} - x) = (0.72)\ (5.0\text{ g})$

Solving for x, we get $x = 3.32$ g

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65. The reaction to be considered is $2Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2$

$$\frac{M_{Pb} + 16\ g\ mol^{-1}}{M_{Pb} + 124\ g\ mol^{-1}} = \frac{67.4}{100}.$$ Solving for M_{Pb}, we get $M_{Pb} = 207\ g\ mol^{-1}$

66. The reaction to be considered is $4K_2Cr_2O_7 \rightarrow 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$

The loss in mass is due to escape of O_2. For 1 mol of $K_2Cr_2O_7$, (3/4) mol of O_2 is released. Hence

$$\frac{\text{mass of (3/4) mol of } O_2}{\text{mass of 1 mol of } K_2\,Cr_2\,O_7} \times 100 = \frac{24\,g}{249\,g} \times 100 = 8\%$$

67. The reaction to be considered is $Pb(NO_3)_2 + 2KI \rightarrow PbI_2 + 2KNO_3$

Amount of $Pb(NO_3)_2 = (0.1\ M)\ (5 \times 10^{-3}\ L) = 5 \times 10^{-4}$ mol

Amount of $KI = (0.02\ M)\ (10 \times 10^{-3}\ L) = 2 \times 10^{-4}$ mol

Limiting reagent is KI. The amount of PbI_2 will be 1×10^{-4} mol.

68. With methyl orange indicator, both Na_2CO_3 and $NaHCO_3$ are neutralized.

69. With phenolphthalene indicator, Na_2CO_3 is neutralized upto the stage of $NaHCO_3$.

70. With phenolphthalene, NaOH and Na_2CO_3 upto the stage of $NaHCO_3$ are neutralized.

71. With methyl orange, both NaOH and Na_2CO_3 are completely neutralized.

72. The reactions are $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

$$A^{n+} + 3H_2O \rightarrow AO_3^- + 6H^+ + (5 - n)e^-$$

Hence, we will have $(5)(1.61 \times 10^{-3}\ mol) = (5 - n)(2.68 \times 10^{-3}\ mol)$

which gives $n = 2$

73. Volume of $K_2Cr_2O_7$ required will be $(15\ mL)\left(\frac{5}{6}\right) = 12.5\ mL$

where 5 is the number of electrons involved in the oxidation reaction with MnO_4^- and 6 is those involved with $Cr_2O_7^{2-}$. The above expression follows from the normality expression.

$$(15\ mL)\ (0.1 \times 5\ N\ MnO_4^-) = (V)\ (0.1 \times 6\ N\ Cr_2O_7^{2-})$$

74. The reaction occurring is $Na_2CO_3 + H^+ \rightarrow NaHCO_3 + Na^+$

Since molarity of Na_2CO_3 and HCl are identical, the volume of HCl required in the above reaction will be the same as that of Na_2CO_3.

75. The reactions occurring are $Na_2CO_3 + 2H^+ \rightarrow 2Na^+ + H_2O + CO_2$

$$NaHCO_3 + H^+ \rightarrow Na^+ + H_2O + CO_2$$

Since molarity of Na_2CO_3, $NaHCO_3$ and HCl are identical, the volume of HCl consumed will be 2×20 mL + 20 mL (= 60 mL).

76. The reaction to be considered is $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$

Amount of $I_2 = (0.01\ mol\ L^{-1})\ (10 \times 10^{-3}\ L) = (1 \times 10^{-4})$ mol

Amount of $S_2O_3^{2-}$ consumed $= 2 \times 10^{-4}$ mol

Volume of $S_2O_3^{2-}$ consumed $= \frac{2 \times 10^{-4}\ mol}{0.01\ mol^{-1}} = 2 \times 10^{-2}\ L = 20\ mL$

77. Normality of oxalic acid $= \left(\frac{6.3\ g}{6.3\ g\ eq^{-1}}\right)\left(\frac{1}{250 \times 10^{-3}\ L}\right) = 0.4\ eq\ L^{-1}$

$$V_{NaOH} = \frac{(10\,mL)\,(0.4\,N)}{(0.1\,N)} = 40\ mL$$

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78. The changes in oxidation numbers are $\overset{+5}{ClO_3^-} + \overset{+5}{2ClO_3} \rightarrow \overset{+7}{ClO_4} + \overset{-1}{Cl^-}$

Chlorine undergoes increase as well decrease in oxidation states. Hence, the reaction is disproportionation reaction.

79. The reaction of $Cr_2O_7^{2-}$ involving the release of I_2 from I^- is

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

Hence, Equivalent mass of $K_2Cr_2O_7 = \dfrac{\text{Molar mass}}{6}$

80. Mn in $KMnO_4$ is already present in the highest oxidation state.

81. The reaction is $\underset{1\,\text{mol}}{Cr_2O_7^{2-}} + 14H^+ + \underset{6\,\text{mol}}{6Fe^{2+}} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$

82. $Ag_2CO_3 \rightarrow Ag_2O + CO_2$; $\left(\dfrac{2\times108+16}{2\times108+12+48}\times2.76\,g\right) = \left(\dfrac{232}{276}\times2.76\,g\right) = 2.32\,g$

83. Only $CaCO_3$ on heating undergoes the reaction $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

Loss of mass is due to escape of $CO_2(g)$

$$\text{Amount of } CO_2 \text{ escaped} = \frac{1.0\,g - 0.67\,g}{44\,g\,mol^{-1}} = \frac{3}{4} \times 10^{-2}\ mol$$

Amount of $CaCO_3(s)$ in mixture will be equal to the amount of CO_2 evolved. Hence, mass of $CaCO_3$ will be

$$m = nM = \left(\frac{3}{4}\times10^{-2}\ mol\right)(100\,g\ mol^{-1}) = 0.75\,g$$

$$\text{Mass percent of } CaCO_3 = \frac{0.75\,g}{1\,g}\times100 = 75\%$$

84. The reactions are $\underset{n_1}{C(s)} + \frac{1}{2}\underset{n_1/2}{O_2(g)} \rightarrow \underset{n_1}{CO(g)}$ and $\underset{n_2}{C(s)} + \underset{n_2}{O_2(g)} \rightarrow \underset{n_2}{CO_2(g)}$

Total mass of C in CO and $CO_2 = (n_1 + n_2)\,(12\,g\ mol^{-1})$

Total mass of oxygen in CO and $CO_2 = (n_1 + 2n_2)\,(16\,g\ mol^{-1})$

Hence $(n_1 + n_2)\,(12\,g\ mol^{-1}) = 6.0\,g$ and $(n_1 + 2n_2)\,(16\,g\ mol^{-1}) = 12.0\,g$

or $n_1 + n_2 = 0.5$ mol and $n_1 + 2n_2 = 0.75$ mol

Solving for n_1 and n_2, we get

$n_1 = 0.25$ mol and $n_2 = 0.25$ mol;

$m_1 = (0.25\ mol)\,(28\,g\ mol^{-1}) = 7\,g\ mol^{-1}$; $m_2 = (0.25\ mol)\,(44\,g\ mol^{-1}) = 11\,g\ mol^{-1}$

$$\text{Mass percent of CO} = \frac{7}{10}\times100 = 63.6$$

85. On explosion, CO and CH_4 is converted to CO_2

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g) \quad \text{and} \quad CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + H_2O(l)$$

Let V_1, V_2 and V_3 be the partial volumes of CO, CH_4 and He in the original 20 cm^3 of the mixture. From the chemical equations given above, we have

$$V_1(CO) \equiv \frac{V_1}{2}\,(O_2) \equiv V_1(CO_2) \quad \text{and} \quad V_2(CH_4) \equiv 2V_2(O_2) = V_2(CO_2)$$

The decrease in volume is due to consumption of O_2 since $V_1(CO)$ and $V_2(CH_4)$ are replaced by equal volumes of $V_1(CO_2)$ and $V_2(CO_2)$, respectively. Hence

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$$\frac{V_1}{2} + 2V_2 = 13 \text{ cm}^3$$

On passing through NaOH(aq), $CO_2(g)$ will be absorbed. Hence $V_1 + V_2 = 14 \text{ cm}^3$

These two equations give $V_1 = 10 \text{ cm}^3$ and $V_2 = 4 \text{ cm}^3$

Thus, $V_3(\text{He}) = (20 - 10 - 4) \text{ cm}^3 = 6 \text{ cm}^3$

Volume percent of CO = (10/20) × 100 = 50%; Volume percent of CH_4 = (4/20) × 100 = 20%

Volume percent of He = (6/20) × 100 = 30%

86. We have $\frac{18x}{18x+152} = \frac{45.5}{100}$. This gives $x = \frac{0.455\times152}{18(1-0.455)} = 6.92$

87. Let n_1 and n_2 be the amounts of SO_3 and H_2SO_4 in the given solution of fuming H_2SO_4. The neutralization reactions are

$$SO_3 + 2OH^- \rightarrow SO_4^{2-} + H_2O \quad \text{and} \quad H_2SO_4 + 2OH^- \rightarrow SO_4^{2-} + 2H_2O$$

We will have

(1) $n_1M_1 + n_2M_2 = 0.5$ g ; (Given mass of mixture)

(2) $2(n_1 + n_2) = (22 \times 10^{-3} \text{ L})\ (0.5 \text{ mol L}^{-1}) = 0.011$ mol (Equivalent H_2SO_4 is consumed)

or $n_1 + n_2 = 0.0055$ mol;

Eliminating n_2 from Eqs (1) and (2), we get

$n_1(80 \text{ g mol}^{-1}) + (0.0055 \text{ mol} - n_1)\ (98 \text{ g mol}^{-1}) = 0.5$ g

or $n_1(80 - 98) \text{ g mol}^{-1} = 0.5 \text{ g} - 0.0055 \times 98 \text{ g} = 0.5 \text{ g} - 0.539 \text{ g}$

$$n_1 = \frac{0.039}{18} \text{ mol} = 0.0022 \text{ mol}; \quad m_1 = (0.0022 \text{ mol})\ (80 \text{ g mol}^{-1}) = 0.176 \text{ g}$$

$$\text{Mass percent of } SO_3 = \frac{0.176}{0.5} \times 100 = 35.2$$

88. Mass of KI in solution $= \left(\frac{16}{100}\right)(1.132 \text{ g mL}^{-1})\ (90 \text{ mL}) = 16.30$ g

$$\text{Amount of KI} = \frac{16.30\text{g}}{(39+127)\text{g mol}^{-1}} = 0.10 \text{ mol}$$

$$\text{Mass of } Pb(NO_3)_2 \text{ in solution} = \left(\frac{20}{100}\right)(1.1 \text{ g mL}^{-1})\ (90 \text{ mL}) = 19.8 \text{ g}$$

$$\text{Amount of } Pb(NO_3)_2 = \frac{19.8\,\text{g}}{\{208+2(14+48)\}\text{ g mol}^{-1}} = 0.06 \text{ mol}$$

The precipitation reactionis $\underset{0.06\text{ mol}}{Pb(NO_3)_2} + \underset{0.1\text{ mol}}{2KI} \rightarrow PbI_2 + 2KNO_3$

Here KI is the limiting reagent. Thus amount of PbI_2 precipitated will be 0.05 mol

89. The neutralization reaction is $M_2CO_3 + 2HCl \rightarrow 2MCl + CO_2 + H_2O$

Amount of H^+ in 100 mL of 0.05 M HCl solution,

$$n = VM = (100 \times 10^{-3} \text{ L})\ (0.05 \text{ mol L}^{-1}) = 0.005 \text{ mol}$$

$$\text{Amount of } M_2CO_3 = \frac{n(\text{HCl})}{2} = \frac{0.005\,\text{mol}}{2} = 0.0025 \text{ mol}$$

Hence $(0.0025 \text{ mol})\ [\{106 + x(18)\} \text{ g mol}^{-1}] = 0.355$ g

This gives $x = 2$

90. $$\text{Amount of } KMnO_4 = \frac{m}{M} = \frac{0.465\text{g}}{155\text{g mol}^{-1}} = 0.003 \text{ mol}$$

The reaction between MnO_4^- and H_2O_2 is $2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5O_2$

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Amount of H_2O_2 in the given solution = $\frac{5}{2} \times 0.003$ mol = 0.0075 mol

Mass of H_2O_2 = (0.0075 mol) (34 g mol^{-1}) = 0.255 g

Mass percent purity of H_2O_2 = $\frac{0.255\,g}{0.34\,g} \times 100 = 75$

91. The neutralization reactions are

Phenolphthalein $OH^- + H^+ \rightarrow H_2O$ Methyl orange $OH^- + H^+ \rightarrow H_2O$

$CO_3^{2-} + H^+ \rightarrow HCO_3^-$ $CO_3^{2-} + 2H^+ \rightarrow CO_2 + H_2O$

The extra 5 mL of HCl used in the methyl orange indicator corresponds to the neutralization reaction

$$HCO_3^- + H^+ \rightarrow H_2O + CO_2$$

Therefore, for the complete neutralization of Na_2CO_3, the volume of HCl used will be 10 mL. The volume used for neutralizing NaOH will be 25 mL – 10 mL = 15 mL.

Amount of HCl in 10 mL HCl solution = (10×10^{-3} L) (0.1 mol L^{-1}) = 10^{-3} mol

Amount of HCl in 15 mL HCl solution = 1.5×10^{-3} mol

Amount of NaOH in the mixture = amount of HCl = 1.5×10^{-3} mol

Amount of Na_2CO_3 in the mixture = $\frac{1}{2}$ (amount of HCl) = 0.5×10^{-3} mol

Mass of NaOH in the mixture = (1.5×10^{-3} mol) (40 g mol^{-1}) = 0.06 g

Mass of Na_2CO_3 in the mixture = (0.5×10^{-3} mol) (106 g mol^{-1}) = 0.053 g

Mass per cent of Na_2CO_3 in the mixture = $\frac{0.053}{0.053+0.06} \times 100 = 47$

92. Amount of NaCl = $\frac{4.68\,g}{58.5\,g\,mol^{-1}}$ = 0.08 mol; Amount of $AgNO_3$ = $\frac{6.8\,g}{170.0\,g\,mol^{-1}}$ = 0.04 mol

Since the amount of $AgNO_3$ is less than that of NaCl, the whole of $AgNO_3$ is precipitated.

Mass of AgCl precipitated = (0.04 mol) (143.5 g mol^{-1}) = 5.74 g

Multiple Correct Choice Type

1. (a) The oxidation state of oxygen in H_2O_2 is –1. It is changed to –2 in water and to zero in O_2.
(b) The oxidation state of S is changed from +7 to +6 whereas that of O is changed from 0 to –2.
(c) An oxidant absorbs electron(s), its oxidation number is decreased.
(d) A reductant releases electron(s), its oxidation number is increased.

2. (a) The element undergoing oxidation causes the release of electron(s). Hence, its oxidation number is increased.
(b) The element undergoing reduction absorbs electron(s). Hence, its oxidation number is decreased.
(d) The oxidation state of Mo is changed from +6 to +5. Thus, H_2MoO_4 is an oxidizing agent.

3. (a) It is decreased by one.
(b) In this case, Mn^{3+} is changed to Mn^{4+} and another Mn^{3+} is changed to Mn^{2+}.
(c) In alkaline medium, the reaction is $MnO_4^- + e^- \rightarrow MnO_4^{2-}$
(d) In neutral medium (or weakly acidic or alkaline), the reaction is

$$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$$

4. (a) In strongly alkaline medium, MnO_4^- undergoes the reaction $MnO_4^- + e^- \rightarrow MnO_4^{2-}$. Hence, its equivalent mass is equal to its molar mass.

(b) The reaction is $2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$

Hence, Equivalent mass = $\frac{2 \times \text{Molar mass}}{2}$ = molar mass

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(c) The reaction is $Ce^{4+} + e^- \rightarrow Ce^{3+}$

(d) The reaction is $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ Equivalent mass = molar mass/6 eq mol^{-1}

5. (a) The reaction is $BrO_3^- + 6H^+ + 6e^- \rightarrow Br^- + 3H_2O$.

(d) The change in oxidation state of iodine in IO_3^- is from +5 to +1.

6. (a) The equivalent mass of a substance may have different values in different reactions. Thus, the reaction has to be considered before determining its equivalent mass.

(b) One mole of $K_4Fe(CN)_6$ produces 4 mol of K^+ and ! mol of $Fe(CN)_6^{4-}$ ions.

(d) As an oxidizing reagent, the reaction is $2H^+ + H_2O_2 + 2e^- \rightarrow 2H_2O$.

As a reducing reagent, the reaction is $H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$.

7. (b) The oxidation state changes from 0 to +6. (d) The equivalent mass is molar mass divided by six.

8. (b) The oxidation state changes from 0 to +1. (e) IO_3^- is oxidizing agent.
(f) I_2 is reducing agent.

9. (b) The equivalent mass is molar mass divided by four.
(d) The equivalent mass is molar mass divided by five.

10. (b) The equivalent mass is molar mass divided by six. (c) The oxidation state of S is zero.

11. (b) There are four species.

13. The mass of 1000 mL solution will be (1000 mL) (1.09 g mL^{-1}) = 1090 g. The mass of sulphuric acid in the solutionis (13/100) (1090 g) = 141.7 g. Amount of sulphuric is 141.7 g/98 g mol^{-1} = 1.446 mol. Hence,

$$\text{Molarity of } H_2SO_4 = \frac{1.446 \text{ mol}}{1\text{L}} = 1.446 \text{ mol L}^{-1}$$

$$\text{Molality of } H_2SO_4 = \frac{1.446 \text{ mol}}{(1090 - 141.7) \times 10^{-3} \text{ kg}} = 1.525 \text{ mol kg}^{-1}$$

14. The burning reaction is $2\,Mg + O_2 \rightarrow 2MgO$

Initial amount of Mg = (1.8 g/24g mol^{-1}) = 0.075 mol

Initial amount of O_2 = (0.8 g/32 g mol^{-1}) = 0.025 mol

In the combustion reaction, whole of O_2 will be used

Amount of MgO formed = 2 × 0.025 mol = 0.050 mol

Amount of O_2 left = 0

Mass of Mg left = [(0.075 – 0.050) mol] [24 g mol^{-1}]

From the reaction $MgO + H_2SO_4 \rightarrow MgSO_4 + H_2O$, we write

$$V(0.25 \text{ M}) = 0.05 \text{ mol} \quad \text{or} \quad V = \frac{0.05}{0.25} \text{L} = 0.2 \text{ L or } 200 \text{ mL}$$

Link Comprehension Type

1. Normality of oxalic acid solution is $N_1 = \dfrac{m_2 / M_{eq}}{V_1} = \dfrac{(0.42\text{ g})/(63\text{ g eq}^{-1})}{(250 \times 10^{-3}\text{ L})} = \dfrac{2}{75}\text{ N}$

(i) Normality of sodium hydroxide solution is $N_2 = \dfrac{N_2 V_1'}{V_2} = \dfrac{(2\text{ N}/75)\,(10\text{ mL})}{(9.6\text{ mL})} = \dfrac{1}{36}\text{ N}$

Normality of sulphuric acid solution is $N_3 = \dfrac{N_2 V_2'}{V_2} = \dfrac{(\text{N}/36)\,(9.0\text{ mL})}{(10\text{ mL})} = \dfrac{1}{40}\text{ N}$

Molarity of sulphuric acid solution = (1/2) (1/40) M = M/80

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(ii) With phenolphthalene, the reaction occurring is $Na_2CO_3 + H^+ \rightarrow NaHCO_3 + Na^+$

To neutralize whole of Na_2CO_3, volume of H_2SO_4 solution will be twice of the given volume of 4.0 mL.

Hence, the normality of Na_2CO_3 in the solution is $N_4 = \dfrac{(2\times 4.0\text{ mL})\,(N/40)}{(10\text{ mL})} = \dfrac{N}{50}\,N$

Mass of Na_2CO_3 in 1L of solution is $m = (N/50)\ (53\text{ g eq}^{-1}) = 1.06\text{ g L}^{-1}$

(iii) Volume of sulphuric acid solution used in neutralizing $NaHCO_3$ will be $(14.0 - 2\times 4.0)$ mL = 6.0 mL.

Hence, the normality of $NaHCO_3$ in the solution is $N_5 = \dfrac{(6.0\text{ mL})\,(N/40)}{(10\text{ mL})} = \dfrac{3}{200}\,N$

Mass of $NaHCO_3$ in 1 L of solution is $m = (3\ N/200)\ (84\text{ g eq}^{-1}) = 1.26\text{ g L}^{-1}$

2. Normality of oxalic acid solution is $N_1 = \dfrac{m_2/M_{eq}}{V_1} = \dfrac{0.63\text{ g}/(63\text{ g eq}^{-1})}{(250\times 10^{-3}\text{ L})} = \dfrac{1}{24}\,N$

(i) Normality of sodium hydroxide solution is $N_2 = \dfrac{N_1V_1'}{V_2} = \dfrac{(N/25)\,(10\text{ mL})}{(9.6\text{ mL})} = \dfrac{1}{25}\,N$

Normality of sulphuric acid solution is $N_3 = \dfrac{N_2V_2'}{V_3} = \dfrac{(N/24)\,(8.4\text{ mL})}{(10\text{ mL})} = \dfrac{7}{200}\,N$

Mass of sulphuric acid present in 1 L of solution $m = \left(\dfrac{7}{200}\text{ eq L}^{-1}\right)\left(\dfrac{98}{2}\text{ g eq}^{-1}\right) = 1.715\text{ g L}^{-1}$

(ii) The reaction occurring are

Phenolphthalein: $CO_3^{2-} + H^+ \rightarrow CO_3^-$; $OH^- + H^+ \rightarrow H_2O$

Methyl orange: $CO_3^{2-} + 2H^+ \rightarrow CO_2 + H_2O$; $OH^- + H^+ \rightarrow H_2O$

Volume of sulphuric acid used to neutralize Na_2CO_3 will be 2(16.0 mL – 12.0 mL) = 8.0 mL

Hence, normality of Na_2CO_3 in solution is $N_4 = \dfrac{(8.0\text{ mL})\,(7\ N/200)}{(10\text{ mL})} = \dfrac{7}{250}\,N$

Mass of Na_2CO_3 in 1L of solution is $m = (7N/250)\ (53\text{ g eq}^{-1}) = 1.484\text{ g L}^{-1}$

(iii) Volume of sulphuric acid used to neutralize NaOH will be 16.0 mL – 8.0 mL = 8.0 mL

Hence, Normality of $NaHCO_3$ in solution is $N_4 = \dfrac{(8.0\text{ mL})\,(7N/200)}{(10\text{ mL})} = \dfrac{7}{250}\,N$

Mass of NaOH in 1 L of solution is $m = (7\ N/250)\ (40\text{g eq}^{-1}) = 1.12\text{ g L}^{-1}$

3. Normality of oxalic acid solution is $N_1 = \dfrac{m_2/M_{eq}}{V_1} = \dfrac{(0.63\text{ g})\,(63\text{ g eq}^{-1})}{(250\times 10^{-3}\text{ mL})} = \dfrac{1}{25}\,N$

(i) Normality of NaOH solution is $N_2 = \dfrac{N_1V_1'}{V_2} = \dfrac{(N/25)\,(10\text{ mL})}{(9.8\text{ mL})} = \dfrac{1}{24}\,N$

Since normality of NaOH is its molarity, the molartiy of NaOH is (1/24) M.

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Normality of $KmnO_4$ solution is $N_3 = \dfrac{N_1V_1''}{V_3} = \dfrac{(N/25)\,(10\text{ mL})}{(9.8\text{ mL})} = \dfrac{1}{24.5}\text{N}$

In the reaction of MnO_4^- with oxalic acid, it undergoes the reaction

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

Molarity of $KMnO_4$ solution $= \dfrac{N_{KMnO_4}}{5\text{ eq mol}^{-1}} = \dfrac{(1/24.5)\text{ eq L}^{-1}}{(5\text{ eq mol}^{-1})} = \dfrac{1}{122.5}\text{ mol L}^{-1}$

(ii) Normality of oxalic acid in the solution containing both oxalic acid and sodium oxalate is

$$N = \frac{(8.5\text{ mL})\,(N/24)}{(10\text{ mL})} = \frac{8.5}{240}\text{ N}$$

Mass of oxalic acid per litre of solution is $m = \left(\dfrac{8.5}{240}\text{N}\right)(63\text{ g eq}^{-1}) = 2.23\text{ g}$

(iii) Normality of sodium oxalate in the solution containing both oxalic acid and sodium oxalate is

$$N = \frac{\{(20.7-8.5)\text{ mL}\}\,(N/24.5)}{(10\text{ mL})} = 0.498\text{ N}$$

Mass of sodium oxalate present per litre of solution is

$$m = (0.0498\text{ N})\,(84\text{ g eq}^{-1}) = 4.18\text{ L}^{-1}$$

4. (i) The reactions between H_2O_2 and MnO_4^- are as follows

$$\begin{aligned} MnO_4^- + 8H^+ + 5e^- &\rightarrow Mn^{2+} + 4H_2O]\times 2 \\ H_2O_2 &\rightarrow O_2 + 2H^+ + 2e^-]\times 5 \\ \hline 2MnO_4^- + 6H^+ + 5H_2O_2 &\rightarrow 2Mn^{2+} + 5O_2 + 4H_2O \end{aligned}$$

Normality of $KMnO_4$ solution $= (5\text{ eq mol}^{-1})\,(\text{mol L}^{-1}/50) = 0.1\text{ eq L}^{-1}$

Normality of H_2O_2 is $N = \dfrac{(0.1\text{ N})\,(28.4\text{ mL})}{(10\text{ mL})} = 0.284\text{ N}$

Molarity of $H_2O_2 = \left(\dfrac{1}{2\text{ eq mol}^{-1}}\right)(0.284\text{ eq L}^{-1}) = 0.142\text{ mol L}^{-1}$

(ii) Mass of 1000 mL of H_2O_2 sample $= (1000\text{ mL})\,(1.2\text{ g mL}^{-1}) = 1200\text{ g}$

Mass of H_2O_2 in this solution $= (0.142\text{ mol})\,(34\text{ g mol}^{-1}) = 4.83\text{ g}$

Mass of solvent in this solution $= (1200\text{ g} - 4.83\text{ g}) = 1195.17\text{ g} = 1.195\text{ kg}$

Molality of $H_2O_2 = \dfrac{0.142\text{ mol}}{1.195\text{ kg}} = 0.119\text{ mol kg}^{-1}$

(iii) The volume strength of H_2O_2 is based on the reaction $2H_2O_2 \rightarrow 2H_2O + O_2$

2 mol of H_2O_2 gives 1 mol of O_2 or 22.414 L of O_2 at STP

Hence, 0.142 mol L^{-1} solution of H_2O_2 will liberate $\dfrac{22.414}{2\text{ M}}\,(0.142\text{ M}) = 1.59$

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ANNEXURE

Subjective Problems for Practice

Balancing Chemical Equations

1. Balance the following equations.

(i) $Cu_2O + H^+ + NO_3^- \rightarrow Cu^{2+} + NO + H_2O$

(ii) $K_4Fe(CN)_6 + H_2SO_4 + H_2O \rightarrow K_2SO_4 + FeSO_4 + (NH_4)_2SO_4 + CO$

(iii) $C_2H_5OH + I_2 + OH^- \rightarrow CHI_3 + HCO_2^- + I^- + H_2O$

Solution

The above equations may be balanced following either oxidation-state change method or ion-electron method. Steps listed in each case are those mentioned earlier in the text.

(i) $Cu_2O + H^+ + NO_3^- \rightarrow Cu^{2+} + NO + H_2O$

Step 1 : $Cu_2O \xrightarrow{\text{oxidation}} Cu^{2+}$ $\qquad$ $NO_3^- \xrightarrow{\text{reduction}} NO$

Step 2 : $Cu_2O \rightarrow \underline{2}Cu^{2+}$ $\qquad$ $NO_3^- \rightarrow NO$

Step 3 : $Cu_2O + \underline{2H^+} \rightarrow 2Cu^{2+} + \underline{H_2O}$ $\qquad$ $NO_3^- + \underline{4H^+} \rightarrow NO + \underline{2H_2O}$

Step 4 : $Cu_2O + 2H^+ \rightarrow 2Cu^{2+} + H_2O + \underline{2e^-}$ $\qquad$ $NO_3^- + 4H^+ + \underline{3e^-} \rightarrow NO + 2H_2O$

Step 5 : $[Cu_2O + 2H^+ \rightarrow 2Cu^{2+} + H_2O + 2e^-] \times \underline{3}$

$[NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O] \times \underline{2}$

Step 6 : $3Cu_2O + 2NO_3^- + 14H^+ \rightarrow 6Cu^{2+} + 2NO + 7H_2O$

(ii) $K_4Fe(CN)_6 + H_2SO_4 + H_2O \rightarrow K_2SO_4 + FeSO_4 + (NH_4)_2SO_4 + CO$

Step 1 : $K_4Fe(\overset{+4-5}{C}\,\overset{+4-5}{N})_6 + H_2SO_4 + H_2O \rightarrow K_2SO_4 + FeSO_4 + (\overset{-3}{N}H_4)_2SO_4 + \overset{+2}{C}O$

Step 2 : $K_4Fe(CN)_6 + H_2SO_4 + H_2O \rightarrow K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$

Step 3 : $K_4Fe(CN)_6 + H_2SO_4 + H_2O \rightarrow K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$

$6(+2) = +12$ $\qquad$ $6(-2) = -12$

Step 4 : $K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O \rightarrow 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$

(iii) $C_2H_5OH + I_2 + OH^- \rightarrow CHI_3 + HCO_2^- + I^- + H_2O$

Step 1 : $\overset{-2}{C_2}H_5OH + \overset{0}{I_2} + OH^- \rightarrow \overset{+2\ -1}{CHI_3} + \overset{+2}{H}CO_2^- + \overset{-1}{I^-} + H_2O$

Step 2 : $C_2H_5OH + 2I_2 + OH^- \rightarrow CHI_3 + HCO_2^- + I^- + H_2O$

Step 3 : $C_2H_5OH + 4I_2 + OH^- \rightarrow CHI_3 + HCO_2^- + 5I^- + H_2O$

$+3 + 5 = +8$ $\qquad$ $(-4) + (-4) = -8$

Step 4 : $C_2H_5OH + 4I_2 + 6OH^- \rightarrow CHI_3 + HCOO^- + 5I^- + 5H_2O$

2. Complete and balance the following equations.

(i) $Zn + NO_3^- \rightarrow Zn^{2+} + NH_4^+$

(ii) $Cr_2O_7^{2-} + C_2H_4O \rightarrow C_2H_4O_2 + Cr^{3+}$

(iii) $HNO_3 + HCl \rightarrow NO + Cl_2$

(iv) $Ce^{3+} + S_2O_8^{2-} \rightarrow SO_4^{2-} + Ce^{4+}$

(v) $Cl_2 + OH^- \rightarrow Cl^- + ClO^-$

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Solution

The above equations may be balanced following either oxidation-state change method or ion-electron method. Steps listed in each case are those mentioned earlier in the text.

(i) $Zn + NO_3^- \rightarrow Zn^{2+} + NH_4^+$

Step 1 : $Zn \xrightarrow{\text{oxidation}} Zn^{2+}$ $\qquad$ $NO_3^- \xrightarrow{\text{reduction}} NH_4^+$

Step 2 : Not required

Step 3 : $Zn \rightarrow Zn^{2+}$ $\qquad$ $NO_3^- + 10H^+ \rightarrow NH_4^+ + 3H_2O$

Steps 4 and 5 : $[Zn \rightarrow Zn^{2+} + 2e^-] \times 4$

$[NO_3^- + 10H^+ + 8e^- \rightarrow NH_4^+ + 3H_2O] \times 1$

Step 6 : $4Zn + NO_3^- + 10H^+ \rightarrow 4Zn^{2+} + NH_4^+ + 3H_2O$

(ii) $Cr_2O_7^{2-} + C_2H_4O \rightarrow C_2H_4O_2 + Cr^{3+}$

Step 1 : $C_2H_4O \xrightarrow{\text{oxidation}} C_2H_4O_2$ $\qquad$ $Cr_2O_7^{2-} \xrightarrow{\text{reduction}} Cr^{3+}$

Step 2 : $C_2H_4O \rightarrow C_2H_4O_2$ $\qquad$ $Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$

Step 3 : $C_2H_4O + H_2O \rightarrow C_2H_4O_2 + 2H^+$ $\qquad$ $Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$

Steps 4 and 5 : $[C_2H_4O + H_2O \rightarrow C_2H_4O_2 + 2H^+ + 2e^-] \times 3$

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

Step 6 : $3C_2H_4O + Cr_2O_7^{2-} + 8H^+ \rightarrow 3C_2H_4O_2 + 2Cr^{3+} + 4H_2O$

(iii) $HNO_3 + HCl \rightarrow NO + Cl_2$

Step 1 : $Cl^- \xrightarrow{\text{oxidation}} Cl_2$ $\qquad$ $NO_3^- \xrightarrow{\text{reduction}} NO$

Step 2 : $2Cl^- \rightarrow Cl_2$ $\qquad$ $NO_3^- \rightarrow NO$

Step 3 : $2Cl^- \rightarrow Cl_2$ $\qquad$ $NO_3^- + 4H^+ \rightarrow NO + 2H_2O$

Steps 4 and 5 : $[2Cl^- \rightarrow Cl_2 + 2e^-] \times 3$

$[NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O] \times 2$

Step 6 : $2NO_3^- + 6Cl^- + 8H^+ \rightarrow 3Cl_2 + 2NO + 4H_2O$ or $2HNO_3 + 6HCl \rightarrow 3Cl_2 + 2NO + 4H_2O$

(iv) $Ce^{3+} + S_2O_8^{2-} \rightarrow SO_4^{2-} + Ce^{4+}$

Step 1 : $Ce^{3+} \xrightarrow{\text{oxidation}} Ce^{4+}$ $\qquad$ $S_2O_8^{2-} \xrightarrow{\text{reduction}} SO_4^{2-}$

Step 2 : $Ce^{3+} \rightarrow Ce^{4+}$ $\qquad$ $S_2O_8^{2-} \rightarrow 2SO_4^{2-}$

Step 3 : Not required

Steps 4 and 5 : $[Ce^{3+} \rightarrow Ce^{4+} + e^-] \times 2$

$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$

Step 6 : $2Ce^{3+} + S_2O_8^{2-} \rightarrow 2SO_4^{2-} + 2Ce^{4+}$

(v) $Cl_2 + OH^- \rightarrow Cl^- + ClO^-$

Step 1 : $Cl_2 \xrightarrow{\text{oxidation}} ClO^-$ $\qquad$ $Cl_2 \xrightarrow{\text{reduction}} Cl^-$

Step 2 : $Cl_2 \rightarrow 2ClO^-$ $\qquad$ $Cl_2 \rightarrow 2Cl^-$

Step 3 : $Cl_2 + 4OH^- \rightarrow 2ClO^- + 2H_2O$ $\qquad$ $Cl_2 \rightarrow 2Cl^-$

Steps 4 and 5 : $Cl_2 + 4OH^- \rightarrow 2ClO^- + 2H_2O + 2e^-$

$Cl_2 + 2e^- \rightarrow 2Cl^-$

Step 6 : $2Cl_2 + 4OH^- \rightarrow 2Cl^- + 2ClO^- + 2H_2O$ or $Cl_2 + 2OH^- \rightarrow Cl^- + ClO^- + H_2O$

3. Complete and balance the following equations.

(i) $Mn^{2+} + PbO_2 \rightarrow MnO_4^- + Pb^{2+} + H_2O$ $\qquad$ (ii) $S + OH^- \rightarrow S^{2-} + S_2O_3^{2-}$

(iii) $ClO_3^- + I^- + H_2SO_4 \rightarrow Cl^- + HSO_4^- + I_2$ $\qquad$ (iv) $Ag^+ + AsH_3 \rightarrow H_3AsO_3 + H^+ + Ag$ (1986)

Solution

The above equations may be balanced following either oxidation-state change method or ion-electron method. Listed steps are those mentioned earlier in the text.

(I) $Mn^{2+} + PbO_2 \rightarrow MnO_4^- + Pb^{2+} + H_2O$

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Step 1 : $Mn^{2+} \xrightarrow{\text{oxidation}} MnO_4^-$ $\qquad$ $PbO_2 \xrightarrow{\text{reduction}} Pb^{2+}$

Step 2 : Not required.

Step 3 : $Mn^{2+} + 4H_2O \rightarrow MnO_4^- + 8H^+$ $\qquad$ $PbO_2 + 4H^+ \rightarrow Pb^{2+} + 2H_2O$

Steps 4 and 5 : $[Mn^{2+} + 4H_2O \rightarrow MnO_4^- + 8H^+ + 5e^-] \times 2$

$[PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O] \times 5$

Step 6 : $2Mn^{2+} + 5PbO_2 + 4H^+ \rightarrow 2MnO_4^- + 5Pb^{2+} + 2H_2O$

(ii) $S + OH^- \rightarrow S^{2-} + S_2O_3^{2-}$

Steps 1 and 2 : $2S \xrightarrow{\text{oxidation}} S_2O_3^{2-}$ $\qquad$ $S \xrightarrow{\text{reduction}} S^{2-}$

Step 3 : $2S + 3H_2O \rightarrow S_2O_3^{2-} + 6H^+$ $\qquad$ $S \rightarrow S^{2-}$

Steps 4 and 5 : $2S + 3H_2O \rightarrow S_2O_3^{2-} + 6H^+ + 4e^-$

$[S + 2e^- \rightarrow S^{2-}] \times 2$

Step 6 : $4S + 3H_2O \rightarrow 2S^{2-} + S_2O_3^{2-} + 6H^+$ $\qquad$ or $\quad 4S + 6OH^- \rightarrow 2S^{2-} + S_2O_3^{2-} + 3H_2O$

(iii) $ClO_3^- + I^- + H_2SO_4 \rightarrow Cl^- + HSO_4^- + I_2$

Steps 1 and 2 : $2I^- \xrightarrow{\text{oxidation}} I_2$ $\qquad$ $ClO_3^- \xrightarrow{\text{reduction}} Cl^-$

Step 3 : $2I^- \rightarrow I_2$ $\qquad$ $ClO_3^- + 3H_2SO_4 \rightarrow Cl^- + 3HSO_4^- + 3H_2O$

Steps 4 and 5 : $2I^- \rightarrow I_2 + 2e^-$

$[ClO_3^- + 3H_2SO_4 + e^- \rightarrow Cl^- + 3HSO_4^- + 3H_2O] \times 2$

Step 6 : $2I^- + 2ClO_3^- + 6H_2SO_4 \rightarrow I_2 + 2Cl^- + 6HSO_4^- + 6H_2O$

(iv) $Ag^+ + AsH_3 \rightarrow H_3AsO_3 + H^+ + Ag$

Steps 1 and 2 : $AsH_3 \xrightarrow{\text{oxidation}} H_3AsO_3$ $\qquad$ $Ag^+ \xrightarrow{\text{reduction}} Ag$

Step 3 : $AsH_3 + 3H_2O \rightarrow H_3AsO_3 + 6H^+$ $\qquad$ $Ag^+ \rightarrow Ag$

Steps 4 and 5 : $AsH_3 + 3H_2O \rightarrow H_3AsO_3 + 6H^+ + 6e^-$

$[Ag^+ + e^- \rightarrow Ag] \times 6$

Step 6 : $AsH_3 + 6Ag^+ + 3H_2O \rightarrow H_3AsO_3 + 6Ag + 6H^+$

4. Balance the following equations.

(i) $As_2S_3 + OH^- + H_2O_2 \rightarrow AsO_4^{3-} + SO_4^{2-} + H_2O$

(ii) $CrI_3 + H_2O_2 + OH^- \rightarrow CrO_4^{2-} + 3IO_4^- + H_2O$

(iii) $P_4 + OH^- + H_2O_2 \rightarrow H_2PO_2^- + PH_3$

(iv) $As_2S_3 + NO_3^- + H^+ + H_2O \rightarrow H_3AsO_4 + NO + S$

Solution

We may arrive at the balanced equations as shown in the following.

(i) $As_2S_3 + OH^- + H_2O_2 \rightarrow AsO_4^{3-} + SO_4^{2-} + H_2O$

Steps 1 and 2 : $As_2S_3 \xrightarrow{\text{oxidation}} 2AsO_4^{3-} + 3SO_4^{2-}$ $\qquad$ $H_2O_2 \xrightarrow{\text{reduction}} 2OH^-$

Step 3 : $As_2S_3 + 40OH^- \rightarrow 2AsO_4^{3-} + 3SO_4^{2-} + 20H_2O$ $\qquad$ $H_2O_2 \rightarrow 2OH^-$

Steps 4 and 5 : $As_2S_3 + 40OH^- \rightarrow 2AsO_4^{3-} + 3SO_4^{2-} + 20H_2O + 28e^-$

$[H_2O_2 + 2e^- \rightarrow 2OH^-] \times 14$

Step 6 : $As_2S_3 + 12OH^- + 14H_2O_2 \rightarrow 2AsO_4^{3-} + 3SO_4^{2-} + 20H_2O$

(ii) $CrI_3 + H_2O_2 + OH^- \rightarrow CrO_4^{2-} + 3IO_4^- + H_2O$

Steps 1 and 2 : $CrI_3 \xrightarrow{\text{oxidation}} CrO_4^{2-} + 3IO_4^-$ $\qquad$ $H_2O_2 \xrightarrow{\text{reduction}} 2OH^-$

Step 3 : $CrI_3 + 32OH^- \rightarrow CrO_4^{2-} + 3IO_4^- + 16H_2O$ $\qquad$ $H_2O_2 \rightarrow 2OH^-$

Steps 4 and 5 : $[CrI_3 + 32OH^- \rightarrow CrO_4^{2-} + 3IO_4^- + 16H_2O + 27e^-] \times 2$

$[H_2O_2 + 2e^- \rightarrow 2OH^-] \times 27$

Step 6 : $2CrI_3 + 10OH^- + 27H_2O_2 \rightarrow 2CrO_4^{2-} + 6IO_4^- + 32H_2O$

(iii) $P_4 + OH^- + H_2O_2 \rightarrow H_2PO_2^- + PH_3$

Steps 1 and 2 : $\frac{1}{4}P_4 \xrightarrow{\text{oxidation}} H_2PO_2^-$ $\qquad$ $\frac{1}{4}P_4 \xrightarrow{\text{reduction}} PH_3$

Step 3 : $\frac{1}{4}P_4 + 2OH^- \rightarrow H_2PO_2^-$ $\qquad$ $\frac{1}{4}P_4 + 3H_2O \rightarrow PH_3 + 3OH^-$

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Steps 4 and 5 : $[\frac{1}{4}P_4 + 2OH^- \rightarrow H_2PO_2^- + e^-] \times 3$

$\frac{1}{4}P_4 + 3H_2O + 3e^- \rightarrow PH_3 + 3OH^-$

Step 6 : $P_4 + 3OH^- + 3H_2O \rightarrow 3H_2PO_2^- + PH_3$

(iv) $As_2S_3 + NO_3^- + H^+ + H_2O \rightarrow H_3AsO_4 + NO + S$

Steps 1 and 2 : $As_2S_3 \xrightarrow{\text{oxidation}} 2H_3AsO_4 + 3S$ $\qquad$ $NO_3^- \xrightarrow{\text{reduction}} NO$

Step 3 : $As_2S_3 + 8H_2O \rightarrow 2H_3AsO_4 + 3S + 10H^+$ $\qquad$ $NO_3^- + 4H^+ \rightarrow NO + 2H_2O$

Steps 4 and 5 : $[As_2S_3 + 8H_2O \rightarrow 2H_3AsO_4 + 3S + 10H^+ + 10e^-] \times 3$

$[NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O] \times 10$

Step 6 : $3As_2S_3 + 4H_2O + 10NO_3^- + 10H^+ \rightarrow 6H_3AsO_4 + 9S + 10NO$

5. Balance the following equations.

(i) $O_2 + Cr \xrightarrow{\text{alkaline medium}} Cr(OH)_4^-$ $\qquad$ (ii) $MnO_4^{2-} + H^+ \rightarrow MnO_2 + MnO_4^-$

(iii) $Ag_2O + AsH_3 \xrightarrow{\text{alkaline medium}} Ag + H_2AsO_3^-$ $\qquad$ (iv) $IO_3^- + Cl^- \rightarrow I_2 + Cl_2$

Solution

(i) $O_2 + Cr \xrightarrow{\text{alkaline medium}} Cr(OH)_4^-$

Steps 1 and 2 : $Cr \xrightarrow{\text{oxidation}} Cr(OH)_4^-$ $\qquad$ $2O_2 \xrightarrow{\text{reduction}} Cr(OH)_4^-$

Step 3 : $Cr + 4OH^- \rightarrow Cr(OH)_4^-$ $\qquad$ $2O_2 + Cr + 4H_2O \rightarrow Cr(OH)_4^- + 4OH^-$

Steps 4 and 5 : $[Cr + 4OH^- \rightarrow Cr(OH)_4^- + 3e^-] \times 5$

$[2O_2 + Cr + 4H_2O + 5e^- \rightarrow Cr(OH)_4^- + 4OH^-] \times 3$

Step 6 : $8Cr + 6O_2 + 8OH^- + 12H_2O \rightarrow 8Cr(OH)_4^-$ $\qquad$ or $4Cr + 3O_2 + 4OH^- + 6H_2O \rightarrow 4Cr(OH)_4^-$

(ii) $MnO_4^{2-} + H^+ \rightarrow MnO_2 + MnO_4^-$

Steps 1 and 2 : $MnO_4^{2-} \xrightarrow{\text{oxidation}} MnO_4^-$ $\qquad$ $MnO_4^{2-} \xrightarrow{\text{reduction}} MnO_2$

Step 3 : $MnO_4^{2-} \rightarrow MnO_4^-$ $\qquad$ $MnO_4^{2-} + 4H^+ \rightarrow MnO_2 + 2H_2O$

Steps 4 and 5 : $[MnO_4^{2-} \rightarrow MnO_4^- + e^-] \times 2$

$MnO_4^{2-} + 4H^+ + 2e^- \rightarrow MnO_2 + 2H_2O$

Step 6 : $3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$

(iii) $Ag_2O + AsH_3 \xrightarrow{\text{alkaline medium}} Ag + H_2AsO_3^-$

Steps 1 and 2 : $AsH_3 \xrightarrow{\text{oxidation}} H_2AsO_3^-$ $\qquad$ $Ag_2O \xrightarrow{\text{reduction}} 2Ag$

Step 3 : $AsH_3 + 7OH^- \rightarrow H_2AsO_3^- + 4H_2O$ $\qquad$ $Ag_2O + H_2O \rightarrow 2Ag + 2OH^-$

Steps 4 and 5 : $AsH_3 + 7OH^- \rightarrow H_2AsO_3^- + 4H_2O + 6e^-$

Step 6 : $[Ag_2O + H_2O + 2e^- \rightarrow 2Ag + 2OH^-] \times 3$

$AsH_3 + 3Ag_2O + OH^- \rightarrow H_2AsO_3^- + 6Ag + H_2O$

(iv) $IO_3^- + Cl^- \rightarrow I_2 + Cl_2$

Steps 1 and 2 : $2Cl^- \xrightarrow{\text{oxidation}} Cl_2$ $\qquad$ $2IO_3^- \xrightarrow{\text{reduction}} I_2$

Step 3 : $2Cl^- \rightarrow Cl_2$ $\qquad$ $2IO_3^- + 12H^+ \rightarrow I_2 + 6H_2O$

Steps 4 and 5 : $[2Cl^- \rightarrow Cl_2 + 2e^-] \times 5$

$2IO_3^- + 12H^+ + 10e^- \rightarrow I_2 + 6H_2O$

Step 6 : $10Cl^- + 2IO_3^- + 12H^+ \rightarrow 5Cl_2 + I_2 + 6H_2O$

6. Arrange the following in order of increasing oxidation number of

(i) Iodine : I_2, HI, HIO_4, ICl $\qquad$ (ii) Manganese : $MnCl_2$, MnO_2, $KMnO_4$

(iii) Nickel : $K_2[Ni(CN)_4]$, $K_2[NiF_6]$, $Ni(CO)_4$ $\qquad$ (iv) Sulphur : S_8, $S_2O_8^{2-}$, $S_2O_3^{2-}$, $S_4O_6^{2-}$.

(i) The oxidation numbers of iodine are shown below alongwith the compounds.

$\overset{0}{I_2}, H\overset{-1}{I}, H\overset{+7}{I}O_4, \overset{+1}{I}Cl$

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Hence, the increasing order of oxidation number of iodine in the compounds is
$HI < I_2 < ICl < HIO_4$

(ii) The oxidation numbers of Mn are shown below alongwith the compounds.

$\overset{+2}{Mn}Cl_2, \overset{+4}{Mn}O_2, K\overset{+7}{Mn}O_4$

Hence, the order is $MnCl_2 < MnO_2 < KMnO_4$

(iii) The oxidation numbers of Ni are shown below alongwith the compounds.

$K_2[\overset{+2}{Ni}(CN)_4], K_2[\overset{+4}{Ni}F_6], \overset{0}{Ni}(CO)_4$

Hence, the order is $Ni(CO)_4 < K_2[Ni(CN)_4] < K_2[NiF_6]$

(iv) The oxidation numbers of S are shown below alongwith the compounds.

$\overset{0}{S_8}, \overset{+7}{S_2}O_8^{2-}, \overset{+2}{S_2}O_3^{2-}, \overset{+2.5}{S_4}O_6^{2-}$

Hence, the order is $S_8 < S_2O_3^{2-} < S_4O_6^{2-} < S_2O_8^{2-}$

Unbalanced Chemical Equations

Complete and balance the following equations adding H^+, OH^- or H_2O as required.

(a) $CrO_4^{2-} + Cu_2O \rightarrow Cr(OH)_4^- + Cu(OH)_2$

(b) $Cu_3P + Cr_2O_7^{2-} \rightarrow Cu^{2+} + H_3PO_4 + Cr^{3+}$

(c) $Fe^{2+} + UO_2^{2+} \rightarrow Fe^{3+} + U^{4+}$

(d) $Cu_2O + NO_3^- \rightarrow Cu^{2+} + NO$

(e) $P_4 + HNO_3 \rightarrow H_3PO_4 + NO_2$

(f) $Pb_3O_4 + H_2SO_4 \rightarrow PbSO_4 + O_2$

(g) $IO_3^- + I^- \rightarrow I_2$

(h) $HNO_3 + I_2 \rightarrow NO_2 + HIO_3$

(i) $P_4O_{11} + HNO_2 \rightarrow HPO_3 + N_2O_5$

(j) $IO_3^- + H_3AsO_3 + Cl^- \rightarrow ICl_2^- + H_3AsO_4$

(k) $Cr^{3+} + MnO_4^- \rightarrow Cr_2O_7^{2-} + Mn^{2+}$

(l) $Mg + HNO_3 \rightarrow Mg(NO_3)_2 + NH_4NO_3$

(m) $SnS_2 + NaOH \rightarrow Na_2SnS_3 + Na_2SnO_3$

(n) $Cr(OH)_4^- + HO_2^- \rightarrow CrO_4^{2-} + OH^- + H_2O$

(o) $Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO$

(p) $Ag + O_2 + CN^- \rightarrow Ag(CN)_2^- + OH^-$

(q) $Zn + NaNO_3 + NaOH \rightarrow NH_3 + Na_2ZnO_2$

(r) $Au + HNO_3 + HCl \rightarrow HAuCl_4 + NO$

(s) $BrO_3^- + Br^- \rightarrow Br_2$

(t) $MnO_4^- + As_2O_3 \rightarrow Mn^{2+} + H_3AsO_4$

(u) $Cu + HNO_3 \rightarrow Cu^{2+} + NO_2 + NO_3^-$

(v) $S + OH^- \rightarrow S^{2-} + S_2O_3^{2-}$

(w) $I_2 + OH^- \rightarrow I^- + IO_3^-$

(x) $P_4 + OH^- \rightarrow H_2PO_4^- + PH_3$

(y) $KClO_3 + H_2SO_4 \rightarrow HClO_4 + KHSO_4 + ClO_2$

(z) $I^- + ClO_3^- + H_2SO_4 \rightarrow Cl^- + HSO_4^- + I_2$

ANSWERS

(a) $2CrO_4^{2-} + 3Cu_2O + 2H^+ + 9H_2O \rightarrow 2Cr(OH)_4^- + 6Cu(OH)_2$

(b) $6Cu_3P + 11Cr_2O_7^{2-} + 124H^+ \rightarrow 18Cu^{2+} + 6H_3PO_4 + 22Cr^{3+} + 53H_2O$

(c) $2Fe^{2+} + UO_2^{2+} + 4H^+ \rightarrow 2Fe^{3+} + U^{4+} + 2H_2O$

(d) $3Cu_2O + 2NO_3^- + 14H^+ \rightarrow 6Cu^{2+} + 2NO + 7H_2O$

(e) $P_4 + 20HNO_3 \rightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$

(f) $2Pb_3O_4 + 6H_2SO_4 \rightarrow 6PbSO_4 + 6H_2O + O_2$

(g) $IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$

(h) $10HNO_3 + I_2 \rightarrow 10NO_2 + 2HIO_3 + 4H_2O$

(i) $2P_4O_{11} + 2HNO_2 + 3H_2O \rightarrow 8HPO_3 + N_2O_5$

(j) $IO_3^- + 2Cl^- + 2H^+ + 2H_3AsO_3 \rightarrow ICl_2 + 2H_3AsO_4 + H_2O$

(k) $10Cr^{3+} + 6MnO_4^- + 22OH^- \rightarrow 5Cr_2O_7^{2-} + 11H_2O + 6Mn^{2+}$

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(l) $4Mg + 10HNO_3 \rightarrow 4Mg(NO_3)_2 + NH_4NO_3 + 3H_2O$

(m) $3SnS_2 + 6NaOH \rightarrow 2Na_2SnS_3 + Na_2SnO_3 + 3H_2O$

(n) $2Cr(OH)_4^- + 3HO_2^- \rightarrow 2CrO_4^{2-} + OH^- + 5H_2O$

(o) $3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

(p) $4Ag + O_2 + 8CN^- + 2H_2O \rightarrow 4[Ag(CN)_2]^- + 4OH^-$

(q) $4Zn + NaNO_3 + 7NaOH \rightarrow NH_3 + 4Na_2ZnO_2 + 2H_2O$

(r) $2Au + 2HNO_3 + 8HCl \rightarrow 2HAuCl_4 + 2NO + 4H_2O$

(s) $BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$

(t) $4MnO_4^- + 5As_2O_3 + 12H^+ + 9H_2O \rightarrow 4Mn^{2+} + 10H_3AsO_4$

(u) $Cu + 4HNO_3 \rightarrow Cu^{2+} + 2NO_3^- + 2NO_2 + 2H_2O$

(v) $4S + 6OH^- \rightarrow 2S^{2-} + S_2O_3^{2-} + 3H_2O$

(w) $6I_2 + 12OH^- \rightarrow 10\,I^- + 2IO_3^- + 6H_2O$

(x) $2P_4 + 3OH^- + 9\,H_2O \rightarrow 3H_2PO_4^- + 5PH_3$

(y) $3\,KClO_3 + 3H_2SO_4 \rightarrow HClO_4 + 3KHSO_4 + H_2O + 2ClO_2$

(z) $6I^- + ClO_3^- + 6\,H_2SO_4 \rightarrow Cl^- + 6\,HSO_4^- + 3I_2 + 3H_2O$

Solved Problems

1. A 1.0 g sample of H_2O_2 solution containing X% H_2O_2 by mass requires X cm^3 of a $KMnO_4$ solution for complete oxidation under acidic conditions. Calculate the normality of $KMnO_4$ solution. (1981)

Solution The equations involved are

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O] \times 2$$
$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-] \times 5$$
$$2\,MnO_4^- + 5H_2O_2 + 6\,H^+ \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O$$

From this equation, we find that

$$\text{Equivalent mass of } H_2O_2, \quad M_{eq} = \frac{\text{Molar mass of } H_2O_2}{2\text{ eq mol}^{-1}} = \frac{34\text{ g mol}^{-1}}{2\text{ eq mol}^{-1}} = 17\text{ g eq}^{-1}$$

$$\text{Mass of } H_2O_2 \text{ in the given 1.0 g sample}, \quad m_{eq} = \frac{X}{100} \times 1.0\text{ g}$$

Amount (in equivalents) of H_2O_2 in the given 1.0 g sample is

$$n_{eq} = \frac{m}{M_{eq}} = \frac{(X/100)\text{ g}}{17\text{ g eq}^{-1}} = \frac{X}{17 \times 100}\text{ eq} \qquad (1)$$

If N_{KMnO_4} is the normality of $KMnO_4$, the amount (in equivalents) of $KMnO_4$ consumed is

$$n'_{eq} = V_{KMnO_4}\, N_{KMnO_4} = \left(\frac{X}{1000}\text{ L}\right) N_{KMnO_4} \qquad (2)$$

Equating Eqs (1) and (2), we get

$$\left(\frac{X}{1000}\text{ L}\right) N_{KMnO_4} = \frac{X}{17 \times 100}\text{ eq} \qquad \text{or} \qquad N_{KMnO_4} = \frac{10}{17}\text{ eq L}^{-1} = 0.588\text{ eq L}^{-1}$$

2. Hydroxylamine reduces iron(III) according to the equation

$$2NH_2OH + 4Fe^{3+} \rightarrow N_2O(g) + H_2O + 4Fe^{2+} + 4H^+$$

Iron(II) thus produced is estimated by titration with a standard permanganate solution. The reaction is

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

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A 10 mL sample of hydroxylamine solution was diluted to 1 litre. 50 mL of this diluted solution was boiled with excess of iron(III) solution. The resulting solution required 12 mL of 0.02 M $KMnO_4$ solution for complete oxidation of iron(II). Calculate the mass of hydroxylamine in one litre of the original solution. (1982)

Solution From the given chemical equations, we find that

$$2 \text{ mol } NH_2OH \equiv 4 \text{ mol } Fe^{2+} \quad \text{and} \quad 1 \text{ mol } MnO_4^- \equiv 5 \text{ mol } Fe^{2+}$$

Amount of MnO_4^- consumed in the oxidation of iron(II)

$$= VM = (12 \text{ mL})\,(0.02 \text{ M}) = \left(\frac{12}{1000} \text{L}\right)(0.02 \text{ mol L}^{-1}) = \frac{12 \times 0.02}{1000} \text{ mol}$$

Since 1 mol $MnO_4^- \equiv 5$ mol Fe^{2+}, we have

Amount of Fe^{2+} formed by the reduction of Fe^{3+} by $NH_2OH = (5)\left(\frac{12 \times 0.02}{1000}\right)$ mol

Now since 2 mol $NH_2OH \equiv 4$ mol Fe^{2+}, we have

Amount of NH_2OH present in 50 mL of diluted solution $= \left(\frac{2}{4}\right)(5)\left(\frac{12 \times 0.02}{1000}\right)$ mol

Amount of NH_2OH present in 1 L of diluted solution $= \left(\frac{1000}{50}\right)\left(\frac{2}{4}\right)(5)\left(\frac{12 \times 0.02}{1000}\right)$ mol

Amount of NH_2OH present in 1 L of undiluted solution $= \left(\frac{1000}{10}\right)\left(\frac{1000}{50}\right)\left(\frac{2}{4}\right)(5)\left(\frac{12 \times 0.02}{1000}\right)$ mol $= 1.2$ mol

Mass of NH_2OH present in 1 L of undiluted solution $= (1.2 \text{ mol})\,(33 \text{ g mol}^{-1}) = 39.6$ g.

3. A mixture weighing 4.08 g of BaO and unknown carbonate XCO_3 was heated strongly. The residue weighed 3.64 g. This was dissolved in 100 mL of 1 N HCl. The excess acid required 16 mL of 2.5 N NaOH solution for complete neutralization. Identify the metal M. (1983)

Solution On heating, we have $XCO_3 \rightarrow XO + CO_2$

The loss of mass (= 4.08 g –3.64 g = 0.44 g) is due to the removal of CO_2. Thus

$$\text{Amount of } CO_2 \text{ released} = \frac{0.44 \text{ g}}{44 \text{ g mol}^{-1}} = 10^{-2} \text{ mol}$$

Hence, Amount of $XO = 10^{-2}$ mol

Now Mass of BaO in the mixture after heating $= 3.64 \text{ g} - (10^{-2} \text{ mol})\,(M_{XO})$
$= 3.64 \text{ g} - (10^{-2} \text{ mol})\,(M_X + 16 \text{ g mol}^{-1})$
$= 3.48 \text{ g} - (10^{-2} \text{ mol})\,(M_X)$

From the dissolution reactions $BaO + 2HCl \rightarrow BaCl_2 + H_2O$ and $XO + 2HCl \rightarrow XCl_2 + H_2O$ we conclude that

$$\text{Amount of HCl consumed for the dissolution process} = 2\left[\frac{3.48 \text{ g} - (10^{-2} \text{ mol})\,M_X}{M_{BaO}} + 10^{-2} \text{ mol}\right]$$

Amount of HCl taken for the dissolution process $= (100 \text{ mL})\,(0.1 \text{ M}) = \left(\frac{100}{1000} \text{L}\right)(1 \text{ mol L}^{-1}) = 0.1$ mol

$$\text{Amount of remaining HCl} = 0.1 \text{ mol} - 2\left[\frac{3.48 \text{ g} - (10^{-2} \text{ mol})\,M_X}{154 \text{ g mol}^{-1}} + 10^{-2} \text{ mol}\right]$$

Since the remaining HCl required 16 mL of 2.5 M NaOH $\left(= \frac{16}{1000} \times 2.5 \text{ mol}\right)$ for complete neutralization, we would have

$$\frac{16 \times 2.5}{1000} \text{ mol} = 0.1 \text{ mol} - 2\left[\frac{3.48 \text{ g} - (10^{-2} \text{ mol})\,M_X}{154 \text{ g mol}^{-1}} + 10^{-2} \text{ mol}\right]$$

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This gives $$M_X = \frac{\left(\frac{16\times 2.5}{1000} - 0.1 + 2\times 10^{-2}\right)\left(\frac{154}{2}\right)\text{g} + 3.48\,\text{g}}{\left(10^{-2}\ \text{mol}\right)} = 40\ \text{g mol}^{-1}$$

Hence, the element X is Ca.

4. A solution containing 2.68×10^{-3} mol of A^{n+} ions requires 1.61×10^{-3} mol of MnO_4^- for the oxidation of A^{n+} to AO_3^- in acidic medium. What is the value of n? (1984)

Solution From the chemical equations

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \quad \text{and} \quad A^{n+} + 3H_2O \rightarrow AO_3^- + 6H^+ + (5 - n)e^-$$

we write

Amount of electrons involved in reducing the given amount of $MnO_4^- = 5 \times 1.61 \times 10^{-3}$ mol

Amount of electrons involved in oxidizing the given amount of $A^{n+} = (5 - n) \times 2.68 \times 10^{-3}$ mol

Equating these two, we get

$$5 \times 1.61 \times 10^{-3}\ \text{mol} = (5 - n) \times 2.68 \times 10^{-3}\ \text{mol}$$

Hence, $$n = \frac{5(2.68 - 1.61)}{2.68} = \frac{5\times 1.07}{2.68} \simeq 2.$$

5. Five mL of 8 N nitric acid, 4.8 mL of 5 N hydrochloric acid and a certain volume of 17 M sulphuric acid are mixed together and made up to 2 L. Thirty mL of this acid solution exactly neutralizes 42.9 mL of sodium carbonate solution containing 1 g of $Na_2CO_3 \cdot 10\ H_2O$ in 100 mL of water. Calculate the mass of SO_4 units in the solution. (1985)

Solution Let V be the volume of sulphuric acid taken while mixing the given acids. We will have

Amount of H^+ in 2 L of acids solution

$$= (5\ \text{mL})\ (8\ \text{M}) + (4.8\ \text{mL})\ (5\ \text{M}) + (V)\ (2 \times 17\ \text{M})$$

$$= \left(\frac{5}{1000}\text{L}\right)\ (8\ \text{mol L}^{-1}) + \left(\frac{4.8}{1000}\text{L}\right)\ (5\ \text{mol L}^{-1}) + (V)\ (2 \times 17\ \text{mol L}^{-1})$$

$$= \left(\frac{1}{1000}\right)\left[5\times 8 + 4.8\times 5 + \left(\frac{V}{\text{mL}}\right)(2\times 17)\right]\ \text{mol} = \left(\frac{1}{1000}\right)\left[64 + 34\left(\frac{V}{\text{mL}}\right)\right]\ \text{mol}$$

Amount of H^+ in 30 mL of acids solution $= \left(\frac{30}{2000}\right)\left(\frac{1}{1000}\right)\left[64 + 34\left(\frac{V}{\text{mL}}\right)\right]$ mol (1)

Mass of sodium carbonate neutralized by 30 mL of acids solution $= \left(\frac{1\,\text{g}}{100\,\text{mL}}\right)\ (42.9\ \text{mL}) = \frac{42.9}{100}\ \text{g}$

Amount of sodium carbonate neutralized $= \frac{(42.9/100)\,\text{g}}{286\,\text{g mol}^{-1}} = \frac{42.9}{100\times 286}$ mol (2)

From the chemical equation $CO_3^{2-} + 2H^+ \rightarrow CO_2 + H_2O$ we find that 1 mol $CO_3^{2-} \equiv 2$ mol H^+

Hence, from Eqs. (1) and (2), we write

$$2\left(\frac{42.9}{100\times 286}\right) = \left(\frac{30}{2000}\right)\left(\frac{1}{1000}\right)\left[64 + 34\left(\frac{V}{\text{mL}}\right)\right]$$

which gives $$\frac{V}{\text{mL}} = \frac{1}{34}\left[2\left(\frac{42.9}{100\times 286}\right)\left(\frac{2000}{30}\right)\left(\frac{1000}{1}\right) - 64\right] = 4 \quad \text{i.e.,} \quad V = 4\ \text{mL}$$

Finally,

Mass of SO_4 unit in 4 mL of 17 M H_2SO_4 solution

$$= (4\ \text{mL})\ (17\ \text{mol L}^{-1})\ (96\ \text{g mol}^{-1}) = \left(\frac{4}{1000}\right)\ (17)\ (96)\ \text{g} = 6.528\ \text{g}.$$

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$$\text{Molarity of } NaHC_2O_4 = \frac{(2.02\text{ g} - x)/112\text{ g mol}^{-1}}{1\text{ L}} = \frac{(2.02\text{ g} - x)}{(112\text{ g})}\text{ mol L}^{-1}$$

$$\text{Amount of oxalic acid in 10 mL solution} = VM = \left(\frac{10}{1000}\text{ L}\right)\left(\frac{x}{90\text{ g}}\text{ mol L}^{-1}\right) = \left(\frac{10}{1000}\right)\left(\frac{x}{90\text{ g}}\right)\text{ mol}$$

$$\text{Amount of } NaHC_2O_4 \text{ in 10 mL solution} = \left(\frac{10}{1000}\right)\left(\frac{2.02\text{ g} - x}{112\text{ g}}\right)\text{ mol}$$

Now from the neutralization reactions

$$H_2C_2O_4 + 2NaOH \rightarrow Na_2C_2O_4 + 2H_2O \quad \text{and} \quad NaHC_2O_4 + NaOH \rightarrow Na_2C_2O_4 + H_2O$$

we find that 1 mol $H_2C_2O_4 \equiv$ 2 mol NaOH and 1 mol $NaHC_2O_4 \equiv$ 1 mol NaOH

Hence,

$$\text{Amount of NaOH equivalent to } H_2C_2O_4 = 2\left(\frac{10}{1000}\right)\left(\frac{x}{90\text{ g}}\right)\text{ mol}$$

$$\text{Amount of NaOH equivalent to } NaHC_2O_4 = \left(\frac{10}{1000}\right)\left(\frac{2.02\text{ g} - x}{112\text{ g}}\right)\text{ mol}$$

Total amount of NaOH equivalent to 10 mL solution containing $H_2C_2O_4$ and $NaHC_2O_4$

$$= \left[2\left(\frac{10}{1000}\right)\left(\frac{x}{90\text{ g}}\right) + \left(\frac{10}{1000}\right)\left(\frac{2.02\text{ g} - x}{112\text{ g}}\right)\right]\text{ mol}$$

This amount will be equal to the amount of NaOH present in 3.0 mL of 0.1 N NaOH solution. Hence,

$$2\left(\frac{10}{1000}\right)\left(\frac{x}{90\text{ g}}\right) + \left(\frac{10}{1000}\right)\left(\frac{2.02\text{ g} - x}{112\text{ g}}\right) = \left(\frac{3.0}{1000}\right) \quad (0.1)$$

Solving for x, we get $x = 0.9$ g

Hence, in the original mixture, we have

Mass of oxalic acid = 0.9 g and Mass of $NaHC_2O_4$ = 2.02 g − 0.9 g = 1.12 g.

9. A solid mixture (5.0 g) consisting of lead nitrate and sodium nitrate was heated below 600 °C until the mass of the residue was constant. If the loss in mass is 28.0 per cent, find the masses of lead nitrate and sodium nitrate in the mixture. (1990)

Solution Let x be the mass of lead nitrate in the mixture. Heating the mixture results into the following reactions.

$$2Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2$$

$$2NaNO_3 \rightarrow 2NaNO_2 + O_2$$

Hence, $$\text{Mass of PbO obtained} = \frac{2M_{PbO}}{2M_{Pb(NO_3)_2}} \times x = \frac{223}{331}\ x$$

$$\text{Mass of } NaNO_2 \text{ obtained} = \frac{2M_{NaNO_2}}{2M_{NaNO_3}}\ (5.0\text{ g} - x) = \left(\frac{69}{85}\right)\ (5.0\text{ g} - x)$$

$$\text{Total mass of residue} = \frac{223}{331}\ x + \frac{69}{85}\ (5.0\text{ g} - x)$$

Since there occurs 28 per cent loss in mass, we would have

$$\frac{223}{331}\ x + \frac{69}{85}\ (5.0\text{ g} - x) = \frac{100 - 28}{100} \times 5.0\text{ g}$$

Solving for x, we get $x = 3.32$ g

Hence, Mass of lead nitrate = 3.32 g and Mass of sodium nitrate = (5.0 − 3.32) g = 1.68 g.

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10. A solution of 0.2 g of a compound containing Cu^{2+} and $C_2O_4^{2-}$ ions on titration with 0.02 M $KMnO_4$ in presence of H_2SO_4 consumes 22.6 mL of the oxidant. The resultant solution is neutralized with Na_2CO_3, acidified with dilute acetic acid and treated with excess KI. The liberated iodine requires 11.3 mL of 0.05 M $Na_2S_2O_3$ solution for complete reduction. Find out the mole ratio of Cu^{2+} to $C_2O_4^{2-}$ in the compound. Write down the balanced redox reactions involved in the above titration. (1991)

Solution The chemical equations involved in the titration of $C_2O_4^{2-}$ with MnO_4^- are :

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O] \times 2$$
$$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-] \times 5$$
$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

From this equation, we conclude 2 mol $MnO_4^- \equiv$ 5 mol $C_2O_4^{2-}$. Hence,

$$\text{Amount of } C_2O_4^{2-} \text{ in the solution} = \left(\frac{5}{2}\right)(22.6 \text{ mL})(0.02 \text{ M}) = \left(\frac{5}{2}\right)\left(\frac{22.6}{1000} \text{ L}\right)(0.02 \text{ mol L}^{-1}) = 0.00113 \text{ mol}$$

The chemical equations involved during the treatment of KI and the titration with $Na_2S_2O_3$ are

$$2Cu^{2+} + 4I^- \rightarrow Cu_2I_2 + I_2 \quad \text{and} \quad I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

From these equations, we conclude

$$2 \text{ mol } Cu^{2+} \equiv 4 \text{ mol } I^- \equiv 1 \text{ mol } I_2 \quad \text{and} \quad 1 \text{ mol } I_2 \equiv 2 \text{ mol } S_2O_3^{2-}$$

Now, $$\text{Amount of } S_2O_3^{2-} \text{ consumed} = (11.3 \text{ mL})(0.05 \text{ M}) = \left(\frac{11.3}{1000} \text{ L}\right)(0.05 \text{ mol L}^{-1})$$

$$= \left(\frac{11.3}{1000}\right)(0.05) \text{ mol} = 0.000565 \text{ mol}$$

Amount of Cu^{2+} equivalent to the above amount of $S_2O_3^{2-}$ = 0.000 565 mol

Hence, $$\frac{\text{Amount of } Cu^{2+}}{\text{Amount of } C_2O_4^{2-}} = \frac{0.000565}{0.00113} = \frac{1}{2}$$

11. A 1.0 g sample of Fe_2O_3 solid of 55.2% purity is dissolved in acid and reduced by heating the solution with zinc dust. The resultant solution is cooled and made up to 100.0 mL. An aliquot of 25.0 mL of this solution requires 17.0 mL of 0.0167 M solution of an oxidant for titration. Calculate the number of electrons taken up by the oxidant in the reaction of the above titration. (1991)

Solution We have

$$\text{Mass of } Fe_2O_3 \text{ in the sample} = (1.0 \text{ g})\left(\frac{55.2}{100}\right) = 0.552 \text{ g}; \qquad \text{Molar mass of } Fe_2O_3 = 159.8 \text{ g mol}^{-1}$$

$$\text{Amount of } Fe_2O_3 = \frac{0.552 \text{ g}}{159.8 \text{ g mol}^{-1}} = 3.454 \times 10^{-3} \text{ mol}; \qquad \text{Amount of } Fe^{3+} \text{ ions} = 2 \times 3.454 \times 10^{-3} \text{ mol}$$

On reduction, we have

$$\text{Amount of } Fe^{2+} \text{ ions} = 2 \times 3.454 \times 10^{-3} \text{ mol}$$

$$\text{Molarity of } Fe^{2+} \text{ ions} = \frac{2 \times 3.454 \times 10^{-3} \text{ mol}}{100 \times 10^{-3} \text{ L}} = 6.908 \times 10^{-2} \text{ mol L}^{-1}$$

If z is the number of electrons taken by the oxidant, we will have

$$(25.0 \text{ mL})(6.908 \times 10^{-2} \text{ mol L}^{-1})(1 \text{ eq mol}^{-1}) = (17.0 \text{ mL})(0.0167 \text{ mol L}^{-1})(z \text{ eq mol}^{-1})$$

which gives $$z = \frac{25.0 \times 6.908 \times 10^{-2}}{17 \times 0.0167} = 6.$$

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12. One gram of commercial $AgNO_3$ is dissolved in 50 mL of water. It is treated with 50 mL of a KI solution. Th silver iodide thus precipitated is filtered off. Excess of KI in the filtrate is titrated with M/10 KIO_3 solution in presen of 6 M HCl till all I^- ions are converted into ICl. It requires 50 mL of M/10 KIO_3 solution. Twenty milliliters of the san stock solution of KI requires 30 mL of M/10 KIO_3 under similar conditions. Calculate the percentage of $AgNO_3$ in th sample. (Reaction: $KIO_3 + 2KI + 6HCl \rightarrow 3ICl + 3KCl + 3H_2O$.) (199

Solution It is given that 20 mL of stock solution of KI requires 30 mL of M/10 KIO_3 solution to convert I^- ions into I according to the reaction

$$KIO_3 + 2KI + 6HCl \rightarrow 3ICl + 3KCl + 3H_2O$$

For 50 mL of KI solution, the required volume of KIO_3 solution would be

$$\frac{30 \text{ mL of } KIO_3 \text{ solution}}{20 \text{ mL of KI solution}} \times 50 \text{ mL of KI solution} = 75 \text{ mL of } KIO_3 \text{ solution}$$

After treating 50 mL of KI solution with 1 g $AgNO_3$ sample, the volume of KIO_3 solution used is 50 mL. This mea KI equivalent to 25 mL of KIO_3 solution is used in precipitating out Ag^+ ions from 50 mL of KI solution.

$$\text{Amount of } KIO_3 \text{ in 25 mL of M/10 } KIO_3 \text{ solution} = (25 \text{ mL}) \left(\frac{1}{10} \text{M}\right) = \left(\frac{25}{1000} \text{L}\right)\left(\frac{1}{10} \text{ mol L}^{-1}\right) = 0.002\,5 \text{ m}$$

$$\text{Amount of KI equivalent to this amount} = 2 \times 0.0025 \text{ mol}$$

$$\text{Mass of } AgNO_3 \text{ precipitated out} = 2 \times 0.0025 \times 170 \text{ g} = 0.85 \text{ g}$$

$$\text{Per cent of } AgNO_3 \text{ in the sample} = \frac{0.85 \text{ g}}{1.0 \text{ g}} \times 100 = 85.$$

13. A 2.0 g sample of a mixture containing sodium carbonate, sodium bicarbonate and sodium sulphate is heate 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 m A 1.5 g of the sample requires 150 mL of M/10 HCl for complete neutralization. Calculate the percentage compositi of the components of the mixture. (199

Solution The evolution of CO_2 on heating the mixture is due to the reaction $2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$

From the liberated volume of CO_2, we calculate

$$\text{Amount of liberated } CO_2 = \frac{pV}{RT} = \frac{\{(750/760) \text{ atm}\}\,(0.1239 \text{ L})}{(0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1})\,(298 \text{ K})} = 0.005 \text{ mol.}$$

From the chemical equation given above, we conclude that

$$\text{Amount of } NaHCO_3 \text{ present in 2.0 g sample of the mixture} = 2 \times 0.005 \text{ mol} = 0.01 \text{ mol}$$

$$\text{Mass of } NaHCO_3 \text{ present in the mixture} = (0.01 \text{ mol})\,(84 \text{ g mol}^{-1}) = 0.84 \text{ g}$$

The treatment of the mixture with HCl solution would cause the following neutralization reactions.

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O \quad \text{and} \quad NaHCO_3 + HCl \rightarrow NaCl + CO_2 + H_2O$$

Now, 1.5 g of the sample required 150 mL of M/10 HCl. For 2.0 g of the sample, volume of HCl required would be 2 mL. Hence,

$$\text{Amount of HCl in 200 mL of M/10 HCl} = (200 \text{ mL})(0.1 \text{ mol L}^{-1}) = \left(\frac{200}{1000} \text{L}\right)(0.1 \text{ mol L}^{-1}) = 0.02 \text{ m}$$

Since the mixture contains 0.01 mol of $NaHCO_3$, 0.01 mol out of 0.02 mol would be consumed for the neutralizati of $NaHCO_3$. The remaining 0.01 mol will used for the neutralization of Na_2CO_3. From the chemical equation giv above, we conclude that

$$\text{Amount of } Na_2CO_3 \text{ present in the 2.0 g sample of the mixture} = \left(\frac{0.01 \text{ mol}}{2}\right) = 0.005 \text{ mol}$$

$$\text{Mass of } Na_2CO_3 \text{ present in 2.0 g sample of the mixture} = (0.005 \text{ mol})\,(106 \text{ g mol}^{-1}) = 0.53 \text{ g}$$

Hence, $\text{Mass per cent of } Na_2CO_3 = \left(\frac{0.53 \text{ g}}{2.0 \text{ g}} \times 100\right) = 26.5$; $\text{Mass per cent of } NaHCO_3 = \left(\frac{0.84 \text{ g}}{2.0 \text{ g}} \times 100\right) = 42$

$$\text{Mass per cent of } Na_2SO_4 = 100 - (26.5 + 42.0) = 31.5.$$

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14. 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. What amount of lead sulphate is formed? Also, calculate the molar concentrations of the species left behind in the final solution. Assume that lead sulphate is completely insoluble. (1993)

Solution To start with, we have

$$\text{Amount of } Pb(NO_3)_2 = MV = (0.25 \text{ mol } L^{-1})(45 \times 10^{-3} \text{ L}) = 11.25 \times 10^{-3} \text{ mol}$$

$$\text{Amount of } Cr_2(SO_4)_3 = (0.1 \text{ mol } L^{-1})(25 \times 10^{-3} \text{ L}) = 2.5 \times 10^{-3} \text{ mol}$$

The reaction occurring is

	$3Pb(NO_3)_2$	+	$Cr_2(SO_4)_3$	$\rightarrow$	$3PbSO_4 \downarrow$	+	$2Cr(NO_3)_3$
$t = 0$	11.25×10^{-3} mol		2.5×10^{-3} mol		0		0

In the above reaction, $Cr_2(SO_4)_3$ has the limiting concentration. Hence, it will be consumed completely.

Thus, $$\text{Amount of } Pb(NO_3)_2 \text{ left} = 11.25 \times 10^{-3} \text{ mol} - 3 \times 2.5 \times 10^{-3} \text{ mol} = 3.75 \times 10^{-3} \text{ mol}$$

$$\text{Amount of } PbSO_4 \text{ precipitated} = 3 \times 2.5 \times 10^{-3} \text{ mol} = 7.5 \times 10^{-3} \text{ mol}$$

$$\text{Amount of } Cr(NO_3)_3 \text{ formed} = 2 \times 2.5 \times 10^{-3} \text{ mol} = 5.0 \times 10^{-3} \text{ mol}$$

Now the volume of the system after mixing $Pb(NO_3)_2$ and $Cr_2(SO_4)_3$ solutions becomes 70.0 mL (= 45.0 mL + 25.0 mL). Hence,

$$[Pb(NO_3)_2] = \frac{3.75 \times 10^{-3} \text{ mol}}{70 \times 10^{-3} \text{ L}} = 0.053\,6 \text{ M} \quad \text{and} \quad [Cr(NO_3)_3] = \frac{5.0 \times 10^{-3} \text{ mol}}{70 \times 10^{-3} \text{ L}} = 0.0714 \text{ M}$$

Assuming $Pb(NO_3)_2$ and $Cr(NO_3)_3$ completely dissociated, we will have

$$[Pb^{2+}] = 0.0536 \text{ M}; \quad [Cr^{3+}] = 0.0714 \text{ M}; \quad [NO_3^-] = (2 \times 0.0536 + 3 \times 0.0714) \text{ M} = 0.3214 \text{ M}$$

$$\text{Amount of } PbSO_4 \text{ formed} = 7.5 \times 10^{-3} \text{ mol.}$$

15. A 20.0 cm^3 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 13.0 cm^3. A further contraction of 14.0 cm^3 occurs when the residual gas is treated with KOH solution. Find out the composition of gaseous mixture in terms of volume percentage. (1995)

Solution Let V_1, V_2 and V_3 be the respective partial volumes of CO, CH_4 and He in the given 20.0 cm^3 of the mixture.

Hence, $$V_1 + V_2 + V_3 = 20.0 \text{ cm}^3 \qquad (1)$$

The combustion reactions are $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$ and $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

Hence, $$V_1 \text{ volume CO} \equiv \frac{V_1}{2} \text{ volume } O_2 \equiv V_1 \text{ volume } CO_2$$

$$V_2 \text{ volume } CH_4 \equiv 2V_2 \text{ volume } O_2 \equiv V_2 \text{ volume } CO_2$$

Since there is no volume change due to the replacement of CO into CO_2 and CH_4 into CO_2, the volume change is due to the consumption of O_2. Hence,

$$\frac{V_1}{2} + 2V_2 = 13.0 \text{ cm}^3 \qquad (2)$$

The treatment of residual gases with KOH solution would cause the absorption of $CO_2(g)$. Hence,

$$V_1 + V_2 = 14.0 \text{ cm}^3 \qquad (3)$$

Solving V_1, V_2 and V_3 from Eqs (1) to (3), we get $V_1 = 10.0 \text{ cm}^3$, $V_2 = 4.0 \text{ cm}^3$, and $V_3 = 6.0 \text{ cm}^3$

Hence, $$\text{Volume percentage of CO} = \frac{10.0 \text{ cm}^3}{20.0 \text{ cm}^3} \times 100 = 50; \quad \text{Volume percentage of } CH_4 = \frac{4.0 \text{ cm}^3}{20.0 \text{ cm}^3} \times 100 = 20$$

$$\text{Volume percentage of He} = 100 - (50 + 20) = 30.$$

16. A 20.0 g of mixture Cu_2S and CuS was treated with 400 cm^3 of 0.75 M $KMnO_4$ solution in acidic medium, producing SO_2, Cu^{2+} and Mn^{2+}. The SO_2 was boiled off and the excess MnO_4^- was titrated against 1.0 M Fe^{2+} solution. The volume consumed of the latter was found to be 350 cm^3. Compute the per cent of Cu_2S in the original mixture.

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The chemical equations involved are:

(i) $MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O] \times 8$

$Cu_2S + 2H_2O \rightarrow 2Cu^{2+} + SO_2 + 4H^+ + 8e^-] \times 5$

$$8MnO_4^- + 5Cu_2S + 44H^+ \rightarrow 8Mn^{2+} + 10Cu^{2+} + 5SO_2 + 22H_2O$$

(ii) $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O] \times 6$

$CuS + 2H_2O \rightarrow Cu^{2+} + SO_2 + 4H^+ + 6e^-] \times 5$

$$6MnO_4^- + 5CuS + 28H^+ \rightarrow 6Mn^{2+} + 5Cu^{2+} + 5SO_2 + 14H_2O$$

(iii) $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

$Fe^{2+} \rightarrow Fe^{3+} + e^-] \times 5$

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

From the above equations, we conclude that

$$8 \text{ mol } MnO_4^- \equiv 5 \text{ mol } Cu_2S \; ; \quad 6 \text{ mol } MnO_4^- \equiv 5 \text{ mol } CuS \quad \text{and} \quad 1 \text{ mol } MnO_4^- \equiv 5 \text{ mol } Fe^{2+}$$

Let n_1 and n_2 be the respective amounts of Cu_2S and CuS in 20.0 g mixture. The amount of MnO_4^- used in the oxidation of Cu_2S and CuS will be given as

$$n_3 = \frac{8}{5} n_1 + \frac{6}{5} n_2$$

This amount will also be given as

n_3 = Total amount of MnO_4^- – amount of MnO_4^- used in oxidation of Fe^{2+}

$$= (400 \text{ cm}^3)\,(0.75 \text{ M}) - \frac{1}{5}\,[(350 \text{ cm}^3)\,(1.0 \text{ M})]$$

$$= \left(\frac{400}{1000} \text{dm}^3\right)\,(0.75 \text{ mol dm}^{-3}) - \frac{1}{5}\left[\left(\frac{350}{1000} \text{dm}^3\right)(1.0 \text{ mol dm}^{-3})\right] = 0.230 \text{ mol}$$

Hence, $\frac{8}{5} n_1 + \frac{6}{5} n_2 = 0.230 \text{ mol}$ (1)

Moreover, $n_1 M_1 + n_2 M_2 = 20.0 \text{ g}$ i.e. $n_1(159.2 \text{ g mol}^{-1}) + n_2(95.6 \text{ g mol}^{-1}) = 20.0 \text{ g}$

or $159.2\, n_1 + 95.6\, n_2 = 20.0 \text{ mol}$ (2)

Solving n_1 and n_2 from Eqs (1) and (2), we get

$$n_1 = 0.0529 \text{ mol} \quad \text{and} \quad n_2 = 0.1212 \text{ mol}$$

$$\text{Per cent of } Cu_2S \text{ in the mixture} = \frac{(0.0529 \text{ mol})\,(159.2 \text{ g mol}^{-1})}{20.0 \text{ g}} \times 100 = 42.1.$$

17. A 8.0 g sample contained Fe_3O_4, Fe_2O_3 and inert materials. It was treated with an excess of aqueous KI solution in acidic medium, which reduced all the iron to Fe^{2+} ions. The resulting solution was diluted to 50.0 cm^3 and a 10.0 cm^3 of it was taken. The liberated iodine in this solution required 7.2 cm^3 of 1.0 M $Na_2S_2O_3$ for reduction to iodide. The iodine from another 25.0 cm^3 sample was extracted, after which the Fe^{2+} ions was titrated against 1.0 M MnO_4^- in acidic medium. The volume of $KMnO_4$ solution used was found to be 4.2 cm^3. Calculate the mass percentages of Fe_3O_4 and of Fe_2O_3 in the original mixture. (Given: Molar mass of Fe = 56 g mol^{-1}.)

Solution The reactions with KI solution in acidic medium are

$$Fe_3O_4 + 2I^- + 8H^+ \rightarrow 3\ Fe^{2+} + 4\ H_2O + I_2 \quad (1)$$

$$Fe_2O_3 + 2I^- + 6H^+ \rightarrow 2\ Fe^{2+} + 3\ H_2O + I_2 \quad (2)$$

The reaction involving I_2 and $S_2O_3^{2-}$ is $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2\ I^-$

From this equation, we conclude 2 mol $S_2O_3^{2-} \equiv 1$ mol I_2

Amount of $S_2O_3^{2-}$ in 7.2 cm^3 of 1.0 M $Na_2S_2O_3$ solution

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$$= (7.2\ \text{cm}^3)\ (1.0\ \text{M}) = \left(\frac{7.2}{1000}\text{L}\right)\ (1.0\ \text{mol L}^{-1}) = \frac{7.2}{1000}\ \text{mol}$$

Amount of I_2 equivalent to the above amount of $S_2O_3^{2-} = \frac{1}{2}\left(\frac{7.2}{1000}\right)\ \text{mol} = 3.6 \times 10^{-3}\ \text{mol}$

The above iodine is present in 10.0 cm^3 of the solution. Hence

Amount of I_2 liberated in 50.0 cm^3 solution $= 5 \times 3.6 \times 10^{-3}\ \text{mol} = 18.0 \times 10^{-3}\ \text{mol}$

If n_1 and n_2 are the respective amounts of Fe_3O_4 and Fe_2O_3 present in the given 8.0 g sample, from Eqs (1) and (2), we can write $n_1 + n_2 = 18.0 \times 10^{-3}\ \text{mol}$ (3)

Now from the chemical equation $MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

we can write 1 mol $MnO_4^- \equiv 5$ mol Fe^{2+}

Amount of MnO_4^- in 4.2 cm^3 of 1.0 M $KMnO_4$ solution

$$= (4.2\ \text{cm}^3)\ (1.0\ \text{M}) = \left(\frac{4.2}{1000}\text{L}\right)\ (1.0\ \text{mol L}^{-1}) = 4.2 \times 10^{-3}\ \text{mol}$$

Amount of Fe^{2+} ions equivalent to the above amount of MnO_4^- ions

$= 5 \times 4.2 \times 10^{-3}\ \text{mol} = 21.0 \times 10^{-3}\ \text{mol}$

This amount of Fe^{2+} ions is present in 25.0 cm^3 of the solution. Hence,

Amount of Fe^{2+} ions in 50.0 cm^3 solution $= 2 \times 21.0 \times 10^{-3}\ \text{mol} = 42.0 \times 10^{-3}\ \text{mol}$

From Eqs (1) and (2), we can now write

$$3n_1 + 2n_2 = 42.0 \times 10^{-3}\ \text{mol} \quad (4)$$

Solving for n_1 and n_2 from Eqs (3) and (4), we get

$n_1 = 6 \times 10^{-3}$ mol and $n_2 = 12 \times 10^{-3}$ mol

Hence, Mass of Fe_3O_4 in 8.0 g sample $= (6 \times 10^{-3}\ \text{mol})\ (232.0\ \text{g mol}^{-1}) = 1.392$ g.

Mass of Fe_2O_3 in 8.0 g sample $= (12 \times 10^{-3}\ \text{mol})\ (160\ \text{g mol}^{-1}) = 1.92$ g.

$$\text{Mass per cent of } Fe_3O_4 \text{ in the sample} = \frac{1.392}{8.0} \times 100 = 17.4$$

$$\text{Mass per cent of } Fe_2O_3 \text{ in the sample} = \frac{1.92}{8.0} \times 100 = 24.0$$

18. 25.0 cm^3 of a solution containing Na_2CO_3 and NaOH required 10 cm^3 of 1.0 M H_2SO_4 for neutralization when phenolphthalein was used as the indicator. Whereas when methyl orange was used, it required 15 cm^3 of the same acid for neutralization. Calculate the masses of Na_2CO_3 and NaOH per dm^3 of the solution.

Solution The neutralization reactions are as follows.

Phenolphthalein indicator $CO_3^{2-} + H^+ \rightarrow HCO_3^-$ and $OH^- + H^+ \rightarrow H_2O$

Methyl orange indicator $CO_3^{2-} + 2H^+ \rightarrow H_2O + CO_2$ and $OH^- + H^+ \rightarrow H_2O$

Let n_1 and n_2 be the respective amounts of Na_2CO_3 and NaOH in 25.0 cm^3 of the solution. From the chemical equations given above, we obtain the following equations.

$n_1 + n_2 =$ Amount of H^+ in 10 cm^3 of 1.0 M H_2SO_4

$2n_1 + n_2 =$ Amount of H^+ in 15 cm^3 of 1.0 M H_2SO_4

As each molecule of H_2SO_4 provides $2H^+$ ions, we have

$$n_1 + n_2 = 2\ (10\ \text{cm}^3)\ (1.0\ \text{M}) = 2\left(\frac{10}{1000}\text{dm}^3\right)\ (1.0\ \text{mol dm}^{-3}) = 2 \times 10^{-2}\ \text{mol}$$

$$2n_1 + n_2 = 2\ (15\ \text{cm}^3)\ (1.0\ \text{M}) = 2\left(\frac{15}{1000}\text{dm}^3\right)\ (1.0\ \text{mol dm}^{-3}) = 3 \times 10^{-2}\ \text{mol}$$

Solving for n_1 and n_2 from the above two equations, we get

$n_1 = 10^{-2}$ mol and $n_2 = 10^{-2}$ mol

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The above amounts is present in 25.0 cm^3 solution. Hence, for 1 dm^3 solution, we have

$$\text{Amount of } Na_2CO_3 = 40 \times 10^{-2} \text{ mol}$$
$$\text{Amount of NaOH} = 40 \times 10^{-2} \text{ mol}$$

Hence, $\text{Mass of } Na_2CO_3 = (40 \times 10^{-2} \text{ mol})\ (106 \text{ g mol}^{-1}) = 42.4 \text{ g}$

$\text{Mass of NaOH} = (40 \times 10^{-2} \text{ mol})\ (40 \text{ g mol}^{-1}) = 16.0 \text{ g}$

19. A solution contains Na_2CO_3 and $NaHCO_3$. Twenty cm^3 of this solution requires 5.0 cm^3 of 0.1 M H_2SO_4 solution for neutralization using phenolphthalein as the indicator. Methyl orange is then added when a further 5.0 cm^3 of 0.2 M H_2SO_4 was required. Calculate the masses of Na_2CO_3 and $NaHCO_3$ in one litre of this solution.

Solution The reaction occurring are as follows.

$$CO_3^{2-} + H^+ \xrightarrow{\text{Phenolphthalein}} HCO_3^- \quad \text{and} \quad HCO_3^- + H^+ \xrightarrow{\text{Methyl orange}} CO_2 + H_2O$$

Let n_1 and n_2 be the respective amounts of Na_2CO_3 and $NaHCO_3$ present in 20 cm^3 of solution. We will have

n_1 = Amount of H^+ in 5.0 cm^3 of 0.1 M H_2SO_4

$n_1 + n_2$ = Amount of H^+ in 5.0 cm^3 of 0.2 M H_2SO_4

That is $$n_1 = 2\left(\frac{5.0}{1000}\text{dm}^3\right)(0.1 \text{ mol dm}^{-3}) = 10^{-3} \text{ mol}$$

$$n_1 + n_2 = 2\left(\frac{5.0}{1000}\text{dm}^3\right)(0.2 \text{ mol dm}^{-3}) = 2 \times 10^{-3} \text{ mol}$$

which gives $n_1 = 10^{-3}$ mol and $n_2 = 10^{-3}$ mol

The above amounts are present in 20 cm^3 of the solution. Hence, for 1 L of the solution, we have

$\text{Amount of } Na_2CO_3 = 50 \times 10^{-3}$ mol and $\text{Amount of } NaHCO_3 = 50 \times 10^{-3}$ mol

Hence, $\text{Mass of } Na_2CO_3 = (50 \times 10^{-3} \text{ mol})\ (106 \text{ g mol}^{-1}) = 5.3 \text{ g}$

$\text{Mass of } NaHCO_3 = (50 \times 10^{-3} \text{ mol})\ (84 \text{ g mol}^{-1}) = 4.2 \text{ g}.$

20. A 50.0 cm^3 portion of a mixture of H_2SO_4 and $H_2C_2O_4$ required 48.9 cm^3 of 0.15 M NaOH solution for titration. Another 50 cm^3 required 38.9 cm^3 of 0.10 N $KMnO_4$ solution for titration. Calculate the masses of H_2SO_4 and $H_2C_2O_4$ present per dm^3 of the solution.

Solution Let N_1 and N_2 be the respective normalities of H_2SO_4 and $H_2C_2O_4$ in the same soution. Applying the normality equation, we get

$$(N_1 + N_2)\ (50.0 \text{ cm}^3) = (0.15 \text{ N})\ (48.9 \text{ cm}^3)$$
$$N_2\ (50.0 \text{ cm}^3) = (0.10 \text{ N})\ (38.9 \text{ cm}^3)$$

Hence, $N_2 = \dfrac{0.10 \times 38.9}{50.0}$ N = 0.0778 N and $N_1 + N_2 = \dfrac{0.15 \times 48.9}{50.0}$ N = 0.1467 N

or $N_1 = 0.1467 \text{ N} - 0.0778 \text{ N} = 0.0689 \text{ N}$

$$\text{Mass of } H_2SO_4 \text{ per dm}^3 \text{ solution} = (0.0689)\left(\frac{98}{2}\text{g}\right) = 3.376 \text{ g}$$

$$\text{Mass of } H_2C_2O_4 \text{ per dm}^3 \text{ solution} = (0.0778)\left(\frac{90}{2}\text{g}\right) = 3.501 \text{ g}$$

Alternatively, we may proceed as follows.
The involved chemical equations are :

(i) $H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$

(ii) $H_2C_2O_4 + 2NaOH \rightarrow Na_2C_2O_4 + 2H_2O$

(iii) $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O] \times 2$

$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-\ ] \times 5$

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

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From these equations, we conclude

$$1 \text{ mol } H_2SO_4 \equiv 2 \text{ mol NaOH} ; \quad 1 \text{ mol } H_2C_2O_4 \equiv 2 \text{ mol NaOH} ;$$

$$2 \text{ mol } MnO_4^- \equiv 5 \text{ mol } C_2O_4^{2-} ; \quad \text{and} \quad 1 \text{ mol } MnO_4^- \equiv 5 \text{ equivalents } MnO_4^-$$

Let n_1 and n_2 be the respective amounts of H_2SO_4 and $H_2C_2O_4$ present in 50.0 cm^3 of the solution. We will have

$$2n_1 + 2n_2 = \frac{48.9}{1000} \times 0.15 \text{ mol} \quad \text{and} \quad \frac{2}{5} n_2 = \frac{38.9}{1000} \times \frac{0.10}{5} \text{ mol}$$

Hence, $$n_2 = \frac{1}{2}\left(\frac{38.9}{1000} \times 0.10\right) \text{ mol} \quad \text{and} \quad n_1 = \frac{1}{2}\left[\frac{48.9}{1000} \times 0.15 - \frac{38.9}{1000} \times 0.10\right] \text{ mol.}$$

The above amounts are present in 50.0 cm^3 of the solution. Hence, in 1 dm^3 of the solution we have

$$\text{Amount of } H_2SO_4 = \frac{1}{2}\left[\frac{48.9}{1000} \times 0.15 - \frac{38.9}{1000} \times 0.10\right]\left(\frac{1000}{50}\right) \text{ mol}$$

$$\text{Amount of } H_2C_2O_4 = \frac{1}{2}\left(\frac{38.9}{1000} \times 0.10\right)\left(\frac{1000}{50}\right) \text{ mol}$$

Hence, $$\text{Mass of } H_2SO_4 = \frac{1}{2}\left[\frac{48.9}{1000} \times 0.15 - \frac{38.9}{1000} \times 0.10\right]\left(\frac{1000}{50}\right)(98 \text{ g}) = 3.376 \text{ g}$$

$$\text{Mass of } H_2C_2O_4 = \frac{1}{2}\left(\frac{38.9}{1000} \times 0.10\right)\left(\frac{1000}{50}\right)(90 \text{ g}) = 3.501 \text{ g.}$$

21. What are the masses of P_4O_6 and P_4O_{10} that will be produced by the combustion of 2.0 g of P_4 in 2.0 g of oxygen leaving no P_4 and O_2?

Solution The equations to be considered are $P_4 + 3O_2 \rightarrow P_4O_6$ and $P_4 + 5O_2 \rightarrow P_4O_{10}$

Let x be the mass of P_4 that is converted into P_4O_6 and rest (= 2.0 g − x) into P_4O_{10}. The mass of oxygen required for these conversions will be $\frac{x}{4 \times 31} \times 96 + \frac{2.0 \text{ g} - x}{4 \times 31} \times 160$ and this will be equal to 2.0 g. Hence, we get

$$\frac{96\,x}{124} + \frac{320.0}{124} \text{ g} - \frac{160\,x}{124} = 2.0 \text{ g}$$

or $$x\,(160 - 96) = (320.0 - 2 \times 124) \text{ g} \quad \text{or} \quad x = \frac{320 - 2 \times 124}{160 - 96} \text{ g} = \frac{72}{64} \text{ g} = 1.125 \text{ g.}$$

Hence, $$\text{Mass of } P_4O_6 \text{ obtained} = \frac{\text{Mass of } P_4}{\text{Molar mass of } P_4} \times \text{Molar mass of } P_4O_6$$

$$= \left(\frac{1.125 \text{ g}}{124 \text{ g mol}^{-1}}\right)(220 \text{ g mol}^{-1}) = 1.996 \text{ g}$$

$$\text{Mass of } P_4O_{10} \text{ obtained} = (4.0 - 1.996) \text{ g} = 2.004 \text{ g.}$$

22. One gram of a moist sample of a mixture of $KClO_3$ and KCl was dissolved in water and made up to 250 mL. 25 mL of this solution was treated with SO_2 to reduce chlorate into chloride and the excess SO_2 was boiled off. When the total chloride was precipitated, 0.1435 g of AgCl was obtained. In another experiment 25 mL of the original solution was heated with 30 mL of 0.2 N solution of $FeSO_4$ and unreacted $FeSO_4$ required 37.5 mL of 0.08 N solution of an oxidizing agent for complete oxidation. Calculate the molar ratio of chlorate and chloride in the given mixture. Fe^{2+} reacts with ClO_3^- according to the equation

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

Also calculate the mass per cent of moisture present in the moist sample.

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Solution Let n_1 and n_2 be the respective amounts of $KClO_3$ and KCl present in the 25 mL of the solution obtained by dissolving the given one gram sample in 250 mL water. The reduction reaction of ClO_3^- with SO_2 is

$$ClO_3^- + 3SO_2 + 3H_2O \rightarrow Cl^- + 3H_2SO_4$$

Thus, the amount of Cl^- obtained by the reduction of ClO_3^- will also be equal to n_1. From the mass of silver chloride obtained, we can write

$$n_1 + n_2 = \frac{0.1435\text{ g}}{M_{AgCl}} = \frac{0.1435\text{ g}}{143.5\text{ g mol}^{-1}} = 10^{-3}\text{ mol}$$

In the second experiment, the amount of Fe^{2+} ions (in equivalents which will also be equal to the amounts in mol) unreacted will be equal to the amount (in equivalent) of the oxidizing agent in 37.5 mL of 0.08 N solution, i.e.

Amount of unreacted Fe^{2+} ions = (37.5 mL) (0.08 N)

$$= \left(\frac{37.5}{1000}\text{ L}\right)(0.08\text{ eq L}^{-1}) = \frac{37.5\times0.08}{1000}\text{ eq} \equiv \frac{37.5\times0.08}{1000}\text{ mol}$$

Amount of Fe^{2+} ions added in the beginning = (30 mL) (0.2 N) $\equiv \left(\frac{30}{1000}\text{ L}\right)(0.2\text{ mol L}^{-1}) = \frac{30\times0.2}{1000}$ mol

Amount of Fe^{2+} ions used in reducing ClO_3^- to Cl^- = $\left(\frac{30\times0.2}{1000} - \frac{37.5\times0.08}{1000}\right)$ mol

From the chemical equation $ClO_3^- + 6Fe^{2+} + 6H^+ \rightarrow Cl^- + 6Fe^{3+} + 3H_2O$, we conclude that

Amount of ClO_3^- ions in 25.0 mL solution, $n_1 = \frac{1}{6}\left(\frac{30\times0.2}{1000} - \frac{37.5\times0.08}{1000}\right)$ mol = 5×10^{-4} mol

Hence, Amount of Cl^- ions in 25.0 mL solution, $n_2 = (10^{-3} - 5\times10^{-4})$ mol = 5×10^{-4} mol

Now, in the 250 mL of the soiution, we will have

Amount of ClO_3^- ions = 5×10^{-3} mol and Amount of Cl^- ions = 5×10^{-3} mol

Hence, $\frac{\text{Amount of } ClO_3^- \text{ ions}}{\text{Amount of } Cl^-} = \frac{5\times10^{-3}\text{ mol}}{5\times10^{-3}\text{ mol}} = \frac{1}{1}$

Now Mass of $KClO_3$ = (5×10^{-3} mol) (122 g mol^{-1}) = 0.61 g

Mass of KCl = (5×10^{-3} mol) (74.5 g mol^{-1}) 0.3725g

Total mass of $KClO_3$ and KCl = (0.61 + 0.3725) g = 0.9825 g

Mass of moisture in 1 g sample = (1 − 0.9825) g = 0.0175 g

Mass per cent of moisture = $\frac{0.0175\text{ g}}{1\text{ g}} \times 100 = 1.75.$

23. A precipitate of AgBr and AgCNS weighing 1.002 g was dissolved in 60.0 cm^3 of 0.25 M KCN solution. The excess cyanide required 16.7 cm^3 of 0.1 M $AgNO_3$ for titration to the turbid end point. Calculate the percentage of AgCNS in the original precipitate.

Solution Let n_1 and n_2 be the respective amounts of AgBr and AgCNS present in the given precipitate. We will have

$$n_1 M_{AgBr} + n_2 M_{AgCNS} = 1.002\text{ g} \quad \text{i.e.} \quad 187.8\, n_1 + 165.9\, n_2 = 1.002\text{ mol} \qquad (1)$$

The dissolution process is due to the reactions

$$AgBr + 2CN^- \rightarrow Ag(CN)_2^- + Br^- \quad \text{and} \quad AgCNS + 2CN^- \rightarrow Ag(CN)_2^- + CNS^-$$

Hence, Amount of CN^- used in the dissolution process = $2n_1 + 2n_2$ (2)

The titration of CN^- versus Ag^+ involves the reaction $Ag^+ + 2\,CN^- \rightarrow Ag(CN)_2^-$

Hence, Amount of excess CN^- = 2(16.7 cm^3) (0.1 M)

$$= 2\left(\frac{16.7}{1000}\text{ dm}^3\right)(0.1\text{ mol dm}^{-3}) = \frac{2\times16.7}{1000}\times0.1\text{ mol}$$

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Amount of CN^- used during dissolution process = (60.0 cm^3) (0.25 M) = $\frac{60.0}{1000} \times 0.25$ mol

Amount of CN^- used in the dissolution process = $\left(\frac{60}{1000} \times 0.25 - \frac{2 \times 16.7}{1000} \times 0.1\right)$ mol = 11.66×10^{-3} mol (3)

Equating Eqs (2) and (3), we get

$$2n_1 + 2n_2 = 11.66 \times 10^{-3} \text{ mol} \quad \text{or} \quad n_1 + n_2 = 5.83 \times 10^{-3} \text{ mol} \tag{4}$$

Solving n_1 and n_2 from Eqs (1) and (4), we get $n_1 = 0.00159$ mol and $n_2 = 0.00424$ mol

Mass per cent of AgCNS = $\frac{0.00424 \times 165.9}{0.00424 \times 165.9 + 0.00159 \times 187.8} \times 100 = \frac{0.7034}{0.7034 + 0.2986} \times 100 = 70.2.$

24. 1.5 g pyrolusite ore was treated with 10 g of Mohr's salt and dilute sulphuric acid resulting into the following equation

$$MnO_2 + 2Fe^{2+} + 4H^+ \rightarrow Mn^{2+} + 2Fe^{3+} + 2H_2O$$

After the reaction is over, the solution was made up to 250 mL. When 50 mL of this solution was titrated against N/10 $K_2Cr_2O_7$ solution, the volume of the latter consumed was found to be 10 mL. Calculate the percentage of MnO_2 in the given pyrolusite sample.

Solution Normality of the solution prepared after the reaction is over can be computed by using the expression

$$N_1V_1 = N_2V_2.$$

Hence, $(N)\ (50\ mL) = \left(\frac{N}{10}\right)\ (10\ mL)$ i.e. $N = 1/50$ N

The normality of Fe^{2+} ions will be same as its molarity. Hence,

$M = 1/50$ M

Amount of Fe^{2+} ions in 250 mL solution

$$= (250\ mL)\left(\frac{1}{50}\ M\right) = \left(\frac{250}{1000}\ L\right)\left(\frac{1}{50}\ mol\ L^{-1}\right) = \frac{1}{200}\ mol = 0.005\ mol$$

Amount of Fe^{2+} ions taken to start with = $\frac{10\ g}{392\ g\ mol^{-1}} = 0.0255$ mol

Amount of Fe^{2+} ions used in reducing MnO_2 = (0.0255 − 0.005) mol = 0.0205 mol

Amount of MnO_2 reduced = $\frac{0.0205}{2}$ mol = 0.01025 mol

Mass of MnO_2 reduced = (0.01025 mol) (86.9 mol^{-1}) = 0.8907 g

Per cent of MnO_2 in the given sample of pyrolusite = $\frac{0.8907\ g}{1.5\ g} \times 100 = 59.4.$

25. Ten grams of a sample of bleaching powder were extracted with water and the solution made upto one litre. 25 mL of this solution was added to 50 mL of N/14 Mohr's salt solution containing enough sulphuric acid. After the reaction was completed, the whole solution required 22 mL of $KMnO_4$ solution containing 2.2571 g of $KMnO_4$ per litre for complete oxidation. Calculate the percentage of available chlorine in the sample of bleaching powder.

Solution The reactions to be considered are :

(i) $Cl_2 + 2Fe^{2+} \rightarrow 2Cl^- + 2Fe^{3+}$

(ii) $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

$Fe^{2+} \rightarrow Fe^{3+} + e^-] \times 5$

$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

Amount of Fe^{2+} ions added in the beginning

$$= (50\ mL)\left(\frac{1}{14}\ M\right) = \left(\frac{50}{1000}\ L\right)\left(\frac{1}{14}\ mol\ L^{-1}\right) = \left(\frac{50}{1000}\right)\left(\frac{1}{14}\right)\ mol$$

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Amount of Fe^{2+} ions oxidized by MnO_4^- = 5 (22 mL) $\left(\frac{2.2571}{M_{KMnO_4}} \text{ mol L}^{-1}\right)$ = 5 $\left(\frac{22}{1000}\right)\left(\frac{2.2571}{158}\right)$ mol

Amount of Fe^{2+} ions oxidized by Cl_2 = $\left[\left(\frac{50}{1000}\right)\left(\frac{1}{14}\right) - 5\left(\frac{22}{1000}\right)\left(\frac{2.2571}{158}\right)\right]$ mol

Amount of Cl_2 gas available = $\frac{1}{2}\left[\left(\frac{50}{1000}\right)\left(\frac{1}{14}\right) - 5\left(\frac{22}{1000}\right)\left(\frac{2.2571}{158}\right)\right]$ mol = 10^{-3} mol.

This amount is present in 25 mL of the solution. Hence,

Amount of Cl_2 gas available in 1 L solution = 40×10^{-3} mol

Mass of Cl_2 gas available in 1 L solution = $71 \times 40 \times 10^{-3}$ g = 2.84 g

Percentage of available Cl_2 = $\frac{2.84\text{ g}}{10\text{ g}} \times 100 = 28.4$.

26. One gram of a mixture of anhydrous Na_2CO_3 and K_2CO_3 was dissolved in water and volume of the solution was made upto 250 mL. 25 mL of this solution required 26.25 mL of HCl of unknown concentration for complete neutralization. The neutral solution so obtained required 16.25 mL of 0.1 M $AgNO_3$ for complete precipitation. Calculate (a) the percentage of K_2CO_3 in the mixture and (b) the concentration of HCl in grams per litre.

Solution Let x be the mass Na_2CO_3 present in one gram of the given mixture. Then

Total amount of CO_3^{2-} ions = $\frac{x}{M_{Na_2CO_3}} + \frac{1.0\text{ g} - x}{M_{K_2CO_3}} = \frac{x}{(106\text{ g mol}^{-1})} + \frac{1.0\text{ g} - x}{(138\text{ g mol}^{-1})}$

Total amount of CO_3^{2-} ions in 25 mL solution = $\frac{1}{10}\left[\frac{x}{(106\text{ g mol}^{-1})} + \frac{1.0\text{ g} - x}{(138\text{ g mol}^{-1})}\right]$

Total amounts of H^+ ions required for complete neutralization (or amount of Cl^- ions produced in the complete neutralization)

$$= (2)\left(\frac{1}{10}\right)\left[\frac{x}{(106\text{ g mol}^{-1})} + \frac{1.0\text{ g} - x}{(138\text{ g mol}^{-1})}\right]$$

This amount of Cl^- ions must be equal to the amount of Ag^+ ions in 16.25 mL of 0.1 M $AgNO_3$ solution. Hence

$$(2)\left(\frac{1}{10}\right)\left[\frac{x}{(106\text{ g mol}^{-1})} + \frac{1.0\text{ g} - x}{(138\text{ g mol}^{-1})}\right] = (16.25\text{ mL})\ (0.1\text{ M})$$

or
$$(2)\left(\frac{1}{10}\right)\left[\frac{x}{(106\text{ g})} + \frac{1.0\text{ g} - x}{(138\text{ g})}\right] = \frac{16.25}{1000} \times 0.1$$

Solving for x, we get

$$x = \frac{1}{32}\left[\left(\frac{1}{2}\right)(10)\left(\frac{16.25 \times 0.1}{1000}\right)(138)\ (106) - 106\right]\text{ g} = 0.4016\text{ g}$$

Hence, Mass per cent of K_2CO_3 = $\frac{0.5984\text{ g}}{1\text{ g}} \times 100 = 59.84$

Molarity of HCl solution used = $\frac{16.25}{26.25} \times 0.1\text{ M} = 0.0619\text{ M}$

Mass of HCl per litre of solution = 0.0619×36.5 g = 2.26 g.

27. Pure $Na_2C_2O_4$ and $KHC_2O_4 \cdot H_2C_2O_4$ are mixed in such a proportion that each gram of the mixture reacts separately with equal volumes of 0.1 M $KMnO_4$ and 0.1 M NaOH. What is the proportion?

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Solution The constituent $KHC_2O_4 \cdot H_2C_2O_4$, which contains three replaceable hydrogen atoms, only reacts with NaOH whereas both the constituents react with $KMnO_4$. The reactions are

(i) $H^+ + OH^- \rightarrow H_2O$

(ii) $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

Hence, it follows that 1 mol $H^+ \equiv$ 1 mol OH^- and 2 mol $MnO_4^- \equiv$ 5 mol $C_2O_4^{2-}$.

Let x and 1.0 g $- x$ be the respective masses of $Na_2C_2O_4$ (molar mass 134 g mol^{-1}) and $KHC_2O_4 \cdot H_2C_2O_4$ (molar mass 218 g mol^{-1}) in one gram of the mixture and let the volume V of $KMnO_4$ solution or NaOH solution that react with one gram of the mixture. We have

$$\text{Amount of } H^+ \text{ in the mixture} = 3\left(\frac{1.0\text{ g} - x}{218\text{ g mol}^{-1}}\right); \quad \text{Amount of } OH^- \text{ reacted} = V\text{ (0.1 M)}$$

Equating these two, we get

$$3\left(\frac{1.0\text{ g} - x}{218\text{ g mol}^{-1}}\right) = V\text{ (0.1 M)} \tag{1}$$

Now $$\text{Amount of } C_2O_4^{2-} \text{ in the mixture} = \frac{x}{134\text{ g mol}^{-1}} + 2 \times \left(\frac{1.0\text{ g} - x}{218\text{ g mol}^{-1}}\right)$$

$$\text{Amount of } MnO_4^- \text{ reacted} = V\text{ (0.1 M)}$$

Now since 2 mol $MnO_4^- \equiv$ 5 mol $C_2O_4^{2-}$, we will have

$$\frac{2}{5}\left[\frac{x}{134\text{ g mol}^{-1}} + 2 \times \left(\frac{1.0\text{ g} - x}{218\text{ g mol}^{-1}}\right)\right] = V\text{ (0.1 M)} \tag{2}$$

Dividing Eq. (1) by Eq. (2), we get

$$\frac{2}{5}\left[\frac{x}{134\text{ g mol}^{-1}} + 2 \times \left(\frac{1.0\text{ g} - x}{218\text{ g mol}^{-1}}\right)\right] = 3\left(\frac{1.0\text{ g} - x}{218\text{ g mol}^{-1}}\right)$$

Solving for x, we get

$$x = \frac{134 \times 11}{134 \times 11 + 2 \times 218}\text{ g} = \frac{1474}{1910}\text{ g} \quad \text{and} \quad 1.0\text{ g} - x = \frac{436}{1910}\text{ g}$$

Hence, the ratio of two masses in 1.0 g mixture is

$$\frac{\text{Mass of } Na_2C_2O_4}{\text{Mass of } KHC_2O_4 \cdot H_2C_2O_4} = \frac{1474}{436} = \frac{3.38}{1}.$$

28. A 0.2 g sample of pyrolusite is analyzed as follows. Add 50.0 mL of a 0.10 M solution of ferrous ammonium sulphate to reduce the MnO_2 to Mn^{2+}. After the reduction is complete, the excess ferrous ion is titrated in acid solution with 0.02 M $KMnO_4$, requiring 15.0 mL. Calculate the percentage of manganese in the sample as MnO_2.

Solution The reactions involved are

$$MnO_2 + 2Fe^{2+} + 4H^+ \rightarrow Mn^{2+} + 2Fe^{3+} + 2H_2O$$

$$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

Hence, 1 mol $MnO_2 \equiv$ 2 mol Fe^{2+} and 1 mol $MnO_4^- \equiv$ 5 mol Fe^{2+}

To start with, amount of Fe^{2+} ions added = $(50.0 \times 10^{-3}\text{ L})\ (0.10\text{ mol L}^{-1}) = 50.0 \times 10^{-4}$ mol

Amount of MnO_4^- used in oxidizing excess of Fe^{2+} ions = $(15.0 \times 10^{-3}\text{ L})\ (0.02\text{ mol L}^{-1}) = 3 \times 10^{-4}$ mol

Since 1 mol $MnO_4^- \equiv$ 5 mol Fe^{2+}, we have

$$\text{Amount of excess } Fe^{2+} \text{ ions} = 5 \times (3 \times 10^{-4}\text{ mol})$$

Amount of Fe^{2+} ions used in the reduction of $MnO_2 = 50 \times 10^{-4}$ mol $- 15 \times 10^{-4}$ mol $= 35 \times 10^{-4}$ mol

Now since 1 mol $MnO_2 \equiv$ 2 mol Fe^{2+}, we will have

$$\text{Amount of } MnO_2 \text{ in 0.2 g sample of pyrolusite} = \frac{1}{2}\ (35 \times 10^{-4}\text{ mol})$$

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$$\text{Mass of } MnO_2 \text{ in the sample} = \frac{1}{2}\ (35 \times 10^{-4} \text{ mol})\ (86.9 \text{ g mol}^{-1}) = 0.152 \text{ g}$$

$$\text{Percentage of } MnO_2 \text{ in the sample} = \frac{0.152\text{ g}}{0.2\text{ g}} \times 100 = 76.0\ \%.$$

29. A mixture containing only $FeCl_3$ and $AlCl_3$ weights 5.95 g. The chlorides are converted into the hydrous oxides and ignited to Fe_2O_3 and Al_2O_3. The oxide mixture weighs 2.62 g. Calculate the percent of Fe and Al in the original mixture.

Solution Let x and y be the masses of $FeCl_3$ and $AlCl_3$ in the 5.95 g mixture, respectively. Thus,

$$x + y = 5.95 \text{ g} \qquad (1)$$

$$\text{Mass of } Fe_2O_3 \text{ obtained from the mass } x \text{ of } FeCl_3 = \frac{x}{M_{FeCl_3}}\left(\frac{1}{2}M_{Fe_2O_3}\right) = x\left(\frac{159.6}{2\times 162.3}\right) = 0.492\ x$$

$$\text{Mass of } Al_2O_3 \text{ obtained from the mass } y \text{ of } AlCl_3 = \frac{y}{M_{AlCl_3}}\left(\frac{1}{2}M_{Al_2O_3}\right) = y\left(\frac{102}{2\times 133.5}\right) = 0.382\ y$$

Hence, $$0.492\ x + 0.382\ y = 2.62 \text{ g} \qquad (2)$$

Solving x and y from Eqs (1) and (2), we get

$$x = \frac{5.95\times 0.382 - 2.62}{0.492 - 0.382}\ \text{g} = 3.155 \text{ g} \quad \text{and} \quad y = 5.95 \text{ g} - 3.155 \text{ g} = 2.795 \text{ g}$$

Now $$\text{Mass of Fe in the mixture} = x\left(\frac{M_{Fe}}{M_{FeCl_3}}\right) = (3.155 \text{ g})\left(\frac{55.8}{162.3}\right) = 1.085 \text{ g}$$

$$\text{Mass percent of Fe in the mixture} = \frac{1.085\text{ g}}{5.95\text{ g}} \times 100 = 18.24$$

$$\text{Mass of Al in the mixture} = y\left(\frac{M_{Al}}{M_{AlCl_3}}\right) = (2.795 \text{ g})\left(\frac{27}{133.5}\right) = 0.565 \text{ g}$$

$$\text{Mass percent of Al in the mixture} = \frac{0.565\text{ g}}{5.95\text{ g}} \times 100 = 9.50.$$

30. 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.

Solution Glauber's salt is $NaSO_4 \cdot 10H_2O$.

$$\text{Molar mass of Glauber's salt} = \{2 \times 23.00 + 32.10 + 4 \times 16.00 + 10\,(2 \times 1.01 + 16.00)\}\ \text{g mol}^{-1}$$

$$= 322.3 \text{ g mol}^{-1}$$

$$\text{Amount of Glauber's salt dissolved, } n_2 = \frac{m}{M} = \frac{8.0575\times 10^{-2}\text{ kg}}{322.3\times 10^{-3}\text{ kg mol}^{-1}} = 0.25 \text{ mol}$$

$$\text{Mass of 1 dm}^3 \text{ solution} = \rho V = (1077.2 \text{ kg m}^{-3})\ (10^{-3} \text{ m}^3) = 1.0772 \text{ kg}$$

$$\text{Mass of } Na_2SO_4 \text{ in 1 dm}^3 \text{ solution, } = n_2\, M_{Na_2SO_4} = (0.25 \text{ mol})\ (2 \times 23 + 32.10 + 4 \times 16.00)\ \text{g mol}^{-1}$$

$$= 35.525 \text{ g} = 3.5525 \times 10^{-2} \text{ kg}$$

$$\text{Mass of solvent in 1 dm}^3 \text{ solution} = (1.0772 - 3.5525 \times 10^{-2}) \text{ kg} = 1.0417 \text{ kg}$$

$$\text{Molarity of solution} = \frac{n_2}{V} = \frac{0.25\text{ mol}}{1\text{ dm}^3} = 0.25 \text{ mol dm}^{-3}$$

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$$\text{Molality of solution} = \frac{n_2}{m_{\text{solvent}}} = \frac{0.25 \text{ mol}}{1.0417 \text{ kg}} = 0.24 \text{ mol kg}^{-1}$$

$$\text{Amount of solvent in 1 dm}^3 \text{ solution, } n_1 = \frac{1.0417 \times 10^3 \text{ g}}{18 \text{ g mol}^{-1}} = 57.87 \text{ mol}$$

$$\text{Mole fraction of } Na_2SO_4 \text{ in solution } \frac{n_1}{n_1 + n_2} = \frac{0.25}{0.25 + 57.87} = 0.0043$$

31. A sample of hard water contains 96 ppm of SO_4^{2-} and 183 ppm of HCO_3^-, with Ca^{2+} as the only cation. How many moles of CaO will be required to remove HCO_3^- from 1000 kg of this water? If 1000 kg of this water is treated with the amount of CaO calculated above, what will be the concentration (in ppm) of residual Ca^{2+} ions? (Assume $CaCO_3$ to be completely insoluble in water.) If the Ca^{2+} ions in one litre of the treated water are completely exchanged with hydrogen ions, what will be its pH? (One ppm means one part of the substance in one million part of water, mass/mass.)

Solution In 10^6 g (= 1000 kg) of the given hard water, we will have

Mass of SO_4^{2-} ions = 96 g; Mass of HCO_3^- ions = 183 g

Thus $\text{Amount of } SO_4^{2-} \text{ ions} = \frac{96 \text{ g}}{96 \text{ g mol}^{-1}} = 1 \text{ mol}$; $\text{Amount of } HCO_3^- \text{ ions} = \frac{183 \text{ g}}{61 \text{ g mol}^{-1}} = 3 \text{ mol}$

These ions are present as $CaSO_4$ and $Ca(HCO_3)_2$. Hence, Amount of Ca^{2+} ions = (1 + 1.5) mol = 2.5 mol.

The addition of CaO causes the following reaction: $CaO + Ca(HCO_3)_2 \longrightarrow 2CaCO_3 + H_2O$

To remove 1.5 mol of $Ca(HCO_3)_2$, 1.5 mol of CaO will be required in the treated water. After this, the solution contains only $CaSO_4$. Thus, 1 mol of Ca^{2+} ions will be present in 10^6 g of water. Hence, its concentration will be 40 ppm.

Molarity of Ca^{2+} ions in the treated water will be 10^{-3} mol L^{-1}. If the Ca^{2+} ions are exchanged by H^+ ions, then

Molarity of H^+ in the treated water = 2×10^{-3} M.

Thus, $pH = -\log (2 \times 10^{-3}) = 2.7$

32. One litre of a mixture of O_2 and O_3 at STP was allowed to react with an excess of acidified solution of KI. The iodine liberated required 40 mL of M/10 sodium thiosulphate solution for titration. What is the mass per cent of ozone in the mixture? Ultraviolet radiation of wavelength 300 nm can decompose ozone. Assume that one photon can decompose one ozone molecule, how many photons would have been required for the complete decomposition of ozone in the original mixture? (1997)

Solution The reaction of O_3 with I^- in acidic medium is $O_3 + 2I^- + 2H^+ \rightarrow I_2 + O_2 + H_2O$

Hence, 1 mol O_3 = 1 mol I_2

The reaction of I_2 with $S_2O_3^{2-}$ is $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$

Hence, 2 mol $S_2O_3^{2-} \equiv$ 1 mol I_2

$$\text{Amount of } S_2O_3^{2-} \text{ consumed} = (40 \times 10^{-3} \text{ L}) \left(\frac{1}{10} \text{ mol L}^{-1}\right) = 40 \times 10^{-4} \text{ mol}$$

Thus 40×10^{-4} mol $S_2O_3^{2-} \equiv 20 \times 10^{-4}$ mol $I_2 \equiv 20 \times 10^{-4}$ mol O_3

Mass of O_3 present in 1 L of mixture = $(20 \times 10^{-4} \text{ mol}) (48 \text{ g mol}^{-1}) = 9.6 \times 10^{-2}$ g

Total amount of O_2 and O_3 present in 1 L of mixture at STP is

$$n_{\text{total}} = \frac{pV}{RT} = \frac{(1 \text{ atm}) (1 \text{ L})}{(0.082 \text{ atm L K}^{-1} \text{ mol}^{-1}) (273 \text{ K})} = 4.462 \times 10^{-2} \text{ mol}$$

Hence,

Amount of O_2 present in 1 L of mixture = $(4.462 \times 10^{-2} - 20 \times 10^{-4})$ mol = 4.262×10^{-2} mol

Mass of O_2 present in 1 L of mixture = $(4.262 \times 10^{-2} \text{ mol}) (32 \text{ g mol}^{-1}) = 1.364$ g

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Mass percent of O_3 in the mixture $= \dfrac{9.6\times10^{-2}}{9.6\times10^{-2}+1.364}\times 100 = 6.575$

Amount of photons required to decompose O_3 = Amount of $O_3 = 20\times10^{-4}$ mol

Number of photons required = $(20\times10^{-4}\text{ mol})\,(6.023\times10^{23}\text{ mol}^{-1}) = 1.205\times10^{21}$

33. An aqueous solution containing 0.10 g KIO_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.

Solution The reaction between KIO_3 and KI is $KIO_3 + 5KI + 6HCl \rightarrow 6KCl + 3H_2O + 3I_2$

The reaction of I_2 with thiosulphate ion is $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$

From these reactions, we can write 1 mol $KIO_3 \cong 3$ mol I_2 and 1 mol $I_2 \cong 2$ mol $S_2O_3^{2-}$

From the given mass of KIO_3, we get Amount of $KIO_3 = \dfrac{0.10\text{ g}}{214.0\text{ g mol}^{-1}} = 4.6729\times10^{-4}$ mol

Amount of I_2 generated $= 3\times4.6729\times10^{-4}$ mol

Amount of $S_2O_3^{2-}$ consumed $= 2(3\times4.6729\times10^{-4}\text{ mol})$ (1)

Let M be the molarity of thiosulphate solution. From the given volume of thiosulphate solution, we get

Amount of $S_2O_3^{2-}$ consumed $= MV = M(45.0\times10^{-3}\text{ L})$ (2)

Equating Eqs (1) and (2), we get

$$M(45.0\times10^{-3}\text{ L}) = 2\,(3\times4.6729\times10^{-4}\text{ mol})$$

$$M = \frac{2(3\times4.6729\times10^{-4}\text{ mol})}{45.0\times10^{-3}\text{ L}} = 0.0623\text{ mol L}^{-1}$$

34. A 3.00 g sample containing Fe_3O_4, Fe_2O_3 and an inert impure substance, is treated with excess KI solution in presence of dilute H_2SO_4. The entire iron is converted into Fe^{2+} along with the liberation of iodine. The resulting solution is diluted to 100 mL. A 20 mL of the diluted solution requires 11.0 mL of 0.5 M $Na_2S_2O_3$ solution to reduce the iodine present. A 50 mL of the diluted solution, after complete extraction of the iodine requires 12.80 mL of 0.25 M $KmnO_4$ solution in dilute H_2SO_4 medium for the oxidation of Fe^{2+}. Calculate the percentages of Fe_2O_3 and Fe_3O_4 in the original sample. (1996)

Solution The reactions with KI solution in acidic medium are

$$Fe_3O_4 + 2I^- + 8H^+ \rightarrow 3Fe^{2+} + 4H_2O + I_2 \quad (1)$$

$$Fe_2O_3 + 2I^- + 6H^+ \rightarrow 2Fe^{2+} + 3H_2O + I_2 \quad (2)$$

The reaction involving I_2 and $S_2O_3^{2-}$ is $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$

From this equation, we conclude 2 mol $S_2O_3^{2-} \equiv 1$ mol I_2

Amount of $S_2O_3^{2-}$ in 11.0 mL of 0.5 M $Na_2S_2O_3$ solution $= (11.0\times10^{-3}\text{ L})\,(0.5\text{ mol L}^{-1}) = 5.5\times10^{-3}$ mol

Amount of I_2 equivalent to the above amount of $S_2O_3^{2-} = \dfrac{1}{2}\,(5.5\times10^{-3}\text{ mol}) = 2.75\times10^{-3}$ mol

The above iodine is present in 20 mL of the solution. Hence

Amount of I_2 liberated in 100 mL solution $= 5\times2.75\times10^{-3}\text{ mol} = 13.75\times10^{-3}$ mol

If n_1 and n_2 are the respective amounts of Fe_3O_4 and Fe_2O_3 present in the given 3.00 g sample, then from Eqs (1) and (2), we can write $n_1 + n_2 = 13.75\times10^{-3}$ mol (3)

Now from the chemical equation $MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

We can write 1 mol $MnO^{-4} \equiv 5$ mol Fe^{2+}

Amount of MnO_4^- in 12.80 mL of 0.25 M $KmnO_4$ solution

$= (12.80\times10^{-3}\text{ L})\,(0.25\text{ mol L}^{-1}) = 3.2\times10^{-3}$ mol

Amount of Fe^{2+} equivalent to the above amount of MnO_4^- ions

$= 5\times3.2\times10^{-3}\text{ mol} = 16.0\times10^{-3}$ mol

This amount of Fe^{2+} ions is present in 50 mL of the solution. Hence

Amount of Fe^{2+} ions in 100 mL solution $= 2\times16.0\times10^{-3}$ mol

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From Eqs. (1) and (2), we can now write

$$3n_1 + 2n_2 = 32.0 \times 10^{-3} \text{ mol} \quad (4)$$

Solving for n_1 and n_2 from Eqs (3) and (4), we get

$$n_1 = 4.5 \times 10^{-3} \text{ mol and } n_2 = 9.25 \times 10^{-3} \text{ mol}$$

Mass of Fe_3O_4 in 3.00 g sample = $(4.5 \times 10^{-3} \text{ mol})\ (232 \text{ g mol}^{-1}) = 1.044$ g
Mass of Fe_2O_3 in 3.00 g sample = $(9.25 \times 10^{-3} \text{ mol})\ (160 \text{ g mol}^{-1}) = 1.48$ g

$$\text{Mass per cent of } Fe_3O_4 \text{ in the sample} = \frac{1.044}{3} \times 100 = 34.8$$

$$\text{Mass per cent of } Fe_2O_3 \text{ in the sample} = \frac{1.048}{3} \times 100 = 49.3$$

35. A 5.0 cm^3 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. (1995)

Solution The involved reaction is $H_2O_2 + 2H^+ + 2I^- \rightarrow I_2 + 2H_2O$
Hence 1 mol $H_2O_2 \equiv$ 1 mol I_2

$$\text{Amount of } I_2 \text{ liberated} = \frac{0.508\text{g}}{(2\times127)\text{g mol}^{-1}} = 2x\ 10^{-3} \text{ mol}$$

Thus Amount of H_2O_2 in 5.0 cm^3 solution = 2×10^{-3} mol

$$\text{Molar concentration of } H_2O_2 = \frac{2\times10^{-3} \text{ mol}}{5\times10^{3} \text{ L}} = 0.4 \text{ mol L}^{-1}$$

The volume strength of H_2O_2 is based on the reaction $2H_2O \times 2H_2O + O_2$
Thus 2 mol $H_2O_2 \equiv$ 1 mol $O_2 \equiv$ 22.4 L O_{2s} at STP
Now 2 molar solution of H_2O_2 has volume strength of 22.4.

Hence, 0.4 molar solution of H_2O_2 has volume strength of $\frac{22.4}{2M}$ x 0.4 M = 4.48

36. How many millilitres of 0.5 M H_2SO_4 are needed to dissolve 0.5 g of copper(II) carbonate? (1999)

Solution Molar mass of $CuCO_3 = (63.5 + 12 + 3 \times 16)$ g $mol^{-1} = 123.58$ g mol^{-1}

$$\text{Amount of given } CuCO_3 = \frac{0.5\text{ g}}{123.5\text{ g mol}^{-1}} = 4.05 \times 10^{-3} \text{ mol}$$

The dissolution reaction is $CuCO_3 + H_2SO_4 \rightarrow CuSO_4 + CO_2 + H_2O$
From the stoichiometric coefficients, we can write
Amount of H_2SO_4 required for dissolution of the given mass of $CuCO_3$, $n = 4.05 \times 10^{-3}$ mol
Volume of 0.5 M H_2SO_4 solution containing 4.05×10^{-3} mol of H_2SO_4

$$= \frac{n}{M} = \frac{4.05\times10^{-3} \text{ mol}}{0.5 \text{ mol L}^{-1}} = 8.1 \times 10^{-3} \text{ L} = 8.1 \text{ mL}$$

37. 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 molar mass. (1999)

Solution Radius of the cylindrical particle is $r = \frac{150\times10^{-8} \text{ cm}}{2} = 75 \times 10^{-8}$ cm

Length of the cylindrical particle is $l = 5000 \times 10^{-8}$ cm
Volume of the cylindrical particle is $V = \pi r^2 l = (3.14)\ (75 \times 10^{-8} \text{ cm})^2\ (500 \times 10^{-8} \text{ cm}) = 8.83 \times 10^{-17} \text{ cm}^3$

Mass of the cylindrical particle is $m = \frac{V}{\rho} = \frac{8.83\times10^{-17} \text{ cm}^3}{0.75 \text{ cm}^3/\text{g}} = 1.18 \times 10^{-16}$ g

Molar mass of the cylindrical particle is $m = m\ N_A = (1.18 \times 10^{-16} \text{ g})\ (6.022 \times 10^{23} \text{ mol}^{-1}) = 7.1 \times 10^7 \text{ g mol}^{-1}$

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38. Hydrogen peroxide solution (20 mL) reacts quantitatively with a solution of $KmnO_4$ (20 mL) acidified with dilute H_2SO_4. The same volume of the $KmnO_4$ solution is just decolourised by 10 mL of $MnSO_4$ in neutral lmedium simultaneously forming a dark brown precipitate of hydrated MnO_2. The brown precipitate is dissolved in 10 mL of 0.2 M sodium oxalate under boiling condition in the presence of dilute H_2SO_4. Write the balanced equations involved in the reactions and calculate the molarity of H_2O_2. (2001)

Solution In acidic medium, MnO_4^- oxidizes H_2O_2 to O_2. The involved reactions are

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O] \times 2$$

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-] \times 5$$

$$2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn_2^+ + 5O_2 + 8H_2O$$

In neutral medium, the reactions of MnO_4^- with Mn^{2+} are as follows.

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-] \times 2$$

$$Mn^{2+}\ 4OH^- \rightarrow MnO_2 + 2H_2O + 2e^-] \times 3$$

$$2MnO_4^- + 3Mn^{2+} + 4OH^- \rightarrow 5MnO_2 + 2H_2O$$

The dissolution of MnO_2 in sodium oxalate in acidic medium involves the following reactions.

$$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O]$$

$$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$$

$$MnO_2 + C_2O_4^{2-} + 4H^+ \rightarrow Mn^{2+} + 2CO_{2+}\ 2H_2O$$

Amount of oxalate used in dissolving MnO_2 is

$$n_1 = V_1M_1 = (10\text{ mL})\ (0.2\text{ M}) = (10\text{ mL})\left(\frac{0.2\text{ mol}}{1000\text{ mL}}\right) = 2 \times 10^{-3}\text{ mol}$$

From the reactions given above, we conclude that

1 mol $C_2O_4^{2-}$ ≡ 1 mol MnO_2; 5 mol MnO_2 ≡ 2 mol MnO_4^-; 2 mol MnO_4^- ≡ 5 mol H_2O_2

Hence, 2×10^{-3} mol $C_2O_4^{2-} \equiv 2 \times 10^{-3}$ mol MnO_2 $\frac{2}{5}$ $(2 \times 10^{-3}$ mol $MnO_4^-)$

$$= \frac{5}{2}\left[\frac{2}{5}(2\times10^{-3}\text{ mol}\,H_2O_2)\right]$$

that is,
2×10^{-3} mol of H_2O_2 was present in 20 mL of hydrogen peroxide solution. Hence, its molarity is

$$M = \frac{n}{V} = \frac{2\times10^{-3}}{20\times10^{-3}\text{ L}} = 0.1\text{ mol L}^{-1}$$

39. What is molarity of water at 4 °C? (2002)

Solution By definition, molarity is the amount of substance (i.e. number of moles) per litre of the solution. To calculate molarity of water, we take 1 L of water and find out the amount of water in this volume. We know that the density of water at 4 °C is 1 g mL^{-1}. Hence, the mass of 1 L of water is

$$m = \rho V = (1\text{ g mL}^{-1})\ (1000\text{ mL}) = 1000\text{ g}$$

The amount of water in this mass is

$$n = \frac{m}{M} = \frac{1000\text{ g}}{18\text{ g mol}^{-1}} = 55.56\text{ mol}$$

Hence, the molarity of water at 4 °C is 55.56 mol L^{-1}.

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40. On dissolving 2.0 g of a metal in sulphuric acid, 4.51 g of the metal sulphate was formed. The specific heat capacity of the metal is 0.057 cal g^{-1}. What is the valency of the metal and its exact relative atomic mass. (2003)

Solution Since the product of relative atomic mass and specific heat capacity is approximate 6.4 cal g^{-1},we have

$$\text{Approximate relative atomic mass of element} = \frac{6.4\,\text{cal g}^{-1}}{0.057\,\text{cal g}^{-1}} = 112.28$$

Let x be the valency of M in the metal sulphate, its reaction with H_2SO_4 may be written as

$$2M + xH_2SO_4 \rightarrow M_2(SO_4)x + xH_2$$

We will have $\dfrac{2M_r + x(96)}{2M_r} = \dfrac{4.51}{2}$ i.e. $\dfrac{2\times112.28 + 96x}{2\times112.28} = \dfrac{4.51}{2}$

Solving for x, we get $x = \dfrac{4.51\times2\times112.28 - 2\times2\times112.28}{2\times96} = 2.94$

Hence, the correct valency of M is 3 and its correct relative atomic mass is

$$M_r = \left(\frac{3}{2.94}\right)(112.28) = 114.57$$

Unsolved Problems

1. A mixture of FeO and Fe_3O_4 when heated in air to a constant mass gains 5 per cent in its mass. Find the composition of the initial mixture.
2. In the analysis of a 0.5 g sample of feldspar, a mixture of NaCl and KCl is obtained which weighs 0.118 g. Subsequent treatment of the mixed chlorides with $AgNO_3$ gives 0.2451 g of AgCl. What are the percentages of Na_2O and K_2O in feldspar?
3. 2.8 g of an ammonium salt when heated with excess of NaOH solution and the gas evolved was passed into 150 cm^3 of 0.25 M H_2SO_4. The residual acid required 63.0 cm^3 of 0.5 M NaOH for complete neutralization. Calculate the percentage of ammonia in the ammonium salt.
4. In a sample of dolomitic limestone containing 5 mass % silica, 3.5 mass % of combined oxides principally of iron and aluminium, and showing 43.0 % loss on ignition, what are the percentages of CaO and MgO, assuming that the loss is entirely due to carbon dioxide from carbonates of calcium and magnesium?
5. A mixture of pure $K_2Cr_2O_7$ and pure $KMnO_4$ weighing 0.561 g was treated with excess of KI in acidic medium. Iodine liberated required 100 mL of 0.15 M of sodium thiosulphate solution for exact oxidation. What is the percentage of each in the mixture?
6. 1.64 g of a mixture of $CaCO_3$ and $MgCO_3$ was dissolved in 50 mL of 0.8 M HCl. The excess of acid required 16 mL of 0.25 M NaOH for neutralization. Calculate the percentage of $CaCO_3$ and $MgCO_3$ in the sample.
7. A solution contains a mixture of sulphuric acid and oxalic acid, 25 mL of the solution requires 35.5 mL of 0.1 M NaOH for neutralization and 23.45 mL of 0.02 M $KMnO_4$ for oxidation. Calculate the molarity of solution with respect to sulphuric acid and oxalic acid.
8. A 0.527 g sample of a mixture containing Na_2CO_3, $NaHCO_3$, and inert impurities is titrated with 0.109 M HCl, requiring 15.7 mL to reach the phenolphthalein end point and a total of 43.8 mL to reach the modified methyl orange end point. What is the per cent each of Na_2CO_3 and $NaHCO_3$ in the mixture?
9. A sample containing amino acid alanine, $CH_3CH(NH_2)COOH$ plus inert matter is analyzed by the Kjeldahl method. A 2.00 g sample is digested, the NH_3 is distilled and collected in 50.0 mL of 0.150 M H_2SO_4, and a volume of 9.0 mL of 0.100 M NaOH is required for back titration. Calculate the per cent alanine in the sample.
10. A 2.50 g sample containing As_2O_5 and Na_2HAsO_3, and inert material is dissolved and the pH is adjusted to neutral with excess $NaHCO_3$. The As(III) is titrated with 0.150 M I_2 solution, requiring 11.3 mL to just reach the end point. Then, the solution (all the arsenic in the +5 state now) is acidified with HCl, excess KI is added,

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and the liberated I_2 is titrated with 0.120 M $Na_2S_2O_3$, requiring 41.2 mL. Calculate the per cent As_2O_5 and Na_2HAsO_3 in the sample?

11. A 0.224 g sample that contained only $BaCl_2$ and KBr required 19.7 mL of 0.100 M $AgNO_3$ to reach the end point. Calculate the per cent of each compound present in the sample?

12. The elemental Se, dispersed in a 5.0 mL sample of detergent for dandruff control, was determined by suspending the sample in a warm, ammoniacal solution that contained 45.0 mL of 0.020 M $AgNO_3$:

$$6Ag^+ + 3Se(s) + 6NH_3 + 3H_2O \rightarrow 2Ag_2Se(s) + Ag_2SeO_3(s) + 6NH_4^+$$

The mixture was next treated with excess nitric acid which dissolved the Ag_2SeO_3 but not the Ag_2Se. The Ag^+ from the Ag_2SeO_3 and the excess $AgNO_3$ consumed 16.74 mL of 0.0137 N KSCN in a Volhard titration. How many milligrams of Se were contained per millilitre of sample?

13. A 0.510 g sample of a pesticide was decomposed by fusion with sodium carbonate and leaching the residue with hot water. The fluoride present in the sample was then precipitated as PbClF by addition of HCl and $Pb(NO_3)_2$. The precipitate was filtered, washed, and dissolved in 5% HNO_3. The Cl^- was precipitated by addition of 50.0 mL of 0.20 M $AgNO_3$. After coating the AgCl with nitrobenzene, the excess Ag^+ was back-titrated with 7.42 mL of 0.176 M NH_4SCN. Calculate the per cent F and the per cent Na_2SeF_6 in the sample.

14. A 0.141 g sample of a phosphorus containing compound was digested in a mixture of HNO_3 and H_2SO_4 which resulted in formation of CO_2, H_2O and H_3PO_4. Addition of ammonium molybdate yielded a solid having the composition $(NH_4)_3PO_4 \cdot 12\ MoO_3$. The precipitate was filtered, washed, and dissolved in 50.0 mL of 0.20 M NaOH :

$$(NH_4)_3PO_4 \cdot 12MoO_3(s) + 26OH^- \rightarrow HPO_4^{2-} + 12MoO_4^{2-} + 14H_2O + 3NH_3(g)$$

After boiling the solution to remove the NH_3, the excess NaOH was titrated with 14.1 mL of 0.174 M HCl. Calculate the per cent of phosphorus in the sample.

15. A 1.21 g sample of commercial KOH, which was contaminated by K_2CO_3, was dissolved in water, and the resulting solution was diluted to 500 mL. A 50.0 mL aliquot of this solution was treated with 40.0 mL of 0.053 M HCl and boiled to remove CO_2. The excess acid consumed 4.74 mL of 0.0498 M NaOH using phenolphthalein as the indicator. An excess of neutral $BaCl_2$ was added to another 50.0 mL aliquot to precipitate carbonate as $BaCO_3$. The solution was then titrated with 28.3 mL of the acid to a phenolphthalein end point. Calculate the per cent KOH, K_2CO_3 and water in the sample, assuming that these are the only compounds present.

16. A 0.646 g sample containing $BaCl_2 \cdot 2H_2O$ was dissolved and an excess of a K_2CrO_4 solution added. After a suitable period, the $BaCrO_4$ was filtered, washed, and redissolved in HCl to convert CrO_4^{2-} to $Cr_2O_7^{2-}$. An excess of KI was added, and the liberated iodine was titrated with 84.7 mL of 0.137 M sodium thiosulphate. Calculate the per cent of $BaCl_2 \cdot 2H_2O$.

17. A 0.517 g sample containing $Ba(SCN)_2$ was dissolved in a bicarbonate solution. 50.0 mL of 0.107 N iodine was added, and the mixture was allowed to stand for 5 min. The solution was then acidified, and the excess I_2 was titrated with 16.3 mL of 0.0965 M sodium thiosulphate. Write a balanced equation for the oxidation of SCN^- by I_2; given that the product obtained from SCN^- are SO_4^{2-} and HCN. Calculate the per cent $Ba(SCN)_2$ in the sample.

18. The chromium in a 1.87 g sample of chromite ($FeO \cdot Cr_2O_3$) was oxidized to the +6 state by fusion with sodium peroxide. The fused mass was treated with water and boiled to destroy the excess peroxide. After acidification, the sample was treated with 50.0 mL of 0.160 M Fe^{2+}. A back titration of 2.97 mL of 0.05 N $K_2Cr_2O_7$ was required to oxidize the excess iron(II). What is the percentage of chromite in the sample?

19. In the presence of fluoride ion, Mn^{2+} can be titrated with MnO_4^-, both reactants being converted to a complex of Mn(III). A 0.545 g sample containing Mn_3O_4 was dissolved, and all manganese was converted to Mn^{2+}. Titration in the presence of fluoride ion consumed 31.1 mL of $KMnO_4$ that was 0.117 N against oxalate. (a) Write a balanced equation for the reaction, assuming that the complex is MnF_4^-. (b) What is the normality of the $KMnO_4$ in the titration? (c) What was the per cent Mn_3O_4 in the sample?

20. The H_2S and SO_2 concentrations of a gas were determined by passage through three absorber solutions connected in series. The first contained an ammoniacal solution of Cd^{2+} to trap the sulphide as CdS. The second contained 10.0 mL of 0.0396 N I_2 to oxidize SO_2 to SO_4^{2-}. The third contained 10.0 mL 0.0345 N thiosulphate solution to retain any I_2 carried over from the second absorber. A 25.0 litre gas sample was passed through the apparatus followed by an additional amount of pure N_2 to sweep the last traces of SO_2

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from the first and second absorber. The soultion from the first absorber was made acidic, and 20.0 mL of the 0.0396 N I_2 were added. The excess I_2 was back-titrated with 7.45 mL of the thiosulphate solution. The solutions in the second and third absorbers were combined and the resultant iodine was titrated with 2.44 mL of the thiosulphate solution. Calculate the concentrations of SO_2 and H_2S in mg/L of the sample.

21. A 1.850 g sample of a mixture of $CuCl_2$ and $CuBr_2$ was dissolved in water and mixed thoroughly with a 1.80 g portion of AgCl. After the reaction, the solid, which now considered a mixture of AgCl and AgBr, was filtered, washed, and dried. Its mass was found to be 2.052 g. What per cent by mass of the original mixture was $CuBr_2$?

22. A mixture of two monoprotic acids, lactic acid ($HC_3H_5O_3$) and caporic acid ($HC_6H_{11}O_2$), was titrated with 0.05 M NaOH. A 0.10 g sample of the mixture required 20.4 mL of the base. What was the mass of each acid in the sample?

23. A mixture of $CaCl_2$ and NaCl weighing 2.385 g was dissolved in water and treated with a solution of sodium oxalate which produced a precipitate of calcium oxalate. The precipitate was filtered from the mixtrue and then dissolved in HCl to give oxalic acid which when titrated against 0.2 M $KMnO_4$ consumed 19.64 mL of the latter. What was percentage by mass of $CaCl_2$ in the original sample?

24. A 3.00 g sample containing Fe_3O_4, Fe_2O_3 and an inert impure substance, is treated with excess KI solution in presence of dilute H_2SO_4. The entire iron is converted into Fe^{2+} along with the liberation of iodine. The resulting solution is diluted to 100 mL. A 20 mL of the diluted solution requires 11.0 mL of 0.5 M $Na_2S_2O_3$ solution to reduce the iodine present. A 50 mL of the diluted solution, after complete extraction of the iodine requires 12.80 mL of 0.25 M $KMnO_4$ solution in dilute H_2SO_4 medium for the oxidation of Fe^{2+}. Calculate the percentages of Fe_2O_3 and Fe_3O_4 in the original sample.

ANSWERS

1. 20.12 mass % FeO and 79.88 mass % Fe_3O_4
2. 3.58 mass % Na_2O and 10.62 mass % K_2O
3. 26.4 mass %
4. 32.37 mass % CaO and 16.08 mass % MgO
5. 43.67 mass % $K_2Cr_2O_7$ and 56.33 mass % $KMnO_4$
6. 52.02 mass % $MgCO_3$ and 47.98 mass % $CaCO_3$
7. 0.0241 M H_2SO_4 and 0.0469 M oxalic acid
8. 34.42% Na_2CO_3 and 21.54% $NaHCO_3$
9. 62.8
10. 3.57 mass % As_2O_5 and 11.52 mass % Na_2HAsO_3
11. 32.4 % $BaCl_2$ and 67.7% KBr
12. 7.94 mg/mL
13. 32.4 % F and 67.9 % Na_2SeF_6
14. 6.38%
15. 69.5 % KOH, 22% K_2CO_3, 8.5% H_2O
16. 84%
17. $SCN^- + 3I_2 + 4H_2O \rightleftharpoons SO_4^{2-} + HCN + 7H^+ + 6I^-$ 15.4 %
18. 15.7%
19. (a) $4\ Mn^{2+} + MnO_4^- + 20\ F^- + 8H^+ \rightleftharpoons 5\ MnF_4^- + 4H_2O$
(b) 0.0936 N
(c) 40.8 %
20. 0.365 H_2S mg/L and 0.311 mg SO_2/L
21. 34.2
22. 0.064 g lactic acid and 0.036 g caporic acid
23. 45.70% $CaCl_2$
24. 34.8% Fe_3O_4 and 49.33% Fe_2O_3

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CHAPTER 2

GASEOUS, LIQUID AND SOLID STATES

SECTION I | GASEOUS STATE

The gaseous state of a matter is characterized by sensitivity of volume change with change in pressure and temperature. This characteristic is due to the larger distance between molecules as compared to their own dimensions. There exists weak intermolecular forces (called van der Waals forces) and the molecules move practically independent of each other with a very large speed (of the order of about 400 m s^{-1}). There exists no boundary surface in the gaseous state and thus molecules try to occupy whole of the volume available for their movement. Experiments and theory have established definite relations between the mass, pressure, volume, density and temperature of the gaseous state. An equation relating pressure, volume, temperature and amount of a gas is known as the *equation of state*.

A few experimentally established expressions relating to the characteristics of gaseous phase are described in the following.

Boyle's Law At constant temperature, the volume of a definite mass of a gas is inversely proportional to its pressure. Mathematically, it is expressed as

$$V \propto 1/p \qquad \text{or} \qquad pV = \text{constant} \tag{1}$$

Charles Law At constant pressure, the volume of a given mass of a gas varies linearly with temperature in degree Celsius. Mathematically, it is written as

$$V_t = a + bt \tag{2}$$

It is found experimentally that $b = \dfrac{V_0/273.15}{1°C}$

where V_0 is the volume of gas at 0 °C. The constant a will also be equal to V_0. With these, Eq. (2) becomes

$$V_t = V_0\left(1+\frac{t/°C}{273.15}\right) = V_0\left(\frac{273.15+t/°C}{273.15}\right) = V_0\left(\frac{T/K}{273.15}\right) = \left(\frac{V_0}{273.15\,K}\right)T \tag{3}$$

where the symbol T stands for kelvin temperature. Equation (2) is also expressed as

$$V_t = (\text{constant})\ T \qquad \text{or} \quad V_t \propto T \tag{4}$$

that is, the volume of a gas is directly proportional to its kelvin temperature.

Gay Lussac's Law An expression similar to Charles law exists between pressure and temperature of the gas at a fixed volume. This law can be expressed as

$$p \propto T \qquad \text{or} \qquad p/T = \text{constant} \tag{5}$$

Equation of State The combination of Boyle's law and Charles law leads to the expression

$$pV = nRT \tag{6}$$

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where n is the amount of gas and R is universal gas constant whose value in different units are given below.

$$\begin{aligned} R &= 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \\ &= 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 8.314 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1} = 8.314 \text{ kPa dm}^3 \text{ K}^{-1} \text{ mol}^{-1} \\ &= 8.314 \text{ MPa cm}^3 \text{ K}^{-1} \text{ mol}^{-1} = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1} \end{aligned}$$

Graham's Law of Diffusion The rate of diffusion of a gas is inversely proportional to the square root of its density or molar mass. Mathematically, it is expressed as

$$r \propto \frac{1}{\sqrt{\rho}} \qquad \text{or} \qquad r \propto \frac{1}{\sqrt{M}}$$

Comparison of the rate of diffusion of two gases under identical conditions provides the relation

$$\frac{r_2}{r_1} = \sqrt{\frac{\rho_1}{\rho_2}} \qquad \text{or} \qquad \frac{r_2}{r_1} = \sqrt{\frac{M_1}{M_2}} \tag{7}$$

If the concentrations (or pressures) of two gases are not identical, the rates of diffusion are related to each other through the expression

$$\frac{r_2}{r_1} = \left(\frac{p_2}{p_1}\right)\left(\frac{M_1}{M_1}\right)^{1/2}$$

Dalton's Law of Partial Pressures The total pressure of a mixture of noninteracting gases is equal to the sum of partial pressures of the constituent gases. Mathematically, it is expressed as

$$p_{\text{total}} = p_1 + p_2 + \cdots \tag{8}$$

By definition, the partial pressure of a gas in a mixture of gases is the pressure which the gas would exert if it is allowed to occupy the whole volume of the mixture at the same temperature. It is also given as

$$p_i = \frac{n_i}{\sum_i n_i} p \tag{9}$$

where n_i is the amount of ith constituent in the mixture of the gases containing total amount equal to $\sum_i n_i$.

The pressure of a gas collected over volatile liquid such as water will be expressed as

$$p_{\text{total}} = p_{\text{air}} + p_{\text{water}} \tag{10}$$

where p_{air} is the partial pressure of dry air and p_{water} is the vapour pressure (i.e. aqueous tension) of water.

Avogadro's Law Equal volume of all gases under identical conditions of temperature and pressure contains equal number of molecules. 1 mol of any gas (assumed to be ideal) occupies 22.414 L of volume under standard conditions (1 atm and 0 °C) and contains atoms/molecules equal to 6.022×10^{23}. This number is represented by the physical quantity known as *Avogadro constant* ($= 6.022 \times 10^{23} \text{ mol}^{-1}$).

Kinetic Theory of Gases

Based on certain postulates regarding the characteristics of an ideal gas, kinetic theory of gases provides a theoretical expression of equation of state of an ideal gas. The postulates are

1. All gases are made up of tiny spherical particles called molecules. For a given gas, the size, shape and mass of molecules are completely identical.
2. The volume occupied by the molecules is negligible in comparison to the total volume of the gas.
3. There exists no forces of attraction and repulsion amongst the molecules of a gas.
4. The molecules are perfectly elastic. Thus, no loss of energy occurs during the molecular collisions.
5. The motions of molecules are completely random.
6. The pressure of a gas is due to the collision of molecules with sides of the vessel.
7. Newton's laws of the motion hold good for the movement of molecules.
8. At any instant, a given molecule may have energy ranging from a small value to a large value, but the average kinetic energy of molecules is directly proportional to kelvin temperature.

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The equation obtained on the basis of above postulates is known as *kinetic gas equation* and is expressed as

$$pV = \frac{1}{3} mN\overline{u^2}$$

where m is the mass of each molecule, N is the number of molecules and $\overline{u^2}$ is the mean square speed defined as

$$\overline{u^2} = \frac{u_1^2 + u_2^2 + \cdots + u_N^2}{N}$$

The various gasesous laws (such as Boyle, Charles, etc.) can be derived from the kinetic gas equation.

Expressions of Some Useful Physical Quantities

The expressions of some useful physical quantities are given in the following.

Root Mean Square Speed This speed is defined as $\sqrt{\overline{u^2}} = \left(\frac{u_1^2 + u_2^2 + \cdots + u_N^2}{N}\right)^{1/2}$

and is given by the expression

$$\sqrt{\overline{u^2}} = \sqrt{\frac{3RT}{M}}$$

An alternative form of the above equation can be derived. For an ideal gas, $RT = pV/n$. With this, the above expression becomes

$$\sqrt{\overline{u^2}} = \sqrt{\frac{3pV}{nM}} = \sqrt{\frac{3p}{m/V}} = \sqrt{\frac{3p}{\rho}}$$

where m is the mass of the given quantity of the gas and ρ is the density of the gas. It may be mentioned that the root mean square speed depends only on the temperature of the gas, i.e. it is independent of pressure and volume variations at constant temperature, since the product pV and the quantity p/ρ are constant at a given temperature.

Average Speed This speed is defined as $\bar{u} = \frac{u_1 + u_2 + \cdots + u_N}{N}$

and is given by the expression

$$\bar{u} = \sqrt{\frac{8RT}{\pi M}}$$

Most Probable Speed This is the the speed corresponding to the maximum fraction of the molecules of a gas. Its expression is

$$u_{mp} = \sqrt{\frac{2RT}{M}}$$

Comparing the three speeds listed above, we find that

$$u_{rms} : u_{av} : u_{mp} :: \sqrt{3} : \sqrt{8/\pi} : \sqrt{2} \qquad \text{that is} \qquad u_{rms} > u_{av} > u_{mp}$$

Average Kinetic Energy The average kinetic energy of gaseous molecules is defined as $(1/2)m\overline{u^2}$. From the kinetic gas equation, we find that

$$pV = \frac{1}{3} mN\overline{u^2} = \frac{2}{3} N\left(\frac{1}{2} m\overline{u^2}\right) \qquad \text{or} \qquad \overline{\text{KE}} = \frac{1}{2} m\overline{u^2} = \frac{3pV}{2N}$$

For one mole of a gas, $V = V_m$, $N = N_A$. Hence,

$$\overline{\text{KE}} = \frac{3pV_m}{2N_A} = \frac{3RT}{2N_A} = \frac{3}{2} kT$$

where $k = R/N_A$ and is known as *Boltzmann constant.*

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Van Der Waals Equation of State

All the gaseous laws mentioned above are strictly valid for an ideal gas under all conditions of temperature and pressure. Real gases show deviations from these gaseous laws, especially when temperature is low and pressure is high. Real gases follow ideal gas laws under the condition of low pressure and high temperature. Van der Waals pointed out that the deviations shown by real gases are due to the following two facts.

1. The volume occupied by the molecules is not negligible in comparison to the total volume of the gas.
2. There exist forces of attraction between the molecules.

Van der Waals systematically corrected the ideal gas equation in the light of the above two facts. The corrected equation is

$$\left(p + n^2 \frac{a}{V^2}\right)(V - nb) = nRT$$

where a and b are two constants, known as van der Waals constants. The units of a and b are L^2 atm mol^{-2} and L mol^{-1}, respectively. In SI units, a and b are expressed in Pa m^6 mol^{-2} and m^3 mol^{-1}, respectively. The constants a and b are characteristic of the given gas. The constant a is a measure of the forces of attraction between gaseous molecules and the constant b is a measure of effective volume occupied by the molecules of 1 mol of a gas. The numerical value of b is four times the actual volume occupied by the molecules in 1 mole of the gas, i.e.

$$b = N_A\,[4(4\pi r^3/3)]$$

where r is the radius of molecule of the gas.

Van der Waals equation accounts for the behaviour of real gases. At low pressures, the gas equation can be written as

$$\left(p + \frac{a}{V_m^2}\right) V_m = RT \qquad \text{or} \qquad Z = \frac{pV_m}{RT} = 1 - \frac{a}{V_m RT}$$

where Z is known as *compression factor*. Its value at low pressures is less than one and it decreases with increase in pressure. For a given value of V_m, Z has more value at higher temperature.

At high pressures, the gas equation can be written as

$$p(V_m - b) = RT \qquad \text{or} \qquad Z = \frac{pV_m}{RT} = 1 + \frac{pb}{RT}$$

Here, the compression factor increases with increase in pressure at constant temperature and it decreases with increase in temperature at constant pressure. For the gases H_2 and He, the above behaviour is observed even at low pressures, since for these gases, the value of a is extremely small.

Reduction of Van Der Waals Gas to Virial Equation

For one mole of a gas, the virial equation of state has the following form

$$Z = \frac{pV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \cdots$$

where B, C, ... are known as second, third, etc., virial coefficients.

For one mole of a gas, the van der Waals equation of state is

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT \quad \text{or} \quad p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

or
$$Z = \frac{pV_m}{RT} = \frac{V_m}{V_m - b} - \frac{a}{V_m RT} = \left(1 - \frac{b}{V_m}\right)^{-1} - \frac{a}{V_m RT} = \left[1 + \frac{b}{V_m} + \left(\frac{b}{V_m}\right)^2 + \cdots\right] - \frac{a}{V_m RT}$$

$$= 1 + \left(b - \frac{a}{RT}\right)\frac{1}{V_m} + \left(\frac{b}{V_m}\right)^2 + \ldots$$

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The second virial coefficient is given by $B = b - \frac{a}{RT}$

At Boyle temperature, the second virial coefficient is zero. Hence, $T_B = \frac{a}{Rb}$

At Boyle temperature, the real gas behaves ideally over a wide range of pressure. This is due to the fact that the effects of size of molecules and intermolecular forces roughly compensate each other.

Some Definitions

Critical temperature (T_c) It is the maximum temperature at which a gas can be liquefied, i.e., the temperature above which a liquid cannot exist.

Critical pressure (p_c) It is the minimum pressure required to cause liquefaction at critical temperature.

Critical volume (V_c) It is the volume occupied by one mole of a gas at critical temperature and critical pressure.

Critical state A gas having critical temperature, critical pressure and critical volume is said to be in the critical state.

For a van der Waals gas, we have

$$T_c = 8a/(27Rb); \quad p_c = a/(27b^2); \quad V_c = 3b; \quad \text{and} \quad p_cV_c/RT_c = 3/8$$

Inversion Temperature (T_i) The temperature at which a real gas does not exhibit cooling or heating when it is passed through a throttling device. If the temperature of the gas is lower than its inversion temperature, it exhibits cooling. At higher temperature, it exhibits heating. For a van der Waals gas, $T_i = 2a/Rb$.

Heat Capacity of Gases Heat capacity of a system is defined as the amount of heat required to increase its temperature by 1 degree Celsius. For a gaseous system, two heat capacities may be defined. These are (i) heat capacity at constant volume (C_V) and (ii) heat capacity at constant pressure (C_p). The molar heat capacity is defined for 1 mol of the substance. One can write

$$C_{V,m} = \text{contribution from (translational + rotational + vibrational) modes}$$

At low temperatures, vibrational modes do not contribute towards heat capacity, its contribution increases with increase in temperature. It is only at higher temperature, it is effective in contributing its full share.

The contributions towards heat capacity are as follows.

$$C_{V,m} = \text{(Translational + Rotational + Vibrational) contributions}$$

Monatomic Gas $$C_{V,m} = \frac{3}{2}R + 0 + 0 = \frac{3}{2}R$$

Polyatomic Gas $$\textit{Linear } C_{V,m} = \frac{3}{2}R + R + (3N-5)R$$

$$\textit{Non-linear } C_{V,m} = \frac{3}{2}R + R + (3N-6)R$$

where N is the number of atoms in the molecule of the gas.

For an ideal gas, $C_{p,m} = C_{V,m} - R$

The ratio of $C_{p,m}$ and $C_{V,m}$ is represented by the symbol γ. We have

Monatomic gas $$\gamma = \frac{C_{p,m}}{C_{V,m}} = \frac{(5/2)R}{(3/2)R} = \frac{5}{3} = 1.667$$

$$\textit{Diatomic gas } \gamma = \frac{(9/2)R}{(7/2)R} = \frac{9}{7} = 1.286$$

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Triatomic gas, Linear $\gamma = \dfrac{(15/2)R}{(13/2)R} = \dfrac{15}{13} \simeq 1.154$

Nonlinear $\gamma = \dfrac{7R}{6R} = \dfrac{7}{6} = 1.167$

The value of γ decreases with increase in atomicity of the molecule.

Mean Free Path The mean free path is the average distance travelled by a molecule between two succesive collisions. it is given by the expression $\lambda = 1/\sqrt{2}\,\pi\,\sigma^2 N^*$, where σ is molecular diameter and N^* is the number of molecules per unit volume of the gas.

Viscosity of Gases The gases also exhibit viscosity due to the migration of momentum from one layer to nearby layers. It is given by the expression $\eta = (m\,k\,T)^{1/2}\,\pi^{3/2}\,\sigma^2$. The viscosity gases unlike liquids increases with increase in temperature.

Straight Objective Type

Gaseous Laws

1. Equal masses 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) (1/3) (273/298) (1981)

2. Equal masses of ethane 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) 1 : 1 (c) 1 : 16 (d) 15 : 16 (1993)

3. Which of the following expressions correctly represents the variation of density of an ideal gas with change in temperature from T_1 to T_2?
(a) $\rho_2 = \rho_1 (T_1\,p_2/T_2\,p_1)$ (b) $\rho_2 = \rho_1 (T_1\,p_1/T_2\,p_2)$
(c) $\rho_2 = \rho_1 (T_2\,p_2/T_1\,p_1)$ (d) $\rho_2 = \rho_1 (T_2\,p_1/T_1\,p_2)$

4. The density of neon will be highest at
(a) STP (b) 0 °C, 2 atm (c) 273 °C, 1 atm (d) 273 °C, 2 atm

5. The volume of a gas
(a) is directly proportional to temperature expressed in Celsius scale
(b) is zero at 0 °C
(c) is inversely proportional to kelvin temperature
(d) changes by $V_0/273.15$ for every 1 °C rise in temperature, where V_0 is the temperature at 0 °C

6. For a fixed mass of a gas,
(a) the plot of volume versus Celsius temperature is linear with zero intercept
(b) the plot of volume versus kelvin temperature is linear with a negative slope
(c) the plot of V/T versus T is linear with a positive slope
(d) the plot of V/T versus T is linear with zero slope

7. The dimensionally correct expression for the conversion of kelvin temperature to Celsius temperature is
(a) $t = T + 273.15$ (b) $t = T - 273.15$
(c) $t/\,°C = T/K + 273.15$ (d) $t/\,°C = T/K - 273.15$

8. Which of the following is the value of R expressed in SI units?
(a) 8.314 J mol^{-1} (b) 8.314 J K^{-1} mol^{-1}
(c) 8.314 J K^{-1} (d) 8.314×10^7 ergs K^{-1} mol^{-1}

9. The value of the Boltzmann constant is
(a) 6.023×10^{23} mol^{-1} (b) 1.36×10^{-23} J K^{-1} $molecule^{-1}$
(c) 1.36×10^{-23} J K^{-1} mol^{-1} (d) 1.36×10^{-23} J K^{-1}

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10. The value of Avogadro constant is
(a) 6.022×10^{23} (b) 6.022×10^{13} (c) 6.022×10^{23} mol^{-1} (d) 6.022×10^{13} mol^{-1}

11. At which of the following four conditions, the density of nitrogen will be largest?
(a) STP (b) 273 K and 2 atm (c) 546 K and 1 atm (d) 546 K and 2 atm

12. The temperature of a given mass of a gas is increased from 19 °C to 20 °C at constant pressure. The volume V of the gas is increased
(a) to $V(20/19)$ (b) by 1/273.15 of its volume at 0 °C.
(c) by 1/273.15 of its volume at 0 K. (d) by a factor of 1/273.15.

13. At a given temperature if $\rho(X) = 3\ \rho(Y)$ and $M(Y) = 2\ M(X)$, where ρ and M, respectively, stand for density and molar mass of the gases X and Y, then the ratio of their pressures would be
(a) $p(X)/p(Y) = 1/4$ (b) $p(X)/p(Y) = 4$ (c) $p(X)/p(Y) = 6$ (d) $p(X)/p(Y) = 1/6$

14. The compression factor for an ideal gas is
(a) 1.5 (b) 1.0 (c) 2.0 (d) ∞ (1997)

15. The degree of dissociation of the reaction $AB_2 \rightleftharpoons A + B_2$ is found to be 0.4 at 400 K and 1 atm pressure. If the molar mass of AB_2 is 200 g mol^{-1}, the density of the system at equilibrium would be
(a) 4.35 g dm^{-3} (b) 4.85 g dm^{-3} (c) 5.35 g dm^{-3} (d) 5.85 g dm^{-3}

16. The ratio of densities of a gas at two conditions of temperature and pressure is given by

(a) $\frac{\rho_2}{\rho_1} = \left(\frac{p_2}{p_1}\right)\left(\frac{T_2}{T_1}\right)$ (b) $\frac{\rho_2}{\rho_1} = \left(\frac{p_2}{p_1}\right)\left(\frac{T_1}{T_2}\right)$ (c) $\frac{\rho_2}{\rho_1} = \left(\frac{p_1}{p_2}\right)\left(\frac{T_1}{T_2}\right)$ (d) $\frac{\rho_2}{\rho_1} = \left(\frac{p_1}{p_2}\right)\left(\frac{T_2}{T_1}\right)$

17. A gaseous mixture of helium and oxygen is found to have a density of 0.5 g dm^{-3} at 300 K and 760 Torr. The mass per cent of helium in the mixture is about
(a) 22% (b) 35% (c) 40% (d) 50%

18. The density of a gas is 1.5 g L^{-1} at STP. Its density at 27 °C and 1000 Torr would be
(a) 1.8 g L^{-1} (b) 2.8 g L^{-1} (c) 3.8 g L^{-1} (d) 4.8 g L^{-1}

19. The density of a gas at STP is 1.5 g L^{-1}. Pressure remaining constant, the temperature at which its density is 0.5 g L^{-1} is
(a) 273 °C (b) 546 °C (c) 819 °C (d) 1000 °C

20. A mixture of $NH_3(g)$ and $N_2H_4(g)$ is placed in a sealed container at 300 K. The pressure within the container is 0.6 atm. The container is heated to 1000 K where the two gases undergo decomposition reactions

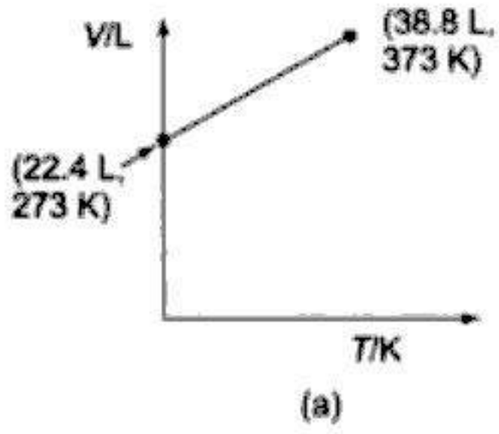
$$2NH_3(g) \rightarrow N_2(g) + 3H_2(g) \quad \text{and} \quad N_2H_4(g) \rightarrow N_2(g) + 2H_2(g).$$

The pressure of the container at this stage becomes 4.8 atm. The mole per cent of $NH_3(g)$ in the original mixture was
(a) 40 (b) 50 (c) 60 (d) 70

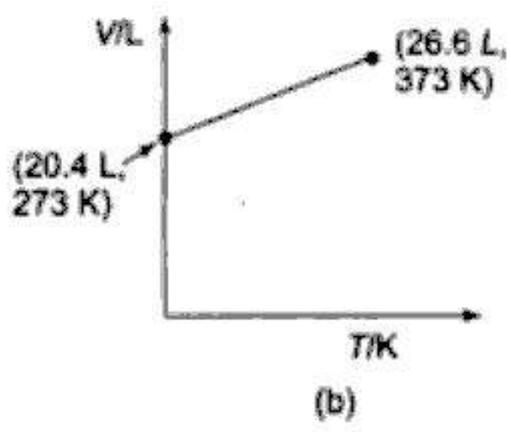
21. The compression factor of an ideal gas.
(a) increases with increase in temperature.
(b) decreases with increase in temperature.
(c) remains constant with change in temperature.
(d) increases with change in temperature in the lower temperature range while it decreases in the higher temperature range.

22. 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}, then the volume occupied by water molecules in 1 litre of steam at this temperature is
(a) 6 cm^3 (b) 60 cm^3 (c) 0.6 cm^3 (d) 0.06 cm^3 (2000)

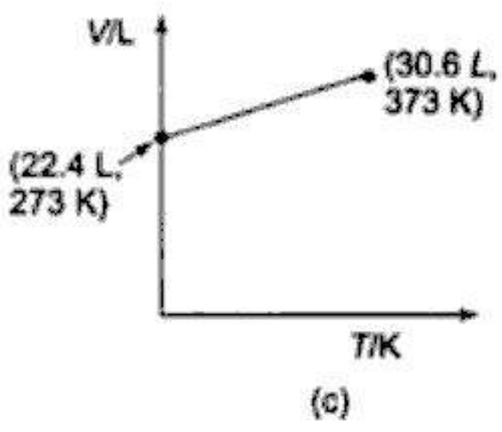
23. Which of the following volume (V)–temperature (T) plots represents the behaviour of one mole of an ideal gas at one atmospheric pressure?



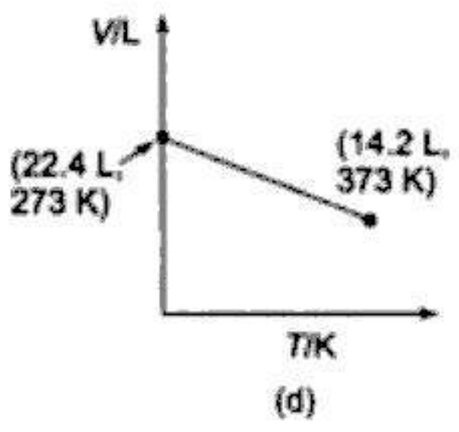
(a)



(b)



(c)



(d)

(2002)

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Diffusion of Gases

24. Rate of diffusion of a gas is
(a) directly proportional to its density
(b) directly proportional to its molar mass
(c) directly proportional to the square root of its molar mass
(d) inversely proportional to the square root of its molar mass (1985)

25. A bottle of dry ammonia and a bottle of dry hydrogen chloride connected through a long tube are opened simultaneously at both ends, the white ammounium chloride ring first formed will be
(a) at the centre of the tube
(b) near the hydrogen chloride bottle
(c) near the ammonia bottle
(d) throughout the length of the tube.

26. The rate of diffusion of methane at a given temperature is twice that of a gas X. The molar mass of X is
(a) 64.0 g mol^{-1} (b) 32.0 g mol^{-1} (c) 4.0 g mol^{-1} (d) 8.0 g mol^{-1} (1990)

27. Three grams of helium diffuses from a container in 15 min. The mass of sulphur dioxide diffusing from the same container over the same time interval will be
(a) 3 g (b) 6 g (c) 9 g (d) 12 g

28. The volume X 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 specified gas under identical conditions is
(a) 10 seconds : He (b) 20 seconds : O_2 (c) 25 seconds : CO (d) 55 seconds : CO_2 (1996)

29. 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) $(p_A/p_B)\,(M_A/M_B)^{1/2}$ (b) $(M_A/M_B)\,(p_A/p_B)^{1/2}$ (c) $(p_A/p_B)\,(M_B/M_A)^{1/2}$ (d) $(M_AM_B)\,(p_B/p_A)^{1/2}$ (1998)

30. The degree of dissociation (α) of the reaction $A_2(g) \rightleftharpoons 2A(g)$ in terms of rate of diffusion (r_{mix}) of equilibrium mixture and that of a reference gas X is given by

(a) $\alpha = \left(\frac{M_{A_2}}{M_X}\right)\left(\frac{r_{mix}}{r_X}\right)^2 - 1$ (b) $\alpha = \left(\frac{M_{A_2}}{M_X}\right)\left(\frac{r_X}{r_{mix}}\right)^2 - 1$

(c) $\alpha = \left(\frac{M_X}{M_{A_2}}\right)\left(\frac{r_X}{r_{mix}}\right)^2 - 1$ (d) $\alpha = \left(\frac{M_X}{M_{A_2}}\right)\left(\frac{r_{mix}}{r_X}\right)^2 - 1$

where M stands for the respective molar masses.

31. A 4:1 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. The composition of the mixture, effusing out initially is about
(a) He : CH_4 :: 1 : 1 (b) He : CH_4 :: 2 : 1 (c) He : CH_4 :: 4 : 1 (d) He : CH_4 :: 8 : 1

32. If methane and helium are allowed to diffuse out of a container under identical conditions of temperature and pressure, the ratio of rate of diffusion of methane to helium is
(a) 4.0 (b) 2.0 (c) 1.0 (d) 0.5

Kinetic Theory of Gases

33. When an ideal gas undergoes unrestrained expansion, no cooling occurs because the molecules
(a) are above the inversion temperature
(b) exert no attractive forces on each other
(c) do work equal to the loss in kinetic energy
(d) collide without loss of energy

34. According to the kinetic theory of gases, for a diatomic molecule
(a) the pressure exerted by the gas is proportional to the mean speed of the molecules
(b) the pressure exerted by the gas is proportional to the root mean square speed of the molecules
(c) the root mean square speed of the molecules is inversely proportional to the temperature
(d) the mean translational kinetic energy of the molecules is proportional to the absolute temperature (1991)

35. At constant volume, for a fixed amount of a gas the pressure of the gas increases with rise of temperature due to
(a) increase in average molecular speed
(b) increased rate of collision amongst molecules
(c) increase in molecular attraction
(d) decrease in mean free path

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36. Which of the following expressions does not represent an ideal gas?

(a) $p = nRT/V$ (b) $p = \rho RT/M$ (c) $pV = \frac{1}{3} m N \overline{u^2}$ (d) $p = \frac{2}{3} N(\text{KE})$

37. Which of the following statements is not a postulate of the kinetic theory of gases?

(a) Gases are made up of tiny particles called molecules
(b) All molecules move with the same speed and have random motion
(c) The molecules are perfectly elastic
(d) There exists no forces of attraction and repulsion amongst gaseous molecules

38. The value of $(pV_m)_{p \to 0}$ at 0 °C for an ideal gas is

(a) 22.414 bar dm^3 (b) 22.71 bar dm^3 (c) 23.414 bar dm^3 (d) 25.0 bar dm^3

39. Which of the following expressions is correct for an ideal gas?

(a) $p = \frac{2}{3}\frac{V}{N}\bar{E}$ (b) $p = \frac{3}{2}\frac{V}{N}\bar{E}$ (c) $p = \frac{2}{3}\frac{N}{V}\bar{E}$ (d) $p = \frac{3}{2}\frac{N}{V}\bar{E}$

Speeds of Gaseous Molecules

40. The ratio of root mean square speed to average speed of a gas molecule at a particluar temperature is

(a) 1.086 : 1 (b) 1 : 1.086 (c) 2 : 1.086 (d) 1.086 : 2 (1981)

41. The average speed of an ideal gas molecules at 27 °C is 0.3 m s^{-1}. The average speed at 927 °C will be

(a) 0.6 m s^{-1} (b) 0.3 m s^{-1} (c) 0.9 m s^{-1} (d) 3.0 m s^{-1} (1986)

42. The expression of root mean square speed of molecules of a gas is given as

(a) $u_{rms} = \sqrt{\frac{3RT}{M}}$ (b) $u_{rms} = \sqrt{\frac{3RT}{m}}$ (c) $u_{rms} = \sqrt{\frac{3kT}{M}}$ (d) $u_{rms} = \sqrt{\frac{8RT}{\pi M}}$

43. The expression of average speed of molecules of a gas is given as

(a) $u_{av} = \sqrt{\frac{8RT}{\pi m}}$ (b) $u_{av} = \sqrt{\frac{8RT}{\pi M}}$ (c) $u_{av} = \sqrt{\frac{8kT}{\pi M}}$ (d) $u_{av} = \sqrt{\frac{8RT}{M}}$

44. The expression of most probable speed of molecules of a gas is given as

(a) $u_{mp} = \sqrt{\frac{2RT}{M}}$ (b) $u_{mp} = \sqrt{\frac{3RT}{M}}$ (c) $u_{mp} = \sqrt{\frac{8RT}{\pi M}}$ (d) $u_{mp} = \sqrt{\frac{8RT}{M}}$

45. For a given gas, which of the following relationships is correct at a given temperature?

(a) $u_{rms} > u_{av} > u_{mp}$ (b) $u_{rms} < u_{av} < u_{mp}$ (c) $u_{rms} > u_{av} < u_{mp}$ (d) $u_{rms} < u_{av} > u_{mp}$

46. The relative ratio of $u_{rms} : u_{av} : u_{mp}$ at a given temperature is

(a) $\sqrt{3} : \sqrt{56/22} : \sqrt{2}$ (b) $\sqrt{56/22} : \sqrt{2} : \sqrt{3}$ (c) $\sqrt{3} : \sqrt{2} : \sqrt{56/22}$ (d) $\sqrt{2} : \sqrt{56/22} : \sqrt{3}$

47. Which of the following gases will have maximum average speed at a given temperature?

(a) Nitrogen (b) Oxygen (c) Helium (d) Carbon dioxide

48. The most probable speed of an ideal gaseous molecules at 27 °C is 0.3 m s^{-1}. The average speed at 927 °C would be

(a) 0.3 m s^{-1} (b) 0.6 m s^{-1} (c) 0.9 m s^{-1} (d) 1.2 m s^{-1}

49. The root mean square speeds of gaseous molecules changes with change in the

(a) temperature of the gas (b) pressure of the gas
(c) volume of the gas (d) density of the gas

50. The root mean square speed of a gaseous molecules is given as $u_{rms} = \sqrt{3p/\rho}$. This shows that at a given temperature

(a) $u_{rms} \propto \sqrt{p}$ (b) $u_{rms} \propto \sqrt{1/\rho}$ (c) $u_{rms} \propto \sqrt{pV_m}$ (d) $u_{rms} \propto \sqrt{p/V_m}$

51. Which of the following is expected to possess the largest root mean square speed at the same temperature?

(a) H_2S (b) NH_3 (c) SO_2 (d) CO_2

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52. The temperature at which root mean square speed of oxygen gas becomes equal to that of SO_2 at 327 °C is
(a) 163.5 °C (b) 654 °C (c) 27 °C (d) 327 °C

53. The ratio between the root means square speed of H_2 at 50 K and that of O_2 at 800 K is
(a) 4 (b) 2 (c) 1 (d) 1/4 (1996)

54. The rms speed of hydrogen is $\sqrt{7}$ times the rms speed of nitrogen. If T is the temperature of the gas, then
(a) $T(H_2) = T(N_2)$ (b) $T(H_2) > T(N_2)$ (c) $T(H_2) < T(N_2)$ (d) $T(H_2) = \sqrt{7}\,T(N_2)$ (2000)

55. The root mean square speed of a gas at 300 K is 490 m s^{-1}. Its average speed at 300 K would be
(a) 451.3 m s^{-1} (b) 475.2 m s^{-1} (c) 502.0 m s^{-1} (d) 520.1 m s^{-1}

56. The average speed of a gas at 300 K is 475 m s^{-1}. Its most probable speed would be
(a) 520.1 m s^{-1} (b) 501.0 m s^{-1} (c) 450 m s^{-1} (d) 420.9 m s^{-1}

57. The temperature at which the average speed of oxygen becomes equal to that of methane at 327 °C is
(a) 627 °C (b) 927 °C (c) 1200 °C (d) 654 °C

58. Helium atom is two times heavier than a hydrogen molecule. At 298 K, the average kinetic energy of a helium atom is
(a) two times that of a hydrogen molecule (b) same as that of a hydrogen molecule
(c) four times that of a hydrogen molecule (d) half that of a hydrogen molecule (1982)

59. Which of the following expressions correctly represents the relationship between the average kinetic energy of CO and N_2 molecules at the same temperature?
(a) $\bar{E}(CO) > \bar{E}(N_2)$
(b) $\bar{E}(CO) < \bar{E}(N_2)$
(c) $\bar{E}(CO) = \bar{E}(N_2)$
(d) Cannot be predicted unless volumes of the gases are given

60. The total energy of a given mass of a gas at a given temperature depends on its
(a) pressure (b) volume (c) density (d) temperature

61. The average kinetic energy of gaseous molecules is
(a) $(1/2)kT$ (b) kT (c) $(3/2)kT$ (d) $(3/2)RT$

62. A molecule of SO_2 is two times heavier than O_2 molecule. At 298 K, the average kinetic energy of SO_2 molecules is
(a) two times that of O_2 molecules (b) half that of O_2 molecules
(c) four times that of O_2 molecules (d) same as that of O_2 molecules

63. The root mean square speed of gaseous molecules (molar mass : M) in terms of their molar kinetic energy (E) is
(a) $u_{rms} = \sqrt{3E/2M}$ (b) $u_{rms} = \sqrt{2E/3M}$ (c) $u_{rms} = \sqrt{2E/M}$ (d) $u_{rms} = \sqrt{E/3M}$ (2004)

64. The root mean square speed of an ideal gas at constant pressure varies (ρ) with density as
(a) ρ^2 (b) ρ (c) $\sqrt{\rho}$ (d) $1/\sqrt{\rho}$ (2001)

Real Gases

65. The temperature at which a real gas obeys the ideal gas laws over a wide range of pressure is
(a) critical temperature (b) Boyle temperature
(c) inversion temperature (d) reduced temperature (1981)

66. In van der Waals equation of state for a nonideal gas the term that accounts for intermolecular forces is
(a) $(V - b)$ (b) $\left(p + \frac{a}{V^2}\right)$ (c) RT (d) $(RT)^{-1}$ (1988)

67. The values of van der Waals constant a for the gases O_2, N_2, NH_3 and CH_4 are 1.360, 1.390, 4.170 and 2.253 L^2 atm mol^{-2}, respectively. The gas which can most easily be liquefied is
(a) O_2 (b) N_2 (c) NH_3 (d) CH_4 (1989)

68. The van der Waals equation for a real gas is
(a) $(p + a/V^2)(V - b) = nRT$ (b) $(p + a/V^2)(V - nb) = nRT$
(c) $(p + na/V^2)(V - nb) = nRT$ (d) $(p + n^2 a/V^2)(V - nb) = nRT$

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69. The unit of van der Waals constant a is
(a) atm (b) atm L^2 (c) atm L^2 mol^{-1} (d) atm L^2 mol^{-2}

70. The unit of van der Waals constant b is
(a) cm^3 (b) cm^3 mol^{-1} (c) cm^3 mol^{-2} (d) $(cm^3\ mol^{-1})^2$

71. In van der Waals equation of state for a nonideal gas, the term that accounts for the molecular volume is
(a) $V - b$ (b) $p + a/V_m^2$ (c) RT (d) $V - nb$

72. The van der Waals constant b is equal to
(a) the molecular volume of 1 mol of the gas
(b) two times the molecular volume of 1 mol of the gas
(c) three times the molecular volume of 1 mol of the gas
(d) four times the molecular volume of 1 mol of the gas

73. The values of van der Waals constant a for the gases O_2, N_2, CO_2 and CH_4 are 1.360, 1.390, 3.640 and 2.253 L^2 atm mol^{-2}, respectively. The gas which can be most easily be liquefied is
(a) O_2 (b) N_2 (c) CO_2 (d) CH_4

74. The temperature above which a real gas cannot be liquefied is known as
(a) critical temperature (b) consolute temperature
(c) Boyle temperature (d) inversion temperature.

75. The behaviour of a real gas is usually depicted by plotting compression factor Z $(= pV_m/RT = V_{real}/V_{ideal})$ versus p at a constant temperature. At low temperature and low pressure, Z is usually less than one. This fact can be explained by van der Waals equation when
(a) the constant a is negligible and not b (b) the constant b is negligible and not a
(c) both the constants a and b are negligible (d) both the constants a and b are not negligible

76. The behaviour of a real gas is usually depicted by plotting compression factor Z $(= pV_m/RT = V_{real}/V_{ideal})$ versus p at a constant temperature. At high temperature and high pressure, Z is usually more than one. This fact can be explained by van der Waals equation when
(a) the constant a is negligible and not b (b) the constant b is negligible and not a
(c) both the constants a and b are negligible (d) both the constants a and b are not negligible

77. At Boyle temperature, the value of compression factor Z $(= pV_m/RT = V_{real}/V_{ideal})$ has a value of one over a wide range of pressure. This is due to the fact that in the van der Waals equation
(a) the constant a is negligible and not b (b) the constant b is negligible and not a
(c) both the constants a and b are negligible (d) the effect produced due to the molecular attraction compensates the effect produced due to the molecular volume

78. A real gas is expected to bahave more or less ideally 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 (1999)

79. A real gas is expected to be behave nonideally 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

80. The most favourable conditions for a real gas to liquefy are
(a) high temperature and low pressure (B) high temperature and high pressure
(c) low temperature and low pressure (d) low temperature and high pressure

81. The compression factor 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 (2000)

82. The unit of second virial coefficient is
(a) m^3 (b) m^3 mol^{-1} (c) Pa (d) Pa m^3

83. At Boyle temperature, the compression factor of a gas is
(a) equal to one over wide range of low pressure
(b) equal to one over wide range of high pressure
(c) more than one and it decreases
(d) less than one and it increases with increase in pressure.

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84. Which of the following expressions between the van der Waals constant b and the radius r of spherical molecules is correct?

(a) $b = \left(\frac{4}{3}\pi r^3\right) N_A$ (b) $b = 2\left(\frac{4}{3}\pi r^3\right) N_A$ (c) $b = 3\left(\frac{4}{3}\pi r^3\right) N_A$ (d) $b = 4\left(\frac{4}{3}\pi r^3\right) N_A$

85. The value of compression factor of a van der Waals gas at critical point is
(a) 8/27 (b) 27/8 (c) 3/8 (d) 8/3

86. Which of the following statements is correct?
(a) Molecular attractions make the pressure of a van der Waals gas smaller than that of an ideal gas.
(b) Molecular attractions makes the pressure of a van der waals gas larger than that of an ideal gas
(c) Molecular size makes the pressure of a van der Waals gas smaller than that of an ideal gas
(d) Molecular attractions and molecular size have no significant effects on the pressure of a van der Waals gas.

87. Which of the following statements is correct?
(a) Molecular size has an effect of increasing the value of volume of a van der Waals gas as compared to that of an ideal gas
(b) Molecular size has an effect of decreasing the value of volume of van der waals gas as compared to that of an ideal gas
(c) Molecular size has no effect on the volume of a van der Waals gas as compared to an ideal gas
(d) Molecular size effects on the volume of a van der Waals gas depends on its temperature and is independent of nature of the gas

88. Negative deviation from ideal behaviour is due to the fact that
(a) there exist molecular interactions and $pV/nRT > 1$
(b) there exist molecular interactions and $pV/nRT < 1$
(c) atoms have finite size and $pV/nRT > 1$
(d) atoms have finite size and $pV/nRT < 1$ (2003)

89. The term that corrects for the attractive forces present in a real gas in the van der Waals equation is
(a) nb (b) n^2a/V^2 (c) $-n^2a/V^2$ (d) $-nb$ (2009)

90. Positive deviation from ideal behaviour is due to the fact that
(a) molecular attractions play dominant role
(b) molecular volume plays dominant role
(c) both molecular attractions and volume play dominant role
(d) molecular attractions cancel the effect of molecular volume

Additional Problems

91. A gas undergoing expansion through a porous plug exhibits heating if its temperature is
(a) more than inversion temperature (b) less than inversion temperature
(c) more than critical temperature (d) more than Boyle temperature

92. A gas undergoing expansion through a porous plug exhibits cooling if its temperature is
(a) more than inversion temperature (b) less than inversion temperature
(c) less than critical temperature (d) less than Boyle temperature

93. A gas undergoing expansion through a porous plug exhibits neither heating nor cooling if its temperature is equal to
(a) Boyle temperature (b) critical temperature
(c) inversion temperature (d) consolute temperature

94. For a monatomic gas,
(a) molar heat capacity at constant volume, $C_{V,m} = \frac{3}{2} R$
(b) molar heat capacity at constant pressure $C_{p,m} = \frac{3}{2} R$
(c) the ratio of $C_{p,m}$ and $C_{V,m}$ is 3/5
(d) the difference between $C_{p,m}$ and $C_{V,m}$ is $2R$

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95. The critical temperature of water is higher than that of O_2 because the H_2O molecule has
(a) few electrons than O_2 (b) two covalent bonds
(c) V-shape (d) dipole moment (1997)

96. For a diatomic gas at low temperatures
(a) molar heat capacity at constant volume, $C_{V,m} < 3.5R$
(b) molar heat capacity at constant pressure, $C_{p,m} = 4.5R$
(c) the ratio of $C_{p,m}$ and $C_{V,m}$ is 7/9
(d) the difference between $C_{p,m}$ and $C_{V,m}$ is $2R$

97. The mean for path of a gas is given by $\lambda = 1/(\sqrt{2}\,\pi\,\sigma^2\,N^*)$ where σ is the molecular diameter and N^* is the number of molecules per unit volume. It implies that
(a) $\lambda \propto p/T$ (b) $\lambda \propto (p/T)^2$
(c) $\lambda \propto T/p$ (d) λ is independent of T and p

98. Let f_1 and f_2 be the fractions of molecules in the range c and $c + dc$ for SO_2 at $2T$ and O_2 at T, respectively. Which of the following expressions is correct?
(a) $f_1 > f_2$ (b) $f_1 < f_2$
(c) $f_1 = f_2$ (d) f_1 and f_2 cannot be correlated

99. The critical volume is related to van der Waals constant b by the expression
(a) $V_c = b$ (b) $V_c = 2b$ (c) $V_c = 3b$ (d) $V_c = 4b$

100. Which of the following expressions between critical constants and van der Waals constants is not correct?
(a) $T_c = 8a/(27Rb)$ (b) $p_c = a(3b^2)$ (c) $p_c V_c = (3/8)\,RT_c$ (d) $V_c = 3b$

101. The total number of bimolecular collisions Z_{11} per unit volume per unit time is given by $Z_{11} = \left(1/\sqrt{2}\right)\pi\,\sigma^2\,\bar{u}\,N^{*2}$ where σ is molecular diameter, $\bar{u}$ is the average speed and N^* is the number of molecules per unit volume. Which of the following facts is correct?
(a) $Z_{11} \propto p/T$ (b) $Z_{11} \propto p^2/T^{3/2}$ (c) $Z_{11} \propto T^{3/2}/p^2$ (d) $Z_{11} \propto p^2\,T^{3/2}$

102. Which of the following facts regarding the viscosity of a gas is correct?
(a) Viscosity of a gas decreases with increasing temperature
(b) Viscosity of a gas is independent of pressure
(c) Viscosity of a gas is due to the intermolecular interactions
(d) Viscosity of a gas is independent of molecular mass

103. For a van der Waals gas, the inversion temperature is given by the expression
(a) $T_i = 2aR$ / b (b) $T_i = a$ / $2Rb$ (c) $T_i = ab$ / $2R$ (d) $T_i = 2a$ / Rb

104. Heat capacity of a diatomic gas in the low temperature range
(a) is independent of its temperature
(b) decreases with increase in temperature
(c) increases with increase in temperature
(d) increases followed by a decrease with increase in temperature.

105. The fraction of molecules having speed in the range c and $c + dc$ follows the pattern
(a) decreases with increase in the value of c at constant temperature
(b) increases with increase in the value of c at constant temperature
(c) increases with increase in the value of c at low speed range while it decreases at high speed range at constant temperature
(d) decreases with increases in the value of c at low speeds while it increases at high speed range at constant temperature.

106. The critical temperature of a gas is related to its Boyle temperature by the expression
(a) $T_c = (8 / 27)\,T_B$ (b) $T_c = (27 / 8)\,T_B$ (c) $T_c = (3 / 8)\,T_B$ (d) $T_c = (8 / 3)\,T_B$

107. The Boyle temperature of a van der Waals gas is given by
(a) $T_B = a/b$ (b) $T_B = a/Rb$ (c) $T_B = Ra/b$ (d) $T_B = Rb/a$

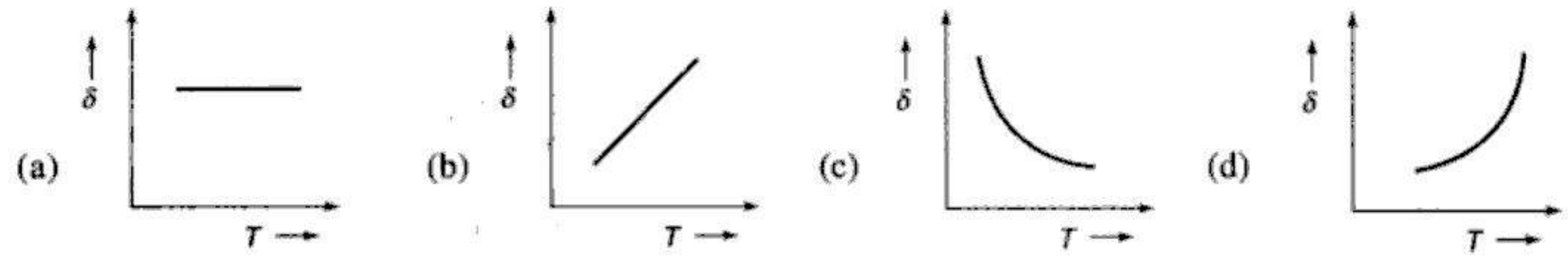
108. At Boyle temperature, the second virial coefficient has a value of
(a) zero (b) positive
(c) negative (d) positive dependent on pressure

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109. Which of the following gases is exhibited to have minimum value of van der Constant a?
(a) H_2 (b) He (c) N_2 (d) O_2

110. Which of the following gases is expected to have maximum value of critical temperature ?
(a) H_2 (b) He (c) O_2 (d) CO_2

111. An ideal gas is initially at temperature T and volume V. Its volume is increased due to an increase in temperature ΔT, pressure remaining constant. The quantity $\delta = \Delta V/(V\,\Delta T)$ varies with temperature as



112. Which of the following statements regarding mean free path of gaseous molecules is correct ?
(a) Directly proportional to the number of molecules per unit volume
(b) Directly proportional to the average speed of molecules
(c) Inversely proportional to the square of molecular diameter
(d) Inversely proportional to the temperature of the gas

Multiple Correct Choice Type

1. Equations of state of an ideal gas is/are
(a) $pV = (1/3)mN$ (b) $pV = nRT$ (c) $p = \rho RT/M$ (d) $p = 3Nk/2V$.

2. The value(s) of universal gas constant is/are
(a) $R = 8.314$ J K^{-1} mol^{-1}
(b) $R = 8.314$ kPa cm^3 K^{-1} mol^{-1}
(c) $R = 8.314$ Pa m^3 K^{-1} mol^{-1}
(d) $R = 0.0821$ dm^3 atm K^{-1} mol^{-1}

3. For a fixed mass of a gas at constant pressure, which of the following statements is/are not correct?
(a) Plot of volume versus Celsius temperature is linear with intercept zero.
(b) Plot of volume versus kelvin temperature is linear with a non-zero intercept.
(c) Plot of V/T versus T is linear with a positive slope.
(d) Plot of V/T versus T is linear with a zero slope.

4. Which of the following facts regarding mean free path of gaseous molecules is/are correct?
(a) Mean free path is derectly proportional to kelvin temperature provided pressure of the gas is held constant.
(b) Mean free path is derectly proportional to pressure provided temperature of the gas is held constant.
(c) Mean free path is inversely proportional to the molecular diameter.
(d) Mean free path is inversely proportional to the number of molecules per unit volume of the gas.

5. Which of the following facts regarding an ideal gas is/are correct?
(a) The mean square speed of gaseous molecules is directly proportional to the square root of kelvin temperature.
(b) The mean square speed is inversely proportional to the molecular mass.
(c) The viscosity of a gas increases with increase in temperature.
(d) The viscosity of a gas independent of its density.

6. Two flasks A and B have equal volumes. Flask A contains hydrogen at 300 K while B contains equal mass of methane at 600 K. Which of the following facts is/are correct if the gases follow ideal behaviour ?
(a) Flask A contains greater number of molecules.
(b) The average speed of molecules in flask B is twice that of molecules in flask A.
(c) Both the gases have the same compression factor
(d) Total kinetic energy of molecules in flask A is greater than that of molecules in flask B.

7. Which of the following statements regarding an ideal gas is/are correct?
(a) The product of pressure and volume of a fixed amount of a gas is independent of temperature.
(b) The increase in the compression factor of a gas with increase of pressure is due to the van der Waals constant b.

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(c) A gas can be liquefied provided its temperature is less than its critical temperature and pressure is more than its critical pressure.
(d) Average speed of molecules of a gas in a container moving only in one dimension is zero.

8. Which of the following statements is/are correct?
(a) The compression factor less than one is due to the van der Waals constant a of a real gas.
(b) The compression factor more than one is due to the excluded volume of the gas.
(c) The excluded volume, which is represented by the van der Waals constant b, is equal to the volume occupied by the molecules of 1 mol of a gas.
(d) At Boyle temperature, the effects caused by the van der Waals constants a and b compensate each other causing the gas to behave ideally over a wide range of pressure.

9. Which of the following statements is/are correct?
(a) The average kinetic energy of oxygen molecules is smaller than that of nitrogen molecules at 298 K.
(b) The average speed of oxygen molecules is smaller than that of nitrogen molecules.
(c) The unit of Boltzman constant is J K^{-1} $molecule^{-1}$.
(d) The negative deviation of a real gas from ideal behaviour is due to the molecular attractions.

10. Which of the following statements is/are correct ?
(a) The value of $C_{p,m}/C_{V,m}$ (where C stands for heat capacity) of gaseous molecules decreases with increase in the number of atoms in the gaseous molecule.
(b) The molar heat capacity of diatomic molecules at low temperature is about $3.5R$.
(c) The molar average energy of helium gas is $1.5RT$.
(d) The average vibrational energy of a diatomic molecule is $(1/2)kT$.

11. Which of the following facts stated along with the given characteristics of two identical gases is/are correct?
(a) Equal p, V, T ; $m_1 > m_2 \quad \Rightarrow \overline{\overline{KE}}_1 = \overline{\overline{KE}}_2$
(b) Equal p, V, T ; $m_1 > m_2 \quad \Rightarrow n_1 > n_2$
(c) Equal p, V, T ; $n_1 > n_2 \quad \Rightarrow T_1 < T_2$
(d) Equal V, N, T ; $m_1 > m_2 \quad \Rightarrow p_1 > p_2$

12. Which of the following statements are correct?
(a) The unit of K in the expression $V = KT$ is m^3 K^{-1}.
(b) A gas is heated at constant pressure from 25 °C to 50 °C, it expands to twice its initial volume.
(c) The volume occupied by 32 g of oxygen is greater than that occupied by 16 g of methane, both being at the same T and p.
(d) All real gases can be liquefied and solidified.

13. Which of the following statements are correct?
(a) A real gas can be liquefied if its temperature is greater than its critical temperature.
(b) A real gas is expected to behave ideally at high temperature and low pressure.
(c) The increase in volume per degree rise in Celsius temperature at constant pressure is $V_0/273.15$, where V_0 is the volume of gas at 0 K.
(d) The rate of diffusion is directly proportional to the square root of its kelvin temperature and also inversely proportional to the square root of its molar mass.

14. Which of the following statements are correct?
(a) The molar mass of a gas may be calculated through the expression $M = (\rho/p)RT$.
(b) The value of ρ/p of an ideal gas at a constant temperature is independent of the pressure of the gas.
(c) The Avogadro constant has a value of 6.626×10^{26} mol^{-1}.
(d) The volume of a fixed mass of gas at constant pressure varies nonlinearly with temperature expressed in Celsius whereas it varies linearly when expressed in kelvin.

15. Which of the following statements are correct?
(a) Equal masses of all gases occupy the same volume at STP.
(b) An ideal gas cannot be liquefied.
(c) Kinetic energy of gaseous molecules is zero at 0 °C.
(d) Gases having very low critical temperatures often show near ideal behaviour at room temperature.

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16. Which of the following statements are **not** correct?

(a) The expression of kinetic gas equation is $pV = \frac{1}{3} mN\overline{u^2}$.

(b) The symbols $\overline{u^2}$ and $\bar{u}^2$ represent one and the same physical quantity.

(c) The density of an ideal gas increases with increase in temperature provided its pressure is constant.

(d) The average kinetic energy of gaseous molecules depends only on temperature and nature of gaseous molecules.

17. Which of the following statements are **not** correct?

(a) At low pressure the molecules of an ideal gas move with slower speed as compared to the gas at high pressure.

(b) The value of gas constant R is 8.314 J K^{-1}.

(c) The value of Boltzmann constant k is 1.38×10^{-23} J K^{-1} $molecule^{-1}$.

(d) The van der Waals constant a is a measure of forces of attraction between gaseous molecules of a gas.

18. Which of the following statements are correct?

(a) The van der Waals constant b is four times the volume occupied by molecules in one mole of a gas.

(b) A gas having comparatively higher value of van der Waals constant a can be liquefied more easily.

(c) The term $V_m - b$ in van der Waals equation represents the available volume where molecules of the gas can move.

(d) The compression factor of an ideal gas is independent of temperature and pressure of the gas.

19. Which of the following statements are correct?

(a) The compression factor of a real gas is equal to one over a wide range of pressure provided the gas is at Boyle temperature.

(b) The mean square speed of a gas is defined as $\left(\frac{u_1 + u_2 + u_3 + \cdots + u_N}{N}\right)^2$

(c) The most probable speed of gaseous molecules is the speed possessed by the maximum fraction of the molecules of a gas.

(d) The average speed of a gas varies linearly with increase of temperature.

20. Which of the following statements are **not** correct?

(a) The kinetic energy of 1 mol of a gas is equal to $(3/2)RT$.

(b) All gases irrespective of their nature have $C_p/C_V = 5/3$.

(c) A real gas obeys $pV = (1/3)\, mN\overline{u^2}$ under all conditions of temperature and pressure.

(d) The ratio of u_{av} and u_{mp} is $\sqrt{56/22} : \sqrt{3}$.

21. Which of the following statements are **not** correct ?

(a) The ratio of u_{av} and u_{mp} is 2 : 3.

(b) The unit of van der Waals constant a is L^2 atm mol^{-1}.

(c) The mean square speed of a gas varies linearly with kelvin temperature.

(d) The increasing order of average, most probable and root mean square speeds is $u_{rms} < u_{av} < u_{mp}$.

22. Which of the following statements are **not** correct?

(a) The product pV has the dimensions of energy.

(b) In the van der Waals equation $\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$, the constant a reflects the actual volume of the gas molecules. (1993)

(c) A mixture of ideal gases is cooled upto liquid helium temperature (4.22 K) to form an ideal solution.

(d) The heat capacity of a monatomic gas is independent of temperature.

23. If a gas is expanded at constant temperature

(a) the pressure decreases

(b) the kinetic energy of the molecules remains the same

(c) the kinetic energy of the molecules decreases

(d) the number of molecules of the gas increases

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24. Which of the following statements are **not** correct?
(a) The rate of diffusion of a gas is inversely proportional to the square of density or molar mass.
(b) The value of pV for 5.6 L of an ideal gas is 0.25 RT at STP.
(c) Eight grams each of oxygen and hydrogen at 27 °C will have the total kinetic energy in the ratio of 1 : 8.
(d) The proportionality constant K in $V = KT$ is given as $V_0/273.15$ K where V_0 is the volume of the gas at 0 K.

25. Which of the following statements are **not** correct?
(a) In SI units, the value of gas constant R is 8.314 J K^{-1} mol^{-1}.
(b) In SI units, the value of Boltzmann constant k is 1.38×10^{-23} J K^{-1} mol^{-1}.
(c) The aqueous tension of water at a given temperature is the vapour pressure of water at the given temperature.
(d) The volume occupied by 22 g of carbon dioxide at STP would be 22.414 L.

26. Which of the following statements are **not** correct ?
(a) The abbreviation STP stands for standard temperature and pressure where temperature is 25 °C and pressure is 1 atm.
(b) Two grams of hydrogen contains as many molecules as in 44 g of carbon dioxide.
(c) For an ideal gas at constant temperature, the ratio ρ/p is dependent on pressure.
(d) For an ideal gas at constant volume, the plot of p/T versus T is linear with slope having a nonzero.

27. Which of the following statements are **not** correct?
(a) For an ideal gas at constant temperature, the plot of pV versus p is linear with slope having a zero value.
(b) The density of an ideal gas increases with increase in temperature of the gas, provided the pressure remains constant.
(c) According to the kinetic theory of gases, the average kinetic energy of gaseous molecules is directly proportional to kelvin temperature.
(d) For a given gas, the expression of mean square speed of its molecules in terms of pressure and density is $2p/\rho$.

28. Which of the following statements are correct?
(a) The average kinetic energy of a gas is independent of the molar mass of the gas.
(b) For a given gas at a constant temperature, the root means square speed of its molecules is greater than their average speed.
(c) For a given gas at a constant temperature, the root mean square speed of its molecules is greater than their most probable speed.
(d) For a given gas at a constant temperature, the average speed of its molecules is greater than their most probable speed.

29. Which of the following statements are correct?
(a) The temperature at which a real gas exhibits ideal behaviour over a wide range of pressure is known as Boyle temperature.
(b) The temperature above which a gas cannot be liquefied is known as critical temperature.
(c) The temperature at which a real gas exhibits neither cooling nor heating when passed through a porous plug is known as inversion temperature.
(d) A real gas is expected to behave ideally at low temperature and high pressure.

30. Which of the following statements are not correct?
(a) A real gas is expected to deviate from ideal behaviour at high temperature and low pressure.
(b) The unit of van der Waals constant a in SI units is Pa m^3 mol^{-1}.
(c) The unit of van der Waals constant b in SI units is m^3 mol^{-1}.
(d) The van der Waals constant b is two times the actual volume occupied by molecules of 1 mol of a gas.

31. Which of the following statements are correct?
(a) For a real gas, the compression factor Z is defined as V_{real}/V_{ideal}.
(b) At low pressure, the variation of compression factor with pressure can be explained from van der Waals equation when the term b is ignored in comparison to the term V_m.

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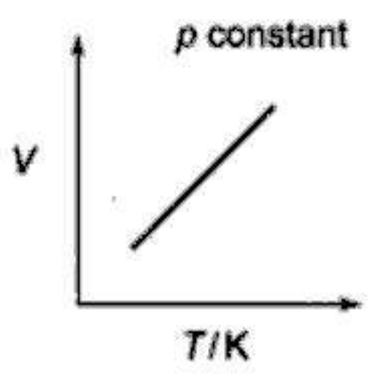
(c) At high pressure, the variation of compression factor with pressure can be explained from the van der Waals equation when the term a is ignored in comparison to the term V_m.
(d) The value 6.022×10^{23} mol^{-1} is assigned to Avogadro constant.

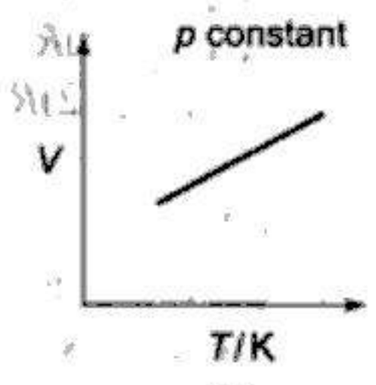
32. Which of the following statements are **not** correct?
(a) The value of $C_p - C_V$ for one mole of an ideal gas is equal to R.
(b) The value of C_p/C_V for one mole of an ideal (monatomic) gas is equal to 7/5.
(c) The value of $C_{V,m}$ for a monatomic gases is $(3/2)R$.
(d) The value of γ(= ratio of heat capacities) of gases increases with increases in the atomicity of gaseous molecule.

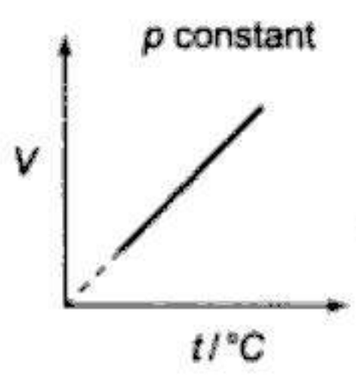
33. Which of the following statements are **not** correct?
(a) The rate of diffusion of helium is about twice that of methane gas.
(b) 0.5 L of a certain gas at STP weighs 0.58 g. Its molar mass is 44 g mol^{-1}.
(c) The root mean square speed of nitrogen gas at 3 atm will be same as that at 1 atm.
(d) The root mean square speed of methane gas will be twice that of helium gas both having the same temperature and pressure.

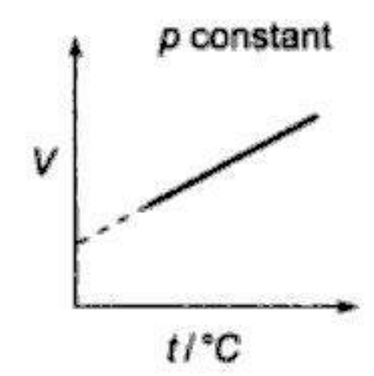
34. Which of the following statements are correct?
(a) The average kinetic energy of a gas at temperature T is given as $(3/2)\ kT$.
(b) The molar kinetic energy of a gas at a temperature T is given as $(3/2)\ RT$.
(c) Of the gases, H_2 and N_2, the larger value of van der Waals constant a would be of H_2 gas.
(d) Of the gases, H_2 and N_2, the larger value of van der Waals constant b would be of N_2 gas.

35. Which of the following graphs represent the behaviour of an ideal gas?

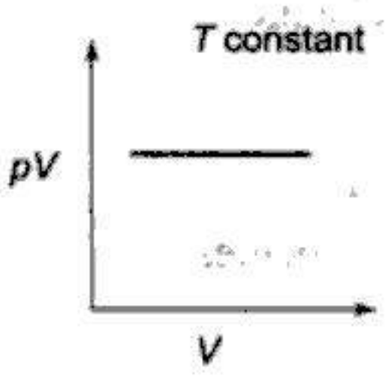
(a) 

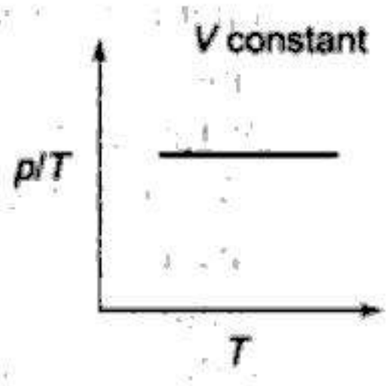
(b) 

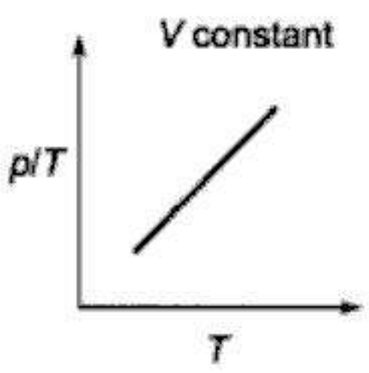
(c) 

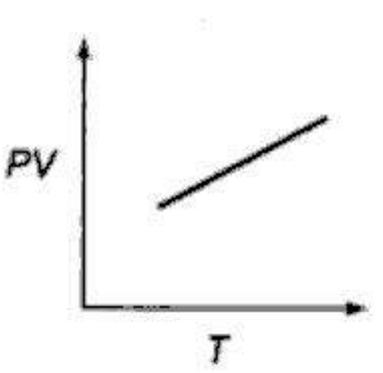
(d) 

36. Which of the following graphs represent the behaviour of an ideal gas?

(a) 

(b) 

(c) 

(d) 

37. Let u_{av}, u_{rms} and u_{mp} respectively denote the average speed, root mean square average speed and most probable speed in an ideal monatomic gas at kelvin temperature T. The mass of an atom is m. Then
(a) no atom can have a speed greater that $\sqrt{2}\ u_{rms}$.
(b) no atom can have a speed less than $u_{mp}/\sqrt{2}$.
(c) $u_{mp} < u_{av} < u_{rms}$
(d) the average kinetic energy of an atom is $(3/4)\ mu^2_{mp}$.

Linked Comprehension Type

1. The behaviour of a real gas is usually depicted by plotting compression factor Z $(= pV_m/RT)$ versus p at a constant temperature. These plots are explained on the basis of van der Waals equation $(p + a/V^2_m)(V_m - b) = RT$.
(i) The value of $Z < 1$ is observed provided
(a) p is low and $T > T_B$ (Boyle temperature)
(b) p is low and $T < T_B$
(c) p is low and $T = T_B$
(d) p is high and $T < T_B$

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(ii) The value of $Z > 1$ is observed provided
(a) p is low and $T < T_c$ (critical temperature) (b) p is low and $T < T_B$
(c) p is low and $T = T_B$ (d) p is high and $T < T_B$

(iii) The value of $Z = 1$ is observed provided
(a) p is low and $T > T_B$ (b) p is low and $T < T_B$
(c) p is low and $T = T_B$ (d) p is high and $T < T_B$

2. The behaviour of a real gas is usually depicted by plotting compression factor Z ($= pV_m/RT$) versus p at a constant temperature. These plots are explainable on the basis of van der Waals equation of state $(p + a/V_m^2)(V_m - b) = RT$.

(i) The value of $Z > 1$ is explained on
(a) ignoring the constant a (b) ignoring the constant b
(c) ignoring both the constants a and b (d) retaining both the constants a and b

(ii) The value of $Z < 1$ is explained on
(a) ignoring the constant a (b) ignoring the constant b
(c) ignoring both the constants a and b (d) retaining both the constants a and b

(iii) The value of $Z = 1$ over wide range of low pressure at Boyle temperature is explained on the basis of
(a) ignoring the constant a (b) ignoring the constant b
(c) ignoring both the constants a and b (d) retaining both the constants a and b

3. The molar heat capacity of a gas may be computed from the average energy of molecules obtained on the basis of law of equipartion of energy.

(i) Which of the following statements for a monatomic gases is not correct?
(a) Molar heat capacity at constant volume, $C_{V,m}$, is $(3/2)R$
(b) Molar heat capacity at constant pressure, $C_{p,m}$, is $(5/2)R$
(c) The ratio of $C_{p,m}/C_{V,m}$ is (5/3)
(d) The ratio of $C_{p,m}/C_{V,m}$ varies with temperature

(ii) Which of the following statements for a diatomic gases is not correct ?
(a) $C_{V,m} = (5/2)R$ and $C_{p,m} = (7/2)R$ at low temperatures
(b) $C_{V,m} = (7/2)R$ and $C_{p,m} = (9/2)R$ at high temperatures
(c) The value of $C_{V,m}$ varies linearly with temperature for smaller change in temperature
(d) The value of $C_{V,m}$ varies nonlinearly with temperature for smaller change in temperature

(iii) Which of the following facts is correct for a triatomic gas?
(a) $C_{V,m}$ is $(13/2)R$ for linear molecules and is $6R$ for non-linear molecules
(b) $C_{V,m}$ is $6R$ for linear molecules and is (13/2) for non-linear molecules
(c) The ratio $C_{p,m}/C_{V,m}$ has the same value for linear and non-linear molecules
(d) The ratio $C_{p,m}/C_{V,m}$ does not vary with temperature

4. The behaviour of a real gas may be represented by Berthelot's equation

$$p = \frac{RT}{V_m - b} - \frac{a}{TV_m^2}$$

Based on this equation, answer the following three questions.

(i) The unit of constant a is
(a) Pa m^6 mol^{-2} (b) Pa m^3 mol^{-1} (c) Pa m^6 $Kmol^{-2}$ (d) atm L^2 mol^{-2}

(ii) If the Berthelot's equation is transformed into the virial equation in V_m, the second virial coefficient will be given by the expression

(a) $B = b - \frac{a}{RT}$ (b) $B = b - \frac{a}{RT^2}$ (c) $B = a - \frac{b}{RT}$ (d) $B = a - \frac{b}{RT^2}$

(iii) The Boyle temperature for the Berthelot's equation is given by the expression

(a) $T_B = a/Rb$ (b) $T_B = a/\sqrt{Rb}$ (c) $T_B = \sqrt{a/Rb}$ (d) $T_B = b/Ra$

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5. The fraction of gaseous molecules having speed in between u and $u + du$ as governed by Maxwell distribution of speeds is given by

$$\frac{dN_u}{N} = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} \exp(-Mu^2/2RT)\, u^2\, du$$

Graphically this distribution is shown in Fig. 2.1.

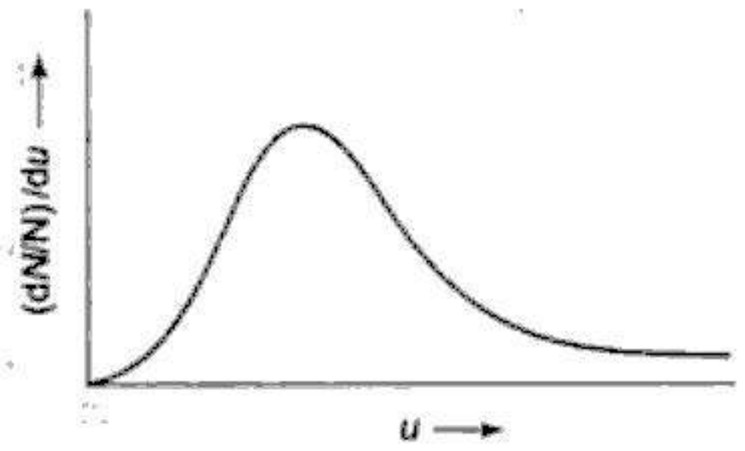


Fig. 2.1

Based on this distribution, answer the following three questions.

(i) With increase in temperature, the quantity $(dN/N)/du$ in the low speed range
(a) increases (b) decreases
(c) shows no change (d) increases or decreases depending upon the gas

(ii) With increase in temperature, the quantity $(dN/N)/du$ in the high speed range
(a) increases (b) decreases
(c) shows no change (d) increases or decreases depending upon the gas

(iii) The maximum value of $(dN/N)/du$ corresponds to most probable speed. With increase in temperature, this maximum fraction
(a) increases (b) decreases
(c) shows no change (d) increases or decreases depending upon the gas

6. At critical temperature and pressure, the van der Waals equation may be written as

$$V_m^3 - \left(b + \frac{RT_c}{p_c}\right)V_m^2 + \frac{a}{p_c}V_m - \frac{ab}{p_c} = 0$$

At these conditions, the above expression yields three identical and real roots. Thus, the above expression is equivalent to $(V_m - V_c)^3 = 0$

Based on the identity of the above expressions, answer the following three questions.

(i) The expression of b in terms of V_c is
(a) $b = V_c/2$ (b) $b = V_c/3$ (c) $b = V_c/4$ (d) $b = V_c/6$

(ii) The expression of a in terms of p_c and T_c is
(a) $a = 27(RT_c)^2/64p_c$ (b) $a = 27RT_c/16p_c$ (c) $a = 64(RT_c)^2/p_c$ (d) $a = 27p_c/(RT_c)^2$

(iii) The value of p_cV_c/RT_c is
(a) 1/2 (b) 3/4 (c) 3/8 (d) 3/16

Assertion and Reason Type

Given below are the two statements. Identify the correct choice from the following.

(a) Statement –1 is correct and Statement –2 is correct and is the correct explanation of the statement –1.
(b) Statement –1 is correct and Statement –2 is correct but not the correct explanation of the statement –1.
(c) Statement –1 is correct and Statement –2 is incorrect.
(d) Statement –1 is incorrect and Statement –2 is correct.

Statement–1	Statement–2
1. The value of van der Waals constant a is larger for ammonia than for hydrogen.	Hydrogen bonding is present in ammonia. (1994)
2. The pressure of a fixed amount of an ideal gas is proportional to the square root of temperature.	Frequency of collision and their impact both increase in proportional to its temperature. (2000)

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3.	Heat capacity of a diatomic gas varies with temperature and attains a constant value at high temperature.	The vibrational contribution to heat capacity varies with temperature.
4.	The compression factor of helium is always greater than one irrespective of its temperature.	The critical temperature of helium is very small.
5.	The fraction of molecules having speed in the range c and $c + dc$ depends on the value of M/T of the gas.	The speed of molecules of a gas depends on the value of M/T of the gas.
6.	The average kinetic energy of gaseous molecules at a fixed temperature is independent of the mass of molecules of the gas.	The mean square speed of gaseous molecules depends inversely on the mass of molecule of a gas.
7.	A real gas behaves ideally over a wide range of pressure at its Boyle temperature.	At Boyle temperature, second virial coefficient of the gas a zero value.
8.	The value of $(pV_m)_{p\to 0}$ of a real gas is independent of its nature.	As $p\to 0$, a real gas behaves as if there exists no molecular attractions and the volume occupied by gaseous molecules is negligible in comparison to its volume.
9.	Pressure of a gas at constant volume increases with increase in temperature.	The speeds of molecules increase causing larger number of collisions with the sides of the vessel.

Matrix Match Type

1. Column II gives the values of van der Waals constant a of a few gases which are shown in Column I. Identify the gas with the corresponding a value.

Column I	Column II
(a) H_2	(p) 137.8 kPa dm^6 mol^{-2}
(b) He	(q) 21.8 kPa dm^6 mol^{-2}
(c) O_2	(r) 364.0 kPa dm^6 mol^{-2}
(d) CO_2	(s) 1304 kPa dm^6 mol^{-2}
	(t) 3.5 kPa dm^6 mol^{-2}

2. Column II gives the values of critical temperatures of a few gases which are shown in Column I. Identify the gas with the corresponding T_c value

Column I	Column II
(a) H_2	(p) 33.3 K
(b) He	(q) 304 K
(c) O_2	(r) 5.3 K
(d) CO_2	(s) 154 K
	(t) 647 K

3. Column II gives the values of $\gamma (= C_{p,m}/C_{V,m})$ at high temperature of gases which are shown in **Column I**. Identify the gas with the corresponding γ value.

Column I	Column II
(a) Monatomic	(p) 1.154
(b) Diatomic	(q) 1.286
(c) Linear Triatomic	(r) 1.167
(d) Nonlinear Triatomic	(s) 1.407
	(t) 1.667

4. For a van der Waals gas, match the entries mentioned in Column I with the correct choice given in Column II.

Column I	Column II
(a) Critical temperature	(p) $2a/Rb$
(b) Inversion temperature	(q) a/Rb
(c) Boyle temperature	(r) T/T_c
(d) Reduced temperature	(s) $8a/(27Rb)$

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ANSWERS

Straight Objective Type

1. (a)	**2.** (d)	**3.** (a)	**4.** (b)	**5.** (d)	**6.** (d)	**7.** (d)
8. (b)	**9.** (d)	**10.** (c)	**11.** (b)	**12.** (b)	**13.** (c)	**14.** (b)
15. (a)	**16.** (b)	**17.** (a)	**18.** (a)	**19.** (b)	**20.** (c)	**21.** (c)
22. (c)	**23.** (c)	**24.** (d)	**25.** (b)	**26.** (a)	**27.** (d)	**28.** (b)
29. (c)	**30.** (a)	**31.** (d)	**32.** (d)	**33.** (b)	**34.** (d)	**35.** (a)
36. (d)	**37.** (b)	**38.** (b)	**39.** (c)	**40.** (a)	**41.** (a)	**42.** (a)
43. (b)	**44.** (a)	**45.** (a)	**46.** (a)	**47.** (c)	**48.** (b)	**49.** (a)
50. (c)	**51.** (b)	**52.** (c)	**53.** (c)	**54.** (c)	**55.** (a)	**56.** (d)
57. (b)	**58.** (b)	**59.** (c)	**60.** (d)	**61.** (c)	**62.** (d)	**63.** (d)
64. (d)	**65.** (b)	**66.** (b)	**67.** (c)	**68.** (d)	**69.** (d)	**70.** (b)
71. (d)	**72.** (d)	**73.** (c)	**74.** (a)	**75.** (b)	**76.** (a)	**77.** (d)
78. (c)	**79.** (b)	**80.** (d)	**81.** (b)	**82.** (b)	**83.** (a)	**84.** (d)
85. (c)	**86.** (a)	**87.** (a)	**88.** (b)	**89.** (b)	**90.** (b)	**91.** (a)
92. (b)	**93.** (c)	**94.** (a)	**95.** (d)	**96.** (a)	**97.** (c)	**98.** (c)
99. (c)	**100.** (b)	**101.** (b)	**102.** (b)	**103.** (d)	**104.** (c)	**105.** (c)
106. (a)	**107.** (b)	**108.** (a)	**109.** (b)	**110.** (d)	**111.** (c)	**112.** (c)

Multiple Correct Choice Type

1. (a), (b), (c)	**2.** (a), (c), (d)	**3.** (a), (b), (c)	**4.** (a), (d)
5. (b), (c), (d)	**6.** (a), (c), (d)	**7.** (b), (c), (d)	**8.** (a), (b), (d)
9. (b), (d)	**10.** (a), (c)	**11.** (a), (c)	**12.** (a), (d)
13. (b), (d)	**14.** (a), (b)	**15.** (b), (d)	**16.** (a), (b), (c)
17. (a), (b), (c)	**18.** (a), (b), (c), (d)	**19.** (a), (c)	**20.** (b), (c), (d)
21. (a), (b), (d)	**22.** (b), (c)	**23.** (a), (b)	**24.** (a), (c), (d)
25. (b), (d)	**26.** (a), (c), (d)	**27.** (b), (d)	**28.** (a), (b)
29. (a), (b), (c)	**30.** (a), (b), (d)	**31.** (a), (b), (d)	**32.** (b), (d)
33. (b), (d)	**34.** (a), (b), (d)	**35.** (a), (d)	**36.** (a), (b)
37. (c), (d)			

Linked Comprehension Type

1. (i) (b)	(ii) (d)	(iii) (c)
2. (i) (a)	(ii) (b)	(iii) (d)
3. (i) (d)	(ii) (c)	(iii) (a)
4. (i) (c)	(ii) (b)	(iii) (c)
5. (i) (b)	(ii) (a)	(iii) (b)
6. (i) (b)	(ii) (a)	(iii) (c)

Assertion and Reason Type

1. (c)	**2.** (b)	**3.** (a)	**4.** (d)	**5.** (c)	**6.** (a)	**7.** (a)
8. (a)	**9.** (b)					

Matrix Match Type

1. (a) – (q); (b) – (t); (c) – (p); (d) – (r)
2. (a) – (p); (b) – (r); (c) – (s); (d) – (q)
3. (a) – (t); (b) – (q); (c) – (p); (d) – (r)
4. (a) – (s); (b) – (p); (c) – (q); (d) – (r)

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Hints and Solutions

Straight Objective Type

1. $n(CH_4) = m/(16\ g\ mol^{-1})$; $n(O_2) = m/(32\ g\ mol^{-1})$

$$\frac{p_{O_2}}{P} = \frac{(m/32\ g\ mol^{-1})}{(m/16\ g\ mol^{-1}) + (m/32\ g\ mol^{-1})} = \frac{(1/32)}{(1/16) + (1/32)} = \frac{16}{32+16} = \frac{1}{3}$$

2. $n(C_2H_6) = m/(30\ g\ mol^{-1})$; $n(H_2) = m/(2\ g\ mol^{-1})$

$$\frac{p(H_2)}{p(H_2) + p(C_2H_6)} = \frac{n(H_2)}{n(H_2) + n(C_2H_6)} = \frac{m/2}{(m/2) + (m/30)} = \left(\frac{1}{2}\right)\left(\frac{60}{32}\right) = \frac{30}{32} = \frac{15}{16}$$

3. $pV = nRT = (m/M)\ RT \Rightarrow pM = \rho RT$. Hence, $\rho_2/\rho_1 = (p_2/T_2)/(p_1/T_1) = T_1p_2/T_2p_1$

4. For an ideal gas $pV = nRT = (m/M)RT \Rightarrow pM = \rho RT$, i.e. $\rho = pM/RT$.

Hence $\rho_{(A)} = (M/R)$ (1 atm/273 K); $\rho_{(B)} = (M/R)$ (2 atm/273 K); $\rho_{(C)} = (M/R)$ (1 atm/546 K)

$\rho_{(D)} = (M/R)$ (2 atm/546 K)

The density will be highest for the choice B.

5. The volume of a gas changes by $V_0/273.15$ for every 1 °C increase in temperature, where V_0 is the volume of the gas at 0 °C.

6. The value of V/T remains constant with change in temperature of a gas. Hence, the plot of V/T versus T is linear with zero slope.

7. The dimensionally correct expression is $t/°C = T/K + 273.15$

8. The value of R expressed in SI units is 8.314 J K^{-1} mol^{-1}.

9. The value of Boltzmann constant is $k = \frac{R}{N_A} = \frac{8.134\ J\ K^{-1}\ mol^{-1}}{6.022 \times 10^{23}\ mol^{-1}} = 1.36 \times 10^{-23}\ J\ K^{-1}$

10. The value of Avogadro constant is $6.022 \times 10^{23}\ mol^{-1}$.

11. $pV = nRT = (m/M)RT$ i.e $pM = \rho RT$ i.e. $\rho = pM/RT$.

Larger the value of p/T, larger the density of a gas. For choice B, p/T has the largest value.

12. The volume of a gas increases by $V_0/273.15$ with an increase of 1°C, where V_0 is the volume of gas at 0 °C.

13. We have $p = \rho RT/M$.

$$\frac{p(X)}{p(Y)} = \frac{\rho(X)}{\rho(Y)}\frac{M(Y)}{M(X)} = (3)\ (2) = 6$$

14. For an ideal gas, the compression factor is equal to one.

15. We have $AB_2 \rightleftharpoons A + B_2$; total amount of gases $= n(1 + \alpha)$

$n(1 - \alpha)$ $n\alpha$ $n\alpha$

Since $pV = nRT$, we have (1 atm) $V = n(1 + \alpha)\ RT = n(1.4)$ (0.082 L atm K^{-1} mol^{-1}) 400 K

or $$\frac{n}{V} = \frac{1\ atm}{(1.4)(0.082)\ L\ atm\ K^{-1}\ mol^{-1})(400\ K)} = 0.0218\ mol\ L^{-1}$$

$$\rho = \frac{m}{V} = \frac{(nM)}{V} = \left(\frac{n}{V}\right)M = (0.0218\ mol\ L^{-1})\ (200\ g\ mol^{-1}) = 4.35\ g\ L^{-1}$$

16. Since $pV = nRT = (m\ /\ M)RT$, we have $\rho = \left(\frac{m}{V}\right) = \frac{pM}{RT}$

This gives $$\frac{\rho_2}{\rho_1} = \left(\frac{p_2}{p_1}\right)\left(\frac{T_1}{T_2}\right)$$

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17. Since $\rho = pM/RT$, we get

$$M_{av} = \frac{\rho RT}{p} = \frac{(0.5\,\text{g L}^{-1})(0.082\,\text{L atm K}^{-1}\text{mol}^{-1})(300\,\text{K})}{1\,\text{atm}} = 12.3\ \text{g mol}^{-1}$$

Since $M_{av} = x_1M_1 + x_2M_2 = M_1 + x_2(M_2 - M_1)$, we get

$$x_2 = \frac{M_{av} - M_1}{M_2 - M_1} = \frac{12.3 - 32}{4 - 32} = 0.70$$

$$m_1 = n_1M_1 = (0.30\ \text{mol})\ (32\ \text{g mol}^{-1}) = 9.6\ \text{g}$$

$$m_2 = n_2M_2 = (0.70\ \text{mol})\ (4\ \text{g mol}^{-1}) = 2.8\ \text{g}.$$

$$\text{Mass per cent of He} = \frac{m_2}{m_1 + m_2} \times 100 = \frac{2.8}{12.4} \times 100 = 22.6$$

18. We have $\rho_2 = \rho_1\left(\frac{p_2}{p_1}\right)\left(\frac{T_1}{T_2}\right) = (1.5\ \text{g L}^{-1})\left(\frac{1000}{760}\right)\left(\frac{273}{760}\right) = 1.8\ \text{g L}^{-1}$

19. We have $T_2 = \left(\frac{\rho_1}{\rho_2}\right)T_1 = \left(\frac{1.5}{0.5}\right)(273\ \text{K}) = 819\ \text{K} \equiv 546\ ^\circ\text{C}$

20. Let x be the mole fraction of NH_3 in the original mixture.

Amount of gas to start with = 1 mol

Amount of gas at the end = $2x$ mol + $3(1 - x)$ mol = $(3 - x)$ mol

Since $pV = nRT$, we have $\frac{n_1T_1}{n_2T_2} = \frac{p_1}{p_2} \Rightarrow \left(\frac{1}{3-x}\right)\left(\frac{300}{1000}\right) = \frac{0.6}{4.8} = \frac{1}{8}$

Hence $x = 0.6$. Mole per cent of NH_3 = 60%

21. The value of compression factor ($= pV_m/RT$) is equal to one.

22. By definition, $\rho = m/V$. Hence,

$$\frac{\rho_l}{\rho_v} = \frac{V_v}{V_l} \quad \text{(for the same mass of the substance)}$$

or $$V_l = \left(\frac{\rho_v}{\rho_l}\right)V_v = \left(\frac{0.0006}{1}\right)(10^3\ \text{cm}^3) = 0.6\ \text{cm}^3$$

23. $V_2 = \left(\frac{V_1}{T_1}\right)T_2 = \left(\frac{22.4\,\text{L}}{273\,\text{K}}\right)(373\ \text{K}) = 30.6\ \text{L}$

24. Rate of diffusion of a gas is inversely proportional to the square root of its molar mass.

25. Since $c_{rms} = \sqrt{3RT/M}$, larger the molar mass, lesser the speed and hence lesser the distance covered. Since $M(HCl) < M(NH_3)$, the ammonium chloride ring will be formed near the hydrogen chloride end.

26. $\frac{r(CH_4)}{r(X)} = 2 = \sqrt{\frac{M(X)}{M(CH_4)}}$. Hence $M(X) = 4\ M(CH_4) = 4 \times 16\ \text{g mol}^{-1} = 64\ \text{g mol}^{-1}$.

27. We have $r_2 = \left(\frac{M_1}{M_2}\right)^{1/2} r_1 = \left(\frac{4}{64}\right)^{1/2} r_1 = \frac{r_1}{4}$

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Since $r = n/t$, we get $r_2/r_1 = n_2/n_1$ i.e. $n_2 = (r_2/r_1)n_1$

$$n_2 = (1/4)(3\text{g}/4\text{g mol}^{-1}) = \frac{3}{16}\text{ mol}; \qquad m_2 = \left(\frac{3}{16}\text{ mol}\right)(64\text{ g mol}^{-1}) = 12\text{ g}.$$

28. $\frac{t_2}{t_1} = \left(\frac{M_2}{M_1}\right)^{1/2}$. For the choice a, $t_2/t_1 = \sqrt{2}$, for the choice b, $t_2/t_1 = 4$. For the choice c, $t_2/t_1 = \sqrt{14}$. For the choice d, $t_2/t_1 = \sqrt{22}$. Thus, the choice b is correct.

29. $\frac{r_A}{r_B} = \left(\frac{p_A}{p_B}\right)\left(\frac{M_B}{M_A}\right)^{1/2}$. The first term is measure of its concentration and the second term is due to Graham's law of diffusion.

30. We have $A_2(g) = 2A(g)$

$n(1-\alpha) \qquad 2n\alpha$

Total amount of gases $= n(1-\alpha) + 2n\alpha = n(1+\alpha)$

$$\text{Average molar mass of gases} = \frac{n(1-\alpha)}{n(1+\alpha)}M_{A_2} + \frac{2n\alpha}{n(1+\alpha)}M_A = \frac{M_{A_2}}{1+\alpha}$$

$$\text{According to Graham's law } \frac{r_{mix}}{r_X} = \left(\frac{M_X}{M_{av}}\right)^{1/2} = \left[\frac{M_X}{M_{A_2}/(1+\alpha)}\right]^{1/2}$$

which gives $\alpha = \left(\frac{M_{A_2}}{M_X}\right)\left(\frac{r_{mix}}{r_X}\right)^2 - 1$

31. We have Partial pressure of He = 16 bar Partial pressure of CH_4 = 4 bar

$$\frac{r_{He}}{r_{CH_4}} = \left(\frac{p_{He}}{p_{CH_4}}\right)\left(\frac{M_{CH_4}}{M_{He}}\right)^{1/2} = \left(\frac{16}{4}\right)\left(\frac{16}{4}\right)^{1/2} = 8$$

32. The relative molar masses of methane and helium are 16 and 4, respectively. Hence

$$\frac{r_{CH_4}}{r_{He}} = \sqrt{\frac{M_{He}}{M_{CH_4}}} = \sqrt{\frac{4}{16}} = \frac{1}{2}$$

33. The molecules of an ideal gas do not exert force of attraction on each other.

34. The mean kinetic energy of the molecules is proportional to the kelvin temperature.

35. The pressure of a gas increases with increase in temperature. This is due to increase in molecular speeds of gaseous molecules, as this results into increase in molecular collisions with sides of the vessel.

36. For an ideal gas, $pV = nRT = (m/M)\,RT$. Hence, $p = \rho RT/M$.

Also $pV = \frac{1}{3}\,mN\,\overline{u^2} = \frac{2}{3}N\left(\frac{1}{2}m\overline{u^2}\right) = \frac{2}{3}N(\overline{\text{KE}})$

37. Molecules in a gas move with all possible speeds.

38. We known that $(pV_m)_{p\to 0} = 22.414$ L atm = (22.414) (1.01325 bar) L = 22.711 L bar

39. We have $pV = \frac{1}{3}\,mN\overline{u^2} = \frac{2}{3}N\left(\frac{1}{2}m\overline{u^2}\right) = \frac{2}{3}N\bar{E}$

40. $c_{rms} = \sqrt{3RT/M}$ and $c_{av} = \sqrt{8RT/\pi M}$. Hence

$$\frac{c_{rms}}{c_{av}} = \sqrt{\frac{3\pi}{8}} = \sqrt{\frac{3\times 3.14}{8}} = \sqrt{\frac{9.42}{8}} = \sqrt{1.165} = 1.086$$

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41. The expression of average speed is $c_{av} = \sqrt{8RT/\pi M}$. For two temperatures, we have

$$\frac{c_2}{c_1} = \sqrt{\frac{T_2}{T_1}} = \sqrt{\frac{927+273}{27+273}} = \sqrt{\frac{1200}{300}} = 2 \quad \Rightarrow \quad c_2 = 2c_1 = 2\ (0.3\ \text{m s}^{-1}) = 0.6\ \text{m s}^{-1}$$

42. The root mean square speeds of gaseous molecule is given by $u_{rms} = \sqrt{3RT/M}$.

43. The average speed of gaseous molecules is given by $u_{av} = \sqrt{8RT/\pi M}$.

44. The most probable speed of gaseous molecules is given by $u_{mp} = \sqrt{2RT/M}$.

45. $u_{rms} : u_{av} : u_{mp} :: \sqrt{3} : \sqrt{8/\pi} : \sqrt{2} :: 1.732 : 1.60 : 1.414$

46. See Q.45

47. Smaller the molar mass, larger the average speed.

48. $u_{mp} = \sqrt{2RT/M} \quad \Rightarrow \quad \sqrt{2R/M} = u_{mp}/\sqrt{T} = (0.3\ \text{m s}^{-1})/(300\ \text{K})^{1/2}$

$u_{av} = \sqrt{8RT/\pi M} = \left(\sqrt{2R/M}\right)\left(2\sqrt{T/\pi}\right) = [(0.3\ \text{m s}^{-1})/(300\ \text{K})^{1/2}]\ [2(1200\text{K}/3.14)^{1/2}]$

$= (0.3\ \text{m s}^{-1})\ \left(4/\sqrt{3.14}\right) = 0.68\ \text{m s}^{-1}$

49. The root mean square speed varies with change in temperature, but not with changes in pressure, volume and density of the gas.

50. The root mean square speed of gaseous molecules is given by $u_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3pV_m}{M}}$.

The choice c is correct. The root mean square speed varies as $\sqrt{p/\rho}$ and not on $\sqrt{p}$ and $\sqrt{1/\rho}$ as the ratio p/ρ remains constant at a given temperature.

51. Since $u_{rms} = \sqrt{3RT/M}$, smaller the value of M, larger the root mean square speed. NH_3 has the least value of molar mass.

52. Since $u_{rms} = \sqrt{3RT/M}$, we have

$$\frac{T(O_2)}{M(O_2)} = \frac{T(SO_2)}{M(SO_2)}; \quad T(O_2) = \frac{T(SO_2)}{M(SO_2)}\ M(O_2) = \left(\frac{600\ \text{K}}{64}\right)(32) = 300\ \text{K} \equiv 27\ ^\circ\text{C}$$

53. $\frac{u_{rms}(H_2)}{u_{rms}(O_2)} = \left[\frac{T(H_2)}{M(H_2)}\frac{M(O_2)}{T(O_2)}\right]^{1/2} = \left[\left(\frac{50}{2}\right)\left(\frac{32}{800}\right)\right]^{1/2} = 1$

54. $\frac{u_{rms}(H_2)}{u_{rms}(N_2)} = \sqrt{7} \quad \Rightarrow \quad \left[\frac{T(H_2)}{M(H_2)}\frac{M(N_2)}{T(N_2)}\right]^{1/2} = \sqrt{7}$. Hence, $\frac{T(H_2)}{T(N_2)} = 7\frac{M(H_2)}{M(N_2)} = 7\left(\frac{2}{28}\right) = \frac{1}{2}$

55. We have $u_{rms} = \sqrt{3RT/M}$ and $u_{av} = \sqrt{8RT/\pi M}$

Hence $u_{av} = \sqrt{8/3\pi}\ u_{rms} = \sqrt{8/(3\times 3.14)}\ (490\ \text{m s}^{-1}) = 451.6\ \text{m s}^{-1}$

56. We have $u_{av} = \sqrt{8RT/\pi M}$ and $u_{mp} = \sqrt{2RT/M}$

Hence $u_{mp} = \sqrt{\pi/4}\ u_{av} = (3.14/4)^{1/2}\ (475\ \text{m s}^{-1}) = 420.9\ \text{m s}^{-1}$

57. Since $u_{av} = \sqrt{8RT/\pi M}$, we have $\frac{T}{(32)} = \frac{\{(327+273)\text{K}\}}{(16)} \quad \Rightarrow \quad T = 600 \times 2\ \text{K} = 1200\ \text{K} \equiv 927\ ^\circ\text{C}$

58. The average molar kinetic energy of a gas is given by $(3/2)RT$. It is independent of the molar mass of the gas.

59. The average kinetic energy of gaseous molecules is independent of the nature of the gas.

60. The total energy of gaseous molecules is given by $E = (3/2)nRT$. It varies with temperature only.

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61. The average kinetic energy is given by $\overline{E} = (3/2)kT$,

62. The average kinetic energy of gaseous molecules depends only on temperature and not on the nature of the gas.

63. The expressions are $u_{rms} = \sqrt{3RT/M}$ and $E = 3RT/2$

Hence, $$u_{rms} = \left[\left(\frac{3RT}{2}\right)\left(\frac{2}{M}\right)\right]^{1/2} = \sqrt{\frac{2E}{M}}$$

64. The expression of root mean square speed is $u_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3pV_m}{M}} = \sqrt{\frac{3p}{M/V_m}} = \sqrt{\frac{3p}{\rho}}$

65. The temperature at which a real gas obeys the ideal gas laws over a wide range of pressure is known as Boyle temperature.

66. The intermolecular forces between gaseous molecules is taken care by the van der Waals constant a.

67. Larger the value of van der Waals constant a, more easily the liquefaction of gas occurs.

68. For the amount n of a real gas, the van der Waals equation is expressed as $(p + n^2a/V^2)(V - nb) = nRT$.

69. The unit of n^2a/V^2 is the same as that of pressure. Hence, the unit of a is L^2 atm mol^{-2}.

70. The unit of nb is the same as that of volume. hence, the unit of b is cm^3 mol^{-1}.

71. The term that accounts for the molecular volume is $V - nb$.

72. The van der Waals constant b is four times the volume occupied by 1 mol of molecules.

73. Larger the value of van der Waals constant a, more easily the gas liquefiable.

74. If the temperature of a gas is more than its critical temperature, it cannot be liquefied.

75. The van der Waals equation of state is $\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT$

If we neglect b in comparison to V_m, we get

$$\left(p + \frac{a}{V_m^2}\right)(V_m) = RT \quad \text{or} \quad Z = \frac{pV_m}{RT} = 1 - \frac{a}{V_m RT}, \quad \text{that is,} \quad Z < 1.$$

76. The van der Waals equation of state is $\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT$

If we ignore a/V^2 in comparison to p, we get

$$p(V_m - b) = RT \quad \text{or} \quad Z = \frac{pV_m}{RT} = 1 + \frac{pb}{RT}, \quad \text{that is,} \quad Z > 1.$$

77. At Boyle temperature, $Z = 1$ over wide range of pressure. This is due to the fact that effects produced by constants a and b compensate each other.

78. High temperature and low pressure conditions favour a gas to behave ideally.

79. Low temperature and high pressure conditions make the gas to behave nonideally.

80. The most favourable conditions for a gas to liquefy is low temperature and high pressure.

81. The compression factor of a real gas is defined as $Z = V_{m,\,real}/V_{m,\,ideal}$. Hence, $V_{m,\,real} < V_{m,\,ideal}$.

82. The second virial coefficient is $B = b - a/RT$. Its unit is the same as that b, that is, m^3 mol^{-1}

83. $Z = 1$ over a wide range of pressure.

84. The van der Waals constant b is four times the molecular volume of one mole of a gas.

85. The value of p_cV_c/RT_c is 3/8.

86. We have $p_{ideal} = p_{real} + a/V_m^2$

87. We have $V_{ideal} = V_{real} - b$

88. Negative deviation means $pV/nRT < 1$. This is possible when the term nb is negligible in comparison to the volume of the gas. In this situation, van der Waals equation is reduced to

$$\left(p + \frac{n^2a}{V^2}\right)(V) = nRT \quad \text{or} \quad \frac{pV}{nRT} = 1 - \frac{na}{VRT}$$

Hence, the constant a (which measures the attraction between molecules) is responsible for making $pV/nRT < 1$.

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89. The van der Waals constants a and b accounts for the forces of attraction amongst gaseous molecules and volume occupied by 1 mol of gaseous molecules, respectively. The van der Waals equation is

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

The terms n^2a/V^2 accounts for the pressure effects due to molecular attractions.

90. Positive deviation means $pV/nRT > 1$. This is possible when the term n^2a/V^2 is negligible in comparison to the pressure of the gas. In this situation, van der Waals equation is reduced to

$$p(V - nb) = nRT \text{ or } \frac{pV}{nRT} = 1 + \frac{pb}{RT}.$$

91. If the temperature of a gas is greater than its inversion temperature, heating is observed.

92. If the temperature of a gas is lower than its inversion temperature, cooling is observed.

93. If a gas exhibits neither heating nor cooling if its temperature is equal to its inversion temperature.

94. For a monatomic gas, we have $C_{V,\,m} = (3/2)R$; $C_{p,\,m} = (5/2)\,R$

95. Water has dipole moment. Because of hydrogen bonding, its T_c is larger.

96. At low temperatures, vibrational modes do not contribute towards heat capacity.

$$C_{V,\,m} = \text{contribution from (translational + rotational) modes}$$
$$= 3\left(\frac{1}{2}R\right) + 2\left(\frac{1}{2}R\right) = \frac{5}{2}R$$

97. We have $\lambda = \dfrac{1}{\sqrt{2}\,\pi\,\sigma^2 N^*}$, where $N^* = \dfrac{N}{V} = \dfrac{N/N_A}{V/N_A} = \dfrac{n}{V/N_A} = \dfrac{pV/RT}{V/N_A} = \dfrac{p}{kT}$

Hence $\lambda \propto T/p$

98. The fraction of molecules having speeds in the range c and $c + dc$ is

$$f = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} \exp\left(-Mc^2/2RT\right)c^2\,dc$$

Since f depends on M/T, both SO_2 at $2T$ and O_2 at T will have the same fracton.

99. The critical volume is three times the van der Waals constant b.

100. The correct expression is $p_c = a/(27/b^2)$

101. Since $N^* = p/kT$ and $\bar{u} = \sqrt{8RT/\pi M}$, we have

$$z_1 \propto \bar{u}\ N^{*2} \propto \sqrt{T}\ (p/T)^2 = p^2/T^{3/2}$$

102. Viscosity of a gas increases with increase in temperature. It is due to the transfer of momentum from one layer to another.

103. The inversion temperature of a van der Waals gas is given by the expression $T_i = 2a/Rb$.

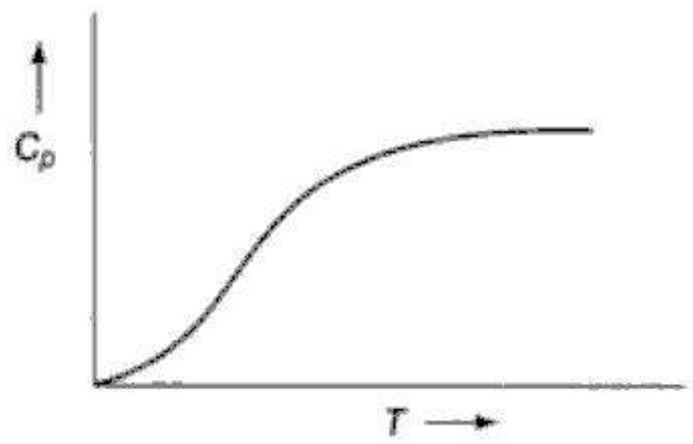


Fig. 2.2

104. Heat capacity variation follows the pattern shown in Fig. 2.2.

105. Fraction of molecules follows the pattern is shown in Fig. 2.3.

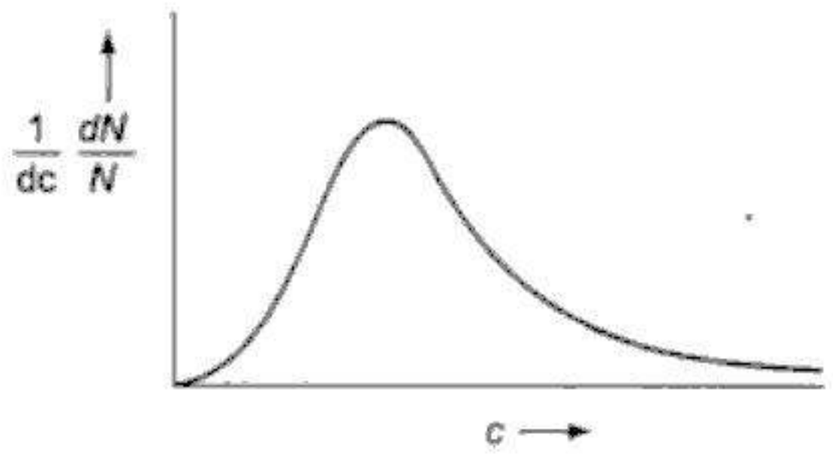


Fig. 2.3

106. We have $T_c = \dfrac{8a}{27\,Rb}$ and $T_B = \dfrac{a}{Rb}$. Hence $T_c = \dfrac{8}{27}\,T_B$

107. The Boyle temperature is given by $T_B = a/Rb$.

108. The second virial coefficient $B(= b - a/RT)$ is zero at Boyle temperature.

109. Helium gas will have minimum a, since it is not easily liquefiable as compared to other given gases.

110. Carbon dioxide is easily liquefiable, hence its critical temperature must be higher than those of the given gases.

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111. For an ideal gas $pV = nRT$ Thus $p\Delta V = nR\Delta T$

or $\dfrac{\Delta V}{\Delta T} = \dfrac{nR}{p} = \dfrac{nR}{nRT/V}$ or $\dfrac{1}{V}\dfrac{\Delta V}{\Delta T} = \dfrac{1}{T}$

With increase in temperature, the value of $(1/V)(\Delta V/\Delta T)$ decreases.

112. The expression of mean free path is $\lambda = \dfrac{1}{\sqrt{2}\,\pi N^* \sigma^2}$

where N^* is the number of molecules per unit volume and σ is the molecular diameter.

Multiple Correct Choice Type

1. The equations of an ideal gas are

$pV = nRT$

$pV = nRT = (m/M)RT;\ p = (m/V)RT/M = \rho RT/M$

$pV = (1/3)\, mN\, \overline{u^2}$

3. (a) $V_t = V_0 + \dfrac{t/^\circ\text{C}}{273} V_o$; intercept is not zero

(b) $V_T = KT$; intercept is zero

(c) $V = KT$; slope is K

4. The expression of mean free path is $\lambda = 1/\sqrt{2}\,\pi\,\sigma^2\,N^*$ where $N^* = \pi/kT$. Hence, $\lambda = kT/\sqrt{2}\,\pi\,\sigma^2\,p$.

5. (a) Mean square speed is given by $\overline{u^2} = 3RT/M = 3kT/M$

(c) The expression of viscosity is $\eta = (mkT)^{1/2}/\pi^{3/2}\sigma^2$.

6. (a) $n(H_2) = m/2$ g mol^{-1}; $n(CH_4) = m/16$ g mol^{-1}. Since $n(H_2) > n(CH_4)$, it follows that $N(H_2) > N(CH_4)$

(b) Average speed depends upon $\sqrt{T/M}$.

$$\frac{u(H_2)}{u(CH_4)} = \left[\frac{T(H_2)}{M(H_2)}\frac{M(CH_4)}{T(CH_4)}\right]^{1/2} = \left[\left(\frac{300\,\text{K}}{2\,\text{g mol}^{-1}}\right)\left(\frac{16\,\text{g mol}^{-1}}{600\,\text{K}}\right)\right]^{1/2} = 2$$

(c) For an ideal gas, compression factor is equal to 1.

(d) $(KE)_{total} = n(KE) = n(1.5\ RT)$

$$\frac{KE(H_2)}{KE(CH_4)} = \frac{(m/2\,\text{g mol}^{-1})(1.5R)(300\,\text{K})}{(m/16\,\text{g mol}^{-1})(1.5R)(600\,\text{K})} = 4$$

7. (a) Since $pV = nRT$, the term pV is dependent on temperature.

(c) If na/V^2 is neglected in the van der Waals equation, we get

$$p(V - nb) = nRT \Rightarrow Z = \frac{pV}{nRT} = 1 + \frac{pp}{RT}$$

8. (a) If nb is neglected in the van der Waals equation, we get

$$(p + n^2a/V^2)V = nRT \Rightarrow Z = pV/nRT = 1 - na/VRT$$

(b) see, Q. 7

(c) The excluded volume is four times the volumes of molecules of 1 mol of a gas.

9. (a) Average energy $(= 1.5kT)$ depends only on temperature

(b) $\bar{u}$ $(=\sqrt{8RT/\pi M}\,)$ is inversely proportional to the square root of molar mass

(c) The unit of Boltzmann constant is J K^{-1}

(d) see Q.8

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10. (b) The molar heat capacity of diatomic molecules is $2.5R$, there is no contribution from vibrational motion
(d) The average vibrational energy of a diatomic molecule is kT, because both kinetic energy and potential energy contribute.

11. (a) Average energy depends only on temperature of the gas.
(b) For $m_1 > m_2$, we will have $n_1 > n_2$.
(c) Since $pV = nRT$, we will have $T_1 < T_2$ for $n_1 > n_2$.
(d) Since $pV = nRT = (m/M)\,RT$, we will have $p_1 > p_2$ for $m_1 > m_2$.

12. (a) The unit of $K = \dfrac{\text{unit of volume}}{\text{unit of temperature}} = \dfrac{\text{m}^3}{\text{K}}$

(b) We have

$$V_2 = V_1\left(\frac{T_2}{T_1}\right) = V_1\left(\frac{273+50}{273+25}\right) = V_1\left(\frac{323}{298}\right) \neq 2\ V_1$$

(c) 32 g of O_2 and 16 g of CH_4, each is equal to 1 mol. Hence, they occupy the same volume.
(b) A real gas can be liquefied provided its temperature is less than its critical temperature.

13. (a) The gas can be liquefied if its temperature is less than its critical temperature.
(b) At high temperature, the effect of intermolecular attractions become insignificant. At low pressue, volume of the gas will be large and thus the volume occupied by gaseous molecules will be negligible.
(c) V_0 is the volume at 0 °C and not at 0 K.
(d) The rate of diffusion will be directly proportional to the average speed (or any other speed such as root mean square speed) of its gaseous molecules which is given as

$$u_{av} = \sqrt{\frac{8RT}{\pi M}} \qquad \text{Hence, } u_{av} \propto \sqrt{T} \text{ and } u_{av} \propto \sqrt{1/M}\,.$$

14. (a) Assming gas to be ideal, we have

$$pV = n\,RT = \left(\frac{m}{M}\right)RT \qquad \text{or} \qquad M = \left(\frac{m}{V}\right)\frac{RT}{p} = \left(\frac{\rho}{p}\right)RT$$

(b) Since $M = \left(\dfrac{\rho}{p}\right)RT$ or $\left(\dfrac{\rho}{p}\right) = \dfrac{M}{RT}$, the term ρ/p is independent of p at constant T.
(c) The value of Avogadro constant is $6.022 \times 10^{23}\ \text{mol}^{-1}$.
(d) The relevant expressions are $V_t = at + b$ and $V_T = KT$

15. (a) It is not equal masses but equal amounts of gases.
(b) An ideal gas does not involve molecular attractions.
(c) It is zero kelvin and not 0 °C.
(d) The room temperatrure is much larger than the critical temperature.

16. (a) The correct expression is $pV = (1/3)\,mN\overline{u^2}$ that is, it involves mean square speed and not square of mean speed.
(b) $\overline{u^2}$ stands for mean square speed whereas $\bar{u}^2$ stands for square of mean speed.
(c) The expression of density is $\rho = Mp/RT$
Thus, density decreases with increase in temperature at constant pressure. The qualitative explanation is that increase in temperature causes increase in volume hence decrease in density (= mass/volume).
(d) According to kinetic theory of gases. $\overline{\text{KE}} = (3/2)\,RT$

17. (a) The speed of molecules depend on the temperature and not on the pressure.
(b) The given value does not carry correct units. The value is $8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$.
(c) The given value does not carry correct units. The value is $1.38 \times 10^{-23}\ \text{J K}^{-1}$.

19. (b) The correct expression is $\overline{u^2} = \dfrac{u_1^2 + u_2^2 + \cdots + u_N^2}{N}$
(d) The expression $u_{av} = \sqrt{8RT/\pi M}$ suggests that $u_{av} \propto \sqrt{T}$.

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20. (a) Since $pV = (1/3)\, mN\overline{u^2}$, we get KE = $N_A\left(\frac{1}{2}m\overline{u^2}\right) = \frac{3}{2}pV_m = \frac{3}{2}RT$

(b) It is only monatomic gases which have $C_{p,m}/C_{V,m} = 5/3$ as $C_{p,m} = (5/2)R$ and $C_{V,m} = (3/2)R$.

(c) The expression $pV = (1/3)\, mN\, \overline{u^2}$ is applicable to an ideal gas.

(d) The expression is $\frac{u_{av}}{u_{mp}} = \frac{\sqrt{8RT/\pi M}}{\sqrt{2RT/M}} = \frac{\sqrt{8/\pi}}{\sqrt{2}}$.

21. (a) $u_{av}/u_{mp} = \sqrt{8RT/\pi M}\,/\sqrt{2RT/M} = 4/\pi$

(b) The unit is L^2 atm mol^{-2}.

(c) $\overline{u^2} = 3RT/M$

(d) The correct order is $u_{mp} < u_{av} < u_{rms}$.

22. (b) The constant a reflects the intermolecular attractions between gaseous molecules. The constant b reflects four times the actual volume occupied by 1 mol of gaseous molecules.

(c) An ideal gas cannot be liquefied as there exists no intermolecular attractions.

(d) The heat capacity of a monatomic gas is due to the contribution from translational motion for which energy levels are very close to each other.

23. The pressure of a gas decreases with increase in volume at constant temperature. The average kinetic energy of the molecules also remains constant at a constant temperature.

37. The expressions of u_{av}, u_{rms} and u_{mp} are

$$u_{av} = \sqrt{\frac{8RT}{\pi m}}; \quad u_{rms} = \sqrt{\frac{3RT}{m}}; \quad u_{mp} = \sqrt{\frac{2RT}{m}}$$

From these, it follows that $u_{mp} < u_{av} < u_{rms}$

The average kinetic energy of gaseous atom is

$$\overline{E} = \frac{1}{2}\, mu_{rms}^2 = \frac{1}{2}\, m\left(\frac{3}{2}u_{mp}^2\right) = \frac{3}{4}\, mu_{mp}^2$$

Linked Comprehension Type

1. The variation of Z with p for a van der Waals gas is shown in Fig. 2.4.

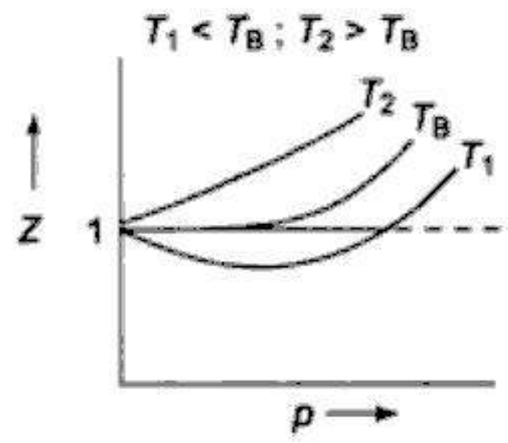


Fig. 2.4

(i) The value is $Z < 1$ provided $T < T_B$ and pressure is low.
(ii) The value is $Z > 1$ provided $T > T_B$ and pressure is high.
(iii) The value is $Z = 1$ provided $T = T_B$ and pressure is low.

2. (i) Ignoring a in the van der Waals equation gives

$$Z = \frac{pV_m}{RT} = 1 + \frac{bp}{RT} \quad \Rightarrow \quad Z > 1$$

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(ii) Ignoring b in the van der Waals equation gives

$$Z = \frac{pV_m}{RT} = 1 - \frac{a}{V_m RT} \quad \Rightarrow \quad Z < 1$$

(iii) At Boyle temperature, the constants satisfy the expression $T_B = a/Rb$.

3. (i) Both $C_{p,m}$ and $C_{V,m}$ vary with temperature

(iii) For triatomic molecules, $N = 3$ in the following expressions

$$\textit{Linear} \quad C_{V,m} = \frac{3}{2}R + R + (3N - 5)R = \frac{13}{2}R$$

$$\textit{Nonlinear} \quad C_{V,m} = \frac{3}{2}R + R + (3N - 6)R = 6R$$

4. (i) The unit of a is the same as that of the expression pTV_m^2, *i.e.* Pa K m^6 mol^{-2}

(ii) The Berthelot's equation is $p = \frac{RT}{V_m - b} - \frac{a}{TV_m^2}$

This gives $\frac{pV_m}{RT} = \frac{V_m}{V_m - b} - \frac{a}{V_m RT^2} = \left(1 - \frac{b}{V_m}\right)^{-1} - \frac{a}{V_m RT^2}$

$$= 1 + \frac{b}{V_m} + \left(\frac{b}{V_m}\right)^2 + \cdots - \frac{a}{V_m RT^2} = 1 + \frac{1}{V_m}\left(b - \frac{a}{RT^2}\right)^2 + \left(\frac{b}{V_m}\right)^2 + \cdots$$

The second virial coefficient is $B = b - \frac{a}{RT^2}$

(iii) At Boyle temperature $B = 0$. This gives $T_B = \sqrt{a/Rb}$

5. (i) In the Maxwell relation, the term $M/(2\pi RT)$ decreases while $\exp(-Mu^2/2RT)$ increases with increase in temperature. In the low speed range, the former is larger than the latter, consequently, the fraction decreases.

(ii) In the high speed range, the reverse of the effects discussd in (i) is observed, consequently, the fraction increases.

(iii) Here, also fraction decreases.

6. Comparing the coefficients of V_m's in the expressions

$$V_m^3 - \left(b + \frac{RT_c}{p_c}\right)V_m^2 + \frac{a}{p_c}V_m - \frac{ab}{p_c} = 0 \quad \text{and} \quad V_m^3 - 3V_c V_m^2 + 3V_c^2 V_m - V_c^3 = 0$$

we find that

(i) $b = V_c/3$; (ii) $a = 27\,(RT_c)^2/64p_c$; (iii) $p_c V_c / RT_c = 3/8$

ANNEXURE

Subjective Problems for Practice

SOLVED PROBLEMS

1. The pressure in a bulb dropped from 2000 to 1500 mmHg in 47 min, when the contained oxygen leaked through a small hole. The bulb was then completely evacuated. A mixture of oxygen and another gas of molar mass 79 g mol^{-1} in the molar ratio 1:1 at a total pressure of 4000 mmHg, was introduced. Find the molar ratio of the two gases remaining in the bulb after a period of 74 min. (1981)

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Solution Since the mixture contains 1:1 molar ratio of oxygen and another gas, partial pressures of oxygen and the second gas would be 2000 mmHg and 2000 mmHg, respectively. Now in 74 min, the decrease in partial pressure of oxygen would be

$$-\Delta p_{O2} = \frac{(2000-1500)\,\text{mmHg}}{47\,\text{min}} \times 74\ \text{min} = 787.2\ \text{mmHg}$$

Hence, Partial pressure of oxygen at the end of 74 min = (2000 – 787.2) mmHg = 1212.8 mmHg

Now, the ratio of rate of diffusion would be $\frac{r_2}{r_1} = \sqrt{\frac{32}{79}} = 0.6364$

Thus $-\Delta p_{\text{unknown gas}} = (0.6364)\ (787.2\ \text{mmHg}) = 501\ \text{mmHg}$

Partial pressure of unknown gas at the end of 74 min = (2000 – 501) mmHg = 1499 mmHg

Now since the amount of the gas remaining will be directly proportional to its partial pressure, we would have

$$\frac{n_2}{n_1} = \frac{1499}{1212.8} = \frac{1.236}{1}.$$

2. Calculate the average kinetic energy, in joules, of the molecules in 8.0 g of methane at 27 °C. (1982)

Solution We have

$$\text{Average kinetic energy of the gas} = \frac{3}{2}RT = \left(\frac{3}{2}\right)(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})\ (300.15\ \text{K}) = 3743\ \text{J mol}^{-1}.$$

3. The density of mercury is 13.6 g cm^{-3}. Calculate approximately the diameter of an atom of mercury assuming that each atom occupying a cube of edge length equal to the diameter of the mercury atom.

Solution Volume of one atom of Hg is

$$v = \frac{\text{mass of one atom}}{\text{density}} = \frac{(200\ \text{g mol}^{-1})/(6.022\times10^{23}\ \text{mol}^{-1})}{13.6\ \text{g cm}^{-3}} = 2.44 \times 10^{-23}\ \text{cm}^3$$

As each atom occupies a cube of edge length equal to the diameter of the Hg atom, we will have

$$d^3 = 2.44 \times 10^{-23}\ \text{cm}^3 \quad \text{or} \quad d = (2.44 \times 10^{-23}\ \text{cm}^3)^{1/3} = 2.90 \times 10^{-8}\ \text{cm}.$$

4. Oxygen is present in 1-litre flask at a pressure of 7.6×10^{-10} mmHg. Calculate the number of oxygen molecules in the flask at 0 °C. (1983)

Solution Using the expression $pV = nRT$, we have

$$n = \frac{pV}{RT} = \frac{\{(7.6\times10^{-10}/760)\text{atm}\}\,(1\text{L})}{(0.0821\ \text{atm L K}^{-1}\ \text{mol}^{-1})(273.15\ \text{K})} = 4.459 \times 10^{-14}\ \text{mol}$$

$$N = nN_A = (4.459 \times 10^{-14}\ \text{mol})\ (6.023 \times 10^{23}\ \text{mol}^{-1}) = 2.686 \times 10^{10}.$$

5. When 2 g of a gas A is introduced into an evacuated flask kept at 25 °C, the pressure is found to be 1 atm. If 3 g of another gas B is then added to the same flask, the total pressure becomes 1.5 atm. Assuming ideal gas behaviour, calculate the ratio of molar masses $M_A : M_B$. (1983)

Solution Since $pV = n\ RT$, we have

$$pV = \frac{m}{M}\ RT \quad \text{or} \quad M = \frac{mRT}{pV}$$

Hence, $M_A = \frac{(2\,\text{g})RT}{(1\,\text{atm})\ V}$ and $M_B = \frac{(3\,\text{g})RT}{(0.5\,\text{atm})\ V}$. Thus, $\frac{M_A}{M_B} = \left(\frac{2}{1}\right)\left(\frac{0.5}{3}\right) = \frac{1}{3}$.

6. Calculate the root mean square speed of ozone kept in a closed vessel at 20°C and 82 cmHg pressure. (1985)

Solution We have

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \left[\frac{3(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(293.15\ \text{K})}{(0.048\ \text{kg mol}^{-1})}\right]^{1/2} = 390.3\ \text{m s}^{-1}.$$

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7. A spherical balloon of 21 cm diameter is to be filled up with hydrogen at STP from a cylinder containing the gas at 20 atm at 27 °C. If the cylinder can hold 2.82 L of water, calculate the number of balloons that can be filled up. **(1987)**

Solution We have,

$$\text{Volume of balloon} = \frac{4}{3}\pi r^3 = \left(\frac{4}{3}\right)\left(\frac{22}{7}\right)\left(\frac{21\,\text{cm}}{2}\right)^3 = 4851\ \text{cm}^3$$

Total volume of the gas available at STP conditions is

$$V = \frac{p_1 V_1}{T_1}\frac{T_0}{p_0} = \frac{(20\,\text{atm})(2.82\,\text{L})}{(300\,\text{K})}\left(\frac{273\,\text{K}}{1\,\text{atm}}\right) = 51.324\ \text{L} = 51324\ \text{cm}^3$$

When the balloons are being filled, the pressure in the cylinder will decrease. We can continue filling from the cylinder till the pressure within the cylinder is also 1 atm. At this stage, the volume of 2820 cm^3 of the gas will remain within the cylinder.

Hence, Volume of the gas which can be transferred to balloons will be = 51324 cm^3 – 2820 cm^3 = 48504 cm^3

$$\text{Number of balloons that can be filled up} = \frac{48504\ \text{cm}^3}{4851\,\text{cm}^3/\text{balloon}} = 10\ \text{balloons.}$$

8. The average speed at T_1 (in kelvin) and the most probable speed at T_2 (in kelvin) of CO_2 gas is 9.0×10^4 cm s^{-1}. Calculate the values of T_1 and T_2. **(1990)**

Solution We have $u_{av} = \sqrt{\frac{8RT}{\pi M}}$

Hence, $\sqrt{\frac{8RT_1}{\pi M}} = 9.0 \times 10^4\ \text{cm s}^{-1}$

or $$T_1 = (9.0 \times 10^2\ \text{m s}^{-1})^2\left(\frac{\pi M}{8R}\right) = (9.0 \times 10^2\ \text{m s}^{-1})^2\left[\frac{(3.14)(44 \times 10^{-3}\ \text{kg mol}^{-1})}{(8)(8.314\,\text{J K}^{-1}\,\text{mol}^{-1})}\right] = 1682.5\ \text{K}$$

For most probable speed, we have

$$\sqrt{\frac{2RT_2}{M}} = 9.0 \times 10^2\ \text{m s}^{-1}$$

Hence, $$T_2 = (9.0 \times 10^2\ \text{m s}^{-1})^2\left(\frac{M}{2R}\right) = (9.0 \times 10^2\ \text{m s}^{-1})^2\left[\frac{44 \times 10^{-3}\ \text{kg mol}^{-1}}{(2)(8.314\,\text{J K}^{-1}\,\text{mol}^{-1})}\right] = 2143.4\ \text{K}$$

9. 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 solidified 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 be have ideally.) **(1992)**

Solution To start with, we have

$$\text{Amount of nitric oxide} = \frac{pV}{RT} = \frac{(1.053\,\text{atm})(0.250\,\text{L})}{(0.0821\,\text{atm L K}^{-1}\,\text{mol}^{-1})(300\,\text{K})} = 0.01069\ \text{mol}$$

$$\text{Amount of oxygen} = \frac{pV}{RT} = \frac{(0.789\,\text{atm})(0.100\,\text{L})}{(0.0821\,\text{atm L K}^{-1}\,\text{mol}^{-1})(300\,\text{K})} = 3.203 \times 10^{-3}\ \text{mol}$$

According to the reaction $2NO + O_2 \rightarrow 2NO_2 \rightarrow N_2O_4$, 1 mol of O_2 reacts with 2 mol of NO. Thus, after the reaction, we will have

Amount of oxygen = 0

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Amount of nitric oxide = $(0.01069 - 2 \times 0.0032)$ mol = 4.283×10^{-3} mol
Amount of N_2O_4 formed = 3.203×10^{-3} mol

Now on cooling, $N_2O_4(g)$ is condensed. Thus, only nitric oxide will be present in the entire volume of 0.350 L. Hence,

$$\text{Pressure of the gas} = \frac{nRT}{V} = \frac{(4.283\times10^{-3}\,\text{mol}^{-1})\,(0.0821\,\text{atm L K}^{-1}\,\text{mol}^{-1})\,(220\,\text{K})}{(0.350\,\text{L})} = 0.221 \text{ atm.}$$

10. A gas bulb of 1 litre capacity contains 2.0×10^{21} molecules of nitrogen exerting a pressure of 7.57×10^3 N m^{-2}. Calculate the root mean square (rms) speed and the temperature of the gas molecules. If the ratio of most probable speed to the root mean square speed is 0.84, calculate the most probable speed for these molecules at this temperature. (1993)

Solution We are given that

$V = 1\ \text{L} \equiv 1\ \text{dm}^3 \equiv 10^{-3}\ \text{m}^3$; $N = 2.0 \times 10^{21}$
$p = 7.57 \times 10^3\ \text{N m}^{-2}$
T = ?; c_{rms} = ?; $c_{mp}/C_{rms} = 0.84$; c_{mp} = ?

Now Amount of gas = $\dfrac{2.0\times10^{21}}{6.022\times10^{23}\,\text{mol}^{-1}}$

Using ideal gas equation, we get

$$T = \frac{pV}{nR} = \frac{(7.57\times10^3\ \text{N m}^{-2})\,(10^{-3}\ \text{m}^3)}{(2.0\times10^{21}/6.022\times10^{23}\ \text{mol}^{-1})\,(8.314\,\text{J K}^{-1}\,\text{mol}^{-1})} = 274.2\ \text{K}$$

Now $$c_{rms} = \sqrt{\frac{3RT}{M}} = \left[\frac{3(8.314\,\text{J K}^{-1}\,\text{mol}^{-1})\,(274.2\,\text{K})}{28\times10^{-3}\,\text{kg mol}^{-1})}\right]^{1/2} = 494.22\ \text{m s}^{-1}$$

$c_{mp} = (0.84)\ (494.22\ \text{ms}^{-1}) = 415.14\ \text{m s}^{-1}$.

11. An LPG (liquefied petroleum gas) cylinder weighs 14.8 kg when empty. When full, it weights 29.0 kg and shows a pressure of 2.5 atm. In the course of use at 27 °C, the mass of the full cylinder is reduced to 23.2 kg. Find out the volume of the gas in cubic meters used up 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. (1994)

Solution Mass of gas used up = (29.0 – 23.2) kg = 5.8 kg
Molar mass of *n*-butane(C_4H_{10}) = 58 g mol^{-1}

$$\text{Amount of gas used up} = \frac{5.8\times10^3\ \text{g}}{58\,\text{g mol}^{-1}} = 10^2\ \text{mol}$$

Using ideal gas equation, $V = nRT/p$, we get

$$V = \frac{(10^2\ \text{mol})\,(0.082\,\text{L atm K}^{-1}\,\text{mol}^{-1})\,(300\,\text{K})}{1\,\text{atm}}$$ (For normal usuage, p = 1 atm)

= 2463 L = 2463 dm^3 = 2.463 m^3.

Final Pressure Inside the Cylinder The cylinder contains liquefied pertroleum gas in equilibrium with its vapours. So long liquid remains present, the pressure inside the cylinder remains constant. Since the cylinder contains 8.4 kg (= 23.2 kg – 14.8 kg) of the remaining LPG, the pressure inside the cylinder would be 2.5 atm.

12. The composition of the equilibrium mixture ($Cl_2 \rightleftharpoons 2\ Cl$), 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. (Relative atomic mass of Kr = 84.) (1995)

Solution Let the initial amount of Cl_2 be n. If α is the fraction of Cl_2 dissociated at equilibrium, we will have

Cl_2	$\rightleftharpoons$	2 Cl
$n(1-\alpha)$		$n(2\alpha)$

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Total amount of species at equilibrium, $n_{total} = n_{Cl_2} + n_{Cl} = n(1-\alpha) + n(2\alpha) = n(1+\alpha)$

Average molar mass of the mixture at equilibrium, $(M_{av})_{mix} = \dfrac{n M_{Cl_2}}{n(1+\alpha)} = \dfrac{M_{Cl_2}}{1+\alpha}$

Accordng to Graham's law of diffusion, we get

$$\frac{r_{mix}}{r_{Kr}} = \left[\frac{M_{Kr}}{(M_{av})_{mix}}\right]^{1/2} = \left[\frac{M_{Kr}(1+\alpha)}{M_{Cl_2}}\right]^{1/2}$$

or $$\alpha = \left(\frac{M_{Cl_2}}{M_{Kr}}\right)\left(\frac{r_{mix}}{r_{Kr}}\right)^2 - 1 = \left(\frac{71}{84}\right)(1.16)^2 - 1 = 1.1374 - 1 = 0.1374.$$

13. A mixture of ethane (C_2H_6) and ethene (C_2H_4) occupies 40 litres at 1.00 atm and 400 K. The mixture reacts completely with 130 g of O_2 to produce CO_2 and H_2O. Assuming ideal gas behaviour, calculate the mole fractions of C_2H_4 and C_2H_6 in the mixture. (1995)

Solution Total amount of the mixture, $n = \dfrac{pV}{RT} = \dfrac{(1.00\,\text{atm})(4.0\,\text{L})}{(0.082\,\text{L atm K}^{-1}\,\text{mol}^{-1})(400\,\text{K})} = 1.295\ \text{mol}$

The combustion reactions are

$$C_2H_6 + \tfrac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O \text{ and } \quad C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$$

Let x be the amount of C_2H_6 in the mixture. As per the above equations, the amount of oxygen consumed would be

$$n(O_2) = \frac{7}{2}x + 3\ (1.295\ \text{mol} - x)$$

This will be equal to the given amount which is 130 g/32 g mol^{-1}, i.e. (130/32) mol. Hence

$$\frac{7}{2}x + 3\ (1.295\ \text{mol} - x) = \frac{130}{32}\ \text{mol} \quad \text{or} \quad \frac{7}{2}x - 3x = \left(\frac{130}{32} - 3\times 1.295\right)\ \text{mol}$$

or $$x = 2(4.0625 - 3.885)\ \text{mol} = 0.355\ \text{mol}$$

$$\text{Mole fraction of } C_2H_6 = \frac{0.355}{1.295} = 0.274 \quad \text{and} \quad \text{Mole fraction of } C_2H_4 = 1.0 - 0.274 = 0.726$$

14. The relative humidity in a room (4 m × 4 m × 3 m) is 65%. Assuming ideal gas behaviour, what mass of water vapour is present in the room at 25 °C. Given : Vapour pressure of water = 23.8 Torr at 25°C.

Solution We have

$$p(H_2O) = 0.65 \times 23.8\ \text{Torr} = \left(\frac{0.65\times 23.8}{760}\times 101\,325\right)\text{Pa} = 2062.5\ \text{Pa}$$

Now $$n_{H_2O} = \frac{p_{H_2O}V}{RT} = \frac{(2062.5\,\text{Pa})(4\times 4\times 3\,\text{m}^3)}{(8.314\,\text{Pa m}^3\,\text{K}^{-1}\,\text{mol}^{-1})(298\,\text{K})} = 39.96\ \text{mol}$$

$$m_{H_2O} = n_{H_2O}\,M_{H_2O} = (39.96\ \text{mol})\ (18\ \text{g mol}^{-1}) = 719.3\ \text{g}.$$

15. The radius of an Xe atom is 1.3×10^{-8} cm. A 100 cm^3 container is filled with Xe at a pressure of 1.0 atm and a temperature of 273 K. Calculate the fraction of the volume that is occupied by Xe atoms.

Solution We have

$$\text{Amount of Xe atoms, } n = \frac{pV}{RT} = \frac{(1\,\text{atm})\,(100\times 10^{-3}\,\text{L})}{(0.0821\,\text{atm L K}^{-1}\,\text{mol}^{-1})\,(273\,\text{K})} = 4.467\times 10^{-3}\ \text{mol}$$

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Number of Xe atoms, $N = nN_A = (4.467 \times 10^{-3}\ \text{mol})\ (6.022 \times 10^{23}\ \text{mol}^{-1}) = 2.69 \times 10^{21}$

Volume occupied by Xe atoms $= N\left(\frac{4}{3}\pi r^3\right) = (2.69 \times 10^{21})\left[\frac{4}{3} \times 3.14 \times (1.38 \times 10^{-8}\,\text{cm})^3\right]$

$$= 2.47 \times 10^{-2}\ \text{cm}^3$$

Fraction of volume occupied by Xe atoms $= \frac{(2.47 \times 10^{-2}\ \text{cm}^3)}{(100\ \text{cm}^3)} = 2.47 \times 10^{-4}$.

16. Calculate the density of hydrogen chloride gas at 30 °C and 5 atm pressure.

Solution Since $pV = nRT = \frac{m}{M}RT$, we have $\rho = \frac{m}{V} = \frac{pM}{RT}$

Hence, $$\rho = \frac{(5\ \text{atm})\ (36.5\ \text{g mol}^{-1})}{(0.082\ \text{atm L K}^{-1}\ \text{mol}^{-1})\ (303.15\ \text{K})} = 7.34\ \text{g L}^{-1}.$$

17. The density of a given gas is 3.41 g L^{-1} at STP. Determine its density at 27 °C and 700 Torr.

Solution Since $\rho = pM/RT$, we have

$$\rho_2 = \left(\frac{p_2}{T_2}\right)\left(\frac{T_1}{p_1}\right)\rho_1 = \left(\frac{700\ \text{Torr}}{300\ \text{K}}\right)\left(\frac{273\ \text{K}}{760\ \text{Torr}}\right)(3.41\ \text{g L}^{-1}) = 2.86\ \text{g L}^{-1}.$$

18. The density of phosphorus vapour at 310 °C and 775 Torr is 2.64 g dm^{-3}. What is the molecular formula of phosphorus?

Solution Since $pV = nRT$, we have

$$pV = \frac{m}{M}RT \quad \text{or} \quad M = \left(\frac{m}{V}\right)\frac{RT}{p} = \rho\frac{RT}{p}$$

Substituting the given values, we get

$$M = \frac{(2.64\ \text{g dm}^{-3})\ (8.314\ \text{kPa dm}^3\ \text{K}^{-1}\ \text{mol}^{-1})\ (583\ \text{K})}{(775/760) \times 101.325\ \text{kPa}} = 123.8\ \text{g mol}^{-1}$$

Now since molar mass of P is 31 g mol^{-1}, we have

$$\text{Number of P atoms in a molelcule of phosphorus} = \frac{123.8}{31} = 4$$

Hence, Molecular formula of phosphorus is P_4.

19. A mixture of ethane (C_2H_6) and ethene (C_2H_4) occupied 35.5 L at 1.0 bar and 405 K. The mixture reacted completely with 110.3 g of O_2 to produce CO_2 and H_2O. What was the composition of the original mixture? Assume ideal gas behaviour.

Solution We have

$$\text{Total amount of the original mixture, } n = \frac{(1.0\ \text{bar})\ (35.5\ \text{L})}{(0.08314\ \text{bar L K}^{-1}\ \text{mol}^{-1})(405\ \text{K})} = 1.054\ \text{mol}$$

$$\text{Amount of } O_2 \text{ used in combustion} = \frac{110.3\ \text{g}}{32\ \text{g mol}^{-1}} = 3.447\ \text{mol}$$

The combustion reactions are

$$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(g) \quad \text{and} \quad C_2H_6(g) + \frac{7}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$$

If n_1 and n_2 are the amounts of $C_2H_4(g)$ and $C_2H_6(g)$ in the given mixture, we will have

$$n_1 + n_2 = 1.054\ \text{mol} \quad \text{and} \quad 3n_1 + \frac{7}{2}n_2 = 3.447\ \text{mol}$$

Solving for n_1 and n_2, we get

$$n_1 = 0.484\ \text{mol} \quad \text{and} \quad n_2 = 0.57\ \text{mol}$$

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20. A gaseous mixture of helium and oxygen is found to have a density of 0.518 g dm^{-3} at 25 °C and 720 Torr. What is the per cent by mass of helium in this mixture?

Solution We have

$$M_{av} = \frac{\rho RT}{p} = \frac{(0.518\ \text{g dm}^{-3})(0.082\ \text{atm dm}^{-3}\ \text{K}^{-1}\ \text{mol}^{-1})(298\ \text{K})}{(720/760)\ \text{atm}} = 13.36\ \text{g mol}^{-1}$$

If x is the mole fraction of helium in the mixture, we will have

$$M_{av} = x\,M_{He} + (1 - x)\,M_{O2} \quad \text{i.e.} \quad 13.36\ \text{g mol}^{-1} = x\ (4\ \text{g mol}^{-1}) + (1 - x)\ (32\ \text{g mol}^{-1})$$

Solving for x, we get $x = \dfrac{32 - 13.36}{28} = 0.666$

Hence, Mass per cent of helium $= \dfrac{0.666 \times 4}{0.666 \times 4 + 0.334 \times 32} \times 100 = 19.95$

21. A mixture of $NH_3(g)$ and $N_2H_4(g)$ is placed in a sealed container at 300 K. The total pressure is 0.5 atm. The container is heated to 1200 K, at which time both substances decompose completely according to the equations

$$2NH_3(g) \rightarrow N_2(g) + 3H_2(g) \qquad \text{and} \qquad N_2H_4(g) \rightarrow N_2(g) + 2H_2(g)$$

After decomposition is complete, the total pressure at 1200 K is found to be 4.5 atm. Find the amount per cent of $N_2H_4(g)$ in the original mixture.

Solution Let the original mixture contain the amounts n_1 and n_2 of NH_3 and N_2H_4, respectively.

Total amount of gases originally present $= n_1 + n_2$

From the given decomposition reactions, we find that

2 mol NH_3 produces a total of 4 mol of N_2 and H_2

1 mol N_2H_4 produces a total of 3 mol of N_2 and H_2

Hence, Total amount of gases after decomposition of gases $= 2n_1 + 3n_2$

Now, using ideal gas law, $pV = nRT$, we get

$$(0.5\ \text{atm})\ V = (n_1 + n_2)\ R\ (300\ \text{K}) \quad \text{and} \quad (4.5\ \text{atm})\ V = (2n_1 + 3n_2)\ R\ (1200\ \text{K})$$

where V is the volume of the container. Dividing the two expressions, we get

$$\left(\frac{2n_1 + 3n_2}{n_1 + n_2}\right)\left(\frac{1200\ \text{K}}{300\ \text{K}}\right) = \frac{4.5\ \text{atm}}{0.5\ \text{atm}}$$

or $$\frac{2n_1 + 3n_2}{n_1 + n_2} = \frac{9}{4} \quad \text{or} \quad \frac{2(n_1 + n_2) + n_2}{n_1 + n_2} = \frac{9}{4} \quad \text{or} \quad \frac{n_2}{n_1 + n_2} = \frac{9}{4} - 2 = \frac{1}{4}$$

Hence, per cent amount of N_2H_4 is $\dfrac{n_2}{n_1 + n_2} \times 100 = 25$.

22. The total pressure of a mixture of H_2 and O_2 is 1.00 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.

Solution For the original mixture, we have $n_1 = \dfrac{(1.00\ \text{bar})\ V}{RT}$

After the reaction, the amount of excess H_2 is given as $n_2 = \dfrac{(0.35\ \text{bar})\ V}{RT}$

The total amount of O_2 and H_2 that have undergone reaction to give water is $n = n_1 - n_2 = \dfrac{(0.65\ \text{bar})\ V}{RT}$

From the chemical equation $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ we conclude that the amounts of $H_2(g)$ and $O_2(g)$ that have reacted are

$$n(H_2) = \left(\frac{2}{3}\right)\left[\frac{(0.65\ \text{bar})\ V}{RT}\right] \qquad \text{and} \qquad n(O_2) = \left(\frac{1}{3}\right)\left[\frac{(0.65\ \text{bar})\ V}{RT}\right]$$

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Now $$n_{\text{total}}(H_2) = \left[(0.35 \text{ bar}) + \frac{2}{3}(0.65 \text{ bar})\right]\left(\frac{V}{RT}\right)$$

Hence, $$x(H_2) = \frac{n_{\text{total}}(H_2)}{n_{\text{total}}(H_2) + n(O_2)} = \frac{0.35 + \frac{2}{3}(0.65)}{\left[0.35 + \frac{2}{3}(0.65) + \frac{1}{3}(0.65)\right]} = 0.35 + \frac{2}{3}(0.65) = 0.78$$

$$x(O_2) = 1 - x(H_2) = 0.22.$$

23. Calculate the root mean square, average and most probable speeds of oxygen molecules at 300 K.

Solution We have

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \left[\frac{3(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(300 \text{ K})}{32 \times 10^{-3} \text{ kg mol}^{-1}}\right]^{1/2} = 483.6 \text{ m s}^{-1}$$

$$u_{\text{av}} = \sqrt{\frac{8RT}{\pi M}} = \left[\frac{8(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(300 \text{ K})}{(3.14)(32 \times 10^{-3} \text{ kg mol}^{-1})}\right]^{1/2} = 445.6 \text{ m s}^{-1}$$

$$u_{\text{mp}} = \sqrt{\frac{2RT}{M}} = \left[\frac{2(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(300 \text{ K})}{(32 \times 10^{-3} \text{ kg mol}^{-1})}\right]^{1/2} = 394.8 \text{ m s}^{-1}.$$

24. The escape velocity, the velocity required by an object to escape from the gravitational field of a body, is given by

$$v_e = \sqrt{2gr}$$

where $r = 6.37 \times 10^6$ m for earth. At what temperature will the v_{rms} of an H_2 molecule attain escape velocity?

Solution Equating v_e with v_{rms}, we get

$$\sqrt{2gr} = \sqrt{\frac{3RT}{M}}$$

or $$T = \frac{2Mgr}{3R} = \frac{2(2.0 \times 10^3 \text{ kg mol}^{-1})(9.81 \text{ m s}^{-2})(6.37 \times 10^6 \text{ m})}{3(8.314 \text{ J K}^{-1} \text{ mol}^{-1})} = 1.02 \times 10^4 \text{ K}.$$

25. Calculate the pressure exerted by 2 mol of CO_2(g) confined to 855 cm^3 volume at 300 K using (a) ideal gas equation, and (b) van der Waals equation. Given: $b(CO_2) = 42.8 \text{ cm}^3 \text{ mol}^{-1}$ and $a(CO_2) = 3.61 \text{ L}^2 \text{ atm mol}^{-2}$.

Solution We have

(a) $$p = \frac{nRT}{V} = \frac{(2 \text{ mol})(0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1})(300 \text{ K})}{(0.855 \text{ L})} = 57.61 \text{ atm}$$

(b) $$p = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2} = \frac{(2 \text{ mol})(0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1})(300\text{K})}{(0.855 \text{ L}) - (2 \text{ mol})(0.0428 \text{ L mol}^{-1})} - \frac{(2 \text{ mol})^2 (3.61 \text{ L}^2 \text{ atm mol}^{-2})}{(0.855 \text{ L})^2}$$

$$= 64.02 \text{ atm} - 19.75 \text{ atm} = 44.27 \text{ atm}.$$

26. Calculate the pressure exerted by 10^{23} gaseous particles each of mass 10^{-22} g in a container of volume 1 dm^3. The root mean square speed of gaseous molecules is 10^5 cm s^{-1}. What are the average and total kinetic energies of gaseous molecules? What will be its temperature?

Solution We have

$N = 10^{23}$ molecules; $m = 10^{-22} \text{ g} = 10^{-25} \text{ kg}$; $V = 1 \text{ dm}^3 = 10^{-3} \text{ m}^3$; $u_{\text{rms}} = 10^5 \text{ cm s}^{-1} = 10^3 \text{ m s}^{-1}$

From the kinetic gas equation, we get

$$p = \frac{1}{3}\frac{mN\overline{u^2}}{V} = \frac{1}{3}\frac{(10^{-25} \text{ kg})(10^{23})(10^3 \text{ m s}^{-1})^2}{(10^{-3} \text{ m}^3)} = \frac{1}{3} \times 10^7 \text{ Pa}$$

Average energy is

$$\overline{\text{KE}} = \frac{1}{2} m \overline{u^2} = \frac{1}{2}(10^{-25} \text{ kg})(10^3 \text{ m s}^{-1})^2 = \frac{1}{2} \times 10^{-19} \text{ J}$$

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Total kinetic energy is

$$\text{KE} = N(\overline{\text{KE}}) = (10^{23})\left(\frac{1}{2}\times 10^{-19}\text{ J}\right) = \frac{1}{2}\times 10^{4}\text{ J}$$

Now since $\overline{\text{KE}} = (3/2)kT$, we get

$$T = \frac{2}{3k}(\overline{\text{KE}}) = \frac{2(0.5\times 10^{-19}\text{ J})}{3(1.38\times 10^{-23}\text{ J K}^{-1})} = \frac{1}{4.14}\times 10^{4}\text{ K} = 2415\text{ K}$$

Alternatively, we may proceed as follows.

Since $u_{\text{rms}} = \sqrt{3RT/M}$, we get

$$T = \frac{M}{3R}u^2_{\text{rms}} = \frac{N_A m}{3R}u^2_{\text{rms}} = \frac{(6.022\times 10^{23}\text{ mol}^{-1})(10^{-25}\text{ kg})}{3(8.314\text{ J K}^{-1}\text{ mol}^{-1})}(10^3\text{ m s}^{-1})^2 = 2415\text{ K}$$

$$\overline{\text{KE}} = \frac{3}{2}kT = \frac{3}{2}(1.38\times 10^{-23}\text{ J K}^{-1})(2415\text{ K}) = 0.5\times 10^{-19}\text{ J}$$

$$\text{KE} = N(\overline{\text{KE}}) = (10^{23})(0.5\times 10^{-19}\text{ J}) = 0.5\times 10^{4}\text{ J}$$

Finally, $$p = \frac{nRT}{V} = \frac{(10^{23}/6.022\times 10^{23}\text{ mol}^{-1})(8.314\text{ J K}^{-1}\text{ mol}^{-1})(2415\text{ K})}{(10^{-3}\text{ m}^3)} = 3.334\times 10^{6}\text{ Pa.}$$

27. A litre gas bulb contains 1.03×10^{23} hydrogen molecules and the pressure exerted by these molecules is 101.325 kPa. Calculate the average square molecular speed of molecules.

Solution We have

$$V = 1\text{ L} = 1\text{ dm}^3;\quad p = 101.325\text{ kPa};\quad N = 1.03\times 10^{23}$$

Hence, $$n = \frac{N}{N_A} = \frac{1.03\times 10^{23}}{6.022\times 10^{23}\text{ mol}^{-1}} = 0.171\text{ mol}$$

$$T = \frac{pV}{nR} = \frac{(101.325\text{ kPa})(1\text{ dm}^3)}{(0.171\text{ mol})(8.314\text{ kPa dm}^3\text{ K}^{-1}\text{ mol}^{-1})} = 71.27\text{ K}$$

$$\overline{u^2} = \frac{3RT}{M} = \frac{3(8.314\text{ J K}^{-1}\text{ mol}^{-1})(71.27\text{ K})}{(2\times 10^{-3}\text{ kg mol}^{-1})} = 8.888\times 10^{5}\text{ (m s}^{-1})^2.$$

28. Calculate molecular diameter of helium from its van der Waals constant $b = 24\text{ mL mol}^{-1}$.

Solution Since $b = 4\times$ volume occupied by molecules of 1 mol of a gas, we have

$$b = 4N_A\left(\frac{4}{3}\pi r^3\right)$$

Therefore, $$r = \left(\frac{3b}{16N_A\pi}\right)^{1/3} = \left[\frac{3\times 24\text{ cm}^3\text{ mol}^{-1}}{16(6.023\times 10^{23}\text{ mol}^{-1})(3.14)}\right]^{1/3} = 1.335\times 10^{-8}\text{ cm} = 133.5\text{ pm}$$

Now Molecular diameter, $d = 2r = 267$ pm.

29. The molar volume of helium at 10.1325 MPa and 273 K is 0.011 075 of its molar volume at 101.325 kPa at 273 K. Calculate the radius of helium atom. The value of a may be neglected.

Solution The van der Waals equation after neglecting a reduces to

$$p(V_m - b) = RT$$

Substituting the given data, we get

At 10.1325 MPa: $(10.1325\text{ MPa})(0.011\,075\,V_m - b) = (8.314\text{ MPa cm}^3\text{ K}^{-1}\text{ mol}^{-1})(273\text{ K})$

$$0.011075\,V_m - b = 224.00\text{ cm}^3\text{ mol}^{-1} \quad (1)$$

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At 101.325 kPa: $(101.325 \text{ kPa})\,(V_m - b) = (8.314 \text{ kPa dm}^3 \text{ K}^{-1} \text{ mol}^{-1})\,(273 \text{ K})$

i.e. $V_m - b = 22.4 \text{ dm}^3 \text{ mol}^{-1} = 22.4 \times 10^3 \text{ cm}^3 \text{ mol}^{-1}$ (2)

Multiplying Eq. (2) by 0.011 075 and then subtracting Eq. (1) from it, we get

$$b - 0.011\,075\,b = (248.08 - 224) \text{ cm}^3 \text{ mol}^{-1}$$

or $$b = \frac{24.08 \text{ cm}^3 \text{ mol}^{-1}}{0.988925} = 24.35 \text{ cm}^3 \text{ mol}^{-1}$$

Hence, from the expression

$$b = \left(\frac{4}{3}\pi r^3\right)(4\,N_A)$$

we get $$r = \left(\frac{3b}{16\pi N_A}\right)^{1/3} = \left(\frac{3 \times 24.35 \text{ cm}^3 \text{ mol}^{-1}}{16 \times 3.14 \times 6.023 \times 10^{23} \text{ mol}^{-1}}\right)^{1/3} = 1.34 \times 10^{-8} \text{ cm} = 134 \text{ pm}$$

30. 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? (1994)

Solution Partial pressure of He $= \frac{4 \text{ mol}}{(4+1) \text{ mol}} \times 20 \text{ bar} = 16 \text{ bar}$

Partial pressure of $CH_4 = 20 \text{ bar} - 16 \text{ bar} = 4 \text{ bar}$

If r_{He} and r_{CH_4} are the rates of effusion of He and CH_4, respectively, then

$$\frac{r_{He}}{r_{CH_4}} = \left(\frac{p_{He}}{p_{CH_4}}\right)\left(\frac{M_{CH_4}}{M_{He}}\right)^{1/2} = \left(\frac{16}{4}\right)\left(\frac{16}{4}\right)^{1/2} = 8$$

Since the rate of effusion of He is eight times more than that of CH_4, the initial mixture issuing out will contain He and CH_4 in the molar ratio of 8 : 1.

31. An evacuated glass vessel weighs 50.0 g when empty, 148.0 g when filled with a liquid of density 0.98 g mL^{-1} and 50.5 g when filled with an ideal gas at 760 mmHg at 300 K. Determine the molar mass or the gas. (1998)

Solution Mass of water filled in the glass vessel, $m_l = (148.0 - 50.0)$ g $= 98.0$ g

Volume of glass vessel, $V = \frac{m_l}{\rho} = \frac{98.0 \text{ g}}{0.98 \text{ g mol}^{-1}} = 100 \text{ mL} = 0.1 \text{ dm}^3$

Mass of gas filled in the vessel, $m = (50.5 - 50.0)$g $= 0.5$ g

If M is the molar mass of the gas, we will have

$$pV = nRT = \frac{m}{M}RT$$

or $$M = \frac{mRT}{pV} = \frac{(0.5 \text{ g})\,(8.314 \text{ J K}^{-1}\text{mol}^{-1})(300 \text{ K})}{(101.325 \text{ kPa})\,(0.1 \text{ dm}^3)} = 123 \text{ g mol}^{-1}$$

32. Using van der Waals equation, calculate the constant a when two moles of a gas confined in a four-litre flask exerts a pressure of 11.0 atm at a temperature of 300 K. The value of b is 0.05 L mol^{-1}. (1998)

Solution Substituting the given data in the van der Waals equation of state

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

we get $$\left[11 \text{ atm} + \frac{(2 \text{ mol})^2 a}{(4 \text{ L})^2}\right][4 \text{ L} - (2 \text{ mol})\,(0.05 \text{ L mol}^{-1})] = (2 \text{ mol})\,(0.082 \text{ L atm K}^{-1} \text{ mol}^{-1})\,(300 \text{ K})$$

or $$\left(11 \text{ atm} + \frac{a}{4} \text{ mol}^2 \text{ L}^{-2}\right)(4 \text{ L} - 0.1 \text{ L}) = 49.2 \text{ L atm}$$

or $$a = 4\left(\frac{49.2}{3.9} \text{ atm} - 11 \text{ atm}\right) \text{L}^2 \text{ mol}^{-2} = 4(12.615 - 11) \text{ L}^2 \text{ atm mol}^{-2} = 6.46 \text{ L}^2 \text{ atm mol}^{-2}$$

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33. The degree of dissociation is 0.4 at 400 K and 1.0 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. (Relative atomic mass of P = 31.0 and that of Cl = 35.5.) (1998)

Solution If we start with 1 mol of PCl_5, we will have

$$\underset{(1\text{ mol})(1-\alpha)}{PCl_5} \rightleftharpoons \underset{(1\text{ mol})\,\alpha}{PCl_3} + \underset{(1\text{ mol})\,\alpha}{Cl_2}$$

Total amount of gases = (1 mol) $(1 + \alpha)$ = 1.4 mol (since $\alpha = 0.4$)

Volume of gaseous mixture would be

$$V = \frac{nRT}{p} = \frac{(1.4\text{ mol})(8.314\text{ J K}^{-1}\text{ mol}^{-1})(400\text{ K})}{(101.325\text{ kPa})} = 45.95\text{ dm}^3$$

Molar mass of PCl_5 = $(31.0 + 5 \times 35.5)$ g = 208.5 g

$$\text{Density of equilibrium mixture} = \frac{208.5\text{ g}}{45.95\text{ dm}^3} = 4.54\text{ g dm}^{-3}$$

34. 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. Determine the molecular formula of the compound. (1999)

Solution The rate of diffusion depends on the following factors.

$$r \propto p \quad \text{and} \quad r \propto \sqrt{1/M}$$

Taking these together, we get

$$\frac{r_2}{r_1} = \frac{p_2}{p_1}\left(\frac{M_1}{M_2}\right)^{1/2}$$

Since $r \propto 1/t$, we can write

$$\frac{t_1}{t_2} = \left(\frac{p_2}{p_1}\right)\left(\frac{M_1}{M_2}\right)^{1/2} \qquad \text{or} \qquad M_2 = \left(\frac{p_2}{p_1}\,\frac{t_2}{t_1}\right)^2 M_1$$

Identifying the script 1 with nitrogen and 2 with unknown gas, we get

$$M_2 = \left(\frac{1.6}{0.8} \times \frac{57}{38}\right)^2 (28\text{ g mol}^{-1}) = 252\text{ g mol}^{-1}$$

Let the molecular formula of the unknown compound be XeF_n. We will have

$$M_{Xe} + nM_F = 252\text{ g mol}^{-1} \qquad \text{i.e.} \quad [131 + n(19)]\text{g mol}^{-1} = 252\text{ g mol}^{-1}$$

$$n = \frac{252 - 131}{19} = 6.36 \simeq 6$$

Hence, the molecular formula of the gas is XeF_6.

35. The pressure exerted by 12 g of an ideal gas at temperature t (expressed in °C) in a vessel of volume V (expressed in litre) is one atm. When the temperature is increased by 10 degree Celsius at the same volume, the pressure increases by 10%. Calculate the temperature t and volume V. (Molecular weight of the gas = 120.) (1999)

Solution From the expression $pV = nRT$, we can write

$$\frac{p_1}{p_2} = \frac{T_1}{T_2} \qquad \text{(since } V \text{ and } n \text{ are constant)}$$

From the given data, we get

$$\frac{1\text{ atm}}{1.1\text{ atm}} = \frac{(273 + t/°\text{C})\text{ K}}{(273 + t/°\text{C} + 10)\text{K}} \qquad \text{or} \qquad 283 + t/°\text{C} = 1.1\ (273 + t/°\text{C})$$

or $$t/°\text{C} = \frac{283 - 1.1 \times 273}{0.1} = -173 \qquad \text{or} \qquad t = -173\ °\text{C}$$

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For the given system,

$$n = \frac{12\text{ g}}{120\text{ g mol}^{-1}} = 0.1\text{ mol} \quad \text{and} \quad T = (273 - 173)\text{K} = 100\text{ K}$$

Hence, $$V = \frac{nRT}{p} = \frac{(0.1\text{ mol})\,(0.082\text{ L atm K}^{-1}\text{ mol}^{-1})(100\text{ K})}{1\text{ atm}} = 0.82\text{ L}$$

Unsolved Problems

1. Two flasks of equal volume connected by a narrow tube (of negligible volume) are at 300 K and contain 0.7 mol of H_2 at 0.5 atm. One flask is immersed into a bath kept at 400 K while the other remains at 300 K. Calculate the final pressure and the amount of H_2 in each flask.
2. Calculate the root mean speed of H_2 molecules. Given that the density of gas at 1 atm is 0.09 g dm^{-3}.
3. The density of a gas is 1 g cm^{-3} at 63 K and 0.5 atm. What will be its density at STP?
4. Find the molar mass of Freon-11 (a chlorofluoromethane) from the fact that 8.29 dm^3 of its vapour at 200 °C and 790 Torr has a mass of 30.5 g.
5. The density of a gas X is 2.194 g dm^{-3} at 850 Torr and 298 K. Calculate its molar mass.
6. Calculate the relative rate of diffusion at a given pressure of carbon dioxide at 0 °C and at 100 °C.
7. Calculate the value of R in the units of cm^3 atm mol^{-1} K^{-1}.
8. A sample of nitrogen, collected over water at 25 °C and 752 Torr occupies 53.5 mL. What is the volume of dry gas at standard conditions? Given: Aqueous tension of water at 25 °C is 23.8 Torr.
9. What is the value of R when pressure is expressed in dyn m^{-2} and volume in mm^3?
10. One mole of a gas in a 10 L vessel exerts a pressure of 185.6 cmHg at 298 K. Calculate the value of van der Waals constant a. Given: $b = 39.1\text{ cm}^3\text{ mol}^{-1}$.
11. A mixture of $CH_4(g)$ and $C_2H_6(g)$ has a total pressure of 0.53 atm. Just enough $O_2(g)$ is introduced in the mixture to bring its complete combustion to $CO_2(g)$ and $H_2O(g)$. The total pressure of these two gases is found to be 2.2 atm. Assuming constant volume and temperature, find the fraction of CH_4 in the mixture.
12. A sample of $C_2H_2(g)$ has a pressure of 7.8 kPa. After some time a portion of it reacts to form $C_6H_6(g)$. The pressure of the mixtrue of gases is then 3.9 kPa. Assuming constant volume and temperature, find the fraction of C_2H_2, that has undergone reaction.
13. Two moles of NH_3 are encolsed in a 5 dm^3 vessel at 300 K. Calculate the pressure exerted by this gas by using van der Waals equation. Given: $a(NH_3) = 422.5\text{ kPa dm}^6\text{ mol}^{-2}$ and $b(NH_3) = 37.1\text{ cm}^3\text{ mol}^{-1}$.
14. A mixture of H_2 and N_2 weighing 0.116 g is collected over water at 50 °C and occupies a volume of 275 cm^3 when the total pressure is 1 atm. Calculate the composition of dry mixture in mole per cent. The vapour pressure of water at 50 °C is 0.122 atm.
15. Flask A contains a mixture of O_2, SO_2 and He in the volume ratio of 32 : 64 : 4. Flask B contains a mixture of the same gases in the mass ratio 32 : 64 : 4. Each flask is at 1.0 atm and 0 °C. Predict which of the two alternatives is true.
    (a) Partial pressures of three gases are same/different in flask A.
    (b) Partial pressures of three gases are same/different in flask B.
    (c) Partial pressure of O_2 in flask A is greater/smaller than that in flask B.
    (d) Partial pressure of SO_2 in flask A is greater/smaller than that in flask B.
    (e) Partial pressure of He in flask A is greater/smaller than that in flask B.
    (f) The average kinetic energy of gases in flask A will be greater/smaller than or equal to that in flask B.
16. One of the best rocket fuels is dimethylhydrazine. When mixed with dinitrogentetroxide, N_2O_4, it reacts according to the equation

$$(CH_3)_2N_2H_2(l) + 2N_2O_4(l) \rightarrow 3N_2(g) + 4H_2O(g) + 2CO_2(g)$$

    If 2.5 mol of dimethylhydrazine reacts completely with N_2O_4 and if the product gases are collected at 20 °C in a 250 L vessel, what is the pressure in the vessel?
17. 120 mL of NH_3 at 25 °C and 750 Torr was mixed with 165 mL of O_2 at 50 °C and 635 Torr and transferred to a 300-mL reaction vessel where they were allowed to react according to the equation

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$$

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What was the total pressure (in Torr) in the reaction vessel at 150 °C after the reaction is over? Assume the reaction goes to completion.

18. A gas is collected by the displacement of water until the total pressure inside a 100-mL flask is 700 Torr at 25 °C. What volume the dry gas would occupy at STP? Given : Aqueous tension of water at 25 °C is 23.8 Torr.

19. A gas, at a total pressure of 800 Torr and a volume of 500 mL over water at 35 °C, is compressed to a volume of 250 mL, also over water at 35 °C. Calculate the final pressure of the wet gas in Torr. Given : Aqueous tension of water at 35 °C is 42.2 Torr.

20. If 250 mL of O_2 over water at 30 °C and a total pressure of 740 Torr is mixed with 300 mL of N_2 over water at 25 °C and a total pressure of 780 Torr, what will be the total pressure if the mixture is in a 500-mL vessel over water at 35 °C? Given : Aqueous tensions of water at 25 °C, 30 °C and 35 °C are 23.8, 31.8 and 42.2 Torr, respectively.

ANSWERS

1. 0.57 atm, 0.4 mol at 300 K and 0.3 mol at 400 K
2. 1838 m s^{-1}
3. 0.46 g cm^{-3}
4. 137 g mol^{-1}
5. 48.0 g mol^{-1}
6. 0.86
7. 82.05 cm^3 atm K^{-1} mol^{-1}
8. 47.0 mL
9. 8.314×10^{14} (dyn m^{-2}) (mm^3) K^{-1} mol^{-1}
10. 1.4 L^2 atm mol^{-2}
11. 0.42 CH_4
12. 75 mol %
13. 944 kPa
14. 58.73 and 41.27
15. (a) different, (b) same, (c) smaller, (d) greater, (e) smaller, (f) same.
16. 1.23 atm
17. 975 Torr
18. 81.5 mL
19. 1557.8 Torr
20. 8.71 Torr

SECTION II | LIQUID STATE

Vapour Pressure

The vapour pressure of a liquid may be defined as the pressure of the vapour in equilibrium with the liquid. The vapour pressure of a liquid increases with the increase in temperature. The governing expression is

$$\log \frac{p_2}{p_1} = -\frac{\Delta_{vap}H_m}{2.303\,R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where $\Delta_{vap}H_m$ is the molar enthalpy of vaporization of the liquid.

The vapour pressure of a solvent invariably decreases when a nonvolatile solute is dissolved in it. This is due to the availability of lesser number of solvent molecules at its surface as compared to that available in pure solvent.

The boiling point of a liquid can be defined as the temperature at which its vapour pressure is equal to the external pressure. If the latter is equal to 1 atm, the corresponding temperature is known as the normal boiling point of the liquid.

Surface Tension

The surface tension of a liquid is defined as the force acting along the surface of a liquid at right angle to any line of unit length. Its SI unit is N m^{-1} and is equal to 10^3 dyn cm^{-1}. The surface tension (symbol: γ) of a liquid decreases with increase in temperature. The governing expression is

$$\gamma\,(Mv)^{2/3} = k(t_c - t - 6)$$

where M is the molar mass, v is the specific volume and t_c is the critical temperature.

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The surface active materials such as soap, salts of higher sulphonic acids and higher amines lower the surface tension of water. The cleansing action of soap or detergent solution is due to the lowering of surface tension between water and grease. The orientation of soap molecules at the surface is specific, —COO groups pointing towards the surface of water and hydrocarbon chains pointing outwardly. These hydrocarbon chains act as a solvent for the grease and thus the latter is detached from the cloth along with the dust.

The capillary action (rise or fall of a liquid level within the capillary tube) is due to the surface tension of the liquid. The expression governing this phenonmenon is given by

$$\gamma = \frac{1}{2} r \rho g l$$

where γ is surface tension, r is the radius of capillary tube, ρ is the density of liquid, g is acceleration due to gravity and l is the rise of liquid level in the capillary tube.

In a laboratory, the surface tension of a liquid can be determined by using a stalagmometer (Fig. 2.5). The liquid taken in the stalagmometer is allowed to fall dropwise. The average weight of the liquid drop is related to its surface tension by the expression

$$mg = (2\pi r)\gamma$$

where r is the radius of capillary tube of the stalagmometer. To avoid the measurement of r, the relative method is used where water (whose surface tension is known) is used as a reference liquid.

We have

For liquid : $m_l g = (2\pi r)\gamma_l$ and For water : $m_w g = (2\pi r)\gamma_w$

Hence $\gamma_l = (m_l/m_w)\gamma_w$ (2.1)

In drop-weight method, the mass of a fixed number of drops falling through the capillary tube is measured. In drop-number method, the number of drops obtained from a fixed volume of liquid is determined. We have

$$V = n\bar{v} = n(m/\rho) \quad \Rightarrow \quad m = V\rho/n$$

Hence, Eq. (2.1) modifies to

$$\gamma_l = (\rho_l/\rho_w)\ (n_w/n_l)\ \gamma_w$$



Fig. 2.5 Stalagmometer

Viscosity

The viscosity of a liquid is due to the forces of attraction between molecules flowing in different layers in a laminar flow of the liquid. The viscosity (or more precisely, the coefficient of viscosity) may be defined as the force per unit area required to maintain a velocity difference of unity between two parallel layers of liquid unit distance apart. Its SI unit is N m^{-2} s. (= Pa s) and is equal to 10 dyn cm^{-2} s (= 10 poise). With increase in temperature, the viscosity of a liquid decreases due to decrease in the molecular attractions. This effect may be compared with the effect observed in gases where viscosity increases with increase in temperature. In case of gases, viscosity is due to the transfer of molecules (along with their momenta) from one layer to another.

The relation governing the variation of viscosity of a liquid with temperature is

$$\eta = A \exp(E/RT)$$

where A is a constant and E is the activation energy for viscous flow.

The viscosity of a liquid invariably increases with impurities. The associated liquids such as water, alcohols and glycerol have higher viscosities as compared to the nonassociated liquids (benzene, toluene, etc.).

In a laboratory, viscosity of a liquid can be determined by using a viscometer (Fig. 2.6). A fixed volume of liquid is taken in the bigger bulb of the viscometer. It is sucked into the smaller bulb and time taken to fall the liquid level from marked A to marked B is noted down. The experiment is repeated with a reference liquid (water). The expressions (known as Poiseuille equation) to be used are

$$\eta_l = \frac{\pi r^4 p_l t_l}{8 l v} \qquad \text{and} \qquad \eta_w = \frac{\pi r^4 p_w t_w}{8 l v}$$

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Hence, $$\eta_l = \left(\frac{p_l t_l}{p_w t_w}\right)\eta_w$$

In the above expressions, p is the pressure due to which liquid flows in the capillary tube of viscometer. At any instant, it may be replaced by the density of the liquid. Hence

$$\eta_l = \left(\frac{\rho_l t_l}{\rho_w t_w}\right)\eta_w$$

Another method involves the falling of a steel ball in the viscous liquid. After some time, ball falls with a constant speed, such that

$$mg = 6\pi\,\eta\, r v \qquad \Rightarrow \qquad \eta = \frac{mg}{6\pi r v}$$

where r is radius of steel ball, v is the velocity the ball in the liquid and m is the mass of steel ball.

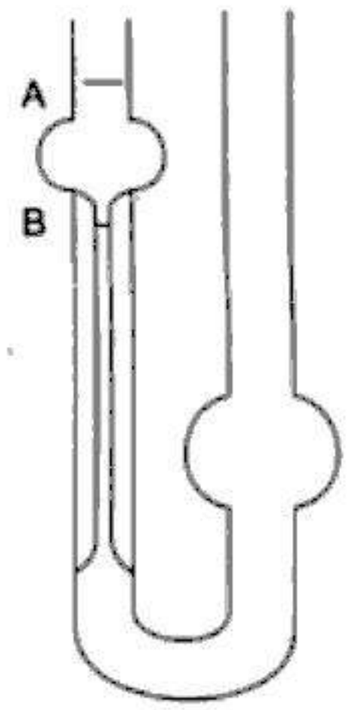


Fig. 2.6 Ostwald Viscometer

Straight Objective Type

1. Which of the following statements regarding a liquid is not correct?
(a) The vapour pressure of a liquid increases with increase in temperature
(b) The vapour pressure of a liquid decreases in the presence of a nonvolatile impurity
(c) The variation of vapour pressure with temperature is given by

$$\log p = \frac{\Delta_{vap} H_m}{2.303\,R}\frac{1}{T} + \text{constant}$$

(d) At the normal boiling point, the vapour pressure of a liquid is 1 atm.

2. Which of the following statements regarding a liquid is not correct?
(a) The surface tension of a liquid is a temperature dependent property
(b) The surface tension of a liquid is an intensive quantity.
(c) The SI unit of surface tension is N m^{-1}.
(d) For a liquid, surface tension and surface energy have different values.

3. Which of the following statements regarding a liquid is not correct?
(a) On dissolving sodium chloride in water, its surface tension decreases
(b) The variation of surface tension of a liquid is given by the expression $\gamma(Mv)^{2/3} = k(t_c - t - 6)$, where the various symbols have their usual meanings.
(c) Soap is a surface active substance
(d) 1 N m^{-1} = 10^3 dyn cm^{-1}

4. Which of the following statements regarding a liquid is not correct?
(a) The SI unit of viscosity is Pa s.
(b) 1 Pa s = 10 Poise.
(c) The viscosity of a liquid decreases with increase in temperature
(d) The viscosity of a gas decreases with increase in temperature

5. Which of the following statements is not correct?
(a) Viscosity of ethanol is smaller than that of glycol
(b) Viscosity of a liquid increases with impurities
(c) The variation of viscosity is given by $\eta = A\exp(-E/RT)$
(d) Capillary action is due to the surface tension of a liquid.

ANSWERS

1. (c) **2.** (d) **3.** (a) **4.** (d) **5.** (c)

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Hints and Solutions

1. The correct expression is

$$\log p = \frac{\Delta_{vap}H_m}{2.303\,R}\frac{1}{T} + \text{constant}$$

2. The surface tension and surface energy has the same numerical value.

3. The surface tension of water increases when sodium chloride is dissolved in it.

4. The viscosity of a gas increases with increase in temperature.

5. The variation of viscosity of a liquid varies with temperature. The governing expression is

$$\eta = A\,\exp(E/RT)$$

ANNEXURE

Subjective Problems for Practice

SOLVED PROBLEMS

Liquid State

1. The normal boiling point of cyclohexane (enthalpy of vaporization: 30.08 kJ mol^{-1}) is 80.75 °C. What will be its vapour pressure at 25 °C?

Solution We have

$$T_1 = 80.75\ °C \equiv 353.9\ K;\quad p_1 = 760\ mmHg;\quad T_2 = 25\ °C \equiv 298.15\ K;\quad p_2 = ?$$

Using the expression

$$\log \frac{p_2}{p_1} = -\frac{\Delta_{vap}H_m}{2.303\,R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

we get $$\log\left(\frac{p_2}{mmHg}\right) = \log\,(760) - \frac{30.08\times10^3\ J\,mol^{-1}}{(2.303)\,(8.314\ J\ K^{-1}\ mol^{-1})}\left[\frac{1}{298.15\ K} - \frac{1}{353.9\ K}\right]$$

This gives $p_2 = 112.4$ mmHg

2. In the determination of the surface tension of a liquid A by the drop-number method, equal volumes of A and water gave 60 and 20 drops, respectively. Calculate the surface tension of A if $\rho(A) = 0.86\ g\ cm^{-3}$ and $\rho(water) = 0.996\ g\ cm^{-3}$. Given: $\gamma(H_2O) = 72.75\times10^{-3}\ N\ m^{-1}$.

Solution Using the expression

$$\gamma_l = \left(\frac{\rho_l}{\rho_w}\frac{n_w}{n_l}\right)\gamma_w$$

we get $$\gamma_l = \left(\frac{0.86}{0.996}\frac{20}{60}\right)(72.75\times10^{-3}\ N\,m^{-1}) = 20.94\times10^{-3}\ N\ m^{-1}$$

3. The viscosity of diethyl ether in millipoise is 2.84 at 0 °C, 2.33 at 20 °C. Calculate the activation energy of diethyl ether for viscous flow and its viscosity at 60 °C.

Solution Using the expression $\eta = A\,\exp(E_a/RT)$, we get

$$\log\frac{\eta_2}{\eta_1} = \frac{E_a}{2.303\,R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Hence $$\log\left(\frac{2.33}{2.84}\right) = \frac{E_a}{(2.303)(8.314\ J\ K^{-1}\ mol^{-1})}\left[\frac{1}{293\ K} - \frac{1}{273\ K}\right]$$

This gives $$E_a = -\frac{\log(2.33/2.84)(293\ K)\,(273\ K)\,(2.303)\,(8.314\ J\ K^{-1}\ mol^{-1}]}{(20\ K)} = 6583\ J\ mol^{-1}$$

For 60 °C, we will have

$$\log\left(\frac{\eta_1}{2.84}\right) = \frac{(6583\ J\,mol^{-1})}{(2.303)(8.314\ J\ K^{-1}mol^{-1})}\left[\frac{1}{333\ K} - \frac{1}{273\ K}\right]$$

This gives $\eta_2 = 1.69$ millipoise

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4. The viscosity of an oil is 0.05 N m^{-2} s and its density is 0.97 g cm^{-3} at 298 K. How long a given liquid of the oil will take to flow through a viscometer if the same volume of water takes 50 s? Given: $\eta(H_2O) = 8.9 \times 10^{-4}$ N m^{-2} s. Take $\rho(H_2O) = 1.0$ g cm^{-3}.

Solution From the expression

$$\eta_l = \left(\frac{\rho_l t_l}{\rho_w t_w}\right)\eta_w$$

we get $$t_l = \left(\frac{\eta_l}{\eta_w}\right)\left(\frac{\rho_w}{\rho_l}\right)t_w = \left(\frac{0.05}{8.9 \times 10^{-4}}\right)\left(\frac{1}{0.97}\right)(50\ \text{s}) = 2\,896\ \text{s}$$

5. A steel ball of density 7.90 g cm^{-3} and 4 mm diameter requires 55 s to fall through a distance of 1 m through a liquid of density 1.10 g cm^{-3}. Calculate the viscosity of the liquid in poise.

Solution Volume of steel ball, $V = \frac{4}{3}\pi r^3 = \frac{4}{3}(3.14)(0.2\ \text{cm})^3$

Mass of steel ball, $m = V\rho = (0.0335\ \text{cm}^3)(7.90\ \text{g cm}^{-3}) = 0.265$ g

The viscosity of liquid is

$$\eta = \frac{mg}{6\pi r v} = \frac{(0.265 \times 10^{-3}\ \text{kg})(9.8\ \text{m/s}^2)}{6(3.14)(2 \times 10^{-3}\ \text{m})(1\ \text{m}/55\ \text{s})} = 3.79\ \text{Pa s} \equiv 37.9\ \text{poise}$$

SECTION III | SOLID STATE

Solids are characterized by their high density and low compressibility as compared to those of the gas phase. The values of these properties for solids indicate that the molecule (or ions) in them are relatively close together. Solids can be broadly classified into two categories, namely, crystalline and amporphous solids. The main characteristics of these are described in the following.

Crystalline Solids The outstanding characteristics of a crystal are its sharp melting point, its flat faces and sharp edges, which, in a well developed form, are usually arranged symmetrically. These properties are due to a high degree of internal order which extends throughout the crystal (a definite pattern constantly repeating in space). This is known as long-range order.

Amorphous Solids Amorphous solids do not have the long-range order but have a short-range order. In the latter, there exists some ordered arrangement around a particular atom or ion which lasts only upto short distances. This characteristics may not be found around a similar atom placed at a distance from the other atom. Examples of amorphous solids are glass, fused silica, rubber and polymers. Amorphous solids do not have the characteristics as possessed by crystalline solids. In many ways, they are more closely related to liquids than to the crystalline solids and are, therefore, regarded as supercooled liquids with high viscosity. A given material may be converted into the amorphous or glassy form by rapidly cooling the melt or freezing the vapour.

Classification of Crystals Based on Bond Type

The properties of most of the crystals are found to conform to one of the four general types of chemical bonds, in terms of which it is possible to classify them into four categories as described in the following.

Molecular Crystals (or van der Waals Crystals) Molecular crystals are those in which the crystalline state is composed of an aggregate of discrete molecules held together by van der Waals forces. Because of these weaker forces, molecular crystals are soft and possess comparatively low melting points. Examples are CO_2, CCl_4, Ar and most of the organic compounds.

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Ionic Crystals Ionic crystals involve electrostatic forces amongst their structural units. Because of stronger forces, ionic crystals are strong and likely to be brittle. The melting points are high, which decrease with increasing size of the ions. In ionic crystals, some of the atoms may be held together by covalent bonds to form ions having definite positions and orientations in crystal lattice.

Covalent Crystals Covalent crystals involve forces of chemical nature (covalent bonds) extended in three dimensions. These forces are strong, and consequently the crystals are strong and hard, with high melting points. Examples are diamond, silicon, etc.

Metallic Crystals Electrons are held loosely in these type of crystals. They are good conductors of electricity. Metallic crystals are strong and can be bent.

Seven Crystal Systems and Fourteen Bravais Lattices

Space Lattice A space lattice represents a three-dimensional translational repetition of the centres of gravity of the unit of pattern in the crystals by means of points (known as lattice points).

Unit Cell A unit cell represents a parallelopiped obtained by connecting the lattice point such that each parallelopiped contains a complete unit of pattern of the crystal. By translation or stacking of the parallelopipeds the entire crystal structure can be generated.

Seven Crystal Systems To describe a unit cell, six parameters are required. These are the three basis vectors along the three crystallographic axes (represented by the symbols a, b and c) and the three angles between the crystallographic axes (represented by the symbols α, β and γ). Based on the presence of certain rotation axes in the unit cell, crystals can be classified into seven categories (known as seven crystal systems). These are described in Table 2.1.

Table 2.1 Seven Crystal Systems

Crystal system	*Minimum Symmetry*	*Parallelopiped dimensions*	*Examples*
Triclinic	1	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90°$	$CuSO_4 \cdot 5H_2O$, $K_2Cr_2O_7$
Monoclinic	2	$a \neq b \neq c$ $\alpha = \beta = 90° \neq \gamma$	S(monoclinic) $CaSO_4 \cdot 2H_2O$ $Na_2SO_4 \cdot 10H_2O$
Orthorhombic	222	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$	S(rhombic), $BaSO_4$, KNO_3, K_2SO_4
Trigonal or Rhombohedral	3	$a = b = c$ $\alpha = \beta = \gamma \neq 90°$	$CaCO_3$
Cubic	3333	$a = b = c$ $\alpha = \beta = \gamma = 90°$	NaCl, diamond, Alums, CaF_2
Tetragonal	4	$a = b \neq c$ $\alpha = \beta = \gamma = 90°$	TiO_2, Sn(white) $ZrSiO_4$
Hexagonal	6	$a = b \neq c$ $\alpha = \beta = 90°$, $\gamma = 120°$	SiO_2, graphite, PbI_2, Mg, ZnO

Note: There is no crystal system with five-fold rotational axis, because the presence of such an axis does not satisfy the translational symmetry.

Fourteen Bravais Lattices In seven crystal systems, points are present at the corners of unit cell. Such a unit cell is known as primitive unit cell. Besides the points at the corners, there are lattices in which points are present at the centre of each face of unit cell (known as face-centered unit cell, symbol: F), or at the body centre of unit cell (known as body centred unit cell, symbol: I) or at the centre of two equivalent opposite faces (known as end-centred unit cell, symbol: C). Each of such unit cells (known as nonprimitive unit cells) also possesses the minimum rotational axes of the corresponding primitive unit cell. If such cells are counted, these are fourteen in all and are known as fourteen Bravais lattices (Table 2.2).

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Table 2.2 Fourteen Bravais Lattices

Unit Cell	*Bravais Lattices*
Triclinic	P
Monoclinic	P and C
Orthorhombic	P, I, C and F
Trigonal	P
Cubic	P, I and F
Tetragonal	P and I
Hexagonal	P

Packing in Crystalline Solids

The structure of crystalline solids is determined by the packing of their constituents. Most metals and nonmetals are found to have three types of packing. These are: (1) body-centred cubic (bcc) lattice packing, (2) hexagonal close-packed (hcp) lattice (ABAB ···, unit cell hexagon), and (3) cubical close-packed (ccp) lattice (ABCABC ···, unit cell face-centred cube). The hcp and ccp constitute the closest packings (Fig. 2.7).

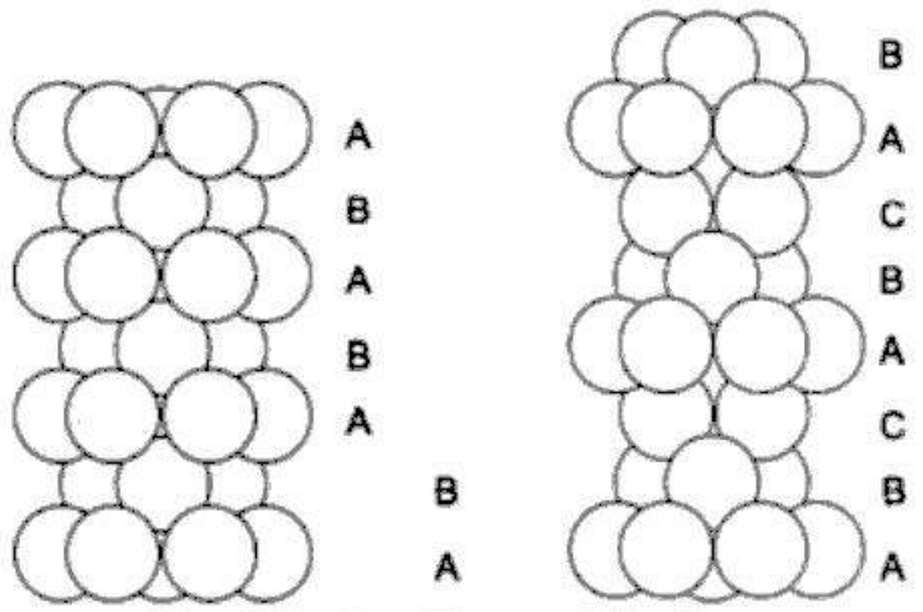


Fig. 2.7 Two Types of Packings

The total number of nearest neighbours of atom in bcc, hcp and ccp are 8, 12 and 12, respectively.

In many of the crystals, the void (or empty) spaces present in the closest-packed structures are also occupied by atoms of smaller sizes. There are two types of voides, namely, tetrahedral and octahedral. In three-dimensional closest-packed structures (hcp and ccp), there are two tetrahedral voids and one octahedral void present per closest packed atom. The two tetrahedral voids are present above and below each atom and the octahedral void is present midway between the two close-packed layers.

Ionic Crystals

In ionic crystals, it is not possible for both cations and anions to have close-packed structures due to their different sizes. However, if one of the ions is bigger than the other, it is common for the bigger ions (usually anions) alone to approach a close-packed structure and smaller ions to fit into holes (or voids) in this structure. The limiting sizes of cations that can fit into these voids without disturbing the closest packing of anions are as follows.

Octahedral void $\frac{r_c}{r_a} = 0.414$ Tetrahedral void $\frac{r_c}{r_a} = 0.225$

A few common ionic lattices are described below.

1. *Rock-Salt Structure* In such a structure, anions form a face-centred cubic unit cell and cations occupy octahedral voids. There are four anions and four cations per unit cell of this structure, and hence, the formula of ionic compound is A_4B_4 or simply AB. Examples are NaCl, KCl, MgO, CaO and SrO.
2. *Anti-Fluorite Structure* In this, anions form a cubical-closest packing arrangement and cations occupy tetrahedral voids. There are four anions and eight cations per unit cell of this structure, and hence, the formula of the ionic compound is A_8B_4 or simply A_2B. Examples are Li_2O, Na_2O, K_2O and Rb_2O.
3. *Zinc-Blende Structure* In such a structure (also known as sphalerite structure), anions form cubical closest-packed structure and cations are present in the half of the tetrahedral holes. There are four anions and four

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cations per unit cell of this structure, and hence, the formula of an ionic compound is A_4B_4 or simply AB. Examples are BeO and ZnS.

There is another polymorph of zinc sulphide in which S^{2-} ions form hexagonally close-packing and Zn^{2+} ions are present in half of the tetrahedral holes. This structure, which is known as *wurtzite structure*, also has (4,4)–coordination. Other examples of wurtzite structure are ZnO, AgI and one polymorph of SiC.

4. *Body-Centred Cubic Structure* In this structure, the cation is located at the body centre of a cube of anions, and the anion is located at the body centre of a cube of cations. There is one cation and one anion present per unit cell, and hence, the formula of an ionic compound is AB. In this structure, each ion has eight positively charged ions as its next nearest neighbours. Hence, the coordination number of each cation and anion is eight. Examples are CsCl, CsBr and CsI.
5. *Fluorite Structure* In this structure, cations form cubical-closest packing and anions occupy tetrahedral holes. Here

   Coordination number of cations = 8 Coordination number of anions = 4

   General formula : $M_{1/8}X_{1/4}$ or MX_2.

   Examples include UO_2, ThO_2 and CaF_2.
6. *Corundum Structure* In this structure, anions form hexagonal closest packing and cations are present in 2/3 of the octahedral holes. The general formula of the compound is $M_{2/3}X$ or M_2X_3. Examples include Fe_2O_3, Al_2O_3 and Cr_2O_3.
7. *Spinel Structure* In this structure, oxides are arranged in cubical-closest packing, one-eighth of the tetrahedral holes are occupied by divalent metal ion (A^{2+}) and one-half of the octahedral holes are occupied by trivalent metal ions (B^{3+}). In a unit cell, we have

   Number of divalent metal ions, $A^{2+} = \frac{1}{8}(8) = 1$ Number of trivalent metal ions, $B^{3+} = \frac{1}{2}(4) = 2$

   Number of oxide ions, $O^{2-} = 4$

   Hence, General formula of the compound: AB_2O_4. Examples are $ZnAl_2O_4$, $MgAl_2O_4$ and $ZnFe_2O_4$.

Stability of Ionic Structure Broadly, speaking, the stability of ionic structures depends upon the radius ratio of r_c and r_a. The structures predicted from the value of r_c/r_a are as follows.

Ratio	*Structure*	*Coordination number*
$\frac{r_c}{r_a} > 0.732$	Body-centred cube	8
$0.732 \geq \frac{r_c}{r_a} \geq 0.414$	face-centred cubic i.e. octahedral	6
$0.414 \geq \frac{r_c}{r_a} \geq 0.225$	tetrahedral	4

For example, chlorides of Li, K and Rb crystallize in the face-centred cubic lattice whereas the chloride of Cs crystallize in the body-centred cubic lattice.

Density of Cubic Crystals

This may be determined by using the expression

$$\rho = \frac{N}{a^3}\left(\frac{M}{N_A}\right)$$

where N is the number of molecules (or atoms) per unit cell, a is the edge length of the unit cell, M is the molar mass of the substance, and N_A is Avogadro's constant ($= 6.022 \times 10^{23}\ mol^{-1}$).

For metallic and nonmetallic crystals, the number of atoms per cubic unit cell and the expression connecting radius of atom (r) and edge length (a) of a unit cell are as follows.

Primitive Cubic Unit Cell Atoms are present at the corners of the cube. Each of the eight atoms present at the eight corners is shared amongst eight unit cells. Hence,

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$$\text{Number of atoms per unit cell} = 8\left(\frac{1}{8}\right) = 1$$

Atoms touch each other along edges. Hence, $r = a/2$

Body-Centred Cubic Unit Cell Besides atoms present at the corners of the cube, there is one atom in the centre of cube which belongs exclusively to this unit cell. Hence,

$$\text{Number of atoms per unit cell} = 8\left(\frac{1}{8}\right) + 1 = 2$$

Atoms touch each other along the cross diagonal of the cube. Hence

$$r = \left(\frac{\sqrt{3}}{4}\right) a$$

Face-Centred Cubic Unit Cell Besides atoms present at the corners of the cube, there are atoms at the centres of six faces, each of which is shared between two unit cells. Hence

$$\text{Number of atoms present per unit cell} = 8\left(\frac{1}{8}\right) + 6\left(\frac{1}{2}\right) = 4$$

Atoms touch each other along the face diagonal. Hence

$$r = \left(\frac{\sqrt{2}}{4}\right) a$$

For ionic crystals, the number of cations and anions (or molecules) per unit cell and the expressions connecting radii of cation and anion with the edge length are as follows.

Rock-Salt Structure There are four anions and four cations (i.e. four molecules) per unit cells. Cations and anions touch each along the edges. Hence,

$$N = 4$$

$$2r_c + 2r_a = a \quad \text{or} \quad r_c + r_a = \frac{a}{2}$$

Body-Centred Structure There is one anion and one cation (i.e. one molecule) per unit cell. Cation and anions touch each other along cross diagonal of the cube. Hence,

$$N = 1$$

$$2r_c + 2r_a = \sqrt{3}\ a \quad \text{or} \quad r_c + r_a = \left(\frac{\sqrt{3}}{2}\right) a.$$

PERCENTAGE OF VOID VOLUME

We calculate here the percentage of void volume in each of the three cubic Bravais lattices.

Primitive Cubic Lattice Here atoms touch each other along the edges, hence $r = a/2$. The number of atoms in a unit cell is one. Hence,

$$\text{Volume of unit cell} = a^3$$

$$\text{Volume occupied by atoms} = \frac{4}{3}\pi(a/2)^3$$

$$\text{Fraction of volume occupied} = \frac{(4/3)\pi(a/2)^3}{a^3} = \frac{\pi}{6} = 0.5236$$

$$\text{Fraction of void volume} = 1 - 0.5236 = 0.4764$$

$$\text{Percentage of void volume} = 47.64\%$$

Body-Centred Cubic Lattice Here atoms touch each other along the body-diagonal of the cube, hence $4r = \sqrt{3}\ a$. The number of atoms in a unit cell is two. Hence,

$$\text{Volume of unit cell} = a^3$$

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$$\text{Volume occupied by atoms} = 2\left[\frac{4}{3}\pi\left(\frac{\sqrt{3}}{4}a\right)^3\right]$$

$$\text{Fraction of volume occupied} = \frac{\sqrt{3}\,\pi}{8} = 0.6802$$

Fraction of void volume = 1 – 0.6802 = 0.3198

Percentage of void volume = 31.98%

Face-Centred Cubic Lattice Here atoms touch each other along the face diagonal of the cube, hence $4r = \sqrt{2}\,a$. The number of atoms in a unit cell is two. Hence

$N = 1$

Volume of unit cell = a^3

$$\text{Volume occupied by atoms} = 4\left[\frac{4}{3}\pi\left(\frac{\sqrt{2}}{4}a\right)^3\right]$$

$$\text{Fraction of volume occupied} = \frac{\sqrt{2}\,\pi}{6} = 0.7405$$

Fraction of void volume = 1 – 0.7405 = 0.2595

Percentage of void volume = 25.95%

Point Defects

The departure from the periodic arrangement around the vicinity of a lattice point is termed point defect. The following two types of point defects are commonly found in the crystalline ionic substances.

Schottky Defects The absence of a cation or anion from the position which it is expected to occupy in the periodic arrangement of ions is known as Schottky defect. The vacant positions give rise to vacancies or voids in the structure of the substance. The Schottky defects are more common in ionic compounds with high coordination numbers and where the positive and negative ions are of similar size, e.g. NaCl, CsCl, KCl and KBr. Since the solid with a Schottky defect contains lesser number of ions as compared to a perfect crystal, the density of the crystal exhibiting Schottky defect will be less as compared to that of the perfect crystal.

Frenkel Defect In this type of defect, the ion, instead of being in its expected location, is found in one of the interstices. Frenkel defects are more common in ionic crystals where size of the cation is such that it can be accommodated in the interstitial sites. That is, this type of defect is favoured by a large difference in size between the positive and negative ions and since the size of cation is smaller than that of the anion, the former can be accommodated in the interstitial position. Examples are ZnS, AgCl, AgBr and AgI. The density of crystals exhibiting Frenkel defects remains unchanged as the ions are present in the interstitial sites without changing the volume of the substance.

Straight Objective Type

Classification of Solids

1. Molecular solids are generally
(a) good conductors of electricity (b) quite hard
(c) quite brittle (d) volatile

2. Ionic solids are generally
(a) good conductor of electricity (b) soft
(c) volatile (d) quite brittle

3. CO_2 belongs to
(a) covalent crystal (b) molecular crystal (c) ionic crystal (d) metallic crystal

4. Which of the followings is an example of molecular crystal?
(a) CCl_4 (b) $CaCO_3$ (c) Silicon (d) Iron

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5. Which of the following is an example of covalent crystal ?
(a) CCl_4 (b) $CaCO_3$ (c) Silicon (d) Iron

6. Which of the following crystal types has generally low melting point?
(a) Ionic crystals (b) Molecular crystals (c) covalent crystals (d) Metallic crystals

7. Which of the following crystal types is a good conductor of heat and electricity ?
(a) Ionic crystals (b) Molecular crystals (c) Covalent crystals (d) Metallic crystals

Crystal Systems

8. In the primitive unit cell, the points are present at the
(a) corners of the unit cell (b) centre of the unit cell
(c) centre of each face of the unit cell (d) one set of faces of the unit cell

9. In the body-centred unit cell, the points are present at the
(a) corners of unit cell only (b) corners and centre of unit cell
(c) corners and centre of each face of the unit cell (d) corners and at one set of faces of unit cell

10. In the face-centred unit cell, the points are present at the
(a) corners of unit cell only (b) corners and centre of the unit cell
(c) corners and face centres of the unit cell (d) face centres of the unit cell

11. Which of the following dimensions of a unit cell represents a cubic unit?
(a) $a = b = c;\ \alpha = \beta = \gamma = 90°$ (b) $a = b = c;\ \alpha = \beta = 90° \neq \gamma$
(c) $a = b \neq c;\ \alpha = \beta = \gamma = 90°$ (d) $a \neq b \neq c;\ \alpha \neq \beta \neq \gamma$

12. The number of crystal systems in which a crystal can be classified is equal to
(a) 5 (b) 7 (c) 8 (d) 10

13. The number of Bravais lattices in a cubic crystal system is equal to
(a) 1 (b) 2 (c) 3 (d) 4

14. The number of Bravais lattices in which a crystal can be classified is equal to
(a) 8 (b) 10 (c) 12 (d) 14

15. Which of the following dimensions of a unit cell represents a tetragonal unit?
(a) $a = b = c;\ \alpha = \beta = \gamma = 90°$ (b) $a = b \neq c;\ \alpha = \beta = \gamma = 90°$
(c) $a = b = c;\ \alpha = \beta = \gamma \neq 90°$ (d) $a \neq b \neq c;\ \alpha \neq \beta \neq \gamma = 90°$

16. $CuSO_4 \cdot 5H_2O$ belongs to
(a) triclinic system (b) cubic system (c) tetragonal system (d) hexagonal system

17. Which of the following dimensions of a unit cell represents a hexagonal unit?
(a) $a = b = c;\ \alpha = \beta = \gamma = 90°$ (b) $a = b \neq c;\ \alpha = \beta = \gamma = 90°$
(c) $a = b \neq c;\ \alpha = \beta = 90°,\ \gamma = 120°$ (d) $a \neq b \neq c;\ \alpha \neq b \neq \gamma \neq 90°$

18. Which of the following dimensions of a unit cell represents a trigonal unit?
(a) $a = b = c;\ \alpha = \beta = \gamma = 90°$ (b) $a = b = c;\ \alpha = \beta = \gamma \neq 90°$
(c) $a \neq b \neq c;\ \alpha \neq \beta \neq \gamma = 90°$ (d) $a \neq b \neq c;\ \alpha = \beta = \gamma = 90°$

19. Which of the following dimensions of a unit cell represents a orthorhomic unit?
(a) $a = b = c;\ \alpha = \beta = \gamma = 90°$ (b) $a = b = c;\ \alpha = \beta = \gamma \neq 90°$
(c) $a \neq b \neq c;\ \alpha \neq \beta \neq \gamma = 90°$ (d) $a \neq b \neq c;\ \alpha = \beta = \gamma = 90°$

20. The minimum rotational symmetry present in a triclinic unit cell is
(a) 1 (b) 2 (c) 3 (d) 4

21. The minimum rotational symmetry present in a cubic unit cell is
(a) 2 (b) 222 (c) four 3 (d) 4

22. The minimum rotational symmetry present in a monoclinic unit cell is
(a) 1 (b) 2 (c) 3 (d) 4

23. Which of the following rotational symmetry is never present in a unit cell?
(a) 2 (b) 3 (c) 4 (d) 5

24. The number of Bravais lattices having monoclinic unit cell is
(a) 2 (b) 3 (c) 4 (d) 6

25. The number of Bravais lattices having tetragonal unit cell is
(a) 2 (b) 3 (c) 4 (d) 6

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46. The closest packed layers in the cubical-closest packing are perpendicular to
(a) the face of its unit cell (b) the face-diagonal of its unit cell
(c) edges of its unit cell (d) the body diagonal of its unit cell

47. The interplanar distance between the closest packed layers in the face-centered cubic unit cell is
(a) equal to the edge length (b) equal to the half of the edge length
(c) equal to the one third of body diagonal (d) equal to the half of face diagonal.

Ionic Solids

48. Which of the following FCC structures contains cations in the alternate tetrahedral voids?
(a) Na_2O (b) ZnS (c) CaF_2 (d) CaO (2005)

49. Which of the following substances does not crystallize in the rock-salt structure?
(a) NaCl (b) KCl (c) MgO (d) CsCl

50. Which of the following statements is correct in the rock-salt structure of an ionic compound?
(a) Coordination number of cation is four whereas that of anion is six
(b) Coordination number of cation is six whereas that of anion is four
(c) Coordination number of each cation and anion is four
(d) Coordination number of each cation and anion is six

51. Which of the following statements is correct in the body-centred cubic structure of an ionic compound?
(a) Coordination number of each cation and anion is two
(b) Coordination number of each cation and anion is four
(c) Coordination number of each cation and anion is six
(d) Coordination number of each cation and anion is eight

52. The general formula of an ionic compound crystallizing in the rock-salt structure is
(a) AB (b) AB_2 (c) A_2B (d) AB_3

53. The general formula of an ionic compound crystallizing in the body-centred cubic structure is
(a) AB (b) AB_2 (c) A_2B (d) AB_3

54. Which of the following statements is correct in the zinc-blende type structure of an ionic compound?
(a) Coordination number of each cation and anion is two
(b) Coordination number of each cation and anion is four
(c) Coordination number of each cation and anion is six
(d) Coordination number of each cation and anion is eight

55. The general formula of an ionic compound crystallizing in zinc-blende structure is
(a) AB (b) AB_2 (c) A_2B (d) AB_3

56. Which of the following statements is correct in the antifluorite structure of an ionic compound?
(a) Coordination number of anion is four and that of cation is eight
(b) Coordination number of anion is eight and that of cation is four
(c) Coordination number of each cation and anion is four
(d) Coordination number of each cation and anion is six

57. The general formula of an ionic compound crystallizing in antifluorite structure is
(a) AB (a) AB_2 (c) A_2B (d) AB_3

58. Which of the following statements is correct in the cubic-fluorite structure of an ionic compound?
(a) Coordination number of anion is four and that of cation is eight
(b) Coordination number of anion is eight and that of anion is four
(c) Coordination number of each cation and anion is four
(d) Coordination number of each cation and anion is six

59. The general formula of an ionic compound having cubic-fluorite structure is
(a) AB (b) AB_2 (c) A_2B (d) AB_3

60. If the anions (A) form hexagonal closest packing and cations (C) occupy only 2/3 octahedral voids in it, then the general formula of the compound is
(a) CA (b) CA_2 (c) C_2A_3 (d) C_3A_2

61. In the spinel structure, oxides ions are cubical-closest packed whereas 1/8th of tetrahedral voids are occupied by A^{2+} cations and 1/2 of octahedral voids are occupied by B^{3+} cations. The general formula of the compound having spinel structure is
(a) $A_2B_2O_4$ (b) AB_2O_4 (c) $A_2B_4O_2$ (d) $A_4B_2O_2$

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62. In a cubic unit cell, seven of the eight corners are occupied by atoms A and centres of faces are occupied by atoms B. The general formula of the compound is
(a) A_7B_6 (b) A_7B_{12} (c) A_7B_{24} (d) $A_{24}B_7$

63. An ionic compound is expected to have octahedral structure if r_c/r_a lies in the range of
(a) 0.414 to 0.732 (b) 0.732 to 0.82 (c) 0.225 to 0.414 (d) 0.155 to 0.225

64. An ionic compound is expected to have tetrahedral structure if r_c/r_a
(a) lies in the range of 0.414 to 0.732 (b) lies in the range of 0.225 to 0.414
(c) lies in the range of 0.155 to 0.225 (d) is more than 0.732

65. An ionic compound is expected to have body-centred cubic unit cell if r_c/r_a
(a) is greater than 0.732 (b) lies in the range of 0.414 to 0.732
(c) lies in the range of 0.225 to 0.414 (d) lies in the range of 0.155 to 0.225

66. A compound formed by elements A and B crystallises in a cubic structure where A atoms are at the corners of a cube and B atoms are the face-centres of the cube. The formula of the compound is
(a) AB_4 (b) AB_3 (c) AB_2 (d) AB

67. The 8 : 8 type packing is present is
(a) NaCl (b) CaF_2 (c) CrCl (d) KCl

68. The coordination number of a metal crystalling in a hexagonal close packed structure is
(a) 12 (b) 4 (c) 8 (d) 6 (2000)

69. In a solid 'AB' having the NaCl structure, 'A' atoms occupy the corners of the cubic unit cell. If all the face-centered 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 (2001)

70. A substance $A_x B_y$ crystallizes in a face centered cubic (FCC) lattice in which atoms 'A' occupy each corner of the cube and atoms 'B' occupy the centres of each face of the cube. Identify the correct composition of the substance $A_x B_y$
(a) AB_3 (b) A_4B_3
(c) A_3B (d) Composition cannot be specified (2002)

71. If $r(Na^+)/r(Cl^-) = 0.5$ and $r(Na^+)/r(K^+) = 0.7$, then the ratio $a(KCl)/a(NaCl)$ of edge lengths of unit cell is about
(a) 1.14 (b) 1.24 (c) 1.34 (d) 1.44

Density of Crystalline Solids

72. The expression to compute the density of metals crystallizing in cubic crystal is
(a) $\rho = \frac{N}{a^3}\left(\frac{M}{N_A}\right)$ (b) $\rho = \frac{N}{a^3}\left(\frac{N_A}{M}\right)$ (c) $\rho = \frac{a^3}{N}\left(\frac{M}{N_A}\right)$ (d) $\rho = \frac{a^3}{N}\left(\frac{N_A}{M}\right)$

73. The number of atoms in a single primitive cubic unit cell is
(a) 1 (b) 2 (c) 4 (d) 8

74. The number of atoms in a single body-centred cubic unit cell is
(a) 1 (b) 2 (c) 4 (d) 8

75. The number of atoms in a single face-centred cubic unit cell is
(a) 1 (b) 2 (c) 4 (d) 6

76. In the primitive cubic unit cell of closest packed atoms, the radius of atom in terms of edge length (a) of unit cell is
(a) $a/2$ (b) $a/2\sqrt{2}$ (c) $\sqrt{3}\ a/4$ (d) $4a/\sqrt{3}$

77. In the body-centred cubic unit cell of closest packed atoms, the radius of atom in terms of edge length (a) of the unit cell is
(a) $a/2$ (b) $a/\sqrt{2}$ (c) $a/2\sqrt{2}$ (d) $\sqrt{3}\ a/4$

78. In the face-centred cubic unit cell of closest packed atoms, the radius of atoms in terms of edge length (a) of the unit cell is
(a) $a/2$ (b) $a/\sqrt{2}$ (c) $a/2\sqrt{2}$ (d) $\sqrt{3}\ a/4$

79. Which of the following expressions is correct in case of a sodium chloride unit cell (edge length, a)?
(a) $r_c + r_a = a$ (b) $r_c + r_a = a/2$ (c) $r_c + r_a = 2a$ (d) $r_c + r_a = \sqrt{2}a$

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80. Which of the following expressions is correct in case of a CsCl unit cell (edge length, a)?
(a) $r_c + r_a = a$ (b) $r_c + r_a = a/\sqrt{2}$ (c) $r_c + r_a = \sqrt{3}\,a/2$ (d) $r_c + r_a = a/2$

81. In a closest Rock-salt structure (edge length, a), which of the following expressions is correct?
(a) $r_a = \sqrt{2}\,a$ (b) $r_a = a/\sqrt{2}$ (c) $r_a = a/\,2\sqrt{2}$ (d) $r_a = a/4$

82. The unit cell length of sodium chloride crystal is 564 pm. Its density would be
(a) 1.082 g cm^{-3} (b) 2.165 g cm^{-3} (c) 3.247 g cm^{-3} (d) 4.330 g cm^{-3}

83. The cubic unit cell of aluminium (molar mass 27.0 g mol^{-1}) has an edge length of 405 pm. Its density is 2.7 g cm^{-3}. The unit cell is
(a) primitive (b) face-centred (c) body-centred (d) end-centred

84. A substance has a density of 1.984 g cm^{-3} and it crystallizes in the face-centred cubic crystal with edge length equal to 630 pm. The molar mass of the substance is
(a) 37.35 g mol^{-1} (b) 56.02 g mol^{-1} (c) 74.70 g mol^{-1} (d) 65.36 g mol^{-1}

85. Ammonium chloride crystallizes in a body-centred cubic lattice with edge length of unit cell equal to 387 pm. If the size of Cl^- ion is 181 pm, the size of NH_4^+ ion would be
(a) 116 pm (b) 154 pm (c) 174 pm (d) 206 pm

86. The edge length of unit cell of sodium chloride is 564 pm. If the size of Cl^- ion is 181 pm, the size of Na^+ ion would be
(a) 101 pm (b) 167 pm (c) 202 pm (d) 383 pm

87. In sodium chloride crystal, the number of nearest neighbours of each Na^+ ion is
(a) 8 Cl^- ions (b) 8 Na^+ ions (c) 6 Cl^- ions (d) 12 Cl^- ions

88. In sodium chloride crystal, the number of next nearest neighbours of each Na^+ ion is
(a) 8 Cl ions (b) 12 Na^+ ions (c) 12 Cl^- ions (d) 24 Cl^- ions

89. If a is the edge length of unit cell of sodium chloride, the distance between the nearest Na^+ and Cl^- ion is
(a) a (b) $\sqrt{2}\,a$ (c) $a/2$ (d) $\sqrt{3}\,a$

90. If a is the edge length of unit cell of sodium chloride, the distance between two nearest Na^+ ions is
(a) a (b) $\sqrt{2}\,a$ (c) $\sqrt{3}\,a$ (d) $a/\sqrt{2}$

91. Lithium iodide occurs as cubical-closest packing. If the edge length of a unit cell is 624 pm, the ionic radii of Li^+ and I^- ions respectively would be
(a) 91.35 pm, 220.65 pm (b) 220.65 pm, 91.35 pm
(c) 182.7 pm, 110.32 pm (d) 110.32 pm, 182.7 pm

92. Chromium crystallizes with a body-centred cubic lattice with unit-cell edge length equal to 287 pm. The atomic radius of chromium atom is about
(a) 143.5 pm (b) 135.0 pm (c) 124.3 pm (d) 95.7 pm

93. A metal crystallises into two cubic phases, FCC and BCC with unit cell length equal to 3.5 Å and 3.0 Å, respectively. The ratio of densities of FCC and BCC is about
(a) 1.15 (b) 1.26 (c) 1.40 (d) 1.51

94. Silver has an atomic radius of 144 pm. The density of silver is 10.6 g cm^{-3}. The type of cubic crystal of silver is
(a) primitive (b) body-centred (c) face-centred (d) end-centred

95. Potassium has a body-centred cubic structure with the nearest neighbour distance 452 pm. Its density would be
(a) 1.01 g cm^{-3} (b) 0.91 g cm^{-3} (c) 0.81 g cm^{-3} (d) 0.71 g cm^{-3}

96. Ammonium chloride crystallizes in a body-centred cubic lattice with a unit distance of 387 pm. If the size of NH_4^+ is 154 pm, the size of Cl^- ion would be
(a) 90.5 pm (b) 119.6 pm (c) 39.5 pm (d) 181 pm

97. The pyknometric density of sodium chloride crystal is 2.165×10^3 kg m^{-3} while its X–ray density is 2.178×10^3 kg m^{-3}. The fraction of unoccupied sites in sodium chloride crystal is
(a) 5.96×10^{-2} (b) 5.96×10^{-1} (c) 5.96×10^{-3} (d) 5.96 (2003)

Void Volume in Cubic Unit Cells

98. The fraction of volume occupied by atoms in a primitive cubic unit cell is
(a) 0.48 (b) 0.52 (c) 0.55 (d) 0.68

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(ii) The unit cell of cubical-closest packing is
(a) primitive cubic (b) body-centred cubic
(c) face-centred cubic (d) not known

(iii) The maximum size of atoms that can be fitted into octahedral voids in terms of radius r of atoms closely packed is
(a) 0.414 r (b) 0.225 r (c) 0.372 r (d) 0.680 r

4. In a cubical packing of atoms, the arrangement of atoms may result into primitive (P), body-centred (I) and face-centred (F) cubical unit cell. Identify the correct choice in the following.

(i) The percentages of void volume follow the expression
(a) P : I : F :: 47.64 : 31.98 : 25.95 (b) P : I : F :: 47.64 : 25.95 : 31.98
(c) P : I : F :: 31.98 : 47.64 : 25.95 (d) P : I : F :: 31.98 : 25.95 : 47.64

(ii) The sizes of atoms in terms of the respective edge-length of the unit cell follow the expression
(a) P : I : F :: $a/2$: $(\sqrt{2}/4)a$: $(\sqrt{3}/4)a$ (b) P : I : F :: $a/2$: $(\sqrt{3}/4)a$: $(\sqrt{2}/4)a$
(c) P : I : F :: $(\sqrt{2}/4)a$: $a/2$: $(\sqrt{3}/4)a$ (d) P : I : F :: $(\sqrt{2}/4)a$: $(\sqrt{3}/4)a$: $a/2$

(iii) The coordination numbers of atoms follow the expression
(a) P : I : F :: 12 : 6 : 8 (b) P : I : F :: 12 : 8 : 6
(c) P : I : F :: 6 : 8 : 12 (d) P : I : F :: 6 : 12 : 8

5. In hexagonal systems of crystals, a frequently encountered arrangement of atoms is described as a hexagonal prism. Here, the top and bottom of the cell are regular hexagons and three atoms are sandwiched in between them. A space-filling model of this structure, called hexagonal close-packed (HCP), is constituted of a sphere on a flat surface surrounded in the same plane by six identical spheres as closely as possible. Three spheres are then placed over the first layer so that they touch each other and represent the second layer. Each one of these spheres touches three spheres of the bottom layer. Finally, the second layer is covered with a third layer that is identical to the bottom layer in relative position. Assume radius of every sphere to be 'r'.

(i) The number of atoms in this HCP unit cell is
(a) 4 (b) 6 (c) 12 (d) 17

(ii) The volume of this HCP unit cell is
(a) $24\sqrt{2}\,r^3$ (b) $16\sqrt{2}\,r^3$ (c) $12\sqrt{2}\,r^3$ (d) $(64/3\sqrt{3})r^3$

(iii) The empty space in this HCP unit cell is
(a) 74% (b) 47.6% (c) 32% (d) 26%

6. One of the common crystal systems has a cubic unit cell. Based on this, answer the following three queries.

(i) The crystallographic dimensions of this unit cell is
(a) $a \neq b \neq c$; $\alpha \neq \beta \neq \gamma \neq 90°$ (b) $a = b \neq c$; $\alpha = \beta = \gamma = 90°$
(c) $a = b = c$; $\alpha = \beta = \gamma = 90°$ (d) $a = b = c$; $\alpha = \beta = \gamma \neq 90°$

(ii) The example of the substance having cubic unit cell is
(a) graphite (b) diamond (c) SiO_2 (d) KNO_3

(iii) The Bravais lattice of this unit cell is/are
(a) P (b) P, F (c) P, F, C (d) P, I, F

Assertion and Reason Type

Given below are the two statements. Identify the correct choice from the following.
(a) Statement –1 is correct and Statement –2 is correct and is the correct explanation of the statement –1.
(b) Statement –1 is correct and Statement –2 is correct but not the correct explanation of the statement –1.
(c) Statement –1 is correct and Statement –2 is incorrect.
(d) Statement –1 is incorrect and Statement –2 is correct.

	Statement–1	Statement–2
1.	The densities of crystals of the same substance exhibiting Frenkel defects remain unchanged.	The ions present in the interstitial sites do not change the overall volume of the substance.
2.	In an ionic solid MX with Schottky defects, the number of positive and negative ions are same.	Equal number of cations and anions vacancies are present.

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Crystal System

8. In a primitive unit cell, the points are present at the corners of the unit cell.
9. In a body-centred unit cell, the points are present at the corners and at the centre of unit cell.
10. In a face-centred unit cell, the points are present at the corners and at the centre of faces of unit cell.
11. For a cubic unit cell $a = b = c$, $\alpha = \beta = \gamma = 90°$.
12. There are seven crystal systems.
13. A cubic crystal system has three Bravais lattices; Primitive, Body-centred, Face-centred.
14. There are fourteen Bravais lattices.
15. For tetragonal unit cell, $a = b \neq c$, $\alpha = \beta = \gamma = 90°$.
16. $CuSO_4 \cdot 5H_2O$ belongs to triclinic system.
17. For a hexagonal unit cell, $a = b \neq c$; $\alpha = \beta = 90°$, $\gamma = 120°$
18. For a trigonal unit cell, $a = b = c$; $\alpha = \beta = \gamma \neq 90°$
19. For a orthorhombic unit cell, $a \neq b \neq c$; $\alpha = \beta = \gamma = 90°$
20. Triclinic unit cell has 1-fold rotational axis.
21. Cubic unit cell is characterised by four 3-fold rotational axes.
22. Monoclinic unit all has 2-fold rotational axis.
23. Five fold rotational axis is never present in a unit cell.
24. Monoclinic unit cell has two Bravais lattices, primitive and end-centred
25. Telragonal unit cell has two Bravais lattices: primitive and body-centred
26. Orthorhomic unit cell has four Bravais lattice : primitive, body-centred, end-centred and face-centred.
27. NaCl, KCl and RbCl crystallize as face-centred cubic lattice while CsCl crystallizes as body-centred cubic until cell
28. There are 32 point groups.
29. There are 230 space groups.
30. Cubic unit cell has only three Bravais lattices: primitive, body-centred and face-centred.
31. Hexagonal unit cell has only primitive unit cell.
32. Triogonal amongst the given unit cells has only primitive unit cell.
33. Monoclinic amongst the given unit cells has Bravais lattices other than primitive one.
34. Triclinic unit cell has all three sides and three angles different from each other.
35. Graphite has hexagonal unit cell.

Packing in Crystalline Solids

36. The packing ABCABC ... is known as face-centred cubical packing.
37. The packing ABAB ... is known as hexagonal packing.
38. The face-centred cubical closing packing involves twelve coordination number.
39. The closest packed layers in the face-centred cubic unit cell are perpendicular to the body diagonal of the cube.
40. The size of octahedral void is greater than that of tetrahedral void.
41. There are two tetrahedral voids and one octahedral void per atom in a cubical-closest packing.
42. The unit cell of diamond is a cube.
43. In the closest packing of atoms A, the size of atom B that can be fitted into tetrahedral void is $0.225r_c$.
44. For the atom B to fit into octahedral void created within the closest packing of atom A is $0.414r_a$.
45. Both ccp and HCP are closest packed, they have the same density.
46. The closest packed layers are along the perpendicular direction of body diagonal of a cube.
47. Along the body diagonal of a cube, there are three closest-packed layers.
48. Na_2O has an anti-fluorite structure in which anions form a cubical-closest packing and cations occupy tetrahedral voids.
ZnS has a zinc-blende structure in which anions form a cubical-closest packing and cations are present in half of the alternate tetrahedral voids.
CaF_2 has a fluorite structure in which cations form cubical-closest packing and anions occupy tetrahedral voids.
CaO has a rock-salt structure in which anions form a face-centred cubic unit cell and cations occupy octahedral voids.

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Ionic Solids

49. CsCl has body-centred cubical packing.

50. The coordination number of each cation and anion is six in the rock-salt structure (which involves face-centred cubic unit cell).

51. The coordination number of each cation and anion is eight in the body-centred cubic structure of an ionic compound.

52. The rock-salt structure involves face-centred cubic unit cell. It has four cations and four anions per unit cell. The formula of ionic compound will be A_4B_4, i.e. AB.

53. In the body-centred cubic unit cell of an ionic compound, there will be one cation and one anions per unit cell. Hence, the formula is AB.

54. In zinc-blende structure, cations are present in tetrahedral holes. Hence, the coordination number of each cation and anion is four.

55. In zinc-blende structure, there are four cations and four anions per unit cell. Hence, the formula will be A_4B_4 or simply AB.

56. Cations occupy tetrahedral holes. The coordination number is four. There are eight tetrahedral holes around an anion; its coordination number is eight.

57. In anti-fluorite structure, anions form cubical-closest packing and cations occupy tetrahedral holes. There are four anions and eight cations per unit cell. Hence, its formula is A_8B_4, i.e. A_2B.

58. In cubic-fluorite structure, cations form face-centred cubical packing and anions occupy tetrahedral holes. There are eight anions and four cations per unit cell. The coordination number of anion is four while that of cation is eight.

59. See Q.58. The formula is AB_2.

60. There is one octahedral hole per atom in closest packing. Hence, the formula is $C_{2/3}A$, i.e. C_2A_3.

61. In cubical-closest packing, there will be four oxide anions, $8 \times 1/8 = 1$ A^{2+} cation and $4 \times 1/2 = 2$ B^{3+} cations. Hence, its structure will be AB_2O_4.

62. The general formula will be $A_{7/8}B_3$, i.e. A_7B_{24}.

63. For the octahedral structure, the ratio r_c/r_a lies in the range of 0.414 to 0.732.

64. For the tetrahedral structure, the ratio r_c/r_a lies in the range of 0.225 to 0.414.

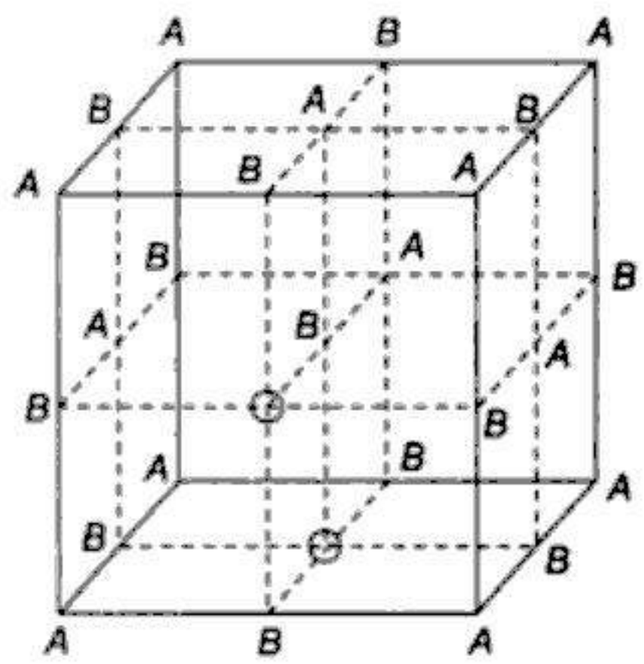
65. For the body-centred cubic structure, the ratio r_c/r_a is greater that 0.732.

66. Three is 1/8th contrubition for the atoms occupying corners and 1/2 contribution from the atoms occupying the centres of faces. Since there are eight corners and six faces of a cube, the molecular formula will be AB_3.

67. Body-centred cubic unit cell has 8:8 coordination numbers. CsCl is such an example.

68. The coordination number of an atom of a metal crystallized in a hexagonal close-packed structure is twelve. There are six atoms in the same plane and three each above and below this plane.

69. The structure of AB is shown in Fig. 2.8


A
B
A
B
A
B

70. Each atom at the corner is shared amongst eight unit cells. Hence, number of atoms A per unit cell is

$$n_A = \text{(Number of corners) (Contribution from each corner)} = 8(1/8) = 1$$

Each atom at the centre of each face is shared between two units cell. Hence, number of atoms B per unit cell is

$$n_B = \text{(Number of faces) (Contribution from each face)} = 6(1/2) = 3$$

The structure of the given substance is AB_3.

71. Given $r_{Na^+}/r_{Cl^-} = 0.5$ and $r_{Na^+}/r_{K^+} = 0.7$. Hence

$$\frac{r_{K^+}}{r_{Cl^-}} = \frac{r_{Na^+}}{r_{Cl^-}}\frac{r_{K^+}}{r_{Na^+}} = \frac{0.5}{0.7} = \frac{5}{7}$$

Now $\dfrac{r_{Na^+}+r_{Cl^-}}{r_{Cl^-}} = \dfrac{3}{2}$ and $\dfrac{r_{K^+}+r_{Cl^-}}{r_{Cl^-}} = \dfrac{12}{7}$. Hence $\dfrac{a_{KCl}}{a_{NaCl}} = \dfrac{2(r_{K^+}+r_{Cl^-})}{2(r_{Na^+}+r_{Cl^-})} = \dfrac{12}{7}\cdot\dfrac{2}{3} = \dfrac{24}{21} = 1.14$

Density

72. The expression is $\text{density} = \dfrac{\text{mass of atoms in a unit cell}}{\text{volume of a unit cell}} = \dfrac{N(M/N_A)}{a^3}$

73. The number of atoms in a single primitive cubic unit is $8 \times 1/8 = 1$.

74. The number of atoms in a body centred cubic unit is $(8 \times 1/8) + 1 = 2$.

75. The number of atoms in a single face-centred cubic unit cell is $(8 \times 1/8) + (6 \times 1/2) = 1 + 3 = 4$.

76. In the primitive cubic unit cell, atoms touch each other along edges. Hence, $2\,r_A = a$.

77. In the body-centred cubic until cell, atoms touch each other along the body diagonal of the cube. Hence, $4\,r_A = \sqrt{3}\,a$, i.e. $r_A = \sqrt{3}\,a/4$.

78. In the face-centred cubic unit cell, atoms touch each other along the face diagonal of the cube. Hence, $4\,r_A = \sqrt{2}\,a$, i.e. $r_A = a/2\sqrt{2}$.

79. In sodium chloride unit cell, anion-cation-anion touch each other along the edges. Hence, $2\,r_c + 2\,r_a = a$, i.e. $r_c + r_a = a/2$.

80. CsCl crystallizes has body-centred cubic unit cell. Hence, $2\,r_c + 2\,r_a = \sqrt{3}\,a$, i.e. $r_c + r_a = \sqrt{3}\,a/2$.

81. In a closest Rock-salt structure, anions touch each other along the face diagonal of a cubic unit cell. Hence, $4r_a = \sqrt{2}\,a$, i.e. $r_a = a/2\sqrt{2}$.

82. In sodium chloride unit cell, there are four Na^+ and four Cl^- ions. Hence

$$\rho = \frac{N}{a^3}\frac{M}{N_A} = \frac{(4)\left\{(23+35.5)\,\text{g mol}^{-1}\right\}}{(564\times10^{-10}\,\text{cm})^3\,(6.022\times10^{23}\,\text{mol}^{-1})} = 2.165\ \text{g cm}^{-3}$$

83.
$$N = \frac{a^3\rho N_A}{M} = \frac{(405\times10^{-10}\,\text{cm})^3\,(2.7\,\text{g cm}^{-3})\,(6.022\times10^{23}\,\text{mol}^{-1})}{(27.0\,\text{g mol}^{-1})} = 4.0$$

84.
$$M = \frac{a^3\rho N_A}{N} = \frac{(630\times10^{-10}\,\text{cm})^3\,(1.984\,\text{g cm}^{-3})\,(6.023\times10^{23}\,\text{mol}^{-1})}{4} = 74.70\ \text{g mol}^{-1}$$

85. In body-centred cubic unit cell, ions touch each other along the body diagonal of the cube.

$$2\,r_+ + 2\,r_- = \sqrt{3}\,a \quad \text{i.e.} \quad 2\,(r_+ + 181\ \text{pm}) = \sqrt{3}\ (387\ \text{pm})$$

$$r_+ = (\sqrt{3}/2)\ (387\ \text{pm}) - 181\ \text{pm} = 154.15\ \text{pm}$$

86. Sodium chloride has a face-centred cubic unit cell. Cation and anion touch each other along the edge of the cube.

$$2\,r_+ + 2\,r_- = a \quad \text{i.e.} \quad 2\,(r_+ + 181\ \text{pm}) = 564\ \text{pm}$$
$$r_+ = (564\ \text{pm}/2) - 181\ \text{pm} = 101\ \text{pm}$$

87. There are six chlorides around each sodium ion.

88. The next nearest neighbours of Na^+ are 12 Na^+ ions.

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100. In a face-centred cubic unit cell, atoms touch each other along the face diagonal of the cube.
Hence, $4\,r_A = \sqrt{2}\,a$. There are four atoms per unit cell. Hence

$$\text{Fraction of volume occupied} = \frac{4\left(\frac{4}{3}\pi r^3\right)}{\left(4r_A/\sqrt{2}\right)^3} = \frac{\pi}{3\sqrt{2}} = 0.74.$$

Point Defects

101. The density of the crystals having Schottky defect is smaller than that of the perfect crystal because of the absence of cation(s) and anion(s) from their expected positions.

102. The density of crystals having Frenkel defect is identical to that of a pure crystal.

103. Let x and y be the Fe^{2+} and Fe^{3+} ions, respectively. We will have

$$x + y = 0.93$$

Also $2x + 3y = 2$ (condition of electroneutrality)

Solving for y, we get $y = 0.14$.

Hence Per cent of Fe^{3+} ions $= (0.14/0.93) \times 100 = 15$

104. Total positive charger per atom of iron will be (1/4) 3 + (3/4) 2 = 2.25
This will be equal to 2x. Hence $x = 2.25/2 = 9/8$

105. Same as Q.101

106. Ferrous oxide forms a nonstoichiometric compound.

107. Bragg equation is $n\lambda = 2\,d \sin\theta$.

Multiple Correct Choice Type

1. The crystals of CsCl has body-centred cubic unit cell. Hence, each ion in this structure has coordination number of eight.
The crystals of NaCl has two interpenetrating face-centred cubic lattices, one composed entirely of Na^+ ions and the other of Cl^- ions. Each Na^+ ion is located halfway between two Cl^- ions and vice versa. A unit cell of NaCl crystals has Cl^- ions at the corners as well as at the face-centres and Na^+ ions are located in octahedral voids. On each edge of cubic unit cell, there are two Cl^- ions and one Na^+ ion. Hence.

$$a = 22\,(r^+_{Na} + r^-_{Cl}) = 2(95\text{ pm} + 181\text{ pm}) = 552\text{ pm}$$

2. In NaCl crystal, each cation and anion has six nearest neighbouring anions and cations, respectively. There are 12 next nearest neighbours of the same type of ions at a distance of $\sqrt{2}\,r$, where r is the distance between neighbouring cation and anion. Next to these, there are eight ions of the type at a distance of $\sqrt{3}\,r$.

3. In bcc cubic lattice, atoms at the corners (say, A) touch each other. Thus, their distance is equal to the edge length a. The unlike atoms touch each other along the body diagonal of the cube. Their arrangement will be ABA. Thus, the distance between A and B will be $\sqrt{3}\,a/2$.

4. The fcc structure of AB will be as shown in Q.2. Therefore, the $d_{A\text{-}A} = d_{B\text{-}B} = \sqrt{2}\,a/2$ and $d_{AB} = a/2$. There will be four molecules of AB in a unit cell. Hence, its density will be given as $\rho = (4/a^3)\,(M_{AB}/N_A)$.

5. (a) Only short-range order is present.
(b) Amorphous solids melt over a range of temperature. Only crystalline solids have sharp melting points.

6. (a) Ionic crystals have long range order.
(b) It is because cations and anions generally have different ionic radii and thus they cannot be packed like atoms in ccp and hcp structures.

7. (a) The coordination number is eight.
(b) There are six chlorides ions as the nearest neighbours of Na^+ ions and these are arranged octahedrally.
(c) In NaCl crystals, Na^+ ions may be assumed to occupy the lattice points in face-centred cubic unit cell with Cl^- ions in the octahedral voids or vice versa. The nearest distance between two Na^+ is (edge–length)/$\sqrt{2}$.

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8. (b) It is 32%.
(c) This is in case of face-centred cubic unit cell.

16. In Frenkel defect, the ion, instead of being in its expected location, is found in one of the interstices. This defect is favoured by a large difference in size between the positive and negative ions.
Schottky defect involves the absence of cation or anion from the postion which it is expected to occupy in the periodic arrangement of ions. This affects the physical properties of solids.

Linked Comprehension Type

1. (i) Since both cubical and hexagonal are closely packed, their densities will be identical
(ii) The coordination of each atom in closest packed structure is twelve.
(iii) The unit cell of cubical closest packing is face centred cubic unit cell for which atoms touch each other along the face diagonal. Hence, $4r = \sqrt{2}\,a$ Also, the distance between closest packed layers is $\sqrt{3}\,a/3$ as three such layers lie along the body diagonal of the cube. Hence.

$$\text{distance} = \frac{\sqrt{3}}{3}a = \frac{\sqrt{3}}{3}\left(\frac{4}{\sqrt{2}}r\right) = \frac{4}{\sqrt{6}}r$$

2. (i) In a closest packing, there is a tetrahedral hole above and below each atom, hence, there are twice as many tetrahedral holes as there are closest packed atoms.
The number of octahedral holes is equal to the number of atoms present and these are located midway between the two closest packed layers.
(ii) The size of tetrahedral hole is smaller than octahedral hole.
(iii) see, part (i) of this question.

3. (i) Cubical closest packing is ABCABC....
(ii) The unit cell of cubical closest packing is face centred cube
(iii) The radius of atom that can be fitted into octahedral void is $0.414r$, where r is the radius of atom colsely packed.

4. (i) The void volumes in primitive, body-centred and face-centred are 47.64, 31.98 and 25.95, respectively.
(ii) In primitive cubic unit cell atoms touch each other along the edges. Hence, $2r = a$

In body-centred cubic unit cell, atoms touch each other along body diagonal.. Hence, $4r = \sqrt{3}\,a$.

In face-centred cubic unit cell, atoms touch each other along face diagonal. Hence, $4r = \sqrt{2}\,a$
(iii) The coordination number of atoms in primitive, body-centred and face diagonal are 6, 8 and 12, respectively.

5. (i) There are 6 atoms per unit cell of HCP. Three atoms are inside the cell, one atom comes from the corners of each of top and bottom of the cell (making a total of two atoms) and half of atom comes from each of the central atom at the top and bottom of unit cell (making a total of one atom).
(ii) The hexagonal base consists of six equilateral triangles, each with side $2r$ and altitude $2r \sin 60°$. Hence,

$$\text{Area of base} = 6[\tfrac{1}{2}(2r)(2r \sin 60°)] = 6\sqrt{3}\,r^3$$

The height of hexagonal is twice the distance between closest-packed layer. This can be determined with reference to the cubical-closest packing. There are three closest-packed layers in its body diagonal, and thus the distance between two closest-packed layers is $\sqrt{3}\,a/3 = a/\sqrt{3}$. The edge length is related to the radius atom by the relation $4r = \sqrt{2}a$ since atoms touch each other along the face diagonal of the cube. Hence, height of HCP unit cell is $2(a/\sqrt{3})$ where $a = 2\sqrt{2}\,r$. Hence

$$\text{Height of unit cell} = 2(2\sqrt{2}\,r/\sqrt{3}) = 4\sqrt{2}\,r/\sqrt{3}$$

$$\text{Volume of unit cell} = (\text{area of base})(\text{height}) = (6\sqrt{3}\,r^2)(4\sqrt{2}\,r/\sqrt{3}) = 24\sqrt{2}\,r^3$$

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ANNEXURE

Subjective Problems for Practice

SOLVED PROBLEMS

Solid State

1. Calculate the radius of molybdenum atom if the element crystallizes as body-centred cubic crystals. Given: Density of Mo = 10.3 g cm^{-3} and molar mass of Mo = 95.94 g mol^{-1}.

Solution In a body-centred cubic unit cell, there are two atoms per unit cell. Hence, from the expression

$$r = \frac{N}{a^3}\left(\frac{M}{N_A}\right)$$

we get $$a^3 = \frac{N}{\rho}\left(\frac{M}{N_A}\right) = \left(\frac{2}{10.3\ \text{g cm}^{-3}}\right)\left(\frac{95.94\ \text{g mol}^{-1}}{6.023\times10^{23}\ \text{mol}^{-1}}\right) = 3.09 \times 10^{-23}\ \text{cm}^3$$

or $$a = 3.13 \times 10^{-8}\ \text{cm} = 313\ \text{pm}$$

Now since in the body-centred cubic unit cell, atoms touch each other along the cross diagonal of the cube, we have

$$4r = \sqrt{3}\,a \quad \text{or} \quad r = (\sqrt{3})(313\ \text{pm})/4 = 135.5\ \text{pm}$$

2. The edge length of a cubic unit cell of metallic calcium is 556 pm. If the density of calcium is 1.54 g cm^{-3} and its molar mass is 40.08 g mol^{-1}, calculate the radius of calcium atom.

Solution From the expression

$$\rho = \frac{N}{a^3}\left(\frac{M}{N_A}\right)$$

we get $$N = \frac{\rho a^3 N_A}{M} = \frac{(1.54\ \text{g cm}^{-3})(556\times10^{-12}\ \text{m})^3\,(6.023\times10^{23}\ \text{mol}^{-1})}{(40.08\ \text{g mol}^{-1})} = 3.98 \simeq 4$$

For $N = 4$, the unit cell is face-centred cube. Since atoms touch each other along the face diagonal in a face-centred cubic unit cell, we have

$$4r = \sqrt{2}\,a \qquad \text{or} \qquad r = \frac{a}{2\sqrt{2}} = \frac{556\ \text{pm}}{2\sqrt{2}} = 196.6\ \text{pm}.$$

3. Caesium chloride may be considered to form interpenetrating simple primitive cubic crystals. The edge length of unit cell is 412 pm. Determine : (a) the density of CsCl, and (b) the ionic radius of Cs^+ if the ionic radius of Cl^- is 181 pm. Given: M(Cs) = 133 g mol^{-1}.

Solution The interpenetrating simple primitive cubic crystals means the unit cell is body-centred where Cl^- ions occupy corners and Cs^+ ion occupy body centre of the cube. There is one Cs^+ ion and one Cl^- ion (or one molecule of CsCl) per unit cell.

From the expression

$$\rho = \frac{N}{a^3}\left(\frac{M}{N_A}\right)$$

we get $$\rho = \frac{1}{(412\times10^{-12}\ \text{m})^3}\left(\frac{168.5\ \text{g mol}^{-1}}{6.023\times10^{23}\ \text{mol}^{-1}}\right) = 0.4 \times 10^7\ \text{g m}^{-3} = 4.0\ \text{g cm}^{-3}$$

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Now since Cs^+ ion touch the two chlorides along the cross diagonal of the cube, we will have

$$2\,r_c + 2\,r_a = \sqrt{3}\,a \quad \text{or} \quad r_c = \left(\frac{\sqrt{3}}{2}\right) a - r_a = \left(\frac{\sqrt{3}}{2}\right) (412\text{ pm}) - (181\text{ pm}) = 175.8\text{ pm}.$$

4. The atomic radius of strontium is 215 pm and it crystallizes with a cubical closest-packed structure. Calculate the density of strontium. The molar mass of strontium is 87.6 g mol^{-1}.

Solution The cubical closest-packed structure has a face-centred cubic unit cell. In the latter atoms touch along the face diagonal of the cube. Hence

$$\sqrt{2}\;a = 4\;r = 4\;(215\text{ pm}) = 860\text{ pm} \quad \text{or} \quad a = \frac{860\text{ pm}}{\sqrt{2}} = 608.2\text{ pm}$$

Now using the expression

$$\rho = \frac{N}{a^3}\left(\frac{M}{N_A}\right)$$

we get

$$\rho = \frac{4}{(608.2\times10^{-12}\text{ m})^3}\left(\frac{87.6\text{ g mol}^{-1}}{6.023\times10^{23}\text{ mol}^{-1}}\right) = 2.586\times10^6\text{ g m}^{-3} \equiv 2.586\text{ g cm}^{-3}$$

5. A solid A^+B^- has an NaCl type closest packed structure. If the radius of the anion is 250 pm, what is the radius of the cation?

Solution The structure of NaCl involves face-centred cubic arrangement of Cl^- ions and its octahedral holes are occupied by Na^+ ions. Now for a closest-packed structure $r_c/r_a = 0.414$. Hence

$$r_c = (0.414)\;r_a = (0.414)\;(250\text{ pm}) = 103.5\text{ pm}$$

6. If the radius of Cs^+ is 169 pm and that of Cl^- is 181 pm, predict the structure of CsCl. What is the coordination number of Cs^+ ion?

Solution We have

$$\frac{r_c}{r_a} = \frac{169}{181} = 0.94$$

Since this value is greater than 0.732, the structure of CsCl involves body-centred cubic unit cell, where Cs^+ is present at the body centre of cube and Cl^- ions are present at the corners. The coordination number of Cs^+ is eight.

7. KCl crystallizes in the same type of lattice as does NaCl. Given that

$$\frac{r_{Na^+}}{r_{Cl^-}} = 0.5 \qquad \text{and} \qquad \frac{r_{Na^+}}{r_{K^+}} = 0.7$$

Calculate (a) the ratio of side of the unit cell for KCl to that for NaCl, and (b) the ratio of density of NaCl to that of KCl.

Solution NaCl crystallizes in the face-centred cubic unit cell, such that

$$r_{Na^+} + r_{Cl^-} = a/2$$

where a is the edge length of unit cell. Now since $r_{Na^+}/r_{Cl^-} = 0.5$ and $r_{Na^+}/r_{K^+} = 0.7$, we will have

$$\frac{r_{Na^+} + r_{Cl^-}}{r_{Cl^-}} = 1.5 \quad \text{and} \quad \frac{r_{K^+}}{r_{Cl^-}} = \frac{r_{K^+}}{r_{Na^+}/0.5} = \frac{0.5}{r_{Na^+}/r_{K^+}} = \frac{0.5}{0.7}$$

or

$$\frac{r_{K^+} + r_{Cl^-}}{r_{Na^+} + r_{Cl^-}} = \frac{1.2}{0.7}\times\frac{1}{1.5} \quad \text{or} \quad \frac{a_{KCl}/2}{a_{NaCl}/2} = \frac{1.2}{0.7\times1.5} \quad \text{or} \quad \frac{a_{KCl}}{a_{NaCl}} = \frac{1.2}{1.05} = 1.143$$

Now since $\rho = \frac{N}{a^3}\left(\frac{M}{N_A}\right)$, we will have

$$\frac{\rho_{NaCl}}{\rho_{KCl}} = \left(\frac{a_{KCl}}{a_{NaCl}}\right)^3\left(\frac{M_{NaCl}}{M_{KCl}}\right) = (1.143)^2\left(\frac{58.5}{74.5}\right) = 1.172.$$

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8. LiI occurs as cubical-closest packing. If the edge length of a unit cell is 624 pm, determine the ionic radii of Li^+ and I^- ions.

Solution The cubical closest packing has a face-centred cubic unit cell. I^- ions occupy the corners and the face centres. These ions touch each other along the face diagonal of the cube. Hence

$$4\, r_{I^-} = \sqrt{2}\ a \quad \text{or} \quad r_{I^-} = \frac{a}{2\sqrt{2}} = \frac{624 \text{ pm}}{2(1.414)} = 220.65 \text{ pm}$$

Now along the edge, we will have $I^- Li^+ I^-$ arrangement, where I^- are at the corners and Li^+ ion at the centre of the edge (octahedral void). Since in closest packing, they touch each other, we will have

$$2\, r_{I^-} + 2r_{Li^+} = a$$

or
$$r_{Li^+} = \frac{a}{2} - r_{I^-} = \frac{624 \text{ pm}}{2} - 220.65 \text{ pm} = 91.35 \text{ pm}$$

9. Calculate the percentage of void volume in the (a) primitive, (b) body-centred, and (c) face-centred cubic metallic crystals.

(a) In the primitive unit cell, atoms are present only at the corners of the cube. Each of the eight atoms is shared amongst eight unit cells. Hence, the number of atoms present in one unit cell is one. Moreover, atoms will touch each other along the edges of the cube. Hence, $2r = a$. Now

Volume of the unit cell $= a^3 = 8r^3$

Volume occupied by the atoms $= 1\left(\frac{4}{3}\pi r^3\right)$

Fraction of volume occupied by the atoms $= \frac{(4/3)\pi r^3}{8r^3} = \frac{\pi}{6} \simeq \frac{22}{42}$

Fraction of volume unoccupied by atoms $= \frac{20}{42}$

Percentage of void volume $= \frac{20}{42} \times 100 = 47.6\%$.

(b) In the body-centred cubic unit cell, atoms are present at the corners and the body centre of the cube. There will be two atoms per unit cells and also atoms touch each other along the cross diagonal of the cube. Hence,

$4r = \sqrt{3}\ a$

Now, Volume of unit cell $= a^3 = \left(\frac{4}{\sqrt{3}} r\right)^3$

Volume occupied by atoms $= 2\left(\frac{4}{3}\pi r^3\right)$

Fraction of volume occupied $= \frac{2(4/3)\pi r^3}{(4/\sqrt{3})^3 r^3} = \frac{\sqrt{3}\pi}{8} = 0.68$

Fraction of volume unoccupied by atoms $= 0.32$

Percentage void volume $= 32\%$

(c) In the face-centred cubic unit cell, atoms are present at the corners as well as at the centres of six faces. Since each atom at the corner is shared amongst eight unit cell and each atom at the centre of face is shared between two unit cells, the number of atoms per unit cell is 4 (= 8(1/8) + 6(1/2)). Moreover, atoms touch each other along the faces of the cube. Hence

$4r = \sqrt{2}\ a$

Now, Volume of unit cell $= a^3 = \left(\frac{4r}{\sqrt{2}}\right)^3 = 16\sqrt{2}\ r^3$

Volume occupied by atoms $= 4\left(\frac{4}{3}\pi r^3\right)$

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$$\text{Fraction of volume occupited by atoms} = \frac{4(4/3)\pi r^3}{16\sqrt{2}\, r^3} = \frac{\pi}{3\sqrt{2}} = 0.74$$

Fraction of volume unoccupied by atoms = 0.26

Percentage of void volume = 26%

10. The composition of a sample of wüstite is $Fe_{0.93}O_{1.00}$. What percentage of the ion is present in the form of Fe(III)? (1995)

Solution The compound $Fe_{0.93}O_{1.00}$ is a non-stoichiometric where electrical neutrality is achieved by converting appropriate Fe^{2+} ions into Fe^{3+} ions. There are 7 Fe^{2+} ions missing out of the expected 100 Fe^{2+} ions. The missing 2×7 positive charge is compensated by the presence of Fe^{3+} ions. Replacement of one Fe^{2+} ions by Fe^{3+} ion increases one positive charge. Thus, 14 positive charges is compensated by the presence of 14 Fe^{3+} ions out of a total of 93 iron ions.

Hence, $$\text{Per cent of } Fe^{3+} \text{ ions present} = \frac{14}{93} \times 100 = 15.05$$

11. A sample of wustite Fe_xO contains one Fe(III) for every three Fe(II). Calculate the value of x.

Solution Let there be 1 mol of iron atom. We will have

Amount of Fe(III) = (1/4) mol and Amount of Fe(II) = (3/4) mol

Total positive charges = (1 mol/4) (3) + (3 mol/4) (2) = (9/4) mol

Let x be the amount of oxygen atoms. We have

Total negative charges = $x(2)$

To satisfy electrical neutrality, we have

Total positive charges = Total negative charges

$$\frac{9}{4} \text{ mol} = 2x \quad \text{or} \quad x = (9/8) \text{ mol}$$

Hence, composition of the composition is $FeO_{9/8}$ or Fe_8O_9.

12. A metallic element crystallises into a lattice containing a sequence of layers of ABABAB . . . . Any packing of spheres leaves out voids in the lattice. What percentage by volume of this lattice is empty space? (1996)

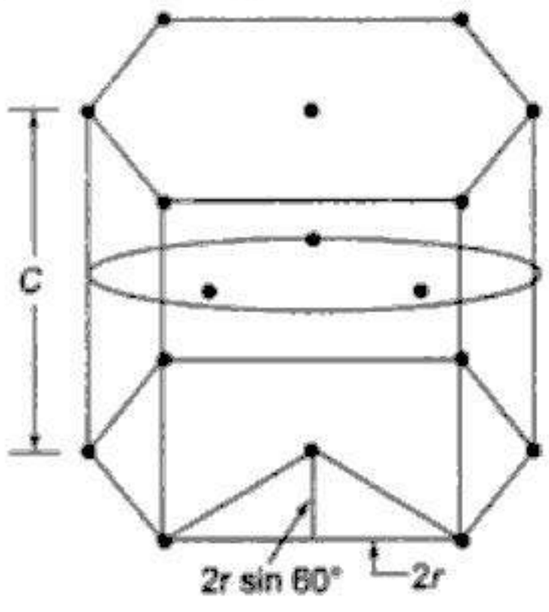


Fig. 2.10

Solution The hexagonal base consists of six equilateral triangles, each with side $2r$ and altitude $2r \sin 60°$. Hence,

$$\text{Area of base} = 6\left[\frac{1}{2}(2r)(2r \sin 60°)\right] = 6\sqrt{3}\, r^2$$

The height of hexagonal is twice the distance between closest-packed layers. The latter can be determined by reference to a face-centred cubic lattice with unit cell length a. In such a lattice, the distance between closest-packed layers is one third the body diagonal, i.e. $\sqrt{3}\, a/3$. Hence

$$C = 2\left(\frac{\sqrt{3}\, a}{3}\right) = \frac{2a}{\sqrt{3}}$$

Now in the face-centred lattice, atoms touch one another along the face diagonal. Thus $4r = \sqrt{2}\, a$

With this, the height of the hexagonal becomes $C = \frac{2}{\sqrt{3}}\left(\frac{4r}{\sqrt{2}}\right) = \left(\frac{4\sqrt{2}}{\sqrt{3}} r\right)$

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Magnetic Quantum Number (Symbol: m) Each magnetic quantum number constitutes a separate orbital within a subshell. It also represents the quantized values of z-component of angular momentum of the electron in an orbital through the expression

$$L_z = m\left(\frac{h}{2\pi}\right)$$

The permitted values of m are $0, \pm1, \pm2, ..., \pm l$. For a given value of l, the total number of permitted values of m is equal to $2l + 1$.

If θ is the angle between z-axis and the angular momentum vector, it is obvious that

$$L_z = L\cos\theta$$

or $$m\left(\frac{h}{2\pi}\right) = \sqrt{l(l+1)}\left(\frac{h}{2\pi}\right)\cos\theta \quad \text{i.e.} \quad m = \sqrt{l(l+1)}\cos\theta$$

Since m is never equal to $\sqrt{l(l+1)}$, $\cos\theta$ is never equal to one or the angle θ is never equal to zero. The quantum number m also fixes the direction of the orbital in space. For example, for p-orbitals, the value of l is equal to 1 and the permitted values of m are -1, 0, and $+1$. This means that there are three p orbitals and these are designated as p_0, p_{+1} and p_{-1}. The plots of p_0, p_x $(= p_{+1} + p_{-1})$ and p_y $(= p_{+1} - p_{-1})$ indicate that the shape of these orbitals are dumb-bell and these point along z-axis, x-axis and y-axis, respectively.

Spin Quantum Number (*Symbmol*: m_s) An electron can also spin around its own axis. Two types of spinning, namely, clockwise and anti-clockwise is possible. These spinning produces angular momentum equal to $\sqrt{s(s+1)}\,(h/2\pi)$, where $s = 1/2$. The direction of angular momentum is governed by the quantized values of z-component of angular momentum which is given as $m_s\,(h/2\pi)$, where m_s is either equal to $+1/2$ (clockwise spinning) or $-1/2$ (anti-clockwise spinning).

Electronic Configurations of Elements

The filling of atomic orbitals by electrons are governed by the three major guidelines. These are aufbau principle, Pauli's exclusion principle and Hund's rule. These are described in the following.

Aufbau Principle Electrons are fillied in various orbitals in the increasing order of their energies. The order is

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p.$$

Pauli's Exclusion Principle No two electrons in an atom can have all the four quantum numbers identical. According to this principle, each orbital can accommodate at the most two electrons with opposite spins.

Hund's Rule This rule operates when the filling of degenerate orbitals (orbitals having identical energies) are carried out. According to this rule, electrons enter one by one till all of them are singly occupied with parallel spins. This is followed by the double occupation of these orbitals.

Besides the above rules, the fact that the half-filled and fully-filled degenerate configurations are more stable than the others is also considered while writing the electronic configurations of some elements. For example, the electronic configurations of Cr and Cu are

$_{24}Cr \quad (1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^1(3d)^5$
$_{29}Cu \quad (1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^1(3d)^{10}$

instead of

$_{24}Cr \quad (1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^2(3d)^4$
$_{29}Cu \quad (1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^2(3d)^9$

SUPPLEMENTARY MATERIAL

The behaviour of electron in hydrogen-like species is described by the solutions of Schrödinger equation

$$\nabla^2\Psi + \frac{8\pi^2 m}{h^2}\left(E - \frac{Ze^2}{(4\pi\varepsilon_0)r}\right)\Psi = 0$$

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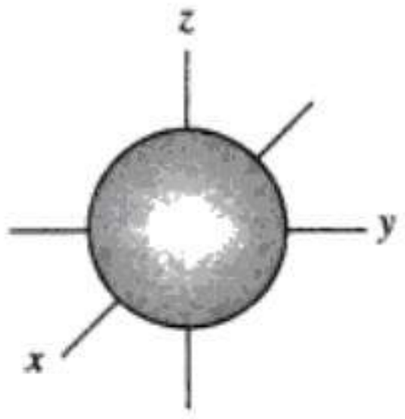


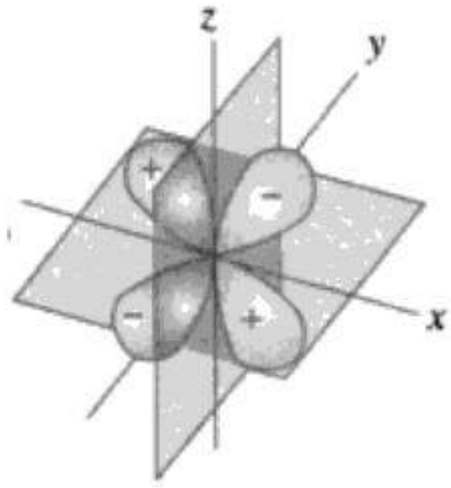
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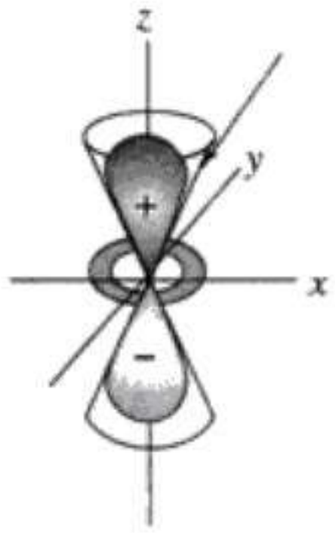


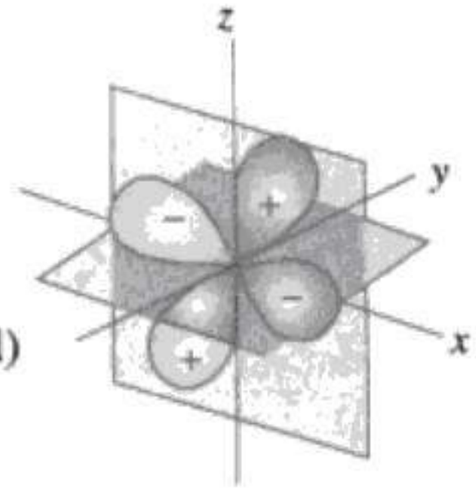
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81. Which of the following orbitals represents $3d_{z^2}$ orbital?

(a) 

(b) 

(c) 

(d) 

82. The orbital angular momentum of an electron in 2s orbital is:

(a) $+\frac{1}{2}\frac{h}{2\pi}$ (b) Zero (c) $\frac{h}{2\pi}$ (d) $\sqrt{2}\frac{h}{2\pi}$

83. For a d-electron, the orbital angular momentum is

(a) $\sqrt{6}\,(h/2\pi)$ (b) $\sqrt{2}\,(h/2\pi)$ (c) $(h/2\pi)$ (d) $2(h/2\pi)$ (1997)

84. In which of the following orbitals, the electrons has the maximum energy?

(a) 3p (b) 4f (c) 4p (d) 4s

85. The correct statement on the aufbau principle is that

(a) $(n-1)$d subshell is always lower in energy than ns orbital

(b) $(n-1)$f subshell always has energy more than np orbital

(c) 5d is lower in energy than 4f

(d) 6p is lower in energy than 5d

86. The quantum numbers +1/2 and –1/2 for the electron spin represent

(a) rotation of the electron in clockwise and anticlockwise direction respectively

(b) rotation of the elctron in anticlockwise and clockwise direction respectively

(c) magnetic moment of the electron pointing up and down respectively

(d) two quantum mechanical spin states which have no classical analogue

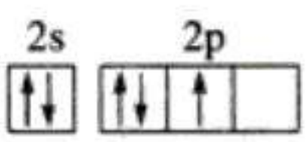
Electronic Configurations

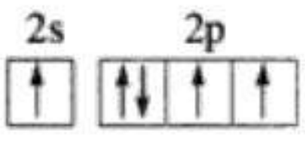
87. Any p-orbital can accommodate upto

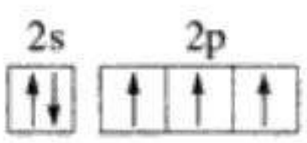
(a) four electrons (b) two electrons with parallel spins

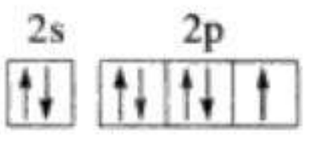
(c) six electrons (d) two electrons with opposite spins

88. The orbital diagram in which the aufbau principle is violated is

(a) 

(b) 

(c) 

(d) 

(1988)

89. The outermost electronic configuration of the most electronegative element is

(a) $(ns)^2(np)^3$ (b) $(ns)^2(np)^4$ (c) $(ns)^2(np)^5$ (d) $(ns)^2(np)^6$ (1988)

90. The correct ground state electronic configuration of chromium atom is

(a) $[Ar](3d)^5(4s)^1$ (b) $[Ar](3d)^4(4s)^2$ (c) $[Ar](3d)^6(4s)^0$ (d) $[Ar](4d)^5(4s)^1$ (1989)

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

	n	l	m_l		n	l	m_l	
(a)	2	1	0	(b)	2	1	1	
(c)	3	1	1	(d)	3	0	0	(1989)

92. The maximum number of electrons that can be accommodated in a quantum shell is equal to

(a) n (b) n^2 (c) $2n^2$ (d) $n(n+1)$

93. The correct set of four quantum numbers for the valence electron of rubidium ($Z = 37$) is

(a) $n = 5,\ l = 0,\ m = 0,\ m_s = +1/2$ (b) $n = 5,\ l = 1,\ m = 0,\ m_s = +1/2$

(c) $n = 5,\ l = 1,\ m = 1,\ m_s = +1/2$ (d) $n = 6,\ l = 0,\ m = 0,\ m_s = +1/2$ (1984)

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36. Photoelectric effect supports quantum nature of light because
(a) there is a minimum frequency of light below which no photoelectron is emitted .
(b) the maximum kinetic energy of photoelectrons depends on the intensity of the light.
(c) even when the metal surface is faintly illuminated, the photoelectrons are emitted
(d) electric charge of the photoelecrons is quantized.

37. When photons of energy 4.25 eV strike the surface of a metal A, the ejected photoelectrons have maximum kinetic energy and de-Broglie wave length is λ_A . The maximum kinetic energy of photoelectrons liberated from another metal B by photons of energy 4.70 eV is $(KE)_B = (KE)_A - 1.50$ eV. If the de-Broglie wavelength of these photoelectrons is $\lambda_B = 2\lambda_A$, then.
(a) the work function of A is 2.25 eV
(b) the work function of B is 4.20 eV
(c) $(KE)_A$=2.00 eV
(d) $(KE)_B$=2.75 eV

38. The electron in a hydrogen atom makes a transition $n_1 \rightarrow n_2$ where n_1 and n_2 are the principal quantum numbers of the two states. Assume the Bohr model to be valid, if the time period of the electron in the initial state is eight times that in the final state then the possible values of n_1 and n_2 are
(a) $n_1 = 4, n_2 = 2$
(b) $n_1 = 8, n_2 = 2$
(c) $n_1 = 8, n_2 = 1$
(d) $n_1 = 6, n_2 = 3$

Linked Comprehension Type

1. Suppose Bohr therory is applicable to a negative particle of mass $2m_e$ and charge $2e$ revolving around a nucleus of charge Ze. Let r_1, v_1 and E_1 be the radius of the orbit, speed of the particle in the orbit and energy of the particle in the orbit, respectively. The values for the electron revolving in the corresponding orbit of hydrogen atom are r, v, and E, respectively.
(i) Which of the following expression regarding the ratio of radii is correct?
(a) $r_1/r = 2$ (b) $r_1/r = 1/2$ (c) $r_1/r = 4$ (d) $r_1/r = 1/4$
(ii) Which of the following expressions regarding the ratio of speeds is correct?
(a) $v_1/v = 2$ (b) $v_1/v = 1/2$ (c) $v_1/v = 4$ (d) $v_1/v = 1/4$
(iii) Which of the following expressions regarding the ratio of energies is correct?
(a) $E_1/E = 4$ (b) $E_1/E = 1/4$ (c) $E_1/E = 8$ (d) $E_1/E = 1/8$

2. In a mixture of H and He^+ gases, H atoms and He^+ ions are excited to their respective first excited states. Subsequently, H atoms transfer their total excitation energy to He^+ ion (by collision). Assuming that the Bohr model is applicable, answer the following three questions.
(i) The qunatum number n of the state finally populated in He^+ ions is
(a) 2 (b) 3 (c) 4 (d) 5
(ii) The wavelength of light emitted in the visible region by He^+ ions after collision with H atoms is
(a) 650 nm (b) 560 nm (c) 480 nm (d) 400 nm
(iii) The ratio of the kinetic energy of the $n = 2$ electron for the H atom to that of He^+ ion is
(a) 1/4 (b) 1/2 (c) 1 (d) 2

3. The Bohr model can account for the spectral transitions in hydrogen-like species. Based on this model, answer the following three questions.
(i) The radius of Bohr orbit is directly proportional to
(a) n/Z^2 (b) n^2/Z (c) n^2/Z^2 (d) n/Z
(ii) The speed of electron in the Bohr orbit is directly proportional to
(a) n/Z (b) n^2/Z (c) Z/n (d) Z/n^2
(iii) The magnitude of energy of an electron is the Bohr orbit is directly proportional to
(a) Z^2/n^2 (b) Z/n^2 (c) Z^2/n (d) Z/n^2

4. A gas of identical hydrogen-like species has some species in the lowest (ground) energy level and some species in a particular upper (excited) energy level and there are no species in any other energy level. The species of the gas make the transition to a higher energy level by absorbing monochromatic radiations of photon energy 2.7 eV. Subsequently, the atoms emit radiation of only six different photon energies. Some of the emitted photons have an energy of 2.7 eV, some have more energy and some less than 2.7 eV. Based on this observation, answer the following three questions.

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8. Match the orbitals given in Column I with the characteristic angular momentum of the electron in the orbital mentioned in Column II.

Column I	Column II
(a) s orbital	(p) $\left(2\sqrt{3}\right)(h/2\pi)$
(b) p orbital	(q) $\left(\sqrt{6}\right)(h/2\pi)$
(c) d orbital	(r) zero
(d) f orbital	(s) $\left(\sqrt{2}\right)(h/2\pi)$

9. Identify the entries mentioned in Column I with the correct entries given in Column II.

Column I	Column II
(a) Identical energies	(p) $n = 2$ of H and $n = 4$ of Be^{3+}
(b) Identical orbit radius	(q) $1 \leftarrow 2$ of H and $2 \leftarrow 4$ of He^{+}
(c) Identical speed of electron	(r) $n = 2$ of H and $n = 1$ of He^{+}
(d) Identical spectral transition	(s) $n = 1$ of H and $n = 2$ of He^{+}
	(t) $2 \leftarrow 3$ of He^{+} and $3 \leftarrow 4$ of Li^{2+}

ANSWERS

Straight Objective Type

1. (c)	**2.** (d)	**3.** (a)	**4.** (b)	**5.** (b)	**6.** (b)	**7.** (a)
8. (a)	**9.** (b)	**10.** (c)	**11.** (b)	**12.** (b)	**13.** (b)	**14.** (d)
15. (c)	**16.** (c)	**17.** (c)	**18.** (b)	**19.** (a)	**20.** (d)	**21.** (b)
22. (a)	**23.** (d)	**24.** (c)	**25.** (a)	**26.** (b)	**27.** (d)	**28.** (c)
29. (a)	**30.** (b)	**31.** (d)	**32.** (a)	**33.** (b)	**34.** (a)	**35.** (a)
36. (a)	**37.** (d)	**38.** (a)	**39.** (c)	**40.** (a)	**41.** (a)	**42.** (b)
43. (b)	**44.** (a)	**45.** (b)	**46.** (d)	**47.** (a)	**48.** (b)	**49.** (d)
50. (a)	**51.** (b)	**52.** (d)	**53.** (d)	**54.** (d)	**55.** (a)	**56.** (b)
57. (a)	**58.** (d)	**59.** (a)	**60.** (c)	**61.** (d)	**62.** (a)	**63.** (a)
64. (a)	**65.** (d)	**66.** (d)	**67.** (a)	**68.** (d)	**69.** (a)	**70.** (a)
71. (c)	**72.** (b)	**73.** (c)	**74.** (c)	**75.** (b)	**76.** (c)	**77.** (d)
78. (d)	**79.** (c)	**80.** (a)	**81.** (c)	**82.** (b)	**83.** (a)	**84.** (b)
85. (b)	**86.** (d)	**87.** (d)	**88.** (b)	**89.** (c)	**90.** (a)	**91.** (c)
92. (c)	**93.** (a)	**94.** (c)	**95.** (d)	**96.** (d)	**97.** (b)	**98.** (c)
99. (a)	**100.** (a)	**101.** (d)	**102.** (c)	**103.** (d)	**104.** (b)	**105.** (a)
106. (c)	**107.** (d)	**108.** (a)	**109.** (a)	**110.** (c)	**111.** (d)	**112.** (d)
113. (c)	**114.** (a)	**115.** (d)	**116.** (b)	**117.** (b)	**118.** (b)	**119.** (c)
120. (d)	**121.** (c)	**122.** (a)	**123.** (b)	**124.** (b)	**125.** (d)	**126.** (a)
127. (d)	**128.** (a)	**129.** (b)	**130.** (b)	**131.** (c)	**132.** (d)	**133.** (a)
134. (c)	**135.** (c)	**136.** (b)	**137.** (a)	**138.** (c)	**139.** (a)	**140.** (c)
141. (d)	**142.** (a)	**143.** (d)	**144.** (a)	**145.** (c)	**146.** (c)	

Multiple Correct Choice Type

1. (a), (c)	**2.** (b), (d)	**3.** (a), (c)	**4.** (a), (b), (c)
5. (a), (b)	**6.** (a), (b), (c), (d)	**7.** (c), (d)	**8.** (a), (b), (d)
9. (a), (c), (d)	**10.** (a), (c)	**11.** (a), (c), (d)	**12.** (a), (b), (d)
13. (a), (b), (d)	**14.** (a), (c), (d)	**15.** (a), (d)	**16.** (a), (b)
17. (b), (c), (d)	**18.** (a), (c), (d)	**19.** (a), (b)	**20.** (a), (c), (d)
21. (a), (d)	**22.** (a), (b), (c)	**23.** (b), (d)	**24.** (a), (b), (d)
25. (b), (c), (d)	**26.** (c), (d)	**27.** (a), (b), (c), (d)	**28.** (a), (d)
29. (a), (b)	**30.** (a), (c)	**31.** (c), (d)	**32.** (c), (d)
33. (a), (b)	**34.** (a), (b), (c)	**35.** (c), (d)	**36.** (a), (c)
37. (a), (b), (c)	**38.** (a), (d)		

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63. Velocity of electron decreases with increase in the value of n in Bohr theory. The electron will have maximum kinetic energy in the $n = 1$ orbit.

64. For Balmer series, the longest wave length corresponds to the transition $3 \leftarrow 2$.

$$\Delta E = R_H hc \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = R_H hc \left(\frac{1}{2^2} - \frac{1}{3^2}\right) = \frac{5}{36} R_H hc$$

$$\lambda = \frac{hc}{\Delta E} = \frac{36}{5 R_H} = \frac{36}{5 \times 1.09678 \times 10^7 \text{ m}^{-7}} = 6.565 \times 10^{-7} \text{ m} = 656.5 \text{ nm}$$

65. After the removal of one electron, the species formed is He^+. The energy required to remove the electron from He^+ is four times the energy required to remove the electron from the hydrogen atom. Thus

$$E_{He^+} = Z^2 E_H = (2)^2 E_H = 4(13.6 \text{ eV}) = 54.4 \text{ eV}$$

Hence, the energy required to remove both the electrons from helium atom is (24.6 eV + 54.4 eV) which is 79.0 eV.

66. As per Bohr model, the ionization energy of an atom (or ion) in the ground state is directly proportional to the square of the atomic number. Hence, $(IE)_{Li^{2+}} = Z^2 (IE)_H = (3^2)\ (13.6 \text{ eV}) = 122.4 \text{ eV}$

67. The various expressions are

$$\text{PE} = -\frac{1}{4\pi\varepsilon_0}\left(\frac{Ze^2}{r}\right); \quad \text{KE} = \frac{1}{2}\frac{1}{4\pi\varepsilon_0}\left(\frac{Ze^2}{r}\right); \quad E = \text{KE} + \text{PE} = -\frac{1}{2}\frac{1}{4\pi\varepsilon_0}\left(\frac{Ze^2}{r}\right)$$

When an electron undergoes transition from an excited state to the ground state, the value of r decreases. From the above expressions, it follows that the electronic kinetic energy increases while its potential and total energies decrease.

68. For a hydrogen-like species, we have $\Delta E = Z^2 R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

Hence $\Delta E_{4 \leftarrow 3} = Z^2 R_H \left(\frac{1}{9} - \frac{1}{16}\right) = \left(\frac{7}{144}\right) Z^2 R_H = 0.049\ Z^2 R_H$

$$\Delta E_{1 \leftarrow 2} = Z^2 R_H \left(\frac{1}{1} - \frac{1}{4}\right) = \left(\frac{3}{4}\right) Z^2 R_H = 0.75\ Z^2 R_H$$

$$\Delta E_{2 \leftarrow 3} = Z^2 R_H \left(\frac{1}{4} - \frac{1}{9}\right) = \left(\frac{5}{36}\right) Z^2 R_H = 0.139\ Z^2 R_H$$

$$\Delta E_{4 \leftarrow 5} = Z^2 R_H \left(\frac{1}{16} - \frac{1}{25}\right) = \left(\frac{9}{400}\right) Z^2 R_H = 0.023\ Z^2 R_H$$

Since $\Delta E_{4 \leftarrow 5} < \Delta E_{4 \leftarrow 3}$, the transition $4 \leftarrow 5$ may result into the emission of infrared radiation.

69. In Bohr model $r = \frac{n^2}{Z}$ (53 pm) where $n = 5$ for $Z = 100$

Hence $r = (25/100)\ (53 \text{ pm}) = (53 \text{ pm})/4$

Thus $m = 1/4$

70. The principal quantum number can be correlated with size of an orbital.

71. The choice c is not correct as the value of m_l cannot be greater than l.

72. The angular momentum of electron in an atom is described by azimuthal quantum number through the expression $L = \sqrt{l(l+1)}\ (h/2\pi)$

73. The z-component of angular momentum of electron in an atom is described by magnetic quantum number through the expression $L_z = m(h/2\pi)$.

74. The number of orbitals in a subshell is equal to $2l + 1$.

75. The orbital p_y is symmetrical about the y-axis.

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19. (a) The number of orbitals for a given value of l is equal to the permitted value of m which can take values, 0, ±1, ±2, ... ±l, a total of $2l + 1$ values.
(c) A diamagnetic atom has no unpaired electrons.
(d) The half-filled and fully-filled electronic configurations are more stable. It is due to the larger exchange energy.

20. (b) The symbol s stands for sharp—a term used in the characterization of spectral lines. The symbols p, d and f stand for principal, diffuse and fundamental, respectively.

21. (b) The expression is $E = hc/\lambda$. Hence, energy and wavelength are inversely related.
(d) Lyman spectral series lies in the ultraviolet region.

22. (b) See Fig. 1.1; (c) See Fig. 1.1; (d) See Fig. 1.1.

23. (a) See Fig. 1.1; (b) See Fig. 1.1.; (c) See Fig. 1.1.
(d) It is due to the fact that the electron interacts in different manner with the external magnetic field.

24. (a) This splitting is known as Zeeman effect.
(c) Bosons does not follow Pauli exclusion principle.
(d) This is in accordance with Hund's rule of maximum multiplicity.

25. (a) It decreases with increase in the value of atomic number as is evident from the expression

$$E = -\frac{1}{n^2}\left[\frac{2\pi^2 m(Ze^2/4\pi\varepsilon_0)^2}{h^2}\right].$$

(c) The deflection in a given electric field depends on the value of e/m. For β-particles, e/m is larger than α-particles because electrons are much lighter than He^{2+} species.

37. The ejected photoelectrons satisfy the expression

Energy of photon = Work function + KE of electron

Hence, $4.25\text{ eV} = (\text{KE})_A + W_A$ and $4.70\text{ eV} = (\text{KE})_B + W_B$

The expression of de Broglie wavelength is $\lambda = \dfrac{h}{p} = \dfrac{h}{\sqrt{2mE}}$ (since $E = \dfrac{1}{2}mv^2 = \dfrac{p^2}{2m}$)

Hence $\dfrac{\lambda_A}{\lambda_B} = \left[\dfrac{(\text{KE})_B}{(\text{KE})_A}\right]^{1/2} = \dfrac{1}{2}\text{(given)} \Rightarrow (\text{KE})_A = 4(\text{KE})_B$

Since $(\text{KE})_B = (\text{KE})_A - 1.50\text{ eV}$, we get $(\text{KE})_B = 4(\text{KE})_B - 1.50\text{ eV}$ or $(\text{KE})_B = 0.50\text{ eV}$

Thus $(\text{KE})_A = 2.00\text{ eV}$

With these, $W_A = 4.25\text{ eV} - (\text{KE})_A = 2.25\text{ eV}$ and $W_B = 4.70\text{ eV} - (\text{KE})_B = 4.20\text{ eV}$

38. The time period of the electron in a Bohr orbit is given by $T = 2\pi r/v$, where v is the speed of the electron in the orbit. Since $mvr = n(h/2\pi)$, we get

$$T = \frac{2\pi r}{nh/(2\pi mr)} = \left(\frac{4\pi^2 m}{nh}\right)r^2$$

The expression of Bohr radius of hydrogen atom is $r = n^2\left(\dfrac{h^2\varepsilon_0}{\pi m e^2}\right)$

Hence $T = \left(\dfrac{4\pi m}{nh}\right)\left(\dfrac{n^4 h^4 \varepsilon_0^2}{\pi^2 m^2 e^4}\right) = n^3\left(\dfrac{4\pi^3 \varepsilon_0^2}{me^4}\right)$

For two orbits $\dfrac{T_1}{T_2} = \dfrac{n_1^3}{n_2^3}$

Since $T_1/T_2 = 8$, we will have $n_1/n_2 = 2$.

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(iii) The maximum in $r^2 R^2$ can be obtained by setting $d(r^2 R^2)/dr = 0$. Thus

$$\frac{d}{dr}\left[r^2\left(2-\frac{r}{a_0^2}\right)^2 e^{-r/a_0}\right] = 0 \qquad \text{i.e.} \qquad \frac{d}{dr}\left[4r^2+\frac{r^4}{a_0^2}-\frac{4r^3}{a_0}e^{-r/a_0}\right] = 0$$

This gives $\left\{\left(8r+\frac{4r^3}{a_0^2}-\frac{12r^2}{a_0}\right)-\frac{1}{a_0}\left(4r^2+\frac{r^4}{a_0^2}-\frac{4r^3}{a_0}\right)\right\}e^{-r/a_0} = 0$

or $$8r+\frac{8r^3}{a_0^2}-\frac{6r^2}{a_0}-\frac{r^4}{a_0^3} = 0 \qquad \text{or} \qquad \left(\frac{r}{a_0}\right)^3-8\left(\frac{r}{a_0}\right)^2+16\left(\frac{r}{a_0}\right)-8 = 0$$

or $$\left[\left(\frac{r}{a_0}\right)^2-6\left(\frac{r}{a_0}\right)+4\right]\left(\frac{r}{a_0}-2\right) = 0$$

The roots are $(r/a_0) = 2$ and $(r/a_0) = 3 \pm\sqrt{5}$

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Table 4.1 Long Form of Periodic Table

Periods	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIII	9 VIII	10 VIII	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	Noble gases 18 0
1	1 H 1.00794																	2 He 4.00260
2	3 Li 6.941	4 Be 9.01218											5 B 10.811	6 C 12.011	7 N 14.00674	8 O 15.9994	9 F 18.99840	10 Ne 20.1797
3	11 Na 22.98977	12 Mg 24.3050											13 Al 26.98154	14 Si 28.0855	15 P 30.97376	16 S 32.066	17 Cl 35.4527	18 Ar 39.948
4	19 K 39.0983	20 Ca 40.078	21 Sc 44.95591	22 Ti 47.88	23 V 50.9415	24 Cr 51.9961	25 Mn 54.9380	26 Fe 55.847	27 Co 58.93320	28 Ni 58.69	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.92159	34 Se 78.96	35 Br 79.904	36 Kr 83.80
5	37 Rb 85.4678	38 Sr 87.62	39 Y 88.90585	40 Zr 91.224	41 Nb 92.90638	42 Mo 95.94	43 Tc 98.9072	44 Ru 101.07	45 Rh 102.90550	46 Pd 106.42	47 Ag 107.8682	48 Cd 112.411	49 In 114.82	50 Sn 118.710	51 Sb 121.75	52 Te 127.60	53 I 126.90447	54 Xe 131.29
6	55 Cs 132.90543	56 Ba 137.327	57 *La 138.9055	72 Hf 178.49	73 Ta 180.9479	74 W 183.85	75 Re 186.207	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.96654	80 Hg 200.59	81 Ti 204.3833	82 Pb 207.2	83 Bi 208.98037	84 Po 208.9824	85 At 209.9871	86 Rn 222.0176
7	87 Fr 223.0197	88 Ra 226.0254	89 ⊕Ac 227.0278	104 Unq 261.11	105 Unp 262.114	106 Unh 263.118	107 Uns 262.12											

*

58 Ce 140.115	59 Pr 140.90765	60 Nd 144.24	61 Pm 144.9127	62 Sm 150.36	63 Eu 151.965	64 Gd 157.25	65 Tb 158.92534	66 Dy 162.50	67 Ho 164.93032	68 Er 167.26	69 Tm 168.93421	70 Yb 173.04	71 Lu 174.967

⊕

90 Th 232.0381	91 Pa 231.0359	92 U 238.0289	93 Np 237.0482	94 Pu 244.0642	95 Am 243.0614	96 Cm 247.0703	97 Bk 247.0703	98 Cf 242.0587	99 Es 252.083	100 Fm 257.0951	101 Md 258.10	102 No 259.1009	103 Lr 260.105

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Table 4.2 Number of elements in the different periods of modern periodic table

*Period Number**	*Orbitals being filled*	*Number of elements*
1	1s	2
2	2s, 2p	8
3	3s, 3p	8
4	4s, 3d, 4p	18
5	5s, 4d, 5p	18
6	6s, 4f, 5d, 6p	32
7	7s, 5f, 6d	incomplete

*Period number is the value of the principal quantum number or the quantum shell which starts filling.

2. *Groups* Each vertical column of the periodic table constitutes a group. According to IUPAC (International Union of Pure and Applied Chemistry) recommendations, the groups are numbered from 1 to 18 (Table 2.1). Group number of an element locates the position of element in the period. Members belonging to any one group have similar outer electronic configurations.

Classification of Elements

The elements can be classified into five types depending on their electronic configurations.

1. *Noble Gases* Noble gases constitute Group 18 of the periodic table. Except the first element of the group, helium (which has $1s^2$ configuration) all other elements, namely, neon, argon, krypton, xenon and radon have $(ns)^2(np)^6$ electronic configuration in the outermost shell. Because of the stable arrangement of electrons in these elements, they exhibit a very low chemical reactivity.

2. s-*Block Elements* Elements belonging to Group 1 (alkali metals; Li, Na, K, ..., Fr) with outermost electronic configuration ns^1 and those belonging to Group 2 (alkaline earth metals : Be, Mg, Ca, ..., Ra) with outermost electronic configuration ns^2 are known as s-block elements.

3. p-*Block Elements* Elements of Group 13 to 17 are known as p-block elements. The outermost electronic configurations of these groups are as follows.

Group	13	14	15	16	17
Configuration	$(ns)^2(np)^1$	$(ns)^2(np)^2$	$(ns)^2(np)^3$	$(ns)^2(np)^4$	$(ns)^2(np)^5$

The elements of s and p blocks taken together are known as the *representative elements*. Noble gases which appear at the end of each period are also included in the representative elements.

4. d-*Block Elements* Elements belonging to Groups 3 to 12 (in the middle of the periodic table) with an outer electronic configuration $(n-1)d^{1-10}\ ns^{1-2}$ constitute the d-block of the periodic table and are called *transition elements*. In these elements, n is 4, 5, or 6 with corresponding filling of 3d, 4d, or 5d orbitals.

5. f-*Block Elements* At the bottom of the periodic table, there are two rows–one of lanthanides or lanthanide series ($Z = 58$ to 71) and the other of actinides or actinide series ($Z = 90$ to 107) containing incomplete 4f and 5f orbitals, respectively. The elements are characterized by the outer electronic configuration $(n-2)f^{1-14}\ (n-1)d^{0-1}\ ns^2$. In these elements, f orbitals are in the process of filling. These elements are also known as *inner transition elements*.

Main Characteristics of Representative Elements

As we move from left to right across a period, there is transition from metals to metalloids to nonmetals. Thus, elements of Groups 1 and 2 are metals, and those at the extreme right (baring noble gases) are nonmetals. Elements B, Si, Ge, As, Sb, Po and At are metalloids. Down a particular group, there is an increase in the metallic character or decrease in the nonmetallic character.

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Main characteristics of Transition Elements

All transition elements are metallic. These are characterized by variable oxidation states, formation of coloured ions and complexes. Many of them behave as catalysts.

Periodicity in Properties

As we move along the elements in the increasing atomic number, we find periodicity in the properties of these elements. Basically, this is due to the repetition of similar outer electronic configurations of atoms. Within a group, elements have similar outer atomic electronic configuration, and thus behave chemically similar. A few periodicity in properties are described in the following.

Atomic radius Atomic radius can be expressed in one of the three following ways.

Van der Waals radius It is half the shortest internuclear distance between two adjacent non-bonded atoms.

Metallic radius It is half the shortest internuclear distance between two atoms in the metallic crystal.

Covalent bond radius It is half the internuclear distance between two identical atoms joined by a single covalent bond.

Covalent-bond radius is always smaller than van der Waals radius, because the covalent bond formation involves the overlapping of orbitals of the outermost shell of adjacent atoms. Metallic radius is about 15 per cent larger than the covalent radius. The covalent radius is known for most elements and the term atomic radius is generally taken for covalent radius.

Atomic radius increases down a group. This is because the outermost shell successively have higher principal quantum number.

Atomic radius decreases across a period. This is due to the increase in the effective nuclear charge with increase in the atomic number across a period.

Ionic radius It is the radius of a cation or an anion. If an atom forms an anion, its radius increases, since the nuclear charge remains the same but the repulsion resulting from the additional electron(s) enlarges the domain of the electronic cloud. On the other hand, a cation is smaller than the neutral atom, since removing one or more electrons reduces electron-electron repulsion and there will be a shrinkage of the electronic cloud.

Ionization energy Ionization energy is defined as the minimum energy required to remove an electron from a gaseous atom in its ground state. This is, infact, the first ionization energy. The second ionization energy is the energy required to remove an electron from the singly charged cation in the gaseous state and so on.

In general, the ionization energy of atom decreases within a group from top to bottom. This is due to the fact that the electron to be removed belongs to the higher successive quantum shell.

Within a period, there is a tendency to increase the ionization energy as one moves from left to right. This is basically due to the increase in the effective nuclear charge. This increase is met with two exceptions where a decrease in ionization energy is observed. The first exception occurs when one moves from Group 2 to 3 and the second exception occurs from Group 15 to 16. These exceptions can be explained on the basis of electronic configurations.

Elements of Group 3 contain one extra electron in p orbital as compared to those of Group 2. The p electron is well-shielded by the inner electrons and ns^2 electrons. Consequently, less energy is required to remove a single p electron than to remove a paired s electrons from the same principal energy level.

Elements of Groups 16 contain one extra electron in p orbital as compared to the stable half-filled p orbitals of Group 15. Consequently, lesser energy is required to remove this extra electron as compared to the removal of electron from the half-filled p orbital.

In general, second ionization energy is always greater than the first one.

Electron affinity Electron affinity is defined as the energy released when an electron is added to an isolated gaseous atom.

In general, the electron affinity increases as we move from left to right across a period. Within a group, there is little change in the electron affinity values. The halogens (Group 17) have the maximum values of electron affinity. This can be explained on the basis that after accepting electron, one gets the stable electronic configuration of the noble gas.

Amongst halogens, chlorine has the maximum value of electron affinity. This is because fluorine, which otherwise is expected to have maximum value, involves more electron-electron repulsion due to the more compact electronic configuration causing the value less than chlorine.

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Electronegativity The electronegativity of an element is a measures of the relative tendency of an atom to attract electrons towards itself when it is chemically bonded with another atom.

Linus Pauling devised a method for calculating relative electronegativities of most elements. According to him

$$\chi_A - \chi_B = (0.1088\ \text{kJ}^{-1/2}\text{mol}^{1/2})\sqrt{\Delta} \qquad \text{where} \qquad \Delta = \varepsilon_{A-B} - \sqrt{\varepsilon_{A-A}\ \varepsilon_{B-B}}$$

where ε's refer to the numerical values of to bond enthalpies expressed in kJ mol^{-1}. The numerical value of $\sqrt{\Delta}$ is a measure of ionic character of the bond A-B. By assigning $\chi_F = 4.0$, χ values of other atoms can be computed. Mullikan's scale uses the expression

$$\chi = \frac{\text{IE} + \text{EA}}{2}$$

to compute electronegativities. However, Pauling scale is most widely used.

The electronegativity increases across a period and decreases down the group.

Atoms of elements with a difference of 2.0 or more in electronegativity values form ionic bond.

Oxidation states Oxidation state (or oxidation number) refers to the number of charges an atom would have in a molecule (or an ionic compound) if electrons were transferred following a set of some rules. Oxidation states can be positive, negative or zero and thus differ from valency which is always positive.

Metallic elements mostly have positive oxidation states, whereas nonmetallic elements may have either positive or negative oxidation states. The highest oxidation state of a representative element is its group number (or group number – 10) in the periodic table. For example, the highest oxidation number of halogen is +7 which is observed for Cl and I. The transition metals usually have several oxidation numbers.

Metallic and Nonmetallic Character

As we travel in a period, the metallic character of element decreases while its nonmetallic character increases. On descending a group, the metallic character increases. Thus, the elements of Groups 1 and 2 are essentially metals. Group 13 starts with a metalloid and ends with a metal. Group 14 and 15 start with a nonmetal, followed by metalloid and ends with a metal. Group 16 starts with a nonmetal and ends with a metal. Elements of Group 17 are nonmetals and ends with an element with a feeble metallic character.

All metals are electropositive elements and have a tendency to lose electrons. On the other side, nonmetals are electronegative elements and have a tendency to gain electrons. Metals form basic oxides while nonmetals form acidic oxides.

LANTHANIDE CONTRACTION

The metallic radii of the lanthanides and their tripositive ionic radii decrease on passing across the lanthanides due to the increase in effective nuclear charge as the 4f shell is successively filled. This is because the 4f electrons shield each other from nuclear charge poorly. As more 4f electrons are added the effective nuclear charge felt by each of them increases. As a consequence, the whole 4f electron shell contracts on passing across the lanthanides. The steady decrease in metallic and ionic radii on crossing the lanthanides is known as the lanthanide contraction.

The effect of lanthanide contraction is of sufficient magnitude to cause the elements which follow in the third transition series (5d series) to have sizes very similar to those of the second row of transition elements (4d series). The normal increase in size from Sc to Y to La disappears after the lanthanides. Thus, the pairs of elements such as Zr-Hf, Nb-Ta, Mo-W have nearly identical sizes. They have similar chemical properties and their separation is very difficult.

The effect of lanthanide contraction is also important in the chemistry of lanthanides themselves. A general decrease in ionic radii on crossing the series results in a corresponding increase in the polarizing power of the ions and in the stability of the complex ions. Increasing polarizing power makes the hydroxides less and less basic on crossing the lanthanides. For example, $La(OH)_3$ is most basic whereas $Lu(OH)_3$ is less basic.

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BRIEF SYNOPSIS OF REPRESENTATIVE ELEMENTS

A brief synopsis of representative elements groupwise is in order.

Group 1 Elements—Alkali Metals

Group 1 contains lithium (Li), sodium (Na), potassium (K), rubidium (Rb), caesium (Cs) and francium (Fr).
All alkali metals contain one electron in their outermost orbitals. Due to contribution of one electron per atom towards the metallic bonding, all the elements are soft and low melting. Because of low ionization energies, the metals are strong reducing agents. The alkali metals dissolve in liquid ammonia and form a deep blue solution when dilute. The blue colour is due to the solvated electrons. The conducting ability of their ions in aqueous solution follows the order: $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$.

The alkali metals are very reactive and tarnish in air to form oxide. They burn in air, Li forms Li_2O, Na forms Na_2O_2 and higher alkali metals form superoxide (MO_2). The oxides of alkali metals are basic in nature. The peroxides are diamagnetic and are oxidizing agents. The superoxides are paramagnetic and are stronger oxidising agents than peroxides.

The melting points of alkali metal halides decrease in the order MF > MCl > MBr > MI. Lithium halides have melting points less than those of sodium halides due to the more covalent character possessed by lithium salts.

The solubilities of carbonates and bicarbonates increase on descending the group.

Group 2 Elements—Alkaline Earth Metals

Group 2 contains beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba) and radium (Ra).

All alkaline earth metals contain two electrons in their outermost orbitals. These are soft. But compared to alkali metals, they are harder and have higher cohesive energy. Their melting points are higher than those of Group 1 elements and vary irregularly because of different structures. The atomic and ionic radii are smaller than those of the elements of Group 1. The alkaline earth metals dissolve in liquid ammonia giving bright blue colour due to the solvated electrons.

Alkaline earth metals are typically divalent and form colourless ionic compounds. When burnt in air, Be, Mg and Ca form monoxide while Sr, Ba and Ra form peroxides. When burnt in oxygen, they all form oxides which are basic in nature. The base strength of hydroxides increases on descending the group. Their solubility also increases on descending the group.

The solubilities of carbonates and sulphates decrease on descending the group. In deciding the solubilities of hydroxides, lattice energy predominates over hydration energy whereas in carbonates and sulphates, hydration energy predominates over lattice energy.

Group 13 Elements—Boron Family

Group 13 contains boron (B), aluminium (Al), gallium (Ga), indium (In), and thallium (Tl). These elements have outer electronic configuration $(ns)^2\ (np)^1$, where n varies form 2 to 6. Boron is nonmetal while others are metals. The atomic litter of Ga, In and Tl are smaller than the expected values due to d-block contraction. The atomic radius of Tl is a little larger than in due to lanthanide contraction. On descending the group, +1 oxidation state becomes more stable than +3 state due to the inert pair effect.

The very high melting point of boron is due to its icosahedral structure. In boron family, gallium has the lowest melting point. The ionization energies do not follow the expected trend of decreasing values on descending the group.

All elements burn in oxygen at high temperatures forming M_2O_3. The reaction of aluminium with oxygen (known as thermite reaction) is strongly exothermic. Aluminium is amphoteric. It dissolves in dilute mineral acids and in aqueous sodium hydroxide.

The acidic character of hydroxides decreases on descending the group.

Boric acid is a very weak monobasic acid. It does not liberate hydrogen ion but accepts a hydroxyl ion. In the presence of *cis*-diol (glycerol, mannitol or sugars), boric acid behaves as a strong acid and can be titrated with NaOH in the presence of phenolphthalein indicator.

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BF_3 is hydrolysed as follows.

$$4BF_3 + 12H_2O \rightarrow 4H_3BO_3 + 12HF$$
$$12HF + 3H_3BO_3 \rightarrow 3H^+ + 3[BF_4]^- + 9H_2O$$

$$4BF_3 + 3H_2O \rightarrow H_3BO_3 + 3H^+ + 3[BF_4]^-$$

Hydrolysis of BCl_3 or BI_3 produces boric acid.

$$BCl_3 + 3H_2O \rightarrow H_3BO_3 + 3HCl$$

The fluorides of Al, Ga, In and Tl are ionic while the other halides are generally covalent and exist as dimer.

The trihalides of boron are electron-deficient compounds. Due to back bonding, the electron density on boron is increased. The tendency to form $p\pi$-$p\pi$ bond is maximum in BF_3 and falls rapidly on passing to BCl_3 to BBr_3. The increasing order of acid strength follows the order $BF_3 < BCl_3 < BBr_3$.

Group 14 Elements—Carbon Family

Group 14 contains carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb). Their outer electronic configuration is $(ns)^2\ (np)^2$, where n varies from 2 to 6. The metallic character of elements increases on descending the group; C and Si are nonmetals, Ge is a nonmetal but also has some metallic characteristics, and Sn and Pb are metals. The melting points decrease on descending the group, with the exception of Pb whose melting point is slightly higher than that of Sn. Carbon has extremely high melting point. This is due to the stronger C—C bonds in the network of carbon atoms.

The ionization energies decrease from C to Si, but then change in an irregular way because of the effects of filling d and f sub-shells.

Carbon forms single, double and triple bonds with carbon itself and with other elements. The tendency to form multiple bond by other elements is rare. However, silicon can form double bond due to back bonding in which the lone pair in p orbitals of an atom is extended to an empty orbital of Si. One of the examples of back bonding is trisilylamine, $N(SiH_3)_3$.

The chemical reactivity of elements decreases down the group. The inert pair effect becomes increasingly effective on descending the group.

The stability of +4 oxidation state decreases while that of the +2 oxidation state increases on descending the group.

C, Si and Ge are unaffected by dilute acids. Sn and Pb react with dilute nitric acid.

$$4Sn + 10HNO_3 \rightarrow 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$$
$$3Pb + 8HNO_3 \rightarrow 3Pb(NO_3)_2 + 2NO + 4H_2O$$

C is not affected by alkalis, Si reacts forming silicates while Sn and Pb form stannate, $[Sn(OH)_6]^{2-}$, and plumbate, $[Pb(OH)_6]^{2-}$, respectively.

All the elements of Group 14 form tetrahalides with the exception of PbI_4, which is not known. The stability of halides decreases down the group. CCl_4 is stable while other halides are hydrolysed. The hydrolysis of $SiCl_4$ produces SiO_2 while SiF_4 produces SiO_2 as well as $[SiF_6]^{2-}$.

The acidic nature of the dioxides of carbon family decreases down the group; CO_2 and SiO_2 are acidic, GeO_2 is weakly acidic and SnO_2 and PbO_2 are amphoteric.

Silicones are organosilicon polymers with general formula $(R_2SiO)_n$, where R may be methyl, ethyl or phenyl group.

Group 15 Elements-Nitrogen Family

Group 15 contains nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb) and bismuth (Bi). Their outer electronic configuration is $(ns)^2\ (np)^3$, where n varies from 2 to 6. The metallic character of these elements increases on descending the group; N and P are nonmetals, As and Sb are metalloids and Bi is a metal. The melting and boiling points follow the order

melting point	N < P < As > Sb > Bi
boiling point	N < P < As < Sb > Bi

Phosphorus has two common allotropic forms; white and red. White phosphorus is more reactive than red form due to highly strained structure (P—P—P angle is 60°).

Black phosphorus is a highly polymerized form and is most stable.

Nitrogen form triple bond in dinitrogen because bond enthalpy $\varepsilon(N \equiv N)$ is greater than three times bond enthalpy $\varepsilon(N—N)$. In phosphorus, the reverse is true, hence, it involves single bonds.

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The melting points of hydrides follow the order $NH_3 > PH_3 < AsH_3 < SbH_3$.

All the five elements of Group 15 form trihalides. Of these nitrogen halides are least stable. All the trihalides with the exception of NF_3 hydrolyse in aqueous solution.

$$NCl_3 + 3H_2O \rightarrow NH_3 + 3HOCl$$
$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$
$$AsCl_3 + 3H_2O \rightarrow H_3AsO_3 + 3HCl$$
$$SbCl_3 + H_2O \rightarrow SbO^+ + 2H^+ + 3Cl^-$$
$$BiCl_3 + H_2O \rightarrow BiO^+ + 2H^+ + 3Cl^-$$

Nitrogen forms many oxides; N_2O, NO, N_2O_3, NO_2 and N_2O_5. The most common oxides of phosphorus are P_4O_6 and P_4O_{10}. Phosphorus trioxide is an acidic oxide and is anhydride of orthophosphorous acid (H_3PO_3). Phosphorus pentoxide is anhydride of phosphoric acid (H_3PO_4).

Nitrogen forms two acids; nitrous acid (HNO_2) and nitric acid (HNO_3). Phosphorus forms two series of oxoacids. These are phosphorus and phosphoric series. In phosphorous series, the acids include pyrophosphorous acid ($H_4P_2O_5$), orthophosphorous acid (H_3PO_3), metaphosphorous acid (HPO_2) and hypophosphorous acid (H_3PO_2). The acids $H_4P_2O_5$ and H_3PO_3 are reducing agents as they involve P—H bond.

In phosphoric series, the acids include orthophosphoric acid (H_3PO_4), pyrophosphoric acid ($H_4P_2O_7$) and polymetaphosphoric acid, $(HPO_3)_n$.

Group 16 Elements—Oxygen Family

Group 16 contains oxygen (O), sulphur (S), selenium (Se), tellurium (Te) and polonium (Po). Their electronic configuration is $(ns)^2 (np)^4$, where n varies from 2 to 6.

The metallic character of these elements increases on descending the group; O and S are nonmetallic, Se and Te are weaker nonmetallic and Po is metallic.

Electron affinity of sulphur is larger than that of oxygen, this is due to the more repulsion experienced by the incoming electron from the smaller, more compact electronic cloud of oxygen atom.

Oxygen is diatomic with two unpaired electrons. Sulphur exists in two allotropic forms—rhombic and monoclinic sulphur. Rhombic sulphur is stable at room temperature while monoclinic sulphur is stable above 369 K. Selenium exists in six allotropic forms. Tellurium has only one crystalline form and polynium has two allotropic forms (cubic and rhombohedral).

Ozone is another allotropic form of oxygen. It is very reactive. It is formed in the upper layer of atmosphere (about 20 km from the earth) by the action of ultraviolet radiation on oxygen. Ozone is a strong oxidizing agent. In organic chemistry, ozone is used to locate the carbon-carbon double and triple bonds. The ozone molecule is angular with bond angle about 117° and bond length 127.8 pm.

The melting and boiling points of hydrogen compounds of elements of Group 16 follow the order $H_2O > H_2S < H_2Se < H_2Te$. The exceptional high values of H_2O is due to hydrogen bondings.

H_2O_2 is a strong oxidizing agent. With stronger oxidizing agents such as $KMnO_4$, KIO_3, O_2, hydrogen peroxide acts as a reducing agent.

Group 17 Elements—Halogen Family

Group 17 contains fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At). Their outer electronic configuration is $(ns)^2 (np)^5$, where n varies from 2 to 6. The trends in this group are as follows.

Covalent and ionic radii—*increase down the group.*

Electronegativity and ionization energy—*decrease down the group.*

Electron affinity—*increases from* F to Cl *followed by a decrease.*

Melting and boiling points—*increase down the group.*

Bond enthalpy ε(X—X)—*increases from* F *to* Cl *followed by a decrease.*

Oxidizing ability—decreases down the group.

Halogens are very reactive and do not occur in free state. Fluorine is most electronegative atom, there exists hydrogen bondings in gaseous HF.

HF is a weak acid and HCl, HBr and HI behave as strong acids. In the glacial acetic acid medium, the acid strength follows the order HI > HBr > HCl > HF.

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Halogens with the exception of F form a number of oxoacids—hypohalous acids (HOX), halous acids (HXO_2), halic acid (HXO_3) and perhalic acid (HXO_4). The acid strength follows the order $HXO_4 > HXO_3 > HXO_2 > HXO$. Fluorine forms only hypofluorous acid (HOF).

Halogens also form interhalgoen compounds AX, AX_3, AX_5 and AX_7. The compounds AX and AX_3 are formed where the electronegativity is not very large. The compounds AX_5 and AX_7 are formed by large Br and I atoms surrounded by small atom F. The molecule AX_3 is T-shaped with two lone pair of electrons at the equilateral positions. The orientations of five pair of electrons around the atom A is trigonal bipyramidal.

The six pairs of electrons around atom A in AX_5 acquire octahedral orientation. The seven pairs of electrons around atom A in AX_7 acquire pentagonal bipyramidal orientation.

Halogens are nonmetallic and have high electron affinity. The nonmetallic character decreases down the group and iodine shows some metallic character. With metals, they form ionic compounds by accepting one electron and with nonmetals covalent compounds are formed by sharing an electron.

All halogens exhibit –1 oxidation state. Except fluorine, rest of the halogens also exhibit 1, +3, +5 and +7 oxidation states. Fluorine is the most electronegative and thus there exists hydrogen bonding in HF with the result that it has exceptionally high melting and boiling points as compared to those of HCl, HBr and HI.

Because of high reactivity, halogens do not exist in the free state.

Group 18 Elements—Noble Gases

The group 18 contains helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and radon (Rn). Their outer electronic configurations is $(ns)^2$ $(np)^6$ with the exception of the electronic configuration of He which is $(1s)^2$. All elements exist as monatomic gas.

Xenon forms a number of fluorides—XeF_2, XeF_4 and XeF_6. The other compounds are XeO_3, $XeOF_4$, XeO_2F_2, XeO_4 and $[XeO_6]^{4-}$

Straight Objective Type

Classification of Elements

1. The fifth period of modern periodic table includes
(a) 8 elements (b) 18 elements (c) 32 elements (d) unknown elements

2. In the sixth period, the orbitals being filled are
(a) 5s, 5p, 5d (b) 6s, 6p, 6d, 6f (c) 6s, 5f, 6d, 6p (d) 6s, 4f, 5d, 6p

3. In Lother Meyer plot of atomic volume versus atomic mass, the peaks are occupied by
(a) alkali metals (b) alkaline earth metals (c) halogens (d) noble gases

4. The number of periods in the long form of periodic table is
(a) 5 (b) 6 (c) 7 (d) 8

5. The elements with atomic numbers 21 to 30 belong to
(a) halogens (b) noble gas
(c) first transition elements (d) lanthanides

6. The atomic number of element next to $_{53}I$ in the same group is
(a) 61 (b) 71 (c) 85 (d) 93

7. The number of elements in the fourth period of the periodic table is
(a) 8 (b) 18 (c) 32 (d) 64

8. An element X belongs to Group 14 and 2nd period of the periodic table. Its atomic number will be
(a) 6 (b) 14 (c) 32 (d) 50

9. The atomic numbers of elements of the second inner transition elements lie in the range of
(a) 88 to 101 (b) 89 to 102 (c) 90 to 103 (d) 91 to 104

10. The total number of elements in Groups 8 to 10 of the periodic table is
(a) 3 (b) 5 (c) 7 (d) 9

11. The atomic numbers of elements of the lanthanide series lie in the range of
(a) 58 to 71 (b) 57 to 70 (c) 59 to 72 (d) 56 to 69

12. An element X belongs to Group 16 and 5th period. Its atomic number is
(a) 34 (b) 50 (c) 52 (d) 85

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13. The atomic number of In is 49. It belongs to
(a) 4th period (b) 5th period (c) 6th period (d) 3rd period

14. the elements $_{30}Zn$, $_{48}Cd$ and $_{80}Hg$ belong to
(a) 10th group (b) 11th group (c) 12th group (d) 13th group

15. The element with atomic number 105 is known as
(a) Unq (b) Unp (c) Unh (d) Uns

Atomic/Ionic Radius

16. Atomic radii of fluorine and neon in Angstrom units are respectively given by
(a) 0.72, 1.60 (b) 1.60, 1.60 (c) 0.72, 0.72 (d) none of these values (1987)

17. Which one of the following is the smallest in size?
(a) N^{3-} (b) O^{2-} (c) F^- (d) Na^+ (1989)

18. Which one of the following has the minimum atomic size?
(a) Li (b) Be (c) Na (d) Mg

19. Atomic sizes of the following elements decreases in the order
(a) B > Be > Li (b) Be > Li > B (c) Li > B > Be (d) Li > Be > B

20. Identify the correct order of increasing ionic sizes
(a) $Al^{3+} < O^{2-} < F^- < Cl^-$ (b) $F^- < O^{2-} < Cl^- < Al^{3+}$
(c) $Al^{3+} < F^- < O^{2-} < Cl^-$ (d) $Al^{3+} < F^- < Cl^- < O^{2-}$

21. The ionic sizes decreases in the order
(a) $K^+ > S^{2-} > Sc^{3+} > V^{5+} > Mn^{7+}$ (b) $S^{2-} > K^+ > Sc^{3+} > V^{5+} > Mn^{7+}$
(c) $Mn^{7+} > V^{5+} > Sc^{3+} > K^+ > S^{2-}$ (d) $Mn^{7+} > V^{5+} > Sc^{3+} > S^{2-} > K^+$

22. The size of Zr is very similar to
(a) La (b) Hf (c) Ta (d) W

23. The size of Nb is very similar to
(a) La (b) Hf (c) Ta (d) W

24. Which of the following elements has the largest size?
(a) Co (b) Ni (c) Cu (d) Zn

25. The size of Mo is very similar to W due to
(a) the difference of atomic number by one
(b) the contraction in size in the first transition series elements
(c) lanthanide contraction
(d) actinide contraction

26. Ionic sizes decreases in the order
(a) $N^{3-} > O^{2-} > F^- > Na^+ > Mg^{2+}$ (b) $N^{3-} > O^{2-} > F^- > Mg^{2+} > Na^+$
(c) $N^{3-} > F^- > O^{2-} > Na^+ > Mg^{2+}$ (d) $O^{2-} > N^{3-} > F^- > Na^+ > Mg^{2+}$

27. Ionic sizes increase in the order
(a) $Ca^{2+} < Cl^- < S^{2-} < Ar$ (b) $Ar < Ca^{2+} < Cl^- < S^{2-}$
(c) $Cl^- < Ca^{2+} < Ar < S^{2-}$ (d) $S^{2-} < Cl^- < Ca^{2+} < Ar$

28. In the isoelectronic species the ionic radii of N^{3-}, O^{2-} and F^- are respectively given by
(a) 136 pm, 140 pm, 171 pm (b) 136 pm, 171 pm, 140 pm
(c) 171 pm, 140 pm, 136 pm (d) 171 pm, 136 pm, 140 pm

29. The sizes of the following ions is in the order
(a) $Mg^{2+} < Na^+ < Al^{3+} < F^-$ (b) $F^- < Al^{3+} < Na^+ < Mg^{2+}$
(c) $Al^{3+} < Mg^{2+} < Na^+ < F^-$ (d) $Na^+ < Al^{3+} < F^- < Mg^{2+}$

30. The correct order of radii is
(a) N < Be < B (b) $F^- < O^{2-} < N^{3-}$ (c) Na < Li < K (d) $Fe^{3+} < Fe^{2+} < Fe^{4+}$ (2000)

31. Ionic radii of
(a) $Ti^{4+} < Mn^{7+}$ (b) $^{35}Cl^- < ^{37}Cl^-$ (c) $K^+ > Cl^-$ (d) $P^{3+} > P^{5+}$ (1999)

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32. The ionic radii of Li^+, Be^{2+} and B^{3+} follow the order
(a) $_3Li^+ < _4Be^{2+} < _5B^{3+}$ (b) $B^{3+} < Be^{2+} < Li^+$ (c) $Li^+ < B^{3+} < Be^{2+}$ (d) $B^{3+} < Li^+ < Be^{2+}$

33. For which of the elements of different groups, the change in nonpolar covalent radii is maximum?
(a) Groups 1 and 2 (b) Groups 13 and 14 (c) Groups 14 and 15 (d) Groups 16 and 17

34. For which of the elements of different groups, the change in nonpolar covalent radii is maximum?
(a) Groups 1 and 2 (b) Groups 14 and 15 (c) Groups 16 and 17 (d) Groups 17 and 18

35. Which of the following orders regarding metallic atomic radii is correct?
(a) $_{28}Ni < _{29}Cu < _{30}Zn$ (b) Ni < Zn < Cu (c) Cu < Ni < Zn (d) Cu < Zn < Ni

36. Which of the following orders regarding metallic atomic radii is correct?
(a) $_{45}Rh < _{46}Pd < _{47}Ag$ (b) Rh < Ag < Pd (c) Pd < Rh < Ag (d) Pd < Ag < Rh

37. Which of the following elements is expected to have the least density?
(a) Co (b) Ni (c) Cu (d) Zn

38. The ionic radii of Na^+, Mg^{2+} and Al^{3+} follow the order
(a) $Na^+ > Mg^{2+} > Al^{3+}$ (b) $Na^+ < Mg^{2+} < Al^{3+}$ (c) $Na^+ > Al^{3+} > Mg^{2+}$ (d) $Al^{3+} < Na^+ < Mg^{2+}$

39. The ionic radii of Cl^-, S^{2-} and P^{3-} follow the order
(a) $Cl^- > S^{2-} > P^{3-}$ (b) $Cl^- < S^{2-} < P^{3-}$ (c) $Cl^- > P^{3-} > S^{2-}$ (d) $Cl^- < P^{3-} < S^{2-}$

Ionization Energy

40. The first ionization potentials in electron volts of nitrogen and oxygen atoms are respectively given by
(a) 14.6, 13.6 (b) 13.6, 14.6 (c) 13.6, 13.6 (d) 14.6, 14.6 (1987)

41. The first ionization potential of Na, Mg, Al and Si are in the order
(a) Na < Mg > Al < Si (b) Na > Mg > Al > Si
(c) Na < Mg < Al > Si (d) Na > Mg > Al < Si (1988)

42. Amongst the following elements (whose electronic configurations are given below), the one having the highest ionization energy is
(a) $[Ne]\ (3s)^2(3p)^1$ (b) $[Ne]\ (3s)^2(3p)^3$ (c) $[Ne]\ (3s)^2(3p)^2$ (d) $[Ar]\ (3d)^{10}(4s)^2(4p)^3$ (1990)

43. The correct order of ionization energy is
(a) C > N > O (b) C > N < O (c) C < N > O (d) C < N < O

44. The correct order of ionization energy is
(a) Si > P > S (b) Si > P < S (c) Si < P > S (d) Si < P < S

45. 1 eV of energy is equivalent to
(a) 1.602×10^{-18} J (b) 1.602×10^{-19} J (c) 1.602×10^{-20} J (d) 1.602×10^{-21} J

46. Which of the following configurations is expected to have maximum difference in second and third ionization energies ?
(a) $(1s)^2(2s)^2(2p)^2$ (b) $(1s)^2(2s)^2(2p)^6(3s)^1$ (c) $(1s)^2(2s)^2(2p)^6(3s)^2$ (d) $(1s)^2(2s)^2(2p)^1$

47. In the periodic table, the ionization energy of elements
(a) decreases (i) from left to right across a period and (ii) on descending a group
(b) decreases from left to right across a period and increases on descending a group
(c) increases, (i) from left to right across period and (ii) on descending a group
(d) increases from left to right across a period and decreases on descending a group.

48. In the plot of ionization energy versus atomic number, the peaks are occupied by
(a) alkali metals (b) alkaline-earth metals (c) noble gases (d) halogens.

49. In the plot of ionization energy versus atomic number, the minimum positions are occupied by
(a) alkali metals (b) alkaline-earth metals (c) noble gas (d) halogens

50. Which of the following orders regarding the ionization energy is correct?
(a) Be > B > C (b) Be < B < C (c) Be > B < C (d) Be < C < B

51. Which of the following orders regarding the ionization energy is correct?
(a) N > O > F (b) F > O > N (c) N > O < F (d) O > F > N

52. The correct order of the second ionization energy of C, N, O and F is
(a) C > N > O > F (b) O > N > F > C (c) O > F > N > C (d) F > O > N > C (1981)

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106. Which of the following orders regarding the melting points of alkali metal halides is correct?
(a) MF > MCl > MBr (b) MF > MBr > MCl (c) MCl > MF > MBr (d) MCl > MBr > MF

107. Which of the following orders regarding the melting points of alkali metals chlorides is correct
(a) LiCl > NaCl > KCl (b) LiCl > KCl > NaCl (c) LiCl > NaCl > KCl (d) LiCl > NaCl < KCl

108. The boiling points of alkali metals follow the order
(a) Li < Na < K < Rb (b) Li > Na > K > Rb (c) Li < K < Na < Rb (d) Li < Rb < K < Na

109. The number of alkaline earth metals is
(a) 4 (b) 5 (c) 6 (d) 7

110. Which of the following statements is not correct?
(a) Alkaline earth metals are harder and denser than alkali metals
(b) The melting and boiling points of alkaline earth metals are higher than those of alkali metals
(c) Alkaline earth metals are more reactive than alkali metals
(d) The reactivities of alkaline earth metals increase down the group

111. Which of the following alkaline earth metal salts does not impart any colour to the Bunsen flame?
(a) Magnesium nitrate (b) Calcium chloride (c) Barium chloride (d) Strontium chloride

112. Which of the following statements is **not** correct?
(a) The standard reduction potentials of alkaline earth metal ions become more negative on descending the group
(b) Beryllium differs considerably from the rest of the alkaline earth metals
(c) Anhydrous salts of beryllium are covalent whereas those of Ca, Ba and Sr are ionic
(d) Be and Mg burn in air to form oxide while Ca, Ba and Sr form peroxides

113. Beryllium shows a diagonal relationship with
(a) magnesium (b) aluminium (c) boron (d) sodium

114. Which of the following statements is **not** correct?
(a) Beryllium does not react with water
(b) Magnesium reacts with boiling water and not with cold water
(c) Calcium reacts even with cold water
(d) The solubility of alkaline earth metal hydroxide decreases on descending the group

115. Which of the following statements is **not** correct?
(a) The basic strength of hydroxides of alkaline earth metal increases down the group
(b) The solubility of sulphates and carbonates of alkaline earth metal increases down the group
(c) The sulphates of alkaline earth metal are stable to heat
(d) The carbonates of alkaline earth metal decompose on heating

116. Which of the following diatomic molecules is **not** observed?
(a) Be_2 (b) B_2 (c) C_2 (d) N_2

117. Which of the following statements is not correct?
(a) The alkaline earth metals are harder and denser than alkali metals
(b) The melting and boiling points of alkaline earth metals are higher than the corresponding nearby alkali metals
(c) Alkaline earth metals are too reactive to occur freely in nature
(d) Magnesium and calcium can be obtained by chemical reduction of their compounds.

118. The order of melting points of Ba, Mg and Ca follow the order
(a) Ba > Mg > Ca (b) Ba > Ca > Mg (c) Ca > Mg > Ba (d) Ca > Ba > Mg

119. Property of the alkaline earth metals that increases with their atomic number is
(a) ionization energy (b) solubility of their hydroxides
(c) solubility of their sulphates (d) electronegativity (1997)

p-Block Elements

120. Which of the following elements does not belong to Group 13 of the periodic table?
(a) Boron (b) Aluminium (c) Gallium (d) Tin

121. The number of elements in Group 13 is
(a) 4 (b) 5 (c) 6 (d) 7

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(c) The elements having electronic configuration $(ns)^2 (np)^5$ are known as halogens.
(d) The electron affinity values of alkaline earth metals are greater than those of alkali metals.

7. Which of the following statements are correct?
(a) Half of the transition elements are metals and others are nonmetals.
(b) Amongst the metals, alkali metals have lowest ionization energies.
(c) In Group 13, the first member is metalloid and the rest are metals.
(d) Inert-pair effect is more effective in the elements of higher atomic numbers.

8. Which of the following statements are correct?
(a) Metalloids do not form ionic compounds.
(b) All halogens are nonmetals.
(c) The electronic configuration of actinides is given as $(4f)^{1-14} (5d)^{0-1} (6s)^2$.
(d) Modern periodic table was developed by Mendeleev.

9. Which of the following statements are **not** correct?
(a) It is possible to determine absolute values of electronegativity of an element.
(b) The second ionization energy of sodium is greater than that of magnesium.
(c) The first and second ionization energies of nitrogen are greater than those of oxygen.
(d) The decreasing order of electron affinity of F, Cl, Br is F > Cl > Br. **(1993)**

10. Which of the following statements are correct?
(a) Lanthanides are known as inner-transition elements and belong to 4f block.
(b) Na^+, Ne and Mg^{2+} contain the same number of electrons. Such species are known as isoelectronic species.
(c) Electron affinity of noble gases is zero..
(d) Most widely used electronegativity scale is due to Linus Pauling.

11. Which of the following statements are **not** correct?
(a) Due to inner-pair effect, +2 oxidation state of lead is more stable than +4 oxidation state.
(b) Amongst Group 15, metalloids are silicon and germanium.
(c) Amongst Group 14, metalloids are assenic and antimony.
(d) Amongst Group 13, metalloids is boron..

12. Which of the following statements are correct?
(a) Amongst Group 16, metalloids are tellurium and polonuim.
(b) The vast majority of the alkali metal and alkaline earth metals form ionic compounds with halogens.
(c) Copper belongs to 4d transition elements.
(d) Silver belongs to 5d transition elements.

13. Which of the following statements are **not** correct?
(a) There are 14 elements in each of inner-transition elements.
(b) There are seven elements known in noble gases.
(c) The atomic number of elements Unq is 104.
(d) Except helium and neon, other noble gases are totally inert chemically.

14. Which of the following statements are **not** correct?
(a) Covalent-bond radius of an atom is larger than van der Waals radius.
(b) The second ionization energy is always larger than the first ionization energy.
(c) The second electron affinity is always larger than the first electron affinity.
(d) Moving down the Group 13, unipositive ion becomes more stable than the tripositive ion.

15. Which of the following facts are correct?
(a) First ionization of calcium is more than that of potassium.
(b) Second ionization of magnesium is more than that of aluminium.
(c) Third ionization of beryllium is larger than that of carbon.
(d) Second ionization of nitrogen is more than that of oxygen.

16. Which of the following statements for the elements $_{21}Sc$ to $_{28}Ni$ is **not** true?
(a) These elements belong to the second transition series with an incompletely filled d sub-shell
(b) These elements are metals with high melting points
(c) The ionization energy decreases in the order $_{21}Sc$ to $_{28}Ni$
(d) These elements are paramagnetic in nature

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19.	Bond enthalpy of Cl—Cl is larger than that of F—F.	Fluorine is more electronegative than chlorine.
20.	Halogens form interhalogen compounds AX_n, where n varies from 1 to 7.	Interhalogens are more reactive than halogens.
21.	Electronegativity of an atom varies slightly with the hybridization involved in the atom.	More the s contribution in the hybridization, lesser the electronegativity.

Matrix Match Type

1. Column I lists the main type of elements in the periodic table. Column II mentions atomic numbers of some of the elements. Match correctly each entry in column I with those given in Column II.

Column I	Column II
(a) s-block element	(p) 63
(b) p-block element	(q) 57
(c) d-block element	(r) 38
(d) f-block element	(s) 50
	(t) 48
	(u) 51

2. Column I includes atomic numbers of some of the elements and column II lists the locations of these elements in the periodic table. Identify the correct choice from Column II for each entry of Column I.

Column I	Column II
(a) 41	(p) 6th period Group 8
(b) 76	(q) 6th period Group 15
(c) 83	(r) 5th period and Group 15
(d) 89	(s) 7th period and Group 3

3. Column I lists some of the facts about ionization energies of two elements A and B and Column II lists the elements A and B. Match each entry of Column I with those listed in Column II.

Column I	Column II	
	Element A	**Element B**
(a) First ionization energy of A is greater than that of B.	(p) Be	B
(b) First ionization energy of A is lesser than that of B.	(q) N	O
(c) Second ionization energy of A is greater than that of B.	(r) Na	Mg
(d) Second ionization energy of A is lesser than that of B.	(s) Al	Si
	(t) P	S
	(u) B	C

4. Column I lists some of the facts about ionization energies of two elements A and B and Column II lists the elements A and B. Match each entry of Column I with those listed in Column II.

Column I	Column II	
	Element A	**Element B**
(a) First ionization energy of A is is greater than that of B.	(p) Be	B
(b) First ionization energy of A is is lesser than that of B.	(q) B	C
(c) Third ionization energy of A is greater than that of B.	(r) C	N
(d) Third ionization energy of A is lesser than that of B.	(s) N	O

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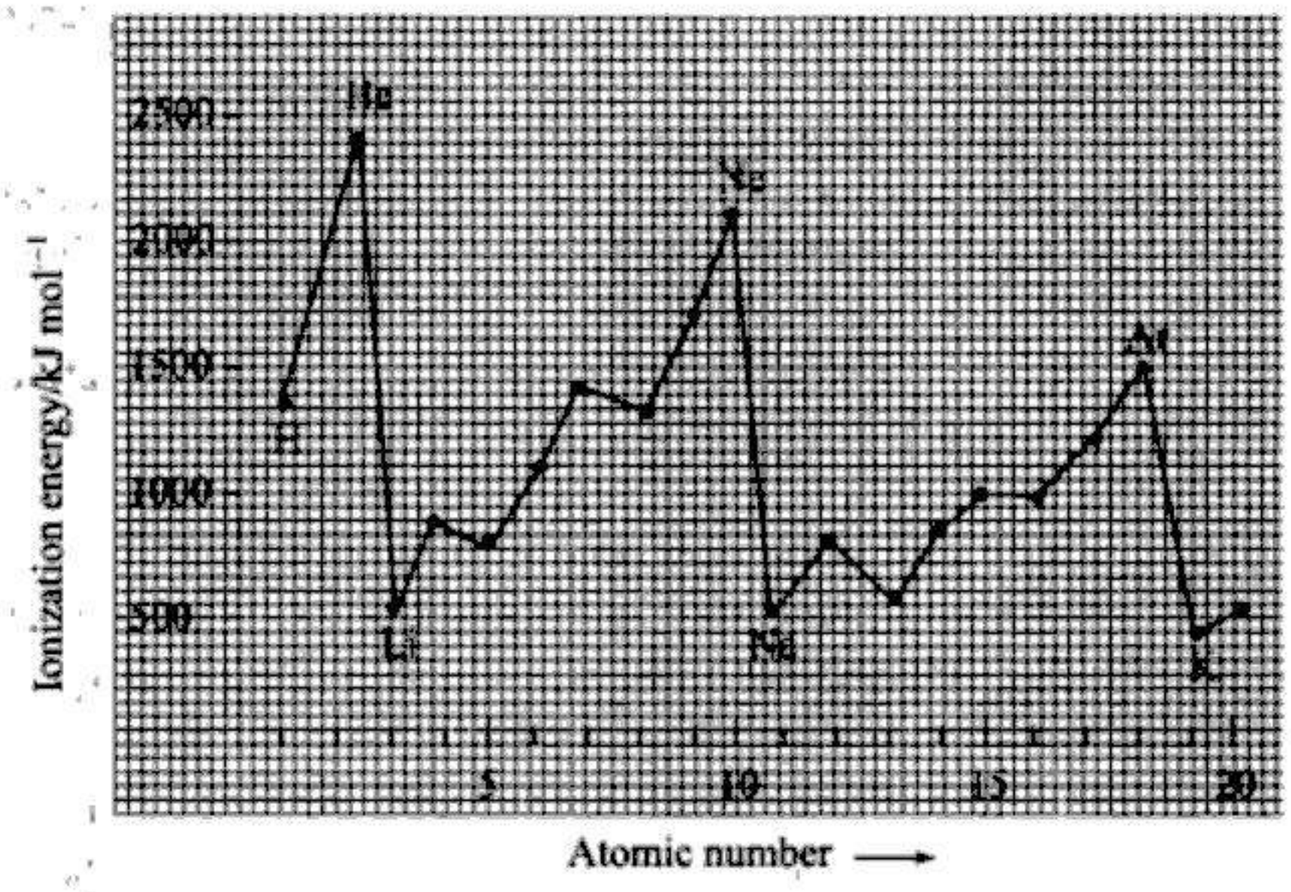
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47. The statement d is correct.

48. The variation of ionization energy versus atomic number is as shown in the following figure.



Peaks are occupied by noble gases as the electron is to be removed from the stable fully occupied sub-shell.

49. The minimum positions are occupied by alkali metals as they contain one extra electron than the stable noble gas configuration. Their removable is easier as the resultant ions are having stable configurations.

50. The electronic configurations are

Be $(1s)2\ (2s)^2$; B $(1s)^2\ (2s)^2\ (2p)^1$; C $(1s)^2\ (2s^2)\ (2p)^2$

Obviously, the ionization energy of Be will be greater than B as here fully-filled 2s orbital (which has lesser energy than 2p orbital) will require more energy for the removal of electron. Boron has lower ionization energy than carbon as the removal of a single electron will lead to more stable configuration, i.e. $(2p)^1$ electron is loosely held as compared to $(2p)^2$ electrons. Moreover, the effective nuclear charge seen by cation valence electron will be more than that of boron.

51. The electronic configurations are

N $(1s)^2\ (2s)^2\ (2p)^3$; O $(1s)^2\ (2s)^2\ (2p)^4$; F $(1s)^2\ (2p)^2\ (2p)^5$

Nitrogen has half-filled electronic configuration and hence more stable than that of oxygen. Hence, the ionization energy of nitrogen will be more than that of oxygen.

52. Boron has the highest melting point due to icosahedral (20-faced) structure with boron atoms at all 12 corners.

53. The second ionization energy implies the removal of electron from O^+, F^+, N^+ and C^+ species. Their configurations are

O^+ : $(1s)^2\ (2s)^2\ (2p)^3$; F^+ : $(1s)^2\ (2s)^2\ (2p)^4$

N^+ : $(1s)^2\ (2s)^2\ (2p)^2$; C^+ : $(1s)^2\ (2p)^2\ (2p)^1$

The species O^+ will have maximum value due to the stable half-filled electronic configuration. The species C^+ will have minimum value as the removal of electron leads to the stable inert-gas configuration.

54. For the configuration $(1s)^2\ (2s)^2\ (2p)^6\ (3s)^2$, the second and third ionizations imply

$(1s)^2\ (2s)^2\ (2p)^6\ (3s)^1 \rightarrow (1s)^2\ (2s)^2\ (2p)^6$

$(1s)^2\ (2s)^2\ (2p)^6 \rightarrow (1s)^2\ (2s)^2\ (2p)^5$

For the second ionization, the removal of 3s electron will require comparatively lesser energy as its removal gives stable electronic configuration.

For the third ionization, the removal of 2p electron will require comparatively higher energy as the electron is to be removed from the stable fully-filled quantum shell.

55. The removal of electron from Mg will require higher energy due to higher nuclear charge.

56. The ionization energy decreases down a group due to the removal of electron from the higher quantum shell which is farther away from the nucleus.

57. Same as Q.56.

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Chapter 5

Bonding and Molecular Structure

The formation of a chemical bond between two atoms implies that the system consisting of these two atoms at stable internuclear distance is energetically more stable than the two isolated atoms. A general study on the reactivity of different elements revealed that noble gases have little tendency to combine with other elements. This leads to the fact that the noble gases have stable outer configuration $(ns)^2(np)^6$ (octet configuration). All other atoms combine to achieve the stable octet configuration either by mutual sharing of electrons (covalent bond) or by complete transfer of electron(s) from one atom to other (ionic bond).

Covalent Bond

Mutual sharing of electrons leads to the formation of covalent bond. A single bond is formed when a single pair of electrons is shared between two atoms, a double bond results when two pairs of electrons are shared and so on. After sharing, each atom has stable octet configuration. This type of bond is formed between two electronegative atoms. Examples include Cl_2, O_2, N_2, CO_2 and so on. Organic compounds also involve covalent bonds between atoms. The sharing of electrons may be shown by *Lewis structures*.

The octet rule holds, with several exceptions in the first two eight-membered periods of the periodic table. A few exceptions are $BeCl_2$, AlF_3, PF_5 and SF_6.

Polar Covalent Bond Because of the difference between the electronegativities of two atoms, the electron pair lies nearer to atom of higher electronegativity. Consequently, this atom acquires a partial negative charge and the other atom (with lesser electronegativity) acquires an equal positive charge. Such a distortion of charges gives rise to a polar covalent bond. The above polarization of bonded electrons is expressed quantitatively with a physical quantity, known as *dipole moment*, which is defined as

$$\boldsymbol{p} = \text{(partial charge on either atom) (distance between the two partial charges)} = (\delta q)r$$

The dipole moment is a vector quantity. Chemists often represent it by an arrow pointing towards the electron pull, i.e. from a lesser electronegative atom to a more electronegative atom. In SI units, the dipole moment has a unit of C m. In CGS units, the dipole moment is expressed in the unit of esu cm. The unit of 10^{-18} esu cm is known as the Debye unit (symbol: D) and its SI equivalent is

$$1 \text{ D} = 3.3356 \times 10^{-30} \text{ C m}$$

The dipole moment of a molecule can be determined experimentally. This, in turn, can be used to determine the per cent ionic character of the molecule. For example, Hydrogen chloride has a dipole moment of 1.03 D. Had the molecule been 100% ionic, its dipole moment would have been

$$\begin{aligned} \boldsymbol{p}_{\text{ionic}} &= \text{(electronic charge) (bond distance of HCl)} = (4.8 \times 10^{-10} \text{ esu})\ (127.5 \times 10^{-10} \text{ cm}) \\ &= 6.12 \times 10^{-18} \text{ esu cm} \equiv 6.12 \text{ D} \end{aligned}$$

But the actual value of dipole moment is 1.03 D. So, its ionic character is

$$\text{Per cent ionic character} = \frac{\boldsymbol{p}_{\text{observed}}}{\boldsymbol{p}_{\text{ionic}}} \times 100 = \frac{1.03 \text{ D}}{6.12 \text{ D}} \times 100 \simeq 17$$

According to Pauling, the per cent ionic character of H–X bond may be computed from the expression $18(\chi_X - \chi_H)^{1.4}$, where χ_X and χ_H are the electronegativity values of atom X and hydrogen, respectively.

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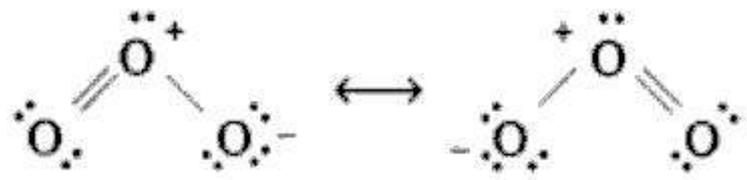
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The actual structure of ozone is the resonance hybrid of the two resonating structures. This is established from the fact that both the oxygen-oxygen bond lengths in ozone are identical.

Molecular Orbital Method

Like atomic orbitals in an atom, there exist molecular orbitals in a molecule. These molecular orbitals belong to whole of the molecule. Electrons in these molecular orbitals are distributed by following aufbau principle, Pauli exclusion principle and Hund's rule.

One of the methods to construct molecular orbitals is the linear combination of atomic orbitals (the abbreviation is LCAO). For example, the ground-state molecular orbital of hydrogen molecule is written as

$$\psi_{MO} = C_1 \psi_{1s(H_a)} + C_2 \psi_{1s(H_b)}$$

It can be shown that the combination of two atomic orbitals gives two molecular orbitals; one involves positive combination, whereas the other involves negative combination. Of these, one involving positive overlap gives a molecular orbital which is more stable than the stabler of the two atomic orbitals and the second one involving negative overlap gives a molecular orbital which is lesser stable than the less stable atomic orbital. The former is known as *bonding* molecular orbital and the latter as *antibonding* molecular orbital.

For homonuclear diatomic molecules involving atoms of the second period, one can construct molecular orbitals from the following combinations.

Combination involving 2s(A) and 2s(B)	Combination involving $2p_x$(A) and $2p_x$(B)
Combination involving $2p_z$(A) and $2p_z$(B)	Combination involving $2p_y$(A) and $2p_y$(B)

The end-to-end overlap leads to σ molecular orbital and side-ways overlap leads to π molecular orbital. Thus, the above combinations lead to σ2s, σ*2s, σ$2p_z$, σ*$2p_z$, π$2p_x$, π*$2p_x$, π$2p_y$ and π*$2p_y$ molecular orbitals, where the orbital with an asterisk represents antibonding molecular orbital. Because of small energy difference between 2s and 2p orbitals, both of them participate jointly in the chemical combination, i.e. a σ2p orbital has some contribution from 2s atomic orbital and σ2s orbital has some contribution from 2p atomic orbital. The relative order of increasing energies of molecular orbital is as follows.

$$E(\sigma 2s) < E(\sigma^* 2s) < E(\pi 2p_x) = E(\pi 2p_y) < E(\sigma 2p_z) < E(\pi^* 2p_x) = E(\pi^* 2p_y) < E^*(\sigma^* 2p_z)$$

The above order is valid from Li_2 to N_2 and for O_2 and F_2, the following sequence is observed.

$$E(\sigma 2s) < E(\sigma^* 2s) < E(\sigma 2p_z) < E(\pi 2p_x) = E(\pi 2p_y) < E(\pi^* 2p_x) = E(\pi^* 2p_y) < E(\sigma^* 2p_z)$$

The electronic configuration of a molecule can be written following aufbau principle, Pauli's exclusion principle and Hund's rule. For example, the electronic configuration of O_2 which contains 12 valence electrons is

$$(\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\sigma 2p_x)^2 (\pi^* 2p_x)^1 (\pi^* 2p_y)^1$$

The characteristics of a molecule can be predicted by using the following facts.

1. The strength of a bond depends on the net excess electrons in bonding orbitals over those of antibonding orbitals. Larger the bond strength, larger the dissociation energy of the molecule.
2. The number of bonds in a molecule is one-half of the net excess of the bonding electrons. The physical quantity to define this is the bond order:

$$\text{Bond order} = \frac{\text{Number (bonding} - \text{antibonding) electrons}}{2}$$

3. The addition of an electron in the bonding orbital makes the molecule more stable, whereas that in the antibonding orbital makes it less stable.
4. The removal of an electron from the bonding molecular orbital makes the molecule less stable and from antibonding orbital makes it more stable.
5. Paramagnetism in a substance is due to the presence of unpaired electron(s) in its molecule.
6. The bond length of a molecule is inversely related to its bond order.

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56. The bonding of S with Cl in SCl_2 molecule involves
(a) sp orbitals (b) sp^2 orbitals (c) sp^3 orbitals (d) sp^3d orbitals

57. The geometry arrangement of CN groups around Ni in $[Ni(CN)_4]^{2-}$ is
(a) tetrahedron (b) square planar (c) trigonal bipyramid (d) octahedran

58. Which of the following species does not involve tetrahedral structure?
(a) SO_4^{2-} (b) SF_4 (c) SeO_4^{2-} (d) SO_2Cl_2

59. Which of the following species involves sp^2 hybridization?
(a) CO_2 (b) N_2O (c) SO_2 (d) H_2S

60. The species ClO_2^- involves
(a) sp hybridization (b) sp^2 hybridization (c) sp^3 hybridization (d) dsp^2 hybridization

61. Which of the following species involves sp^3 hybridization?
(a) PCl_3 (b) SO_3 (c) NO_4^- (d) BF_3

62. The species ClO_3^- involves
(a) sp hybridization (b) sp^2 hybridization (c) sp^3 hybridization (d) dsp^3 hybridization

63. Which of the following statements is correct?
(a) BF_3 involves sp^3 hybridization and NF_3 involves sp^2 hybridization
(b) BF_3 involves sp^2 hybridization and NF_3 involves sp^3 hybridization
(c) Both BF_3 and NF_3 involve sp^3 hybridization
(d) Both BF_3 an^d NF_3 involve sp^2 hybridization

64. The hybridization in OF_2 is
(a) sp (b) sp^2 (c) sp^3 (d) dsp^2

65. Which of the following species involves the smallest bond angle?
(a) NH_3 (b) H_2O (c) BeF_2 (d) CH_4

66. Which of the following species involves the largest bond angle?
(a) H_2Se (b) H_2S (c) H_2O (d) SO_2

67. The bond angle in PH_3 is expected to be
(a) 90° (b) 105° (c) 109° (d) 120°

68. On hybridization of one s and one p orbitals, we get
(a) two mutually perpendicular orbitals (b) two orbitals at 180°
(c) four orbitals directed tetrahedrally (d) three orbitals in a plane. (1984)

69. Among the following species, identify the isostructural pairs. NF_3, NO_3^-, BF_3, H_3O^+, HN_3
(a) [NF_3, NO_3^-] and [BF_3, H_3O^+] (b) [NF_3, HN_3] and [NO_3^-, BF_3]
(d) [NF_3, H_3O^+] and [NO_3^-, BF_3] (d) [NF_3, H_3O^+] and [HN_3, BF_3] (1996)

70. The geometry and the type of hybrid orbitals present about the central atom in BF_3 is
(a) linear, sp (b) trigonal planar, sp^2 (c) tetrahedral, sp^3 (d) pyramidal, sp^3 (1998)

71. The correct order of hybridisation of the central atom in the following species NH_3, $[PtCl_4]^{2-}$, PCl_5 and BCl_3 is
(a) dsp^2, dsp^3, sp^2 and sp^3 (b) sp^3, dsp^2, dsp^3, sp^2
(c) dsp^2, sp^2, sp^3, dsp^3 (d) dsp^2, sp^3, sp^2, dsp^3 (2001)

72. Specify the coordination geometry around and hybridization of N and B atoms in a 1 : 1 complex of BF_3 and NH_3
(a) N : tetrahedral, sp^3 ; B : tetrahedral, sp^3 (b) N : pyramidal, sp^3 ; B : pyramidal, sp^3
(c) N : pyramidal, sp^3 ; B : planar, sp^2 (d) N : pyramidal, sp^3 ; B : tetrahedral, sp^3 (2002)

73. Total number of lone pair of electrons in XeF_4 is
(a) 0 (b) 1 (c) 2 (d) 3 (2004)

74. Which of the following contains maximum number of lone pairs of electrons on the central atom?
(a) ClO_3^- (b) XeF_4 (c) I_3^- (d) SF_4 (2005)

75. The percentage of p-character in the orbitals forming P—P bonds in P_4 is
(a) 25 (b) 33 (c) 50 (d) 75 (2007)

76. The hybridization involved in the molecules PCl_5 and BrF_5, respectively, are
(a) dsp^3, dsp^3 (b) dsp^3, d^2sp^3 (c) d^2sp^3, dsp^3 (d) d^2sp^3, d^2sp^3

77. The hybridization involved in the molecules OSF_4 and $XeOF_4$, respectively, are
(a) sp^3d and sp^3d^2 (b) sp^3d^2, sp^3d (c) sp^3d and sp^3d (d) sp^3d^2, sp^3d^2

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2. Column I lists oxidation/reduction of O_2 and N_2. Column II lists some of the properties associated with these oxidation/reduction reactions. Match each entry of Column I with those listed in Column II.

Column I	**Column II**
(a) $N_2 \rightarrow N_2^+$	(p) Bond order increases
(b) $N_2 \rightarrow N_2^-$	(q) Bond order decreases
(c) $O_2 \rightarrow O_2^+$	(r) paramagnetism increases
(d) $O_2 \rightarrow O_2^-$	(s) paramagnetism decreases
	(t) no change in bond order

3. Column I lists some of hybridization schemes and Column II lists some of the compounds. Match each entry of Column I with the compounds mentioned in Column II.

Column I	**Column II**
(a) sp^3	(p) $Ni(CN)_4$
(b) dsp^2	(q) XeO_3
(c) dsp^3	(r) SO_3^{2-}
(d) d^2sp^3	(s) X_eF_2
	(t) XeF_4
	(u) XeO_2F_2

4. Column I lists some of the common geometries of inorganic species. Column II includes the list of inorganic species. Match correctly each entry of Column I with the examples listed in Column II.

Column I	**Column II**
(a) Linear	(p) CO_3^{2-}
(b) Bent	(q) I_3^-
(c) Tetrahedral	(r) O_3
(d) Planar	(s) XeF_2
	(t) OF_2
	(u) XeF_4
	(v) SO_3

ANSWERS

Straight Objective Type

1. (b)	**2.** (b)	**3.** (d)	**4.** (c)	**5.** (a)	**6.** (d)	**7.** (c)
8. (b)	**9.** (a)	**10.** (b)	**11.** (b)	**12.** (b)	**13.** (b)	**14.** (a)
15. (a)	**16.** (b)	**17.** (a)	**18.** (b)	**19.** (b)	**20.** (d)	**21.** (c)
22. (d)	**23.** (c)	**24.** (c)	**25.** (b)	**26.** (b)	**27.** (b)	**28.** (b)
29. (c)	**30.** (c)	**31.** (c)	**32.** (d)	**33.** (a)	**34.** (a)	**35.** (b)
36. (c)	**37.** (a)	**38.** (a)	**39.** (b)	**40.** (a)	**41.** (c)	**42.** (a)
43. (c)	**44.** (c)	**45.** (c)	**46.** (c)	**47.** (d)	**48.** (b)	**49.** (b)
50. (b)	**51.** (c)	**52.** (b)	**53.** (c)	**54.** (d)	**55.** (b)	**56.** (c)
57. (b)	**58.** (b)	**59.** (c)	**60.** (c)	**61.** (a)	**62.** (c)	**63.** (b)
64. (c)	**65.** (b)	**66.** (d)	**67.** (c)	**68.** (b)	**69.** (c)	**70.** (b)
71. (b)	**72.** (a)	**73.** (c)	**74.** (c)	**75.** (d)	**76.** (b)	**77.** (a)
78. (b)	**79.** (a)	**80.** (a)	**81.** (b)	**82.** (a)	**83.** (c)	**84.** (d)
85. (d)	**86.** (c)	**87.** (a)	**88.** (b)	**89.** (d)	**90.** (c)	**91.** (d)
92. (b)	**93.** (a)	**94.** (b)	**95.** (b)	**96.** (a)	**97.** (a)	**98.** (a)
99. (d)	**100.** (a)	**101.** (a)	**102.** (b)	**103.** (b)	**104.** (a)	**105.** (c)
106. (a)	**107.** (b)	**108.** (d)	**109.** (a)	**110.** (b)	**111.** (b)	

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64. The number of valence electrons in OF_2 is $6 + 2 \times 7 = 20$. These are distributed as $:\ddot{\underset{\cdot\cdot}{F}}:\ddot{\underset{\cdot\cdot}{O}}:\ddot{\underset{\cdot\cdot}{F}}:$. There are four paired of electrons around O. Hence, it involves sp^3 hybridization.

65. NH_3, H_2O and CH_4 involves sp^3 hybridization whereas BeF_2 involves sp hybridization (bond angle 180°). Amongst NH_3, H_2O and CH_4, the molecule H_2O is expected to have minimum bond angle due to larger repulsion between two lone pairs of electrons which forces bond angle to decreases from the regular tetrahedron structure.

66. SO_2 involves sp^2 hybridization making angle near to 120°

67. The number of valence electrons in PH_3 is $5 \times 3 = 8$. These are distributed as $H:\ddot{\underset{H}{\underset{\cdot\cdot}{P}}}:H$. There are four paired of electrons around P. Hence, it involves sp^3 hybridization. The bond angles are expected to be 109°.

69. Isostructural pairs have similar structures.

NF_3: Lewis structure, $F-\ddot{\underset{F}{N}}-F$; tetrahedron structure, geometry-triangle pyramidal

NO_3^-: Lewis structure, $\left[:\ddot{O}-N=\ddot{O}\ ;\ \ddot{\underset{\cdot\cdot}{O}}:\right]^-$; triangular planar

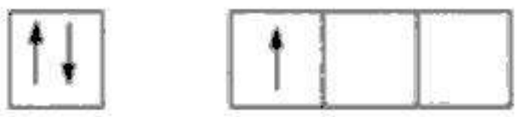
BF_3; Lewis structure, $F-\underset{F}{B}-F$; triangular planar

H_3O^+; Lewis structure, $H-\ddot{\underset{H}{O}}^{+}-H$; tetrahedron structure

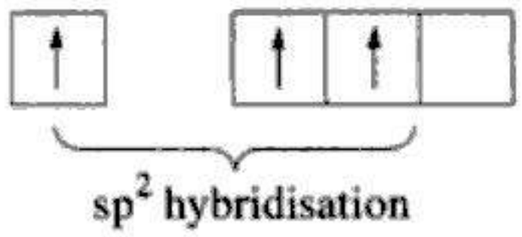
HN_3; Lewis structure, $H-\ddot{N}=N\equiv N:$; linear

Thus, isostructural pairs are $[NF_3, H_3O^+]$ and $[NO_3^-, BF_3]$

70. Outer electronic configuration of boron atom



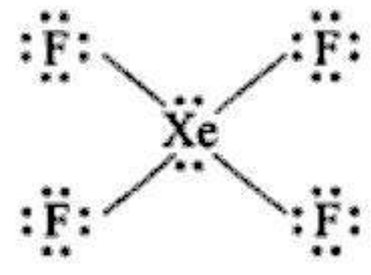
Electronic configuration of boron atom in BF_3



The geometry corresponding to sp^2 hybridisation is trigonal planar.

71. The structures of NH_3, $[PtCl_4]^{2-}$, PCl_5 and BCl_3 are tetrahedral, square planar, triangle bipyramid and triangular planar, respectively. Hence, the central atoms respectively involve sp^3, dsp^2, dsp^3 and sp^2 hybrid orbitals.

73. The total number of valence electrons in XeF_4 are 36 ($= 8 + 4 \times 7$). These are distributed as follows.



Thus, Xe contains six line pair of electrons around Xe out of which two are lone pairs. According VSEPR, these six pairs of electrons are distributed in the octahedral geometry.

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The species CO, NO^+, CN^- and N_2 have the same number (= 10) of valence electrons while NO^- has 12 electrons. Thus, NO^- will have different bond order.

110. In the given compounds, oxygen is present as O_2, O_2^+ and O_2^-, respectively. For these species, we have

O_2 KK $(\sigma 2s)^2$ $(\sigma^* 2s)^2$ $(\sigma 2p)^2$ $(\pi 2p_x)^2$ $(\pi 2p_y)^2$ $(\pi^* 2p_x)^1$ $(\pi^* 2p_y)^1$

O_2^+ KK $(\sigma 2s)^2$ $(\sigma^* 2s)^2$ $(\sigma 2p)^2$ $(\pi 2p_x)^2$ $(\pi 2p_y)^2$ $(\pi^* 2p_x)^1$

O_2^- KK $(\sigma 2s)^2$ $(\sigma^* 2s)^2$ $(\sigma 2p)^2$ $(\pi 2p_x)^2$ $(\pi\ 2p_y)^2$ $(\pi^* 2p_x)^2$ $(\pi^* 2p_y)^1$

The bond orders of these species as given by the expression

$$BO = (1/2)\ [\text{Number of (bonding} - \text{antibonding) electrons}]$$

are as follows.

For O_2 $\quad BO = \frac{1}{2}(8 - 4) = 2$ $\qquad$ For O_2^+ $\quad BO = \frac{1}{2}(8 - 3) = 2.5$

For O_2^- $\quad BO = \frac{1}{2}(8 - 5) = 1.5$

Since bond length is inversely proportional bond order, the increasing order of bond length of O—O is

$$O_2[AsF_6] < O_2 < KO_2$$

111. The species CN^- and NO^+ are isoelectronic (valence electrons = 10). They are expected to have identical electronic configuration and hence identical bond order.

Multiple Correct Choice Type

1. Carbon dioxide, mercuric chloride and acetylene are linear molecules.
2. CN^- and NO^+ have the same number of electrons.
3. The species H_3O^+, NH_3 and CH_3^- have same number of electrons.
5. (a) It is present within the molecule.
(b) It occurs between two different/identical molecules.
6. (a) Hybrid orbitals are obtained by mixing orbitals centred on the same atom.
(b) The structure of CO molecule is $:C\equiv O:$
(d) SO_2 does not have linear geometry.
7. (a) (Fluorine is the most electronegative element. A strong polarization of bonding electrons occurs in HF leading to hydrogen bonding even in the gaseous state.
(c) Due to the resonance, both bonds are identical.
8. (a) Be_2 would contain equal number of bonding and antibonding electrons.
(b) There are more bonding electrons than antibonding electrons.
(c) CH_3F involes lesser C—F distance but more charge separation as compared to those in CH_3Cl. Here, bond distance has more dominating effect causing dipole moment of CH_3Cl greater than that of CH_3F.
(d) Stronger the hydrogen bonding, weaker the base.

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For example, for a pure substance we have

$$\Delta_{vap}S = \frac{\Delta_{vap}H}{T_b} \qquad \text{and} \qquad \Delta_{fus}S = \frac{\Delta_{fus}H}{T_m}$$

where the subscripts vap and fus represent vaporization and fusion, respectively.

Third Law of Thermodynamics According to third law of thermodynamics, every pure perfectly crystalline substance has zero entropy at 0 K, since these involve perfectly ordered arrangements of their constituent particles. However, the substance such as CO, NO, H_2 and ice do not have ordered arrangements at 0 K and thus have nonzero value of entropy. This is known as residual entropy.

Gibbs Function Gibbs function (or energy) or simply free energy is defined as $G = H - TS$

For a process occurring at constant T and p, the change in Gibbs function is given by $\Delta G = \Delta H - T\Delta S$

For a process to be spontaneous, the value of ΔG is negative. For a nonspontaneous reaction, ΔG is positive.

For a reaction at equilibrium, $\Delta G = 0$ and temperature at which the system occurs at equilibrium is given by

$$T_{eq} = \Delta H/\Delta S$$

Standard States of a Substance

For a pure gas, the standard state at a given temperature is the ideal gas at one bar pressure.

For a pure liquid, the standard state at a given temperature is the pure liquid at one bar pressure.

For a pure crystalline substance, the standard state at a given temperature is the pure crystalline substance at one bar pressure.

For a substance or ion in solution, the standard state at a given temperature is the unit molality of the species in ideal solution at one bar pressure.

The standard free energy change of a reaction is related to its equilibrium constant by the expression $\Delta_r G^\circ = -RT \ln K_p^\circ$.

Pressure-Volume Work

An ideal gas can undergo expansion or compression under isothermal or adiabatic conditions. The expansion and compression may be carried out under reversible or irreversible conditions. We give below the expressions of p-V work under different conditions. In a reversible process, system as well as surrourolings can be restored back by following the reverse path. In an irreversible process, this is not possible.

Isothermal *p-V* Work In this case, temperature of the system remains constant, i.e. $\Delta T = 0$.

For irreversible condition: $w = -p_{ext}(V_2 - V_1)$; For reversible condition: $w = -nRT \ln (V_2/V_1)$

Adiabatic *p-V* Work In this case, heat can neither enter to or leave from the system, i.e. $q = 0$. From first law of thermodynamics, it follows that $\Delta U = w$

where ΔU is given by $\Delta U = C_V(T_2 - T_1)$

For a gas undergoing adiabatic irreversible volume change, the expression of work is given by

$$w = -p_{ext}(V_2 - V_1)$$

For an ideal gas undergoing adiabatic reversible expansion/compression, we also have

$$pV^\gamma = \text{constant}; \qquad pT^{\gamma(1-\gamma)} = \text{constant}; \qquad \text{and} \qquad TV^{\gamma-1} = \text{constant}$$

where $\gamma = C_{p,m}/C_{V,m}$. The symbols $C_{p,m}$ and $C_{V,m}$ represent molar heat capacities at constant pressure and volume conditions, respectively.

For a monatomic ideal gas: $C_{V,m} = (3/2)R$; $C_{p,m} = (5/2)R$; and $\gamma = 5/3$

For a diatomic ideal gas: $C_{V,m} = (5/2)R$; $C_{p,m} = (7/2)R$; and $\gamma = 7/5$

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43. For which one of the following equations is $\Delta_r H^\circ$ equal to $\Delta_f H^\circ$?

(a) $CH_4(g) + 2Cl_2(g) \longrightarrow CH_2Cl_2(1) + 2HCl(g)$ (b) $Xe(g) + 2F_2(g) \longrightarrow XeF_4(g)$

(c) $2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$ (d) $N_2(g) + O_3(g) \longrightarrow N_2O_3(g)$ (2003)

Enthalpy of Combusion

44. The products of combustion of an aliphatic thiol (RSH) at 298 K are

(a) $CO_2(g)$, $H_2O(g)$ and $SO_2(g)$ (b) $CO_2(g)$, $H_2O(l)$ and $SO_2(g)$

(c) $CO_2(l)$, $H_2O(l)$ and $SO_2(g)$ (d) $CO_2(g)$, $H_2O(l)$ and $SO_2(l)$ (1992)

45. Which of the following equations corresponds to the enthalpy of combustion at 298 K?

(a) $C_2H_6(g) + \frac{7}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$ (b) $2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(g)$

(c) $C_2H_6(g) + \frac{7}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$ (d) $2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l)$

46. Which of the following reactions corresponds to the definition of enthalpy of combustion at 25 °C?

(a) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ (b) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

(c) $CH_4(l) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$ (d) $CH_4(l) + 2O_2(l) \rightarrow CO_2(l) + 2H_2O(l)$

Enthalpy of Reaction

47. For the equations

$C(\text{diamond}) + 2H_2(g) \rightarrow CH_4(g)$ ΔH_1

$C(g) + 4H(g) \rightarrow CH_4(g)$ ΔH_2

predict whether

(a) $\Delta H_1 = \Delta H_2$ (b) $\Delta H_1 > \Delta H_2$

(c) $\Delta H_1 < \Delta H_2$ (d) $\Delta H_1 = \Delta H_2 + \Delta_{vap}H(C) + \Delta_{diss}H(H_2)$

48. The expression $\Delta_{sub}H^\circ = \Delta_{fus}H^\circ + \Delta_{vap}H^\circ$ is true at all

(a) temperatures (b) pressures

(c) temperatures and pressures (d) temperatures and 1 bar pressure conditions

49. Which of the following expressions is true?

(a) $\Delta_f H^\circ(CO, g) = \frac{1}{2}\ \Delta_f H^\circ(CO_2, g)$

(b) $\Delta_f H^\circ(CO, g) = \Delta_f H^\circ(C, \text{graphite}) + \frac{1}{2}\ \Delta_f H^\circ(O_2, g)$

(c) $\Delta_f H^\circ(CO, g) = \Delta_f H^\circ(CO_2, g) - \frac{1}{2}\ \Delta_f H^\circ(O_2, g)$

(d) $\Delta_f H^\circ(CO, g) = \Delta_c H^\circ(C, \text{graphite}) - \Delta_c H^\circ(CO, g)$

50. The $\Delta_f H^\circ$ 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 for the reaction $CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$ is

(a) 524.1 kJ mol^{-1} (b) 41.2 kJ mol^{-1} (c) -262.5 kJ mol^{-1} (d) -41.2 kJ mol^{-1} (2000)

51. In an endothermic reaction

(a) the enthalpy of reactants is more than that of products

(b) heat is given out of the system

(c) ΔH has a positive value

(d) ΔU has a negative value

52. Given:

$HCO_3^-(aq) + OH^-(aq) \rightarrow H_2O(l) + CO_3^{2-}(aq)$; $\Delta H_1 = -41.84$ kJ mol^{-1}

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$; $\Delta H_2 = -57.32$ kJ mol^{-1}

The enthalpy change for the reaction $HCO_3^-(aq) \rightarrow H^+(aq) + CO_3^{2-}(aq)$ would be

(a) $(-41.84 - 57.32)$ kJ mol^{-1} (b) $(-41.84 + 57.32)$ kJ mol^{-1}

(c) $(41.84 + 57.32)$ kJ mol^{-1} (d) $(41.84 - 57.32)$ kJ mol^{-1}

53. The reaction of cyanamide, $NH_2CN(s)$, with oxygen was run in a bomb calorimeter and ΔU at 300 K was found to be -743 kJ mol^{-1}. The value of ΔH at 300 K for the combustion reaction $NH_2CN(s) + (3/2)\ O_2(g) \rightarrow N_2(g) + CO_2(g) + H_2O(l)$ would be

(a) -741.75 kJ mol^{-1} (b) -743 kJ mol^{-1} (c) -744.25 kJ mol^{-1} (d) -740.5 kJ mol^{-1}

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4. Which of the following statements is/are correct?
(a) Enthalpy of combustion of most species is an exothermic process.
(b) Amongst cyclopropane, cyclobutane and cyclopentane, the enthalpy of combustion per CH_2 group is maximum for cyclopropane.
(c) The enthalpy of formation of acetylene is positive.
(d) The entropy of all substances at 25 °C is positive.

5. Which of the following statements are correct?
(a) First law of thermodynamics is not adequate in predicting the direction of the process.
(b) In an exothermic reaction, the total enthalpy of products is greater than that of reactants.
(c) In an endothermic reaction, the total enthalpy of products is greater than that of reactants.
(d) The standard enthalpy of formation of diamond is zero at 298 K and 1 atm pressure.

6. Which of the following statements are correct?
(a) The standard enthalpy of formation of $Br_2(g)$ is taken to be zero at standard conditions of 298 K and 1 atm.
(b) The magnitude of enthalpy of neutralization of a weak acid is smaller than that of a strong acid.
(c) In the relation $\Delta H = \Delta U + (\Delta v_g)RT$, the units of Δv_g is mol.
(d) The terms, bond enthalpy and bond dissociation enthalpy stand for one and the same thing.

7. Which of the following statements are correct?
(a) At 298 K, the enthalpy of combustion of CH_4 corresponds to the reaction

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$$

(b) For an exothermic reaction, ΔH is positive.
(c) For an endothermic reaction, ΔH is positive.
(d) The calorific value of a fat is greater than that of a carbohydrate.

8. Which of the following statements are correct?
(a) For a reaction involving condensed phases $\Delta H = \Delta U$.
(b) It is possible to calculate the value of ΔH for the reaction $H_2(g) + Br_2(l) \rightarrow 2HBr(g)$ from the bond-enthalpy data alone.
(c) The enthalpy of combustion of diamond and enthalpy of formation of carbon dioxide has the same value.
(d) The reaction $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ is accompanied with decrease in entropy.

9. Which of the following statements are **not** correct?
(a) In an exothermic reaction, the total enthalpy of reactants is lesser than that of products.
(b) In an endothermic reaction, the total enthalpy of reactant is lesser than that of products.
(c) The standard molar enthalpy of formation of a substance is the enthalpy of formation of the substance at 1 atm pressure and at specified temperature.
(d) The conventional standard molar enthalpy of formation of an element in its stable state of aggregation at 273 K is taken to be zero.

10. Which of the following statements are **not** correct?
(a) The products of combustion of a hydrocarbon at 298 K are $H_2O(l)$ and $CO_2(g)$.
(b) The products of combustion of a hydrocarbon at 398 K are $H_2O(l)$ and $CO_2(g)$.
(c) The enthalpy of neutralization is about – 52.5 kJ mol^{-1}.
(d) The magnitude of enthalpy of neutralization of a weak acid is smaller than that of a strong acid. The difference of the latter from the former is known as enthalpy of ionization of the weak acid.

11. Which of the following statements are correct?
(a) The heat released when the requisite amounts of ions in the gaseous state combine to given 1 mol of crystal lattice is known as lattice energy.
(b) Enthalpy of fusion of KCl is larger than that of naphthalene.
(c) The stable state of aggregation of carbon at 298 K and 1 bar pressure is diamond.
(d) The stable state of aggregation of sulphur at 298 K and 1 bar pressure is rhombic sulphur.

12. Identify the intensive quantities from the following: (1993)
(a) Enthalpy (b) Temperature (c) Volume (d) Refractive index

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8. The heat released in the neutralization of a weak acid with a strong base is always less than that released in the neutralization of a strong acid with a strong base.
   Weak acid is partly ionized in solution while strong acid is completely ionized in solution.
9. For every chemical reaction at equilibrium, standard Gibbs energy of reaction is zero.
   At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy.
10. There is a natural asymmetry between converting work to heat and converting heat to work.
    No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work.

Matrix Match Type

1. The entries in Column I is related with the $\gamma (= C_{p,m}/C_{V,m})$ values given in Column II. Match each entry of Column I with those given in Column II.

Column I	Column II
(a) Monatomic gas	(p) 9/7
(b) Diatomic gas	(q) 7/6
(c) Linear triatomic gas	(r) 5/3
(d) Nonlinear triatomic gas	(s) 15/3

2. The signs of $\Delta_r H$ and $\Delta_r S$ of chemical reactions are given in Column I. Match each of these entries with the correct characteristic of the reactions given in column II.

Column I	Column II
(a) ΔH = +ve ; ΔS = +ve	(p) Spontaneous at low temperature
(b) ΔH = +ve ; ΔS = –ve	(q) Spontaneous at high temperature
(c) ΔH = –ve ; ΔS = +ve	(r) Nonspontaneous at low temperature
(d) ΔH = –ve ; ΔS = –ve	(s) Nonspontaneous at high temperature

3. Column I lists a few physical processes and their expressions to compute these physical processes are listed in Column II. Match the correct choices.

Column I	Column II
(a) $\Delta_r G^\circ$	(p) $\Delta_r U + (\Delta \nu_g)RT$
(b) $\Delta_r H$	(q) $RT \ln(p_1/p_2)$
(c) $\Delta_r S$	(r) q_{rev}/T
(d) $w_{reversible}$	(s) $-RT \ln K^\circ$
	(t) $-nFE^\circ$
	(u) $nC_{p,m}\Delta T$

4. Column I list expansion of an ideal gas under different conditions and the corresponding expressions to be used are listed in Column II. Identify the correct choice.

Column I	Column II
(a) Reversible isothermal expansion	(p) $-p_{ext}(V_2 - V_1)$
(b) Reversible adiabatic expansion	(q) $-nRT \ln(V_2/V_2)$
(c) Irreversible isothermal expansion against a constant pressure	(r) $C_V \Delta T$
(d) Irreversible adiabatic expansion	(s) $-nRT \ln (p_1/p_2)$
	(t) pV^γ = constant

5. Column I lists four thermodynamic quantities and their natural independent variables are listed in Column II. Identify the correct choices.

Column I	Column II
(a) U	(p) T
(b) H	(q) p
(c) A	(r) V
(d) G	(s) S

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19. For a monoatomic gas, $C_V = (3/2)\ R$ and $C_p = (5/2)\ R$

Hence $\gamma = \dfrac{C_p}{C_V} = \dfrac{5}{3}$

Thus, for adiabatic expansion of a monoatomic gas $pV^{\gamma} = pV^{5/3} = \text{constant}$.

20. $(C_{p,m})_{mix} = \left(\dfrac{1}{3\,mol}\right)\left[(1\,mol)\left(\dfrac{5}{2}R\right)+(2\,mol)\left(\dfrac{7}{2}R\right)\right]$ and $(C_{V,m})_{mix} = \left(\dfrac{1}{3\,mol}\right)\left[(1\,mol)\left(\dfrac{3}{2}R\right)+(2\,mol)\left(\dfrac{5}{2}R\right)\right]$

$$\gamma = \frac{(C_{p,m})_{mix}}{(C_{V,m})_{mix}} = \frac{19}{13} = 1.46$$

21. Heat used in increasing the internal energy $= C_V \Delta T$. Heat absorbed at constant pressure to increase the temperature by $\Delta T = C_p\ \Delta T$

Hence, Fraction of heat used in increasing the internal energy $\varphi = \dfrac{C_V\ \Delta T}{C_p\ \Delta T} = \dfrac{C_V}{C_p}$

For a diatomic gas, $C_{V,m} = (5/2)\ R$ and $C_{p,m} = (7/2)\ R$. Hence $\varphi = \dfrac{(5/2)R}{(7/2)R} = \dfrac{5}{7}$

22. For an adiatomic process, $pV^{\gamma} = \text{constant}$. Also $\gamma\ (= C_{p,m}/C_{V,m})$ for a diatomic gas (= 7/5) is smaller than that of a monatomic gas (= 5/3). Hence, for given volume. $(V^{\gamma})_{\text{diatomic gas}} < (V^{\gamma})_{\text{monatomic gas}}$
Since at any instant, $pV = \text{constant}$, we will have $p_{\text{diatomic gas}} > p_{\text{monatomic gas}}$
Hence, the curve 1 is meant for a diatomic gas and the curve 2 for a monatomic gas.

23. From first law of thermodynamics, we get $dU = dq + dw$
For an given data of an ideal gas, we get $dU = (\ <0) + 0 = (\ <0)$
Since for an ideal gas, the internal energy changes only due to change in temperature, it may be concluded that $\Delta T < 0$, i.e. temperature decreases.

24. The conservation of heat gives $m_i C_i\ (20\ K) + m'_1\ \Delta_{fus}H - m_W C_W\ (20\ K) = 0$

$(4\ kg)\ (2.092\ kJ\ J^{-1}\ kg^{-1})\ (20\ K) + m'_1\ (334.7\ kJ\ kg^{-1}) - (10\ kg)\ (4.184\ kJ\ K^{-1}\ kg^{-1})\ (20\ K) = 0$
This gives

$$m'_1 = \left[\frac{(10)(4.184)(20)-(4)(2.092)(20)}{334.7}\right] kg = \left(\frac{836.8-167.36}{334.7}\right) kg = \left(\frac{669.44}{334.7}\right) kg = 2.0\ kg$$

Hence, mass of water in the container is $m' = (10\ kg) + (2\ kg) = 12\ kg$.

25. In the Fig. 6.4, the curve ab represents isothermal expansion from p_1, V_1 to p_2, V_2. In adiabatic compression from V_2 to V_1, the temperature of the gas will be larger than the temperature at the state a.
Consequently, the pressure of the gas after the gas has undergone compression will be larger than that existing at the state a. Thus, the adiabatic compression will be represented by the curve bc. The total work done is given by $W = W_{\text{isothermal}} + W_{\text{adiabatic}}$
where $W_{\text{isothermal}}$ has a negative value as it involves expansion of the gas.
Since the magnitude of work is given by the area under the curve, the total work will carry positive sign.

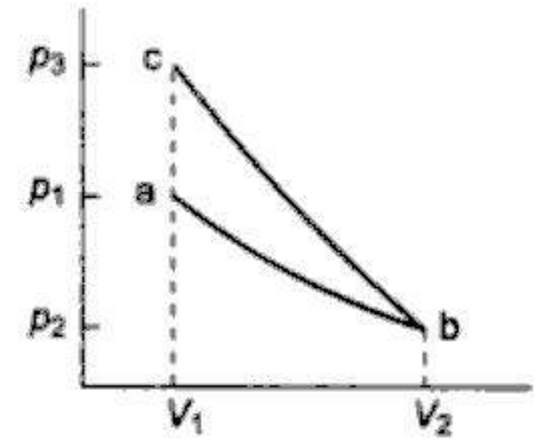


Fig. 6.4

26. $\Delta H - \Delta U = (\Delta \nu_g)RT = (-3)(8.314 \times 10^{-3}\ kJ\ K^{-1}\ mol^{-1})(298\ K) = -7.43\ kJ\ mol^{-1}$

27. For the given reaction, $\Delta \nu_g = -1/2$. Hence $\Delta H - \Delta U = (\Delta \nu_g)\ RT$ = negative. Hence, $\Delta H < \Delta U$.

28. The 'standard' implies pressure equal to 1 bar.

29. For $\Delta H = \Delta U$, we must have $\Delta \nu_g = 0$. Thus, choice b is correct.

30. By definition, $H = U + pV$.

31. $\Delta H = \Delta U + \Delta(pV)$

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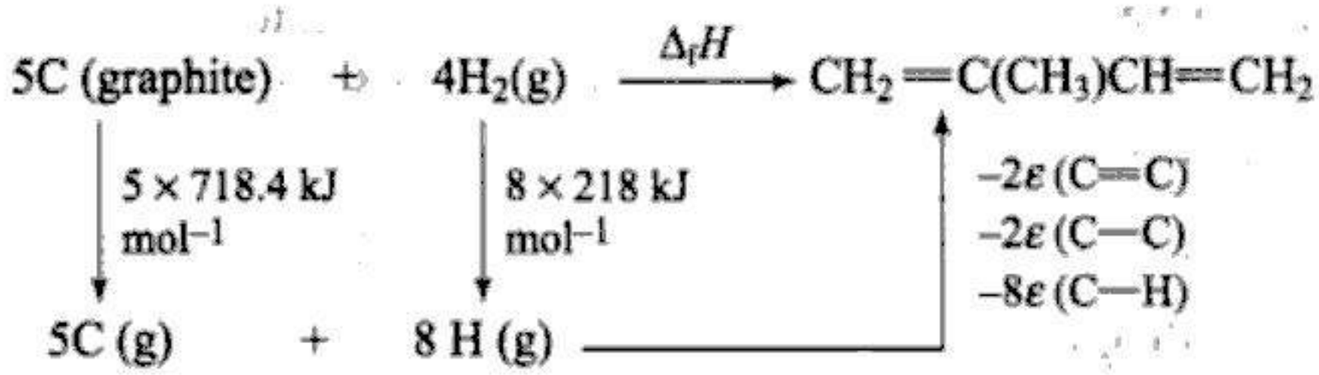
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69. In polymerization breaking one double bond generates two single bonds. Hence
$$\Delta H = \{590 - 2(331)\} \text{ kJ mol}^{-1} = -72 \text{ kJ mol}^{-1}$$

70. The formation reaction is



Hence $\Delta_f H = 5 \times 718.4 + 8 \times 218 - 2 \times 615.1 - 2 \times 347.7 - 8 \times 413.4)$ kJ mol^{-1}
$= 103.2$ kJ mol^{-1}

71. We have

$$\text{S(rhombic)} \rightarrow \text{S(g)} \quad ; \quad \Delta_f H = 275 \text{ kJ mol}^{-1}$$
$$\text{F}_2\text{(g)} \rightarrow \text{F(g)} \quad ; \quad \Delta_f H = 80 \text{ kJ mol}^{-1}$$
$$\text{S(rhombic)} + 3\text{F}_2\text{(g)} \rightarrow \text{SF}_6\text{(s)} \quad ; \quad \Delta_f H = -1100 \text{ kJ mol}^{-1}$$

We have to determine the value of $\frac{\Delta H}{6}$ for $\text{SF}_6\text{(g)} \rightarrow \text{S(g)} + 6\text{F(g)}$

which is equal to $\frac{1}{6}[275 + 6 \times 80 + 1100] = 309.2$ kJ mol^{-1}

72. We have to calculate ΔH for the equation $\text{OH(g)} \rightarrow \text{H(g)} + \text{O(g)}$

$$\Delta H = \Delta_f H(\text{H, g}) + \Delta_f H(\text{O, g}) - \Delta_f H(\text{OH, g}) = (218 + 248 - 42) \text{ kJ mol}^{-1} = 424 \text{ kJ mol}^{-1}$$

73. H—F bond is the strongest.

74. At room temperature, C(graphite) is more stable that C(diamond).

75. Decrease in disorderliness would result into the decrease in entropy.

76. For an irreversible process $\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$ = positive. Hence $|\Delta S_{\text{sys}}| > |\Delta S_{\text{surr}}|$

77. H_2, CO and NO have residual entropies.

78. The combustion reaction is an exothermic process. Hence, ΔH = –ve. The reaction occurs with Δv_g positive. Hence, ΔS = +ve. Since $\Delta G = \Delta H - T\Delta S$ = –ve – T (+ve) = –ve.

79. $\Delta H^\circ = \Delta U^\circ + (\Delta v_g)RT = -10.0$ kJ mol^{-1} + (– 1) (8.314 × 10^{-3} kJ K^{-1} mol^{-1}) (300 K) = – 12.49 kJ mol^{-1}

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -12.49$ kJ mol^{-1} – (300 K) (– 45 × 10^{-3}) kJ K^{-1} mol^{-1} J

$= (-12.45 + 13.5)$ kJ mol^{-1}= positive

81. Δv_g is negative, entropy change will also be negative.

82. $\Delta S = \Delta H/T = 40.63 \times 10^3$ J mol^{-1}/373 K = 108.9 J K^{-1} mol^{-1}

83. For a spontaneous process, ΔG is negative. Since $\Delta G = \Delta H - T\Delta S$, ΔG will always be negative if and only if ΔH is negative and ΔS is positive.

85. In the reversible isothermal reaction, temperature of the system and surroundings are taken to be identical. Since heat absorbed by the system is equal to the heat lost by surroundings, ΔS_{sys} and ΔS_{surr} will have equal value but carry opposite sign.

86. CO has residual entropy due to orientations CO and OC in the crystal lattice.

87. $\Delta S = \Delta H/T = (37300 \text{ J mol}^{-1})/(373 \text{ K}) = 100 \text{ J K}^{-1} \text{ mol}^{-1}$

89. Adiabatically implies $q = 0$. Expansion against vacuum implies $w = 0$. Hence, $\Delta U = q + w = 0$.

92. $K_p = p_B/p_A = 1/4$. Since $\Delta G^\circ = -RT \ln K_p^\circ$, we will have $\Delta G^\circ = RT \ln 4$

93. $T = \Delta H/\Delta S = (25 \times 10^3 \text{ J mol}^{-1})/(100 \text{ J K}^{-1} \text{ mol}^{-1}) = 250$ K

94. $\Delta S(\text{A} \rightarrow \text{B}) = \Delta S(\text{A} \rightarrow \text{C}) + \Delta S(\text{C} \rightarrow \text{D}) + \Delta S(\text{D} \rightarrow \text{B}) = \Delta S(\text{A} \rightarrow \text{C}) + \Delta S(\text{C} \rightarrow \text{D}) - \Delta S(\text{B} \rightarrow \text{D})$

$= (60 + 20 - 10)$ eu = 70 eu

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(ii) The final pressure computed by the expression $p_3V_3 = p_1V_1$ is

$$p_3 = \frac{p_1V_1}{V_3} = \frac{(24.9\times10^4\,\text{Pa})(0.02\,\text{m}^3)}{(0.113\,\text{m}^3)} = 4.41 \times 10^4\ \text{Pa}$$

(iii) In isobaric expansion, $w_1 = -p_{ext}(V_2 - V_1) = -(24.9 \times 10^4\ \text{Pa})\{(0.04 - 0.02)\ \text{m}^3\} = -4980\ \text{J}$
In adiabatic expansion $w_2 = \Delta U = nC_{V,m}\,\Delta T = (2\ \text{mol})\,(\frac{3}{2} \times 8.314\ \text{J K}^{-1}\ \text{mol}^{-1})\,(300\ \text{K} - 600\ \text{K})$
$= -7470\ \text{J}$
Total work done by the gas is $w = w_1 + w_2 = -4980\ \text{J} - 7470\ \text{J} = -12450\ \text{J}$

6. (i) From the first law of thermodynamics, we have

$\Delta U_1 = q_1 + w_1 = 5960\ \text{J} - 2200\ \text{J} = 3760\ \text{J};\quad \Delta U_2 = q_2 + w_2 = -5585\ \text{J} + 825\ \text{J} = -4760\ \text{J}$

$\Delta U_3 = q_3 + w_3 = -2980\ \text{J} + 1100\ \text{J} = -1880\ \text{J};\quad \Delta U_4 = 3645\ \text{J} + w_4$

Since the process is cyclic, the net ΔU $(= \Delta U_1 + \Delta U_2 + \Delta U_3 + \Delta U_4)$ will be equal to zero.
Hence $3760\ \text{J} - 4760\ \text{J} - 1880\ \text{J} + (3645\ \text{J} + w_4) = 0$
This gives $w_4 = -765\ \text{J}$

(ii) $\Delta U_{net} = 0$. See part (i)

(iii) Step 1st and 2nd taken together will accompany with a net decrease in the internal energy of the gas.

7. (i) The combustion reaction is $C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$

$\Delta_cG^\circ = 6\Delta_fG^\circ(CO_2, g) + 6\Delta_fG^\circ(H_2O, l) - \Delta_fG^\circ(\text{glucose})$
$= [6(-395) + 6(-237) - (-900)]\ \text{kJ mol}^{-1} = -2892\ \text{kJ mol}^{-1}$

(ii) Since $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, we get

$$\Delta S^\circ = \frac{1}{T}(\Delta H^\circ - \Delta G^\circ) = \frac{1}{298\,\text{K}}(-2815.8 + 2892)\ \text{kJ mol}^{-1} = 0.256\ \text{kJ K}^{-1}\ \text{mol}^{-1} = 256\ \text{J K}^{-1}\ \text{mol}^{-1}$$

(iii) The entropy change for the combustion reaction is

$$\Delta_cS^\circ = 6S^\circ(CO_2, g) + 6S^\circ(H_2O, l) - S^\circ(C_6H_{12}O_6, s) - 6S^\circ(O_2, g)$$

Hence

$S^\circ(\text{glucose}) = 6S^\circ(CO_2, g) + 6S^\circ(H_2O, l) - 6S^\circ(O_2, g) - \Delta_cS^\circ$
$= [6(213.6) + 6(69.96) - 6(205) - 256]\ \text{J K}^{-1}\ \text{mol}^{-1} = 215.4\ \text{J K}^{-1}\ \text{mol}^{-1}$

8. The reactions to be considered are

$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$ $\qquad \Delta H^\circ = -110\ \text{kJ mol}^{-1}$

$C(s) + O_2(g) \rightarrow CO_2(g)$ $\qquad \Delta H^\circ = -395\ \text{kJ mol}^{-1}$

(i) If x is the amount of C giving CO, then

$[x\,(-110) + (1.0\ \text{mol} - x)(-395)]\ \text{kJ mol}^{-1} = -315\ \text{kJ}$

$$x = \frac{-315+395}{395-110}\ \text{mol} = \frac{80}{285}\ \text{mol} \simeq 0.28\ \text{mol}$$

Mass of C reacted to give CO = $(0.28\ \text{mol})\,(32\ \text{g mol}^{-1}) \simeq 9.0\ \text{g}$

(ii) Amount of C yielding $CO_2 = 1.0\ \text{mol} - 0.28\ \text{mol} = 0.72\ \text{mol}$
Mass of O_2 reacted yielding $CO_2 = (0.72\ \text{mol})(32\ \text{g mol}^{-1}) \simeq 23\ \text{g}$

(iii) Mass of O_2 reacted yielding $CO = \left(\frac{0.28\,\text{mol}}{2}\right)(32\ \text{g mol}^{-1}) = 4.5\ \text{g}$

Mass of total O_2 reacted = 23 g + 4.5 g = 27.5 g

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Now $\Delta H_{(i)} = -\varepsilon_{C-C} - 6\varepsilon_{C-H} = -2828.3 \text{ kJ mol}^{-1}$

$\Delta H_{(ii)} = -2\varepsilon_{C-C} - 8\varepsilon_{C-H} = -4000.5 \text{ kJ mol}^{-1}$

Solving for ε_{C-C} and ε_{C-H}, we get $\varepsilon_{C-H} = 414.0 \text{ kJ mol}^{-1}$ and $\varepsilon_{C-H} = 344.3 \text{ kJ mol}^{-1}$.

11. A gas mixture consisting of 3.67 litres of ethylene and methane on complete combustion at 25 °C produces 6.11 litres of CO_2. Find out the amount of heat evolved on burning one litre of the gas mixture. The heats of combustion of ethylene and methane are – 1423 and – 891 kJ mol^{-1}, respectively, at 25 °C. (1991)

Solution The combustion reactions are

$$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$$

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

Let V be the volume of $C_2H_4(g)$ in the gaseous mixture of 3.67 L. From the chemical equations, we find that

Volume of $CO_2(g)$ produced due to the combustion of $C_2H_4(g) = 2V$

Volume of $CO_2(g)$ produced due to the combustion of $CH_4(g) = 3.67 \text{ L} - V$

Equating the latter with 6.11 L – 2 V, we get

$3.67 \text{ L} - V = 6.11 \text{ L} - 2V$ or $V = 2.44 \text{ L}$

Hence, in the original mixture, we have

$$\text{Volume of } C_2H_4(g) \text{ per litre of the mixture} = \left(\frac{2.44 \text{ L}}{3.67 \text{ L}}\right)(1 \text{ L}) = 0.665 \text{ L}$$

$$\text{Volume of } CH_4(g) \text{ per litre of the mixture} = 1.0 \text{ L} - 0.665 \text{ L} = 0.335 \text{ L}$$

Now, $$\text{Volume of 1 mol of any gas at 25 °C} = (22.414 \text{ L})\left(\frac{298 \text{ K}}{273 \text{ K}}\right) = 24.467 \text{ L}$$

Hence, $$\text{Heat released due to the combustion of } C_2H_4(g) = (1423 \text{ kJ})\left(\frac{0.665 \text{ L}}{24.467 \text{ L}}\right) = 38.68 \text{ kJ}$$

$$\text{Heat released due to the combustion of } CH_4(g) = (891 \text{ kJ})\left(\frac{0.335 \text{ L}}{24.467 \text{ L}}\right) = 12.20 \text{ kJ}$$

Total heat released = (38.68 + 12.20) kJ = 50.88 kJ.

12. Determine the enthalpy of the reaction $C_3H_8(g) + H_2(g) \rightarrow C_2H_6(g) + CH_4(g)$ at 25 °C using the given enthalpy of combustion values under standard conditions:

Compound:	$H_2(g)$	$CH_4(g)$	$C_2H_6(g)$	C(graphite)
$\Delta_c H$/kJ mol^{-1}:	– 285.8	– 890.0	– 1560.0	– 393.5

The standard enthalpy of formation of $C_3H_8(g)$ is – 103.8 kJ mol^{-1}. (1992)

Solution The given data are:

(i)	$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$	$\Delta H = -285.8 \text{ kJ mol}^{-1}$
(ii)	$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$	$\Delta H = -890.0 \text{ kJ mol}^{-1}$
(iii)	$C_2H_6(g) + \frac{7}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$	$\Delta H = -1560.0 \text{ kJ mol}^{-1}$
(iv)	$C(\text{graphite}) + O_2(g) \rightarrow CO_2(g)$	$\Delta H = -393.5 \text{ kJ mol}^{-1}$
(v)	$3C(\text{graphite}) + 4H_2(g) \rightarrow C_3H_8(g)$	$\Delta H = -103.8 \text{ kJ mol}^{-1}$

We have to determine ΔH of the reaction $C_3H_8(g) + H_2(g) \rightarrow C_2H_6(g) + CH_4(g)$

This equation can be obtained by the following manipulations.

– Eq. (v) – Eq. (iii) – Eq. (ii) + 3 Eq. (iv) + 5 Eq. (i)

Carrying out the corresponding manipulations on ΔH s, we get

$\Delta H = (103.8 + 1560 + 890 - 3 \times 393.5 - 5 \times 285.8) \text{ kJ mol}^{-1} = -55.7 \text{ kJ mol}^{-1}$.

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Solution The given reaction may be visualized to take place as shown in the following.

$$C_2H_4(g) + 3O_2(g) \xrightarrow{\Delta H} 2CO_2(g) + 2H_2O(g)$$

$$\Delta H_1 \downarrow \qquad\qquad \uparrow \Delta H_2$$

$$2C(g) + 4H(g) + 6O(g)$$

Obviously, $\Delta H = \Delta H_1 + \Delta H_2$

Now $\Delta H_1 = \varepsilon(C{=}C) + 4\varepsilon(C{-}H) + 3\varepsilon(O{=}O) = (619 + 4 \times 414 + 3 \times 499)$ kJ mol^{-1}

$= 3772$ kJ mol^{-1}

$\Delta H_2 = -4\varepsilon(C{=}O) - 4\varepsilon(O{-}H) = (-4 \times 724 - 4 \times 460)$ kJ mol^{-1}

$= -4736$ kJ mol^{-1}

Hence, $\Delta H = (3772 - 4736)$ kJ mol^{-1} $= -964$ kJ mol^{-1}.

24. Using the bond enthalpy data given below, compute the enthalpy of formation of gaseous isoprene $CH_2{=}C(CH_3)CH{=}CH_2$.

$\varepsilon(C{-}H) = 413.4$ kJ mol^{-1}; $\varepsilon(C{-}C) = 347.7$ kJ mol^{-1}; $\varepsilon(C{=}C) = 615.1$ kJ mol^{-1}

Enthalpy of sublimation of C(graphite) = 718.4 kJ mol^{-1}

Enthalpy of formation of H(g) = 218.0 kJ mol^{-1}

Solution We have to compute the enthalpy change of the following reaction:

$$5C(\text{graphite}) + 4H_2(g) \rightarrow CH_2{=}C(CH_3)CH{=}CH_2(g)$$

The provided data are

$C{-}H(g) \rightarrow C(g) + H(g)$	$\Delta H = 413.4$ kJ mol^{-1}
$C{-}C(g) \rightarrow 2C(g)$	$\Delta H = 347.7$ kJ mol^{-1}
$C{=}C(g) \rightarrow 2C(g)$	$\Delta H = 615.1$ kJ mol^{-1}
$C(\text{graphite}) \rightarrow C(g)$	$\Delta H = 718.4$ kJ mol^{-1}
$\frac{1}{2} H_2(g) \rightarrow H(g)$	$\Delta H = 218.0$ kJ mol^{-1}

The given reaction may be thought to occur through the following alternative path.

$$5C(\text{graphite}) + 4H_2(g) \xrightarrow{\Delta H_1} CH_2{=}\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}{-}CH{=}CH_2(g)$$

$$\Delta H_2 \downarrow \qquad\qquad \uparrow \Delta H_3$$

$$5C(g) + 8H(g)$$

Obviously,

$$\Delta H_1 = \Delta H_2 + \Delta H_3$$

where $\Delta H_2 = (5 \times 718.4 + 8 \times 218.0)$ kJ mol^{-1} $= 5336$ kJ mol^{-1}

and $\Delta H_3 = -2\varepsilon(C{-}C) - 2\varepsilon(C{=}C) - 8\varepsilon(C{-}H)$

$= [-2 \times 347.7 - 2 \times 615.1 - 8 \times 413.4]$ kJ mol^{-1} $= -5232.8$ kJ mol^{-1}

Hence, $\Delta H_1 = (5336 - 5232.8)$ kJ mol^{-1} $= 103.2$ kJ mol^{-1}

25. Find the bond enthalpy of S—S bond from the following data :

$C_2H_5{-}S{-}C_2H_5(g)$	$\Delta_f H^\circ = -147.2$ kJ mol^{-1}
$C_2H_5{-}S{-}S{-}C_2H_5(g)$	$\Delta_f H^\circ = -201.9$ kJ mol^{-1}
S(g)	$\Delta_f H^\circ = 222.8$ kJ mol^{-1}

Solution We are given that

(i) $4C(\text{graphite}) + 5H_2(g) + S(s) \rightarrow C_2H_5{-}S{-}C_2H_5(g)$ $\Delta H = -147.2$ kJ mol^{-1}

(ii) $4C(\text{graphite}) + 5H_2(g) + 2S(s) \rightarrow C_2H_5{-}S{-}S{-}C_2H_5(g)$ $\Delta H = -201.9$ kJ mol^{-1}

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33. 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 J K^{-1} mol^{-1}. (2000)

Solution: For a reversible expansion of an ideal gas, we have

$$T_2\ V_2^{\gamma-1} = T_1\ V_1^{\gamma-1} \qquad \text{where} \qquad \gamma = C_{p,m}/C_{V,m}$$

For a monatomic gas (assumed to be ideal),

$$\gamma = \frac{C_{p,m}}{C_{V,m}} = \frac{C_{V,m} + R}{C_{V,m}} = 1 + \frac{R}{C_{V,m}} = 1 + \frac{8.314}{12.48} = 1.6662$$

Hence, $$T = \left(\frac{V_1}{V_2}\right)^{\gamma-1} T_1 = \left(\frac{1.25}{2.50}\right)^{0.6662} (300\ \text{K}) = 189.0\ \text{K}$$

The enthalpy change in the given process would be $\Delta H = nC_{p,m}\,\Delta T$

where $$n = \frac{pV}{RT} = \frac{(101.325\ \text{kPa})\ (1.25\ \text{dm}^3)}{(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})\ (300\ \text{K})} = 0.0508\ \text{mol}$$

$$C_{p,m} = C_{V,m} + R = (12.48 + 8.314)\ \text{J K}^{-1}\ \text{mol}^{-1} = 20.794\ \text{J K}^{-1}\ \text{mol}^{-1}$$

$$\Delta T = T_2 - T_1 = (189.0 - 300)\ \text{K} = -111\ \text{K}$$

Hence $$\Delta H = nC_{p,m}\,\Delta T = (0.0508\ \text{mol})\ (20.794\ \text{J K}^{-1}\ \text{mol}^{-1})\ (-111\ \text{K}) = -117.25\ \text{J}$$

34. Show that the reaction $CO(g) + (1/2)O_2(g) \rightarrow CO_2(g)$ 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. (2000)

Solution For the given reaction, we have

$$\underset{\Delta_f G^\circ}{\underset{-137.2\ \text{kJ mol}^{-1}}{CO(g)}} + \frac{1}{2}O_2(g) \rightarrow \underset{-394.4\ \text{kJ mol}^{-1}}{CO_2(g)} \qquad \Delta_r S^\circ = -0.094\ \text{kJ K}^{-1}\ \text{mol}^{-1}$$

The standard free-energy change of the reaction is

$$\Delta_r G^\circ = \Delta_f G^\circ(CO_2, g) - \Delta_f G^\circ(CO, g) = (-394.4) + 137.2)\ \text{kJ mol}^{-1} = -257.2\ \text{kJ mol}^{-1}$$

Since $\Delta_r G^\circ$ is negative, the reaction is spontaneous. The enthalpy change of the reaction is

$$\Delta_r H^\circ = \Delta_r G^\circ - T\Delta_r S^\circ = (-257.2 + (300)\ (-0.094)\ \text{kJ mol}^{-1} = -285.4\ \text{kJ mol}^{-1}$$

Since $\Delta_r H^\circ$ is negative, the reaction is exothermic.

35. 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.

$2B(s) + (3/2)\ O_2(g) \rightarrow B_2O_3(s)$ $\qquad \Delta H = -1273\ \text{kJ mol}^{-1}$.

$H_2(g) + (1/2)O_2(g) \rightarrow H_2O(l)$ $\qquad \Delta H = -286\ \text{kJ mol}^{-1}$

$H_2O(l) \rightarrow H_2O(g)$ $\qquad \Delta H = 44\ \text{kJ mol}^{-1}$

$2B(s) + 3H_2(g) \rightarrow B_2H_6(g)$ $\qquad \Delta H = 36\ \text{kJ mol}^{-1}$ (2000)

Solution

The given reaction can be obtained as follows.

$B_2H_6(g) \rightarrow 2B(s) + 3H_2(g)$	$\Delta H = -36\ \text{kJ mol}^{-1}$
$2B(s) + (3/2)\ O_2(g) \rightarrow B_2O_3(s)$	$\Delta H = -1273\ \text{kJ mol}^{-1}$
$3[H_2O(l) \rightarrow H_2O(g)]$	$\Delta H = 3 \times 44\ \text{kJ mol}^{-1}$
$3[H_2(g) + (1/2)O_2(g) \rightarrow H_2O(l)]$	$\Delta H = -3 \times 286\ \text{kJ mol}^{-1}$
Add	
$B_2H_6(g) + 3O_2(g) \rightarrow B_2O_3(s) + 3H_2O(g)$	$\Delta H = -2035\ \text{kJ mol}^{-1}$

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In thermodynamics, the equilibrium constant carries no unit as the pressures are expressed in terms of standard unit of 1 atm or 1 bar. In fact, the expression of K_p involves the term p/p°, where p is the pressure of the gaseous substance and p° is the standard unit pressure. This type of equilibrium constant is known as standard (or thermodynamic) equilibrium constant and is represented as K_p°.

Equilibrium Constant in Units Other than Partial Pressures

Equilibrium constant of a reaction is also expressed in units other than that of partial pressure. For example, if the concentrations are used, one gets the constant K_c. Equation (1) is the expression of K_c for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$. The standard equilibrium constant K_c° involves the use of c/c°, where c° is the standard unit concentration of 1 mol L^{-1}.

Likewise, one can define the constants K_x and K_n where the subscripts x and n stand for mole fraction and amount of substance, respectively. For the reaction mentioned above, we have

$$K_x = \frac{x_{NH_3}^2}{x_{N_2}\, x_{H_2}^3} \quad \text{and} \quad K_n = \frac{n_{NH_3}^2}{n_{N_2}\, n_{H_2}^3}$$

Relations Between Equilibrium Constants The various equilibrium constants are related to each other through the following expressions.

Equilibrium constants K_p and K_c are related to each other through the expression

$$K_p = K_c\,(R\,T)^{\Delta\nu_g} \tag{3}$$

where $\Delta\nu_g$ is the change in the stoichiometric numbers of gaseous molecules during the conversion of reactants to products and is defined as $\Delta\nu_g = \Sigma\nu_g(\text{product}) - \Sigma\nu_g(\text{reactant})$ (4)

The equilibrium constants K_p and K_c are quite often used to deal with the reactions at equilibrium. If K_p is expressed in terms of "atm" unit, the value of R to be used is 0.082 L atm K^{-1} mol^{-1}.

The expressions involving standard equilibrium constants are as follows.

$$K_p^\circ = K_c^\circ\,(c^\circ\, RT/p^\circ)^{\Delta\nu_g};\quad K_p^\circ = K_x\,(p_{total}/p^\circ)^{\Delta\nu_g},\quad \text{and}\quad K_p^\circ = K_n^\circ\,(n^\circ/n_{total})^{\Delta\nu_g}\,(p_{total}/p^\circ)^{\Delta\nu_g}$$

where $n^\circ = 1$ mol.

Simultaneous Equilibrium Reactions with a Common Species

Consider the following reactions occurring simultaneously in a system

$$X(g) \rightleftharpoons A(g) + B(g) \quad \text{and} \quad Y(g) \rightleftharpoons A(g) + C(g)$$

Let the reactions be initiated with the partial pressures a and b of X and Y, respectively. Let the partial pressures x and y of X and Y, respectively, are transformed into the respective products at equilibrium. We will have

$$\underset{a-x}{X(g)} \rightleftharpoons \underset{x+y}{A(g)} + \underset{x}{B(g)};\qquad K_{p1} = \frac{p_A\, p_B}{p_X} = \frac{(x+y)x}{a-x}$$

$$\underset{b-y}{Y(g)} \rightleftharpoons \underset{x+y}{A(g)} + \underset{y}{C(g)};\qquad K_{p2} = \frac{p_A\, p_C}{p_Y} = \frac{(x+y)y}{b-y}$$

Equilibrium Constant of a Reaction Involving Condensed Phases The expression of the equilibrium constant of a reaction involving condensed (solid or liquid) and gaseous states is obtained by considering the concentrations or partial pressures of only the gaseous species. The concentration of condensed phases being constant are merged with the equilibrium constant.

Variation of K_p° with Temperature The equilibrium constant K_p° of a reaction at equilibrium varies with change in temperature and the relation governing this change is

$$\ln K_p^\circ = -\frac{\Delta_r H^\circ}{RT} + I$$

where I is a constant and $\Delta_r H^\circ$ is the standard enthalpy change of the reaction.

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21. For the reaction $NH_3(g) \rightleftharpoons \frac{1}{2} N_2(g) + \frac{3}{2} H_2(g)$, the degree of dissociation in terms K_p is

(a) $\alpha = \left(1+\frac{3\sqrt{3}}{4}\frac{p}{K_p}\right)^{-1/2}$ (b) $\alpha = \left(1-\frac{3\sqrt{3}}{4}\frac{p}{K_p}\right)^{-1/2}$

(c) $\alpha = \left(1+\frac{3\sqrt{3}}{4}\frac{K_p}{p}\right)^{-1/2}$ (d) $\alpha = \left(1-\frac{3\sqrt{3}}{4}\frac{K_p}{p}\right)^{-1/2}$

22. For the reaction $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$, the degree of dissociation at equilibrium pressure p and temperature T is given by

(a) $\alpha = (\rho\, p\, M_{COCl_2}/RT) + 1$ (b) $\alpha = (\rho\, p\, M_{COCl_2}/RT) - 1$

(c) $\alpha = (p\, M_{COCl_2}/\rho RT) + 1$ (d) $\alpha = (p\, M_{COCl_2}/\rho RT) - 1$

where ρ is the density of the gases at equilibrium.

23. An exothermic reaction proceeding towards equilibrium is associated with

(a) the absorption of heat

(b) an increase in the enthalpy of reaction

(c) a decrease in the value of equilibrium constant with increase in temperature

(d) a decrease in the value of equilibrium constant with the variation of pressure at a constant temperature.

24. An endothermic reaction proceeding towards equilibrium is associated with

(a) the release of heat

(b) a decrease in the enthalpy of reaction

(c) a decrease in the value of K_p° with increase in temperature

(d) an increase in the value of K_p° with increase in temperature

25. For a reaction at equilibrium

(a) K_p° varies linearly with temperature with a positive slope

(b) K_p° varies linearly with inverse of temperature with a positive slope

(c) ln K_p° varies linearly with a temperature

(d) ln K_p° varies linearly with inverse of temperature

Relation Between K_p and K_c

26. For the reaction $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$, which of the following facts holds good?

(a) $K_p = K_c$ (b) $K_p > K_c$

(c) $K_p < K_c$ (d) K_p and K_c cannot be correlated unless pressure of the system is given

27. For the reaction $2N_2O_5(g) \rightleftharpoons 4NO_2(g) + O_2(g)$, which of the following facts holds good?

(a) $K_p = K_c$ (b) $K_p > K_c$

(c) $K_p < K_c$ (d) K_p and K_c cannot be correlated unless pressure of the system is provided

28. For the reaction $4NO_2(g) + O_2(g) \rightleftharpoons 2N_2O_5(g)$, which of the following facts holds good?

(a) $K_p = K_c$ (b) $K_p > K_c$

(c) $K_p < K_c$ (d) K_p and Kc cannot be correlated unless pressure of the system is provided

29. The equilibrium constants K_p and K_c for a gaseous reactions are related to each other by the expression

(a) $K_p = K_c(RT)^{-\Delta v_g}$ (b) $K_p = K_c(RT)^{\Delta v_g}$ (c) $K_p = K_c(R)^{-\Delta v_g}$ (d) $K_p = K_c(R)^{\Delta v_g}$

30. The K_p of the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ was found to be 11.45 kPa at 298 K. Its K_c would be

(a) 4.62×10^{-2} M (b) 4.62×10^{-3} M (c) 4.62×10^{-4} M (d) 4.62×10^{-5} M

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72. Given the following reaction at equilibrium. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$. Some inert gas at constant pressure is added to the system. Predict which of the following facts will be affected?
(a) More $NH_3(g)$ is produced
(b) Less $NH_3(g)$ is produced
(c) No affect on the equilibrium
(d) K_p of the reaction is decreased

73. For the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, ΔH = –ve. The formation of $NH_3(g)$ is favoured at
(a) high pressure and low temperature
(b) low pressure and high temperature
(c) low pressure and low temperature
(d) high pressure and high temperature

74. For the reaction $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$, $\Delta H = -180$ kJ mol^{-1}. Which of the following facts does not hold good?
(a) The pressure changes at constant temperature do not affect the equilibrium constant
(b) The volume changes at constant temperature do not affect the equilibrium constant
(c) The dissociation of NO is favoured more at high temperature
(d) The dissociation of NO is favoured less at high temperature

75. For the reaction $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$, $\Delta H = 93.6$ kJ mol^{-1}. Which of the following facts does not hold good?
(a) The pressure changes at constant temperature does not affect the equilibrium constant
(b) The volume changes at constant temperature does not affect the equilibrium constant
(c) The dissociation of NH_3 is more favoured at high temperature
(d) The dissociation of NH_3 is less favoured at high temperature

76. For an equilibrium $H_2O(s) \rightleftharpoons H_2O(l)$, which of the following statements is true?
(a) The pressure changes do not affect the equilibrium
(b) More of ice melts if pressure on the system is increased
(c) More of liquid freezes if pressure on the system is increased
(d) The pressure changes may increase or decrease the degree of advancement of the reaction depending upon the temperature of the system

77. Solids $CaCO_3$ and CaO and gaseous CO_2 are placed in a vessel and allowed to reach equilibrium

$$CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s) \qquad \Delta H = -180 \text{ kJ mol}^{-1}$$

The quantity of CaO in the vessel could be increased by
(a) adding more of $CaCO_3$
(b) removing some of CO_2
(c) lowering the temperature
(d) reducing the volume of the vessel

78. For a given equilibrium reaction, an increase in temperautre will
(a) increase the rate of the exothermic reaction more than that of the endothermic reaction.
(b) increase the rate of the endothermic reaction more than that of the exothermic reaction.
(c) increase both rates equally.
(d) decreases both rates equally.

79. For an equilibrium reaction $A(g) + B(g) \rightleftharpoons C(g) + D(g)$, ΔH = –ve. An increase in temperature would cause
(a) an increase in the value of K_{eq}
(b) a decrease in the value of K_{eq}
(c) no change in the value of K_{eq}
(d) a change in K_{eq} which cannot be qualitatively predicted

80. For an equilibrium reaction $A(g) + B(g) \rightleftharpoons C(g) + D(g)$, ΔH = +ve. An increase in temperature would cause
(a) an increase in the value of K_{eq}
(b) a decrease in the value of K_{eq}
(c) no change in the value of K_{eq}
(d) a change in K_{eq} which cannot be qualitatively predicted

81. For the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, $\Delta H = -93.6$ kJ mol^{-1}. The concentration of H_2 at equilibrium will increase if
(a) the temperature is lowered
(b) the volume of the system is decreased
(c) N_2 is added at constant volume
(d) NH_3 is removed

82. For the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, $\Delta H = -93.6$ kJ mol^{-1}. The amount (i.e. number of mole) of H_2 at equilibrium will increase if
(a) volume is increased
(b) volume is decreased
(c) O_2 is added at constant volume
(d) NH_3 is removed.

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(i) The degree of dissociation of PCl_5 is
(a) 1/3 (b) 2/3 (c) 1/2 (d) 3/4
(ii) The equilibrium constant of the reaction is
(a) 60 kPa (b) 70 kPa (c) 80 kPa (d) 90 kPa
(iii) The free energy change of the reaction is
(a) 910 J mol^{-1} (b) 928 J mol^{-1} (c) 952 J mol^{-1} (d) 998 J mol^{-1}

7. The standard free energies of formation of $N_2O_4(g)$ and $NO_2(g)$ are 97.89 and 51.31 kJ mol^{-1}, respectively. For the reaction $N_2O_4(g) \rightleftharpoons NO_2(g)$ at 300 K and 1 atm pressure, answer the following three questions. Take p° = 100 Pa.
(i) The value of K_p° for the reaction is
(a) 0.10 (b) 0.12 (c) 0.15 (d) 0.18
(ii) The value of K_c° for the reaction is
(a) 6.1×10^{-3} (b) 6.8×10^{-3} (c) 7.5×10^{-3} (d) 8.5×10^{-3}
(iii) The value of K_x for the reaction is
(a) 0.168 (b) 0.148 (c) 0.128 (d) 0.108

8. The value of K_p° = 1.8 at 500 K for the reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$. The equilibrium pressure is 100 kPa. Based on this information, answer the following three questions. Take p° = 100 kPa
(i) The degree of dissociation of $PCl_5(g)$ is
(a) 0.6 (b) 0.7 (c) 0.8 (d) 0.85
(ii) The density of the reaction at equilibrium is
(a) 2.8 g dm^{-3} (b) 2.4 g dm^{-3} (c) 1.9 g dm^{-3} (d) 1.5 g dm^{-3}
(iii) The standard free energy change of the reaction at equilibrium is
(a) – 1.20 kJ mol^{-1} (b) – 1.80 kJ mol^{-1} (c) – 2.44 kJ mol^{-1} (d) – 2.98 kJ mol^{-1}

9. $COCl_2$ gas dissociates as $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$
The density of the gas mixture at equilibrium is.1.2 g dm^{-3} when T = 700 K and p = 100 kPa. Based on this information, answer the following three questions.
(i) The degree of dissociation of $COCl_2(g)$ is
(a) 0.25 (b) 0.30 (c) 0.36 (d) 0.42
(ii) The equilibrium constant K_p° for the reaction is
(a) 0.214 (b) 0.294 (c) 0.364 (d) 0.394
(iii) The standard free energy change of the reaction is
(a) 8.0 kJ mol^{-1} (b) 8.98 kJ mol^{-1} (c) 9.8 kJ mol^{-1} (d) 10.5 kJ mol^{-1}

Assertion and Reason Type

In the following questions, two statements are given. For each question, select the correct choice from the following.
(a) Statement-1 is True. Statement-2 is True. Statement-2 is correct explanation for Statement-1.
(b) Statement-1 is True. Statement-2 is True. Statement-2 is NOT a correct explanation for Statement-1.
(c) Statement-1 is True. Statement-2 is False.
(d) Statement-1 is False. Statement-2 is True.

	Statement–1	**Statement–2**
1.	(a) For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, the values of K_p° and K_c° are identical.	The reaction has the same number of gaseous species on either sides of equilibrium.
2.	The formation of NH_3 ($\Delta_f H^\circ = -46.11$ kJ mol^{-1}) is favoured at high pressure and low temperature.	The formation of NH_3 is accompanied with decreases in gaseous molecules and release of heat.
3.	The value of K_p is greater than that of K_c for a reaction involving $\Delta\nu_g$ = +ve.	The relation between K_p and K_c is $K_c = K_p (RT)^{\Delta\nu_g}$.
4.	The addition of an inert gas at constant volume does not affect the equilibrium of a reaction provided $\Delta\nu_g = 0$.	Addition of NH_3 at constant volume increases the pressure of the gaseous mixture of a reaction at equilibrium.

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$$p(H_2S) = \frac{2(1-\alpha)}{2+\alpha}p; \quad p(H_2) = \frac{2\alpha}{2+\alpha}p; \quad p(S_2) = \frac{\alpha}{2+\alpha}p$$

$$K_p = \frac{\{2(\alpha)\,p/(2+\alpha)\}^2\,\{\alpha p/(2+\alpha)\}}{\{2(1-\alpha)\,p/(2+\alpha)\}^2} = \frac{\alpha^3 p}{(2+\alpha)(1-\alpha)^2}$$

11. The equilibrium constant is independent of individual concentrations.

12. The equilibrium constant is independent of volume of the container.

14. K_p of an equilibrium reaction depends only on temperature. However, the degree of dissociation will change in accordance with Le-Chatelier's principle.

15. The given reaction can be obtained as follows.

$$\begin{aligned} &-[N_2 + 3H_2 \rightleftharpoons 2NH_3] \\ &+[N_2 + O_2 \rightleftharpoons 2NO] \\ &+3[H_2 + \tfrac{1}{2}\,O_2 \rightleftharpoons H_2O] \\ \hline &2NH_3 + \tfrac{5}{2}\,O_2 \rightleftharpoons 2NO + 3H_2O \end{aligned}$$

Hence $K = K_2\,K_3^3/K_1$

16. The given reaction will be exothermic in nature due to the formation of three X-Y bonds from the gaseous atoms. The reaction is also accompanied with the decrease in the gaseous species. Hence, the reaction will be affected by both temperature and pressure. The use of catalyst does not affect the equilibrium concentrations of the species in the chemical reaction.

17. For the reaction A + B → C + D, the reaction quotient is defined as $Q = \dfrac{[C][D]}{[A][B]}$

In the final stage of the reaction, the reaction is at equilibrium and thus the value of Q remains constant with time.

18. We have

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

$n(1-\alpha)$ $\quad$ $n(2\alpha)$; Total amount of gases $= n(1+\alpha)$

$$K_p = \frac{p^2_{NO_2}}{p_{N_2O_4}} = \frac{[\{2\alpha/(1+\alpha)\}P]^2}{\{(1-\alpha)/(1+\alpha)\}P} = \frac{4\alpha^2 P}{1-\alpha^2} \quad \text{or} \quad \alpha = \sqrt{K_p/(4p+K_p)}$$

19. We have $\Delta G^\circ = -RT \ln K_p^\circ = -2.303\,RT \log K_p^\circ$

This gives $K_p^\circ = \text{antilog}\,(-\Delta G^\circ/2.303\,RT) = \text{antilog}\,\{16\,600/(2.303 \times 8.314 \times 298)\}$

20. We have

$$\begin{matrix} A(g) & \rightleftharpoons & B(g) & + & C(g) \\ a-x & & x & & x; \end{matrix} \qquad \text{Total amount} = a + x$$

$$p_A = \left(\frac{a-x}{a+x}\right)P; \quad p_B = p_C = \frac{x}{a+x}\,P$$

$$K_p = \frac{p_B p_C}{p_A} = \frac{\{x/(a+x)\}^2 P^2}{\{(a-x)/(a+x)\}P} = \frac{x^2 P}{a^2 - x^2}$$

21. We have

$$NH_3(g) \rightleftharpoons \frac{1}{2}\,N_2(g) + \frac{3}{2}\,H_2(g)$$

$n(1-\alpha)$ $\quad$ $n(\alpha/2)$ $\quad$ $n(3\alpha/2)$; $\quad$ Total amount $= n(1+\alpha)$

$$p_{NH_3} = \{(1-\alpha)/(1+\alpha)\}P; \quad p_{N_2} = \{\alpha/2(1+\alpha)\}P; \quad p_{H_2} = \{3\alpha/2\,(1+\alpha)\}\,P$$

$$K_p = \frac{p^{1/2}_{N_2}\,p^{3/2}_{H_2}}{p_{NH_3}} = \left[\frac{\alpha}{2(1+\alpha)}P\right]^{1/2}\left[\frac{3\alpha}{2(1+\alpha)}P\right]^{3/2}\left[\frac{1+\alpha}{1-\alpha}\frac{1}{P}\right] = \frac{3\sqrt{3}\,\alpha^2}{4(1-\alpha^2)}P$$

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51. Molar mass of N_2O_4 = 92 g mol^{-1}

Amount of N_2O_4 = 11.5 g/92 g mol^{-1} = 0.125 mol

	$N_2O_4(g)$	$\rightleftharpoons$	$2NO_2(g)$
$t = 0$	0.125 mol		
t_{eq}	(1 – 0.66) 0.125 mol = 0.0425 mol		(2 × 0.66) 0.125 mol = 0.165 mol

Total amount of gases = (0.0425 + 0.165) mol = 0.2075 mol

$$V = \frac{nRT}{p} = \frac{(0.2075\ \text{mol})(0.082\ \text{L atm K}^{-1}\ \text{mol}^{-1})(300\ \text{K})}{1\ \text{atm}} = 5.1\ \text{L}$$

52. The given reaction may be obtained by subtracting half of the first reaction from the second. Hence

$$K_c^\circ = \frac{1.55}{(2.4\times10^{30})^{1/2}} = 1.0 \times 10^{-15}$$

53. $N_2O_5(g) \rightleftharpoons 2NO_2(g) + \frac{1}{2}\ O_2(g)$

600mmHg – p $\quad$ $2p$ $\quad$ $p/2$

Pressure at any time = (600 mmHg – p) + ($2p$) + ($p/2$) = 600 mmHg + 1.5 p

Hence, 600 mmHg + 1.5 p = 960 mmHg $\Rightarrow$ p = 240 mmHg

$$x(N_2O_5) = \frac{240\ \text{mmHg}}{600\ \text{mmHg}} = 0.40$$

54.

	$CO_2(g)$ +	$H_2(g)$	$\rightleftharpoons$	$CO(g)$ +	$H_2O(g)$
$t = 0$	0.6 mol	0.4 mol			
t_{eq}	0.35 mol	0.15 mol		0.25 mol	0.25 mol

$$K_p = \frac{(0.25)^2}{(0.35)(0.15)} = 1.2$$

55. For the given concentrations, we have

$$\frac{[NO][SO_3]}{[SO_2][NO_2]} = \frac{(0.30)(0.02)}{(0.04)(0.50)} = 0.3$$

This value is less than the equilibrium constant. Hence, to attain equilibrium, the reaction will proceed to right side.

56.

	$2NO(g)$ +	$Cl_2(g)$	$\rightleftharpoons$	$2NOCl$ (g)
$t = 0$	0.4 atm	0.3 atm		
t_{eq}	0.4 atm – $2p$	0.3 atm – p		$2p$

Total pressure at equilibrium, 0.7 atm – p = 0.6 atm (given).

Hence, p = 0.1 atm

$$K_p = \frac{p^2_{NOCl}}{p^2_{NO}\ p_{Cl_2}} = \frac{(0.2\ \text{atm})^2}{(0.2\ \text{atm})^2\ (0.2\ \text{atm})} = 5\ \text{atm}^{-1}$$

57. $K_{eq} = k_f/k_b = 3.2/0.12 = 26.7$

58. $E_{a(b)}$ = (208 + 536) kJ mol^{-1} = 744 kJ mol^{-1}.

59.

$2HI(g)$	$\rightleftharpoons$	$H_2(g)$ +	$I_2(g)$
0.78 mol		0.11 mol	0.11 mol

Since $\Delta\nu_g = 0$, $K_p = K_n$ = (0.11 mol)^2/(0.78 mol)^2 = 0.02

60. $\Delta G^\circ = -RT\ \text{lm}\ K_p^\circ = -$ (8.314 J K^{-1} mol^{-1}) (900 K) ln (0.05) = 22400 J mol^{-1}

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Linked Comprehension Type

1. (i) $K^\circ = \dfrac{[Ag(NH_3)_2^+][Cl^-]}{[NH_3]^2} = \dfrac{(s)(s)}{(1\,M)} = 2.79\times10^{-3}$; $s = \sqrt{2.79\times10^{-3}}\ M = 0.053\ M$

(ii) $K^\circ = \dfrac{[Ag(NH_3)_2^+][Cl^-]}{[NH_4OH]^2} = \dfrac{(s)(s)}{(1\,M)^2} = 8.46\times10^{-7}$; $s = \sqrt{8.46\times10^{-7}}\ M = 9.2\times10^{-4}\ M$

(iii) Subtracting the given reactions, we get

$$2NH_3 + 2H_2O \rightarrow 2NH_4OH \qquad K^\circ = \frac{2.79\times10^{-3}}{8.46\times10^{-7}} = 3298$$

For $NH_3 + H_2O \rightarrow NH_4OH$, $\qquad K^\circ = \sqrt{3298} = 57.43$

2. (i) $\Delta_r H^\circ = 2\Delta_f H^\circ(N_2O_5, g) - 4\Delta_f H^\circ(NO_2, g) = (2\times11.3 - 4\times33.2)\ kJ\ mol^{-1} = -110.2\ kJ\ mol^{-1}$

(ii) Since the reaction is exothermic, the reaction will proceed to left side on increasing temperature.

(iii) Since ΔH° = – ve and $\Delta\nu_g = -3$, the yield of N_2O_5 will increase on increasing temperature and high pressure. At high pressure, the equilibrium will shift in a direction of lesser gaseous molecules as this direction will tend to decrease pressure.

3. (i) $\Delta_r G^\circ = 2\Delta_r G^\circ(N_2O_5, g) - 4\Delta_r G^\circ(NO_2, g) = (2\times115.1 - 4\times51.3)\ kJ\ mol^{-1} = 25.0\ kJ\ mol^{-1}$

(ii) $K_p^\circ = \text{antilog}\left(-\dfrac{\Delta G^\circ}{2.303\,RT}\right) = \text{antilog}\left(-\dfrac{25\times10^3}{2.303\times8.314\times298}\right) = \text{antilog}\ (-4.38) = 4.15\times10^{-5}$

(iii) $K_c^\circ = K_p^\circ\,(RT)^{-\Delta\nu_g} = (4.15\times10^{-5})\,(0.082\times298)^3 = 0.61$

4. (i) $\Delta_r H^\circ = 2\Delta_f H^\circ(SO_2, g) - 2\Delta_f H^\circ(SO_3, g) = [2\,(-296.8) - 2(-395.7)]\ kJ\ mol^{-1} = 197.8\ kJ\ mol^{-1}$

(ii) Since the reaction is endothermic, increasing temperature will cause the reaction to shift towards right side.

(iii) Since ΔH° = + ve and $\Delta\nu_g$ = + 1, the decomposition of SO_3 will be favoured on increasing temperature and decreasing pressure.

5. (i) $\Delta_r G^\circ = 2\Delta_f G^\circ(SO_2, g) - 2\Delta_f G^\circ(SO_3, g) = [2\,(-300.2) - 2\,(-371.1)]\ kJ\ mol^{-1} = 141.8\ kJ\ mol^{-1}$

(ii) $K_p^\circ = \text{antilog}\left(-\dfrac{\Delta G^\circ}{2.303\,RT}\right) = \text{antilog}\left(-\dfrac{141.8\times10^3}{2.303\times8.314\times298}\right) = 1.41\times10^{-25}$

(iii) $K_c^\circ = K_p^\circ\,(RT)^{-\Delta\nu_g} = (1.41\times10^{-25})\,(0.082\times298)^{-1} = 5.77\times10^{-27}$

6. (i) We have

$$\underset{n(1-\alpha)}{PCl_5(g)} \rightleftharpoons \underset{n\alpha}{PCl_3(g)} + \underset{n\alpha,}{Cl_2(g)} \qquad \text{Total amount} = n(1+\alpha)$$

From the given T, p and V, we get

$$n' = \frac{pV}{RT} = \frac{(100\,kPa)(2.08\,dm^3)}{(8.314\,kPa\,dm^3\,K^{-1}\,mol^{-1})(500\,K)} = 0.05\ mol$$

Hence $\qquad n(1+\alpha) = 0.05 \qquad$ or $\qquad \alpha = \dfrac{0.05\ mol}{n} - 1 = \dfrac{0.05}{0.03} - 1 = 0.667$

(ii) $x_{PCl_5} = \dfrac{1-\alpha}{1+\alpha}\,p$; $\qquad p_{PCl_3} = p_{Cl_2} = \dfrac{\alpha}{1+\alpha}\,p$

$$K_p = \frac{p_{PCl_3}\,p_{Cl_2}}{p_{PCl_5}} = \frac{\alpha^2 p}{1-\alpha^2} = \frac{(2/3)^2(100\,kPa)}{1-(2/3)^2} = 80\ kPa$$

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Hence, $$K_p = \frac{p(PCl_3)\cdot p(Cl_2)}{p(PCl_5)} = \frac{(0.41\,atm)^2}{0.82\,atm} = 0.205\ atm$$

3. The equilibrium constant of the reaction $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$ at 100 °C is 50. If a one-litre flask containing one mole of A_2 is connected to a two-litre flask containing two moles of B_2, what amount of AB will be formed at 373 K? (1985)

Solution We have

	$A_2(g)$	+	$B_2(g)$	$\rightleftharpoons$	$2AB(g)$
$t = 0$	1 mol		2 mol		
t_{eq}	1 mol − x		2 mol − x		$2x$

Since for the given reaction, $\Delta\nu_g = 0$, we will have

$$K_p = K_n = \frac{n_{AB}^2}{n_{A_2} n_{B_2}} = \frac{(2x)^2}{(1\,mol - x)(2\,mol - x)} = 50$$

or $46\,x^2 - 50\,(3\ mol)\,x + 100\ mol^2 = 0$ which gives $x = 0.934$ mol

Hence, $n(AB) = 2x = 1.868$ mol.

4. At a certain temperature, equilibrium constant (K_c) is 16 for the reaction

$$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$$

If we take one mole of each of all the four gases in a one litre container, what would be the equilibrium concentrations of NO and NO_2? (1987)

Solution We have

	$SO_2(g)$	+	$NO_2(g)$	$\rightleftharpoons$	$SO_3(g)$	+	$NO(g)$
$t = 0$	1 mol		1 mol		1 mol		1 mol
t_{eq}	1 mol − x		1 mol − x		1 mol + x		1 mol + x

Hence, $$K_c = \frac{[SO_3][NO]}{[SO_2][NO_2]} = \frac{\{(1\,mol + x)/1\,L\}^2}{\{(1\,mol - x)/1\,L\}^2} = 16$$

or $$\frac{1\,mol + x}{1\,mol - x} = 4 \quad \text{or} \quad x = \frac{3}{5}\ mol = 0.6\ mol$$

Hence, $[NO_2] = 0.4\ mol\ L^{-1}$ and $[NO] = 1.6\ mol\ L^{-1}$.

5. N_2O_4 is 25% dissociated at 37 °C and 1 atm pressure. Calculate (i) K_p and (ii) the precentage dissociation at 0.1 atm and 37 °C. (1988)

Solution If α is the degree of dissociation of N_2O_4, we will have

	N_2O_4	$\rightleftharpoons$	$2\ NO_2$
$t = 0$	n		
t_{eq}	$n(1 - \alpha)$		$n(2\alpha)$

Total amount of gases = $n\ (1 + \alpha)$

Now $$p_{N_2O_4} = \frac{1-\alpha}{1+\alpha}\,p \quad \text{and} \quad p_{NO_2} = \frac{2\alpha}{1+\alpha}\,p$$

and $$K_p = \frac{(p_{NO_2})^2}{p_{N_2O_4}} = \frac{[2\alpha\ p/(1+\alpha)]^2}{(1-\alpha)\ p/(1+\alpha)} = \frac{4\alpha^2}{1-\alpha^2}\,p$$

It is given that when $p = 1$ atm, $\alpha = 0.25$. Hence,

$$K_p = \frac{4(0.25)^2}{1-(0.25)^2}\ (1\ atm) = 0.267\ atm$$

Now when $p = 0.1$ atm, we will have

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from the reaction $NO(g) + \frac{1}{2} Br_2(g) \rightleftharpoons NOBr(g)$ $K_c'' = 1.4$

Hence, K_c of the new reaction would be

$$K_c = \frac{K_c''}{\sqrt{K_c'}} = \frac{1.4}{\sqrt{2.4 \times 10^{30}}} = 9.04 \times 10^{-16}.$$

15. For the reaction $NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$ show that the degree of dissociation of NH_3 is given as

$$\alpha = \left(1 + \frac{3\sqrt{3}}{4} \frac{p}{K_p}\right)^{-1/2}$$

where p is the equilibrium pressure. If K_p of the above reaction is 78.1 atm at 400 °C, determine the value of K_c.

Solution Let α be the degree of dissociation of $NH_3(g)$. We will have

	$NH_3(g)$	$\rightleftharpoons$	$\frac{1}{2}N_2(g)$	+	$\frac{3}{2}H_2(g)$
$t = 0$	n				
t_{eq}	$n(1 - \alpha)$		$n\alpha/2$		$n(3\alpha/2)$

Total amount of gases $= n(1 + \alpha)$

Now Partial pressure of $NH_3 = \frac{1-\alpha}{1+\alpha} p$; Partial pressure of $N_2 = \frac{\alpha/2}{1+\alpha} p$

Partial pressure of $H_2 = \frac{(3/2)\alpha}{1+\alpha} p$

Hence, $$K_p = \frac{(p_{N_2})^{1/2} (p_{H_2})^{3/2}}{p_{NH_3}} = \frac{\left(\frac{\alpha/2}{1+\alpha} p\right)^{1/2} \left(\frac{3\alpha/2}{1+\alpha} p\right)^{3/2}}{\left(\frac{1-\alpha}{1+\alpha} p\right)} = \left(\frac{3\sqrt{3}}{4} p\right)\left(\frac{\alpha^2}{1-\alpha^2}\right)$$

or $$4 (1 - \alpha^2) K_p - 3\sqrt{3}\ \alpha^2 p = 0 \quad \text{or} \quad \alpha^2 (4 K_p + 3\sqrt{3}\ p) = 4 K_p$$

or $$\alpha = \left(\frac{4K_p}{4K_p + 3\sqrt{3}\ p}\right)^{1/2} = \left(\frac{1}{1 + 3\sqrt{3}\ p/4K_p}\right)^{1/2} = \left(1 + \frac{3\sqrt{3}\, p}{4K_p}\right)^{-1/2}$$

Now for the equilibrium reaction, $\Delta\nu_g = +1$. Hence using the expression $K_p = K_c(RT)^{\Delta\nu_g}$, we get

$$K_c = K_p(RT)^{-\Delta\nu_g} = (78.1 \text{ atm}) \{(0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}) (673 \text{ K})\}^{-} = 1.413 \text{ mol L}^{-1}.$$

16. H_2S dissociates according to the equation $2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$ If α is the degree of dissociation of H_2S, show that K_p of the reaction is given as $K_p = \frac{\alpha^3 p}{2(1-\alpha)^2 (1+\alpha/2)}$

At 1125 °C, the value of the α is found to be 0.31 when the equilibrium pressure is 1 atm. Determine the values of K_p and K_c.

Solution We have

$$2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$$

$n(1 - \alpha)$ $n\alpha$ $n(\alpha/2)$; Total amount of gases $= n(1 + \alpha/2)$

Hence, $$p_{H_2S} = \frac{1-\alpha}{1+\alpha/2} p; \quad p_{H_2} = \frac{\alpha}{1+\alpha/2} p; \quad p_{S_2} = \frac{\alpha/2}{1+\alpha/2} p$$

Thus, $$K_p = \frac{(p_{H_2})^2 (p_{S_2})}{(p_{H_2S})^2} = \frac{\left(\frac{\alpha}{1+\alpha/2} p\right)^2 \left(\frac{\alpha/2}{1+\alpha/2} p\right)}{\left(\frac{1-\alpha}{1+\alpha/2} p\right)^2} = \frac{\alpha^3 p}{2(1-\alpha)^2 (1+\alpha/2)}$$

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23. The equilibrium constant for the reaction $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ is 0.3 atm at 1000 K. One mole of SO_2 and two moles of O_2 are placed in a vessel that is maintained at a pressure of 4 atm. How much SO_3 is present at equilibrium?

Solution We have

	$2SO_3(g)$	$\rightleftharpoons$	$2SO_2(g)$	+	$O_2(g)$
$t = 0$	0		1 mol		2 mol
t_{eq}	$2x$		1 mol $- 2x$		2 mol $- x$

Total amount of gases at equilibrium $= 2x + (1 \text{ mol} - 2x) + (2 \text{ mol} - x) = 3 \text{ mol} - x$

Now $$p_{SO_3} = \frac{2x}{3\,\text{mol} - x} P; \quad p_{SO_2} = \frac{1\,\text{mol} - 2x}{3\,\text{mol} - x} P; \quad p_{O_2} = \frac{2\,\text{mol} - x}{3\,\text{mol} - x} P$$

$$K_p = \frac{p^2_{SO_3}\, p_{O_2}}{p^2_{SO_3}} = \frac{(1\,\text{mol} - 2x)^2\,(2\,\text{mol} - x)\,P}{(2x)^2\,(3\,\text{mol} - x)}$$

At $P = 4$ atm, we get $$\left(\frac{1\,\text{mol} - 2x}{x}\right)^2 = \frac{0.3\,(3\,\text{mol} - x)}{(2\,\text{mol} - x)} \qquad (1)$$

To start with, we may assume $x \ll 2$ mol. With this, Eq. (1) becomes

$$\left(\frac{1\,\text{mol} - 2x}{x}\right)^2 = \frac{0.3 \times 3}{2} \quad \text{or} \quad \frac{1\,\text{mol} - 2x}{x} = \sqrt{0.45} = 0.671 \quad \text{or} \quad x = \frac{1\,\text{mol}}{2.671} = 0.374 \text{ mol}$$

Substituting this value of x in the right hand side of Eq. (1), we get

$$\left(\frac{1\,\text{mol} - 2x}{x}\right)^2 = \frac{0.3 \times 2.626}{1.626} = 0.484\,5 \quad \text{or} \quad \frac{1\,\text{mol} - 2x}{x} = 0.696 \quad \text{or} \quad x = \frac{1\,\text{mol}}{2.696} = 0.371 \text{ mol}$$

Repeating again with this new value of x, we again get $x = 0.371$ mol.

Hence, the concentration of SO_3 at equilibrium is 2×0.371 mol $= 0.742$ mol.

24. A sample of air consisting of N_2 and O_2 was heated to 2500 K until the equilibrium

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

was established with an equilibrium constant $K_c = 2.1 \times 10^{-3}$. At equilibrium, the mole % of NO was 1.8. Estimate the initial composition of air in mole fractions of N_2 and O_2. (1997)

Solution Let there be 100 mol of the three gases at equilibrium. We will have

$$\underbrace{N_2(g) + O_2(g)}_{98.2\text{ mol}} \rightleftharpoons \underbrace{2NO(g)}_{1.8\text{ mol}}$$

Let x be the amount of N_2 in the mixture. Then

$N_2(g)$	+	$O_2(g)$	$\rightleftharpoons$	$2NO(g)$
x		98.2 mol $- x$		1.8 mol

Using the equilibrium constant, we get

$$\frac{[NO]^2}{[N_2][O_2]} = 2.1 \times 10^{-3} \qquad \text{i.e.} \qquad \frac{(1.8\text{ mol})^2}{x(98.2\text{ mol} - x)} = 2.1 \times 10^{-3}$$

Solving for x, we get $x = 78.56$ mol

In the original air sample. We will have

Amount of $N_2 = (78.56 + 0.9)$ mol $= 79.46$ mol
Amount of $O_2 = (98.2 - 78.56 + 0.9)$ mol $= 20.54$ mol
Mole fraction of $N_2 = 0.79$ and Mole fraction of $O_2 = 0.21$

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22. If the decomposition reaction $4HNO_3(g) \rightleftharpoons 4NO_2(g) + 2H_2O(g) + O_2(g)$ is started with pure HNO_3, then show that

$$K_p = \frac{1024\,(p_{O_2})^7}{(p - 7p_{O_2})^4}$$

where p is the total pressure at equilibrium.

23. A 2-L flask maintained at 700 K contains 0.1 mol of CO and a catalyst for the reaction

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

Hydrogen is introduced until the equilibrium total pressure is 7 atm at which point 0.06 mol of methanol is formed. Calculate K_p° of the reaction. What would be the final pressure if the same amounts of CO and H_2 are used, but no catalyst is present such that no reaction occurs.

24. It is required to pass CO and H_2O vapours at 10 atm and 5 atm, respectively, into a reaction chamber at 973 K and to withdraw CO_2 and H_2 at partial pressures of 15 atm each. Is this theoretically possible? K_p° for the reaction $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ is 0.71.

25. NOCl(g) was introduced in a 1 L vessel and heated so as to attain equilibrium

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

At equilibrium, [NOCl] = 0.1 M. Now more of NOCl is introduced till a new equilibrium is reached such that [NOCl] = 0.8 M. How are the concentrations of NO and Cl_2 get affected?

ANSWERS

1. $50.08\ atm^{-1}$
2. 0.0582 atm
3. 0.245
4. 25 L
5. No, forward, 0.079 mol O_2, 0.236 mol SO_2 and 0.811 mol SO_3
6. $p(NO_2) = 0.64$ atm and $p(N_2O_4) = 0.095$ atm
7. 2.026×10^3 atm
8. 3.7×10^{-6}
9. $5.76\ g\ dm^{-3}$
10. 34.95 mmHg
11. (a) 0.335, (b) 0.271
12. 0.341 mol
13. 23.1 bar
14. (a) 0.672 mol, (b) 0.802 mol
15. No, right direction
16. 0.115, $3.08 \times 10^{-3}\ kPa^{-1}$, 72.6
17. 1.602
18. 0.109,0.1
19. 0.023
20. 0.14
21. 0.01445, 69.22, 0.1202
23. 0.088, 10.44 atm
24. No
25. The concentrations of each of NO and Cl_2 becomes four times.

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For a salt formed from a weak acid and a weak base, such as ammonium acetate, we have

$$NH_4^+ + Ac^- + H_2O \rightleftharpoons NH_4OH + HAc$$

$$K_h = \frac{[NH_4\,OH][HAc]}{[NH_4^+][Ac^-]} = \frac{[NH_4OH]}{[NH_4^+][OH^-]}\,\frac{[HAc]}{[Ac^-][H^+]}\,[H^+][OH^-] = \frac{K_W}{K_a K_b}$$

To determine the pH of such a solution, we set $[NH_4OH] = [HAc]$ and $[NH_4^+] = [Ac^-]$

Thus get $\frac{[HAc]^2}{[Ac^-]^2} = \frac{K_w}{K_a K_b}$ i.e. $\frac{[H^+]^2}{K_a^2} = \frac{K_w}{K_a K_b}$ or $[H^+] = \sqrt{\frac{K_w K_a}{K_b}}$

or $pH = \frac{1}{2}\,(pK_w^\circ + pK_a^\circ - pK_b^\circ)$

Buffer Solutions A solution which resists the change in its pH value when a small amount of acid or alkali is added to it is known as buffer solution. Such a solution can be prepared by mixing weak acid with the salt of its conjugate base (acidic buffer solution) or mixing weak base with the salt of its conjugate acid (alkaline buffer solution). A solution of salt of a weak acid and a weak base, such as ammonium acetate, also has buffer characteristics.

The pH of a buffer solution containing weak acid and salt of its conjugate base is given by the expression

$$pH = pK_a^\circ + \log\frac{[salt]}{[acid]}$$

For a buffer solution containing a weak base and salt of its conjugate acid, the expression is

$$pOH = pK_b^\circ + \log\frac{[salt]}{[base]}$$

The above expressions of pH and pOH are known as Henderson's equations.

Straight Objective Type

pH of a Solution

1. At 25 °C the pH of a 10^{-8} molar solution of HCl in water is
(a) 8 (b) −8 (c) between 7 and 8 (d) between 6 and 7 (1981)

2. At 90 °C pure water has $[H_3O^+] = 10^{-6}$ mol litre^{-1}. The value of K_w° at 90 °C is
(a) 10^{-6} (b) 10^{-12} (c) 10^{-14} (d) 10^{-8} (1981)

3. Which of the following solutions will have pH close to 1.0?
(a) 100 mL of (M/10) HCl + 100 mL of (M/10) NaOH
(b) 55 mL of (M/10) HCl + 45 mL of (M/10) NaOH
(c) 10 mL of (M/10) HCl + 90 mL of (M/10) NaOH
(d) 75 mL of (M/5) HCl + 25 mL of (M/5) NaOH (1992)

4. The pH of pure water is 6.5. Its temperature is
(a) more than 25 °C (b) less than 25 °C (c) equal to 25 °C (d) zero kelvin

5. The equivalence point in a titration of 40.0 mL of a solution of a weak monoprotic acid occurs when 35.0 mL of a 0.10 M NaOH solution has been added. The pH of the solution is 5.75 after the addition of 20.0 mL of NaOH solution. The pK_a of the acid is about
(a) 4.6 (b) 5.6 (c) 6.0 (d) 6.2

6. The pH of the solution when 200 mL of an aqueous solution of HCl (pH = 2.0) is mixed with 300 mL of an aqueous solution of NaOH (pH = 12.0) will be about
(a) 9.3 (b) 10.3 (c) 11.3 (d) 11.8

7. The ionic product of water at 100 °C is 49 times that at 25 °C. The pH of pure water at 100 °C is about
(a) 5.15 (b) 5.75 (c) 7.15 (d) 6.15

8. On adding 10^{-3} mol of NaOH to 1.0 dm^3 of water at 25°C, the pH of water
(a) increases about by 2 (b) increases about by 4
(c) decreases about by 2 (d) decreases about by 4

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Concept of Solubility Product

59. The precipitate of CaF_2 ($K_{sp}^{o} = 1.7 \times 10^{-10}$)is obtained when equal volumes of the following are mixed

(a) 10^{-4} M Ca^{2+} + 10^{-4}M F^- (b) 10^{-2} M Ca^{2+} + 10^{-3} M F^-

(c) 10^{-5} Ca^{2+} + 10^{-3} M F^- (d) 10^{-3} M Ca^{2+} + 10^{-5} M F^- (1982)

60. The ion that cannot be precipitated by both HCl and H_2S is

(a) Pb^{2+} (b) Cu^{2+} (c) Ag^+ (d) Sn^{2+} (1982)

61. Which one among the following pairs of ions cannot be separated by H_2S in dilute hydrochloric acid?

(a) Bi^{3+}, Sn^{4+} (b) Al^{3+}, Hg^{2+} (c) Zn^{2+}, Cu^{2+} (d) Ni^{2+}, Cu^{2+} (1986)

62. When equal volumes of the following solutions are mixed precipitation of AgCl ($K_{sp}^{o} = 1.8 \times 10^{-10}$) 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^- (1988)

63. Amongst the following hydroxides, the one which has the lowest value of K_{sp} at ordinary temperatures (about 25 °C) is

(a) $Mg(OH)_2$ (b) $Ca(OH)_2$ (c) $Ba(OH)_2$ (d) $Be(OH)_2$ (1990)

64. The reagents, NH_4Cl and aqueous NH_3 will precipitate

(a) Ca^{2+} (b) Al^{3+} (c) Bi^{3+} (d) Mg^{2+}

(e) Zn^{2+} (1991)

65. The solubility product of magnesium phosphate is given as

(a) $K_{sp} = [Mg^{2+}]\ [PO_4^{3-}]$ (b) $K_{sp} = [Mg^{2+}]\ [PO_4^{3-}]^3$

(c) $K_{sp} = [Mg^{2+}]^3\ [PO_4^{3-}]^2$ (d) $K_{sp} = \dfrac{[Mg^{2+}][PO_4^{3-}]}{[Mg_3(PO_4)_2]}$

66. If s_0, s_1, s_2 and s_3 are the solubilities of AgCl in water, 0.01 M $CaCl_2$, 0.01 M NaCl and 0.05 M $AgNO_3$ solutions, respectively, then

(a) $s_0 > s_1 > s_2 > s_3$ (b) $s_0 > s_2 > s_1 > s_3$ (c) $s_0 > s_2 > s_3 > s_1$ (d) $s_0 > s_1 = s_2 > s_3$

67. A solution contains 0.05 M each of NaCl and Na_2CrO_4. Solid $AgNO_3$ is gradually added to it. Which of the following facts is true? Given: $K_{sp}(AgCl) = 1.7 \times 10^{-10}$ M^2 and $K_{sp}(Ag_2CrO_4) = 1.9 \times 10^{-12}$ M^3.

(a) Cl^- ions are precipitated first

(b) CrO_4^{2-} ions are precipitated first

(c) Both Cl^- and CrO_4^{2-} ions are precipitated together

(d) The second ion starts precipitating when half of the first ion is precipitated

68. The pH of $Mg(OH)_2$ is 10.45 at 25 °C. The solubility product of magnesium hydroxide would be

(a) 2.24×10^{-11} M^3 (b) 3.36×10^{-11} M^3 (c) 1.12×10^{-11} M^3 (d) 5.60×10^{-12} M^3

69. The solubility product of A_2X_3 is 1.08×10^{-23}. Its solubility will be

(a) 1.0×10^{-3} M (b) 1.0×10^{-4} M (c) 1.0×10^{-5} M (d) 1.0×10^{-6} M

70. A solution is saturated with respect to $SrCO_3$ and SrF_2. The $[CO_3^{2-}]$ was found to be 1.2×10^{-3} M. The concentration of F^- in the solution would be

(a) 1.3×10^{-3} M (b) 2.6×10^{-2} M (c) 3.7×10^{-2} M (d) 5.8×10^{-7} M

(Given : $K_{sp}(SrCO_3) = 7.0 \times 10^{-10}$ M^2, $K_{sp}(SrF_2) = 7.9 \times 10^{-10}$ M^3.)

71. The maximum pH of a solution which is 0.10 M in Mg^{2+} from which $Mg(OH)_2$ is not precipitated is

(a) 4.96 (b) 6.96 (c) 7.54 (d) 9.04

(Given: $K_{sp}(Mg(OH)_2) = 1.2 \times 10^{-11}$ M^3.)

72. The solubility of sparingly soluble electrolyte M_mA_a in water is given by the expression

(a) $s = \left(\dfrac{K_{sp}}{m^m a^a}\right)^{m+a}$ (b) $s = \left(\dfrac{K_{sp}}{m^m\ a^a}\right)^{1/(m+a)}$ (c) $s = \left(\dfrac{K_{sp}}{m^a\ a^m}\right)^{m+a}$ (d) $s = \left(\dfrac{K_{sp}}{m^a\ a^m}\right)^{1/(m+a)}$

73. In a saturated solution of calcium phosphate, the concentration of PO_4^{3-} ions is 3.3×10^{-7} M. The K_{sp} of $Ca_3(PO_4)_2$ will be

(a) 1.32×10^{-31} (b) 1.32×10^{-32} (c) 1.32×10^{-33} (d) 1.32×10^{-35}

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115. Which of the following species is not a Lewis acid?
(a) BF_3 (b) Cu^{2+} (c) NH_3 (d) $AlCl_3$

116. In aqueous solution, which of the following orders regarding acid strength is correct?
(a) $HCN < CH_3COOH < HCl < HClO_4$ (b) $HCN < CH_3COOH < HClO_4 < HCl$
(c) $HCN < HClO_4 < HCl < CH_3COOH$ (d) $HClO_4 < CH_3COOH < HCl < HCN$

117. In aqueous solution, which of the following orders regarding base strength is correct?
(a) $CH_3COO^- < HS^- < NH_3 < CO_3^{2-}$ (b) $CH_3COO^- > HS^- > NH_3 > CO_3^{2-}$
(c) $CH_3COO^- > HS^- > NH_3 < CO_3^{2-}$ (d) $CH_3COO^- > HS^- > CO_3^{2-} > NH_3$

118. The decreasing base strength of OH^-, NH_2^-, $HC{\equiv}C^-$ and $CH_3CH_2^-$ is
(a) $CH_3CH_2^- > NH_2^- > HC{\equiv}C^- > OH^-$ (b) $HC{\equiv}C^- > CH_3CH_2^- > NH_2^- > OH^-$
(c) $OH^- > NH_2^- > HC{\equiv}C^- > CH_3CH_2^-$ (d) $NH_2^- > HC{\equiv}C^- > OH^- > CH_3CH_2^-$

119. The compound that is not a Lewis acid is
(a) BF_3 (b) $AlCl_3$ (c) $BeCl_2$ (d) $SnCl_4$ (1985)

120. Of the given anions, the strongest Bronsted base is
(a) ClO^- (b) ClO_2^- (c) ClO_3^- (d) ClO_4^- (1981)

Multiple Correct Choice Type

1. Which of the following statement(s) is (are) correct?
(a) The pH of 1.0×10^{-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^o.

2. For pure water at 25°C
(a) $[H_2O] = 55.56$ mol dm^{-3} if density of water is 1 g cm^{-3}.
(b) $K_w = 1.0 \times 10^{-14}$ (mol dm^{-3})^2
(c) degree of dissociation, $\alpha = 1.8 \times 10^{-9}$
(d) ionization constant, $K_{ioniz} = 1.8 \times 10^{-16}$ mol dm^{-3}.

3. Which of the following statements is/are correct for an aqueous solution having pH = 7 at 298 K?
(a) $[H^+] = 10^{-7}$ mol L^{-1}
(b) $[OH^-] = 10^{-7}$ mol L^{-1}
(c) $K_w = 10^{-14}$ (mol L^{-1})^2
(d) The solution becomes alkaline on diluting the solution.

4. Which of the following expressions is/are **not** correct for a solution of sodium acetate in water?
(a) The pH of the solution is given by the expression $pH = pK_w^o + pK_a^o + \log (c/c^o)$
(b) The degree of hydrolysis of acetate ions is given by $\log \alpha = pK_a^o - pK_w^o - \log (c/c^o)$
(c) The pOH of the solution decreases with increase in the concentration of sodium acetate.
(d) The ionization constant of acetate is given by
K_b(acetate) = K_w/K_a (acetic acid).

5. For a solution of ammonium acetate, which of the following expressions is/are correct?
(a) The expression of $[H_3O^+]$ is $[H_3O^+] = \left(\frac{K_w K_h}{K_a}\right)^{1/2}$
(b) The degree of hydrolysis of salt is given by $\alpha = \frac{\sqrt{K_h}}{1+\sqrt{K_h}}$ where $K_h = \frac{K_w}{K_a K_b}$
(c) pH of the solution is given by $pH = pK_a^o + \frac{1}{2} pK_h^o$
(d) pOH of the solution increases with increase in the concentration of ammonium acetate.

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6. A solution is 0.1 M in each of PO_4^{3-}, SO_4^{2-} and Cl^- ions. Solid $AgNO_3$ is added to this solution which causes no change in volume of the solution. Given: K_{sp}° (AgCl) = 1.8×10^{-10}, K_{sp}° (Ag_2SO_4) = 1.21×10^{-5} and K_{sp}° (Ag_3PO_4) = 2.7×10^{-18}.

(i) The sequence of ions precipitated is

(a) Cl^-, PO_4^{3-}, SO_4^{2-} (b) Cl^-, SO_4^{2-}, PO_4^{3-} (c) PO_4^{3-}, Cl^-, SO_4^{2-} (d) PO_4^{3-}, SO_4^{2-}, Cl^-

(ii) The concentrations of first and third ions when the second ion starts precipitated, respectively, are

(a) 0.1 M, 0.1 M (b) 6×10^{-5} M, 0.1 M

(c) 1.64×10^{-8} M, 0.1 M (d) 2.03×10^{-12} M, 1.64×10^{-8} M

(iii) The concentrations of first and second ions when the third starts precipitated, respectively, are

(a) 0.1 M, 0.01 M (b) 6×10^{-5} M, 0.1 M

(c) 1.64×10^{-8} M, 2.03×10^{-12} M (d) 2.03×10^{-12} M, 1.64×10^{-8} M

Assertion and Reason Type

Given below are the two statements. Identify the correct choice from the following.

(a) Statement –1 is correct and Statement –2 is correct and is the correct explanation of the statement 1.
(b) Statement –1 is correct and Statement –2 is correct but not the correct explantation of the statement –1.
(c) Statement –1 is correct and Statement –2 is incorrect.
(d) Statement –1 is incorrect and Statement –2 is correct.

	Statement–1	Statement–2
1.	The solubility of $Zn(OH)_2$ is enhanced in acidic as well as in basic medium as compared to water.	$Zn(OH)_2$ is an amphoteric hydroxide.
2.	pH of water decreases with increasing temperature.	The extent of ionization of water increases with increase in temperature giving more of H^+ ions.
3.	Silver chloride is soluble in ammonium hydroxide.	Silver chloride in NH_4OH exists as Ag^+ and Cl^- ions.
4.	In acid-base titrations, the use of indicator helps locating the end point of the titration.	The pH transition range of the indicator coincides with the steep portion of the titration curve.
5.	The pH of sulphuric acid solution can be computed by considering the ionization $H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$.	Sulphuric acid ionizes in stepwise manner.
6.	The hydrolysis of a salt formed from a weak acid and a weak base exhibits extensive hydrolysis.	The hydrolysis of cation drags the hydrolysis of anion and vice versa.
7.	Oxalic acid ($K_{a_1}^{\circ} = 5.9 \times 10^{-2}$ and $K_{a_2}^{\circ} = 6.4 \times 10^{-5}$) exhibits stepwise neutralization with NaOH.	A dibasic acid exhibits stepwise dissociation provided $K_{a1}^{\circ}/K_{a_2}^{\circ} \geq 10^2$
8.	The pH of water decreases with increase in temperature.	The ionization of water is temperature dependent.
9.	A solution of ammonium aceate has characteristics of a buffer solution.	The ions furnished by ammonium acetate are strong conjugate acid and base and have tendencies to react with OH^- and H^+, respectively.
10.	The end point of the titration between weak acid and weak base cannot be determined by using a suitable indicator.	The pH of the solution at the end point does not have a definite value.
11.	Silver chromate is more soluble in water as compared to silver chloride.	The solubility product of silver chromate is larger than that of silver chloride.

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22. The corresponding acids are HI, HCl, HNO_2 and HCN. Their acid strength follows the order HI > HCl > HNO_2 > HCN. Hence, their conjugate base follows the reverse order.

23. The resultant solution will be 0.1 molar sodium acetate. The acetate ions undergo hydrolysis reaction:
$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$

24. Sodium acetate solution is alkaline and thus has maximum pH.

25. Smaller ionization constant with larger concentration of acid involves lesser dissociation.

26. At 100 °C, more of water will ionize and $[H^+]$ will be more that 10^{-7} M and K_w will be more that 10^{-14} M^2 and thus pK_w° will be less than fourteen.

27. pOH 10 $\Rightarrow$ pH = 4 $\Rightarrow$ $[H^+] = 10^{-4}$ M. In 1 mL of solution, $n(H^+) = 10^{-7}$ mol.

$$N = (10^{-7}\ \text{mol})\ (6.023 \times 10^{23}\ \text{mol}^{-1}) = 6.023 \times 10^{16}$$

28. The concentration of H^+ in 200 mL acid solution = 10^{-2} M

The concentration of H^+ in 800 mL acid solution = 10^{-3} M

$$\text{Total amount of } H^+ = \left(\frac{10^{-2}\text{mol}}{1000\ \text{mL}}\right)(200\ \text{mL}) + \left(\frac{10^{-3}\text{mol}}{1000\ \text{mL}}\right)(800\ \text{mL}) = (2 \times 10^{-3}\ \text{mol} + 8 \times 10^{-4}\ \text{mol})$$

$$= 2.8 \times 10^{-3}\ \text{mol}$$

Total volume of solution = 200 mL + 800 mL = 1000 mL = 1 L

$$\text{Concentration of } H^+ \text{ in solution} = \frac{2.8 \times 10^{-3}\ \text{mol}}{1\ \text{L}} = 2.8 \times 10^{-3}\ \text{M}$$

pH of solution = $-\log (2.8 \times 10^{-3}) = 2.55$

29. The pH of stomach is lesser than pK_a° while that of small intestine is greater than pK_a°. Hence, aspirin is unionized in stomach while in small intestine it is present in the ionized form.

30. The expression of Ostwald dilution law is $\alpha = \sqrt{K_a/c}$.

31. We have

$$A_x B_y \rightleftharpoons xA^{y+} + yB^{x-}$$

$$c(1-\alpha) \qquad c(x\alpha) \quad c(y\alpha)$$

$$K_{eq} = \frac{[A^{y+}]^x [B^{x-}]^y}{[A_xB_y]} = \frac{(cx\alpha)^x (cy\alpha)^y}{c(1-\alpha)}$$

For a concentrated solution $K_{eq} = c^{x+y-1} x^x y^y \alpha^{x+y}$

Hence $\alpha = [K_{eq}/c^{x+y-1} x^x y^y]^{1/(x+y)}$

32. We have

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

$$K_{a1} K_{a2} = \frac{[H^+]^2 [S^{2-}]}{[H_2S]} \quad \Rightarrow \quad [S^{2-}] = \frac{K_{a1}K_{a2}[H_2S]}{[H^+]^2}$$

$$[S^{2-}] = \frac{(1.1 \times 10^{-21}\ \text{M}^3)(0.1\ \text{M})}{(0.1\ \text{M})^2} = 1.1 \times 10^{-20}\ \text{M}$$

$$\text{Number of } S^{2-} = (1.1 \times 10^{-20}\ \text{mol})\ (6.023 \times 10^{23}\ \text{mol}^{-1}) = 6.625 \times 10^3$$

33. The addition of sodium acetate to acetic acid solution suppresses the ionization of acid. Due to decrease in the concentration of H^+, its pH will increase.

34. The addition of NH_4Cl in water makes the solution acidic. Due to two sources of H^+, the pH of the solution will show a slight decrease.

35. The solution will contain 0.1 M HAc and 0.4 M NaAc. The pH of solution will be

$$pH = pK_a^\circ + \log \frac{[\text{salt}]}{[\text{acid}]} = -\log (1.8 \times 10^{-5}) + \log \left(\frac{0.4}{0.1}\right) = 4.75 + 0.60 = 5.35$$

36. The solution will contain 0.1 M NH_4OH and 0.4 M NH_4Cl. Its pH will be 14 – 5.35 = 8.65, where 5.35 is pOH of the solution which can be determined using Henderson's equation. See Q.35.

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69. We have

$$K_{sp} = [A^{3+}]^2\,[X^{2-}]^3 = (2x)^2\,(3x)^3 = 108\,x^5$$

$$x = \left(\frac{K_{sp}}{108}\right)^{1/5} = \left(\frac{1.08\times10^{-23}\ M^5}{108}\right)^{1/5} = 1\times10^{-5}\ M$$

70. We have

$$[Sr^{2+}] = \frac{K_{sp}(SrCO_3)}{[CO_3^{2-}]} = \frac{7.0\times10^{-10}\ M^2}{1.2\times10^{-3}\ M} = 5.8\times10^{-7}\ M$$

$$[F^-] = \left[\frac{K_{sp}(SrF_2)}{Sr^{2+}}\right]^{1/2} = \left(\frac{7.9\times10^{-10}\ M^3}{5.8\times10^{-7}\ M}\right)^{1/2} = (1.36\times10^{-3}\ M^2)^{1/2} = 3.7\times10^{-2}\ M$$

71. The concentration of OH^- required to precipitate $Mg(OH)_2$ is

$$[OH^-] = \left(\frac{K_{sp}}{[Mg^{2+}]}\right)^{1/2} = \left(\frac{1.2\times10^{-11}\ M^3}{0.10\ M}\right)^{1/2} = 1.1\times10^{-5}\ M$$

$$pOH = -\log(1.1\times10^{-5}) = 4.96 \quad \text{and} \quad pH = 14 - 4.96 = 9.04$$

72. We have

$$M_mA_a \rightleftharpoons \underset{(ms)}{mM^{a+}} + \underset{(as)}{aA^{m-}}$$

$$K_{sp} = (ms)^m\,(as)^a; \qquad s = \left(\frac{K_{sp}}{m^m a^a}\right)^{1/(m+a)}$$

73. We have

$$Ca_3(PO_4)_2 \rightleftharpoons \underset{3s}{3Ca^{2+}} + \underset{2s}{2PO_4^{3-}}$$

$$K_{sp} = [Ca^{2+}]^3\,[PO_4^{3-}]^2 = \left(\frac{3}{2}\times3.3\times10^{-7}\ M\right)^3\,(3.3\times10^{-7}\ M)^2 = 1.32\times10^{-32}\ M^5$$

74. We have

$$Hg_2Cl_2 \rightleftharpoons \underset{s}{Hg_2^{2+}} + \underset{2s}{2Cl}$$

$$K_{sp} = [Hg_2^{2+}]\,[Cl^-]^2 = (s)\,(2s)^2 = 4s^3; \qquad s = (K_{sp}/4)^{1/3}$$

75. We have

$$A_2X_3 \rightleftharpoons \underset{2y}{2A^{3+}} + \underset{3y}{3X^{2-}}$$

$$K_{sp} = [A^{3+}]^2\,[X^{2-}]^3 = (2y)^2\,(3y)^3 = 108\,y^5$$

76. From the solubility expression of $MgCO_3$, we find that

$$[CO_3^{2-}] = \left(\frac{K_{sp}(MgCO_3)}{[Mg^{2+}]}\right)^{1/2} = \frac{1.6\times10^{-6}\ M^2}{3.2\times10^{-5}\ M} = 0.05\ M$$

Hence $$[Ag^+] = \left(\frac{K_{sp}(Ag_2CO_3)}{[CO_3^{2+}]}\right)^{1/2} = \left(\frac{8.2\times10^{-12}\ M^3}{0.05\ M}\right)^{1/2} = 1.28\times10^{-5}\ M$$

77. If x is the solubility of $Pb(OH)_2$ in water, we will have

$$Pb(OH)_2\ (s) \rightleftharpoons \underset{x}{Pb^{2+}}(aq) + \underset{2x}{2OH^-}(aq); \quad K_{sp} = x\,(2x)^2 = 4x^3$$

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$$\log \{H^+/c^\circ\} = \frac{1}{2} [\log K_w^\circ + \log K_a^\circ - \log (c/c^\circ)]$$

$$pH = \frac{1}{2} [pK_w^\circ + pK_a^\circ + \log (c/c^\circ)]$$

5. (a) The correct expression is $[H^+] = \sqrt{K_w K_a / K_b}$

(b) See Q.56 of straight objective questions

(c) $pH = pK_a^\circ + \frac{1}{2} pK_h^\circ = pK_a + \frac{1}{2} (pK_w^\circ - pK_a^\circ - pK_b^\circ) = \frac{1}{2} (pK_w^\circ + pK_a^\circ - pK_b^\circ)$

(d) See Q. 4.(c)

6. (a) $K_a(HCN) < K_a(CH_3COOH)$. Since $K_h = K_w/K_a$, K_h for CN^- ions is larger than CH_3COO^- ions.

(d) The solution of NH_4CN is alkaline and CN^- undergoes more hydrolysis than NH_4OH.

7. Larger the temperature, larger the ionization of water yielding $[H^+] > 10^{-7}$ mol dm^{-3} and thus pH < 7.

8. (c) $NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$

$c(1 - \alpha)$ $\quad c\alpha \quad c\alpha$

$$K_h = \frac{(c\alpha)(c\alpha)}{c(1-\alpha)} \approx c\alpha^2 \quad \text{or} \quad \alpha = \sqrt{\frac{K_h}{c}} = \sqrt{\frac{K_w}{K_b c}}$$

9. (a) Lewis acid accepts pair of electrons and does not donate them.

(b) This is due to formation of $Na^+AgCl_2^-$.

10. (a) $Zn(OH)_2$ is an amphoteric species. In acidic medium, it exists as Zn^{2+} while in alkaline solution as $Zn(OH)_4^{2-}$.

(b) This is known as levelling effect.

(c) Since all are stronger than H_3O^+.

(d) Only acids stronger than H_3O^+ are levelled in water.

11. (d) Reaction proceeds in a direction favouring weak acids and bases. So, CN^- is also a weaker base than OH^-.

12. (b) The base strength of conjugate bases follows the reverse order of the acid strength. Since HI > HBr > HCl > HF, the correct sequence of base strength would be $I^- < Br^- < Cl^- < F^-$.

(c) The self-ionization of NH_3 is $NH_3 \rightleftharpoons NH_4^+ + NH_2^-$
In NH_3, NH_4^+ is the strongest acid and NH_2^- is the strongest base.

(d) Perchloric acid is stronger acid than sulphuric acid.

Linked Comprehension Type

1. (i) $HA \rightleftharpoons H^+ + A^-$; $K_a = \frac{[H^+][A^-]}{[HA]} = \frac{x^2}{1.0\,M - x}$

$1.0\,M - x$ $\quad x \quad x$

Assuming $x < 1.0$ M, we get

$$\frac{x^2}{1.0\,M} = 1.0 \times 10^{-4}\,M \Rightarrow x = 1.0 \times 10^{-2}\,M \Rightarrow pH = -\log x/M = 2$$

If the pH is doubled, then $[H^+] = 1.0 \times 10^{-4}$ M. Hence

$$\frac{(1.0\times10^{-4}\,M)^2}{c - 1.0\times10^{-4}\,M} = 1.0 \times 10^{-4}\,M \quad \text{i.e.} \quad 1.0 \times 10^{-8}\,M^2 = c(1.0 \times 10^{-4}\,M) - 1.0 \times 10^{-8}\,M^2$$

or $$c = \frac{2.0\times10^{-8}\,M}{1.0\times10^{-4}\,M} = 2.0 \times 10^{-4}\,M$$

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ANNEXURE II

Subjective Problems for Practice

SOLVED PROBLEMS

1. What amount of sodium propanate should be added to one litre of an aqueous solution containing 0.02 mol of propanoic acid to obtain a buffer solution of pH 4.75? What will be the pH if 0.01 mol of hydrogen chloride is dissolved in the above buffer solution? Compare the last pH value with the pH of 0.01 molar HCl solution. Dissociation constant of propanoic acid at 25 °C is 1.34×10^{-5}M. (1981)

Solution Using the expression

$$\text{pH} = \text{p}K_a^\circ + \log \frac{[\text{salt}]}{[\text{acid}]}$$

we get $$4.75 = -\log (1.34 \times 10^{-5}) + \log \frac{[\text{salt}]}{0.02\,\text{M}} \quad \text{which gives} \quad 4.75 = 4.87 + \log \frac{[\text{salt}]}{0.02\,\text{M}}$$

or $$\frac{[\text{salt}]}{0.02\,\text{M}} = 0.76 \quad \text{or} \quad [\text{salt}] = 1.52 \times 10^{-2}\,\text{M}$$

Hence, Amount of sodium propanoate to be added $= 1.52 \times 10^{-2}$ mol

The addition of 0.01 mol of hydrogen chloride convert the equivalent amount of sodium propanoate into propanoic acid. Hence, we will have

$$\text{pH} = 4.87 + \log \frac{(0.0152 - 0.01)\,\text{mol L}^{-1}}{(0.02 + 0.01)\,\text{mol L}^{-1}} = 4.87 + \log (0.173) = 4.87 - 0.76 = 4.11$$

The pH of 0.01 molar HCl solution would be

$$\text{pH} = -\log (0.01) = 2.$$

2. Twenty mL of 0.2 M NaOH is added to 50 mL of 0.2 M acetic acid to give 70 mL of the solution. What is the pH of the solution? Calculate the additional volume of 0.2 M NaOH required to make pH of the solution 4.74. The ionization constant of acetic acid is 1.8×10^{-5}M. (1982)

Solution The addition of NaOH converts equivalent amount of acetic acid into sodium acetate. Hence,

$$\text{Concentration of acetic acid after the addition of sodium hydroxide} = \frac{30}{70} \times 0.2\,\text{M}$$

$$\text{Concentration of sodium acetate after the addition of sodium hydroxide} = \frac{20}{70} \times 0.2\,\text{M}$$

Hence, using the expression $\text{pH} = \text{p}K_a^\circ + \log \frac{[\text{salt}]}{[\text{acid}]}$, we get (1)

$$\text{pH} = -\log (1.8 \times 10^{-5}) + \log \left(\frac{20}{30}\right) = 4.745 - 0.177 = 4.568$$

Let V be the additional volume of 0.2 M NaOH that need to be added to make pH of the solution equal to 4.74. Substituting this value in Eq. (1), we would get

$$4.74 = 4.745 + \log \left(\frac{20\,\text{mL} + V}{30\,\text{mL} - V}\right)$$

or $$\log \frac{20\,\text{mL} + V}{30\,\text{mL} - V} = -0.005 \quad \text{or} \quad \frac{20\,\text{mL} + V}{30\,\text{mL} - V} = 0.9866$$

or $$V = \frac{30\,\text{mL} \times 0.9866 - 20\,\text{mL}}{1.9866} = 4.83\ \text{mL}.$$

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With this, Eq. (5) is simplified to

$$\alpha = 2x \tag{6}$$

Substituting this in Eq. (3), we get

$$\frac{(0.25\,\text{M} - 2x)(z)}{0.05\,M + 2x} = 1.8 \times 10^{-5}\,\text{M}$$

Replacing x in terms of z from Eq. (1), we get

$$\frac{\left(0.25\,\text{M} - \dfrac{2 \times 8.9 \times 10^{-12}\,\text{M}^3}{z^2}\right)(z)}{0.05\,M + 2\left(\dfrac{8.9 \times 10^{-12}\,\text{M}^3}{z^2}\right)} = 1.8 \times 10^{-5}\,\text{M}$$

$$(0.25\ \text{M})\ z^3 - (0.05\ \text{M})\ (1.8 \times 10^{-5}\ \text{M})\ z^2 - (2)\ (8.9 \times 10^{-12}\ \text{M}^3)\ z - 2\ (8.9 \times 10^{-12}\ \text{M}^3)\ (1.8 \times 10^{-5}\ \text{M}) = 0$$

or $$z^3 = (3.6 \times 10^{-6}\ \text{M})z^2 + (7.12 \times 10^{-11}\ \text{M}^2)\ z + 1.28 \times 10^{-15}\ \text{M}^3$$

The above expression may be solved by the method of successive approximation. We may start with $z = 10^{-5}$ M and substitute this in the right hand side of the above expression and then take cube root of this to get new refined value of z. This refined value is again substituted in the right hand side and get the second refined value. This is continued till the two successive values of z agree within the allowed accuracy, say up to two decimals. Carrying out the above approximation, we get

Cycle No.	$[OH^-]$/M
1	1.0×10^{-5}
2	1.33×10^{-5}
3	1.42×10^{-5}
4	1.45×10^{-5}
5	1.45×10^{-5}

Thus, taking $[OH^-] = 1.45 \times 10^{-5}$ M, we get

From Eq. (1) $$[Mg^{2+}] = \frac{8.9 \times 10^{-12}\,\text{M}^3}{(1.45 \times 10^{-5}\,\text{M})^2} = 0.042\,3\ \text{M}$$

From Eq. (2) $$[Al^{3+}] = \frac{6 \times 10^{-32}\,\text{M}^4}{(1.45 \times 10^{-5}\,\text{M})^3} = 1.97 \times 10^{-17}\,\text{M}$$

From the above results, the approximations made in solving the above problem is justified as

$$[Al^{3+}] \ll [Mg^{2+}] \quad \text{and} \quad [OH^-] \ll 2\,[Mg^{2+}]$$

10. What is the pH of a 1.0 M solution of acetic acid? To what volume must one litre of this solution be diluted so that the pH of the resultant solution will be twice the original value. Given : K_a°(acetic acid) = 1.8×10^{-5}. (1990)

Solution We have

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{[H^+]^2}{[CH_3COOH]_0 - [H^+]} \simeq \frac{[H^+]^2}{[CH_3COOH]_0}$$

Hence, $$[H^+] = (K_a\,[CH_3COOH]_0)^{1/2} = (1.8 \times 10^{-5})^{1/2}\ \text{mol L}^{-1} = 4.30 \times 10^{-3}\ \text{mol L}^{-1}$$

$$\text{pH} = -\log\{[H^+]/\text{mol L}^{-1}\} = -\log(4.3 \times 10^{-3}) = 2.37$$

Now the pH of the diluted solution would be $\text{pH} = 2 \times 2.37$

which gives $-\log\{[H^+]/\text{mol L}^{-1}\} = 2 \times 2.37$

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$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+]^2}{[HA]_0 - [H^+]} \simeq \frac{[H^+]^2}{[HA]_0}$$

or $[H^+] = \sqrt{K_a [HA]_0} = [(1.8 \times 10^{-5}\ M)\ (0.5\ M)]^{1/2} = 3.0 \times 10^{-3}\ M$

$pH = -\log (3.0 \times 10^{-3}) = 2.523$

(a) Now to double the pH, we will have

$[H^+] = \text{antilog}\ (-2 \times 2.523) = 9.0 \times 10^{-6}\ M$

Now from the expression $K_a = \frac{[H^+]^2}{[HA]_0 - [H^+]}$ we get $1.8 \times 10^{-5}\ M = \frac{(9.0 \times 10^{-6}\ M)^2}{[HA]_0 - (9.0 \times 10^{-6}\ M)}$

This gives $[HA]_0 = \frac{(9.0 \times 10^{-6}\ M)^2 + (1.8 \times 10^{-5}\ M)(9.0 \times 10^{-6}\ M)}{(1.8 \times 10^{-5}\ M)} = \frac{8.0 \times 10^{-11}\ M^2 + 1.62 \times 10^{-10}\ M^2}{1.8 \times 10^{-5}\ M}$

$$= \frac{2.42 \times 10^{-10}\ M^2}{1.8 \times 10^{-5}\ M} = 1.344 \times 10^{-5}\ M$$

$$\text{Dilution factor} = \frac{0.5\ M}{1.344 \times 10^{-5}\ M} = 3.72 \times 10^4$$

(b) To double the $[OH^-]$, we have

$$[H^+] = \frac{1}{2} \times 3.0 \times 10^{-3}\ M$$

Hence, $[HA]_0 = \frac{[H^+]^2}{K_a} = \frac{(1.5 \times 10^{-3}\ M)^2}{(1.8 \times 10^{-5}\ M)} = 0.125\ M$

$$\text{Dilution factor} = \frac{0.5\ M}{0.125\ M} = 4.$$

18. Consider a 0.5 M NH_4Cl solution. What is its pH? To what volume must 1 L of this solution be diluted to get a solution of pH = 6.0? Given: $K_b(NH_4OH) = 1.8 \times 10^{-5}$ M.

Solution We have

$$\underset{0.5\ M - x}{NH_4^+} + H_2O \rightleftharpoons \underset{x}{NH_4OH} + \underset{x}{H^+}$$

$$K_h = \frac{K_w}{K_b} = \frac{[NH_4OH][H^+]}{[NH_4^+]} = \frac{(x)(x)}{0.5\ M - x}$$

Now $\frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}\ M^2}{1.8 \times 10^{-5}\ M} = 5.56 \times 10^{-10}\ M$

Hence, $\frac{x^2}{0.5\ M - x} = 5.56 \times 10^{-10}\ M$

Ignoring x in comparison to 0.5 M, we get

$x^2 = 0.5 \times 5.56 \times 10^{-10}\ M$ or $x = 1.67 \times 10^{-5}\ M$

Now $pH = -\log \{[H^+]/\text{mol L}^{-1}\} = -\log (1.67 \times 10^{-5}) = 4.78$

To have pH = 6, we must have

$[H^+] = 10^{-6}\ M$

Hence, $[NH_4^+] = \frac{[H^+]^2}{K_h} = \frac{1.0 \times 10^{-12}\ M^2}{5.56 \times 10^{-10}\ M} = 1.80 \times 10^{-3}\ M$

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$$\frac{(5.0\times10^{-33}\text{M}^4)[\text{OH}^-]}{[\text{Al(OH)}_4^-]} = 1.3\times10^{-34}\text{M}^4$$

Hence, for the present problem we get

$$[\text{OH}^-] = \frac{1.3\times10^{-34}}{5.0\times10^{-33}}\ (10^{-3}\ \text{mol L}^{-1}) = 2.6\times10^{-5}\ \text{mol L}^{-1}$$

$$\text{p(OH)} = -\log\{[\text{OH}^-]/\text{M}\} = -\log(2.6\times10^{-5}) = 4.6$$

Thus, $\text{pH} = 14.0 - 4.6 = 9.4$

When $Al(OH)_3$ dissolves as Al^{3+}, we will have $[Al^{3+}] = 10^{-3}\ \text{mol L}^{-1}$

Substituting this in Eq. (2), we get

$$[\text{OH}^-] = \left(\frac{K_{sp}}{[\text{Al}^{3+}]}\right)^{1/3} = \left(\frac{5.0\times10^{-33}}{10^{-3}}\text{M}^3\right)^{1/3} = 1.71\times10^{-10}\ \text{mol L}^{-1}$$

$$\text{p(OH)} = -\log(1.71\times10^{-10}) = 9.78$$

$$\text{pH} = 14 - \text{p(OH)} = 4.22.$$

28. What is the pH of a 0.50 M aqueous NaCN solution? pK_b of CN^- is 4.70. (1996)

Solution The CN^- ions undergo hydrolysis as

$$\text{CN}^- + \text{H}_2\text{O} \rightleftharpoons \text{HCN} + \text{OH}^-$$

Hence, $$K_b = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]} \simeq \frac{[\text{OH}^-]^2}{[\text{CN}]_0}$$

or $$-\log K_b^\circ = -2\log([\text{OH}^-]/\text{M}) + \log([\text{CN}^-]_0/\text{M})$$

$$4.70 = 2\ \text{pOH} + \log(0.50)$$

or $$\text{pOH} = \frac{4.70 + 0.30}{2} = 2.5$$

$$\text{pH} = 14 - \text{pOH} = 14 - 2.5 = 11.5$$

29. A sample of AgCl was treated with 5.00 mL of 1.5 M Na_2CO_3 solution to give Ag_2CO_3. The remaining solution contained 0.0026 g of Cl^- per litre. Calculate the solubility product of AgCl. Given: $(K_{sp}(Ag_2CO_3) = 8.2\times10^{-12}\text{M}^3.)$ (1997)

Solution The involved reaction is

$$2\text{AgCl} + \text{CO}_3^{2-}(\text{aq}) \rightleftharpoons \text{Ag}_2\text{CO}_3(\text{s}) + 2\text{Cl}^-(\text{aq})$$

$$1.5\ \text{M} \qquad\qquad 0.0026\ \text{g L}^{-1} = 7.324\times10^{-5}\ \text{M}$$

Assuming $[CO_3^{2-}] \simeq 1.5$ M as very small quantity ($= 3.662\times10^{-5}$ M) of CO_3^{2-} combines, we get

$$[\text{Ag}^+] = \left(\frac{K_{sp}(\text{Ag}_2\text{CO}_3)}{[\text{CO}_3^{2-}]}\right)^{1/2} = \left(\frac{8.2\times10^{-12}\ \text{M}^3}{1.5\ \text{M}}\right)^{1/2} = 2.338\times10^{-6}\ \text{M}$$

Hence, $$K_{sp}(\text{AgCl}) = [\text{Ag}^+]\ [\text{Cl}^-] = (2.338\times10^{-6}\ \text{M})\ (7.324\times10^{-5}\ \text{M}) = 1.71\times10^{-10}\ \text{M}^2$$

30. An acid indicator, HIn differs in colour from its conjugate base (In^-). The human eye is sensitive to colour differences only when the ratio $[In^-]/[HIn]$ is greater than 10 or smalles than 0.1. What should be the minimum change in the pH of the solution to observe a complete colour change ($K_a^\circ = 1.0\times10^{-5}$)? (1997)

Solution Using the Henderson's equation $\text{pH} = pK_a^\circ + \log\{[In^-]/[HIn]\}$, we get

$$\text{pH}_1 = -\log(1.0\times10^{-5}) + \log(1/10) = 5 - 1 = 4$$

$$\text{pH}_2 = -\log(1.0\times10^{-5}) + \log(10/1) = 5 + 1 = 6$$

The pH of the solution should change from 4 to 6.

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$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{(c\alpha + 0.05\,M)(c\alpha)}{c(1-\alpha)} = \frac{c(\alpha+1)\alpha}{1-\alpha}$$

Assuming $\alpha << 1$, we get

$$\alpha = \sqrt{\frac{K_a}{c}} = \left(\frac{1.75\times10^{-5}\,M}{0.05\,M}\right)^{1/2} = 3.5 \times 10^{-4}$$

$$[H^+] = c\alpha = (0.05\ M)\ (3.5 \times 10^{-4}) = 1.75 \times 10^{-5}\ M$$

$$pH = -\log\{[H^+]/M\} = -\log(1.75 \times 10^{-5}) = 4.76$$

(alternatively, one can use the expression

$$pH = pK_a^\circ + \log\{[salt]/[acid]\}$$

since [salt] = [acid], we get $pH = pK_a^\circ$.

Unsolved Problems

1. The degree of dissociation of water was found to be 1.8×10^{-9} at 25 °C. Calculate its ionization constant and ionic product at 25 °C.
2. The ionic product of water at 100 °C is 55 times that at 25 °C. Calculate the pH of pure water at 100 °C. A given solution at 100 °C has a pH value of 7.0. Indicate whether this solution is acidic, alkaline or neutral.
3. Calculate K_a for an acid whose 0.1 M solution has a pH of 4.50.
4. Calculate the pH of 10^{-8} M HCl solution.
5. What is the pH of a 0.1 M solution of acetic acid? To what volume must one litre of this solution be diluted so as to have pH twice as that of original solution? Given: K_a(acetic acid) = 1.8×10^{-5} M.
6. Calculate the pH of each of the following solutions at 25 °C.
   (a) 0.25 M NaCN : $K_a(HCN) = 4.8 \times 10^{-15}$ M
   (b) 0.015 M NH_4Cl : $K_b(NH_4OH) = 1.8 \times 10^{-5}$ M.
   (c) 0.015 M CH_3COONa : $K_a(CH_3COOH) = 1.8 \times 10^{-5}$ M
7. Calculate $[H^+]$, $[HS^-]$ and $[S^{2-}]$ in 0.1 M solution of H_2S. Given: $K_{a1}^\circ = 1.1 \times 10^{-7}$ and $K_{a2}^\circ = 1.0 \times 10^{-14}$.
8. Calculate the degree of hydrolysis and pH of (a) 0.1 M ammonium acetate solution. Given : $K_b(NH_4OH) = K_a(CH_3COOH) = 1.8 \times 10^{-5}$ M, and (b) 0.1 M anilinium acetate; Given; K_a(acetic acid) = 1.8×10^{-5} M and K_b(aniline) = 4.6×10^{-10} M.
9. Calculate the pH change when 100 mL of (a) 0.05 M NaOH and (b) 0.05 M HCl are added to 400 mL of a buffer solution that is 0.2 M in NH_3 and 0.3 M in NH_4Cl.
10. What volumes of 0.5 M acetic acid ($K_a^\circ = 1.75 \times 10^{-5}$) and 0.426 M sodium hydroxides should be mixed to get 100 mL of a buffer solution having pH = 5.0?
11. A weak base (50.0 mL) was titrated with 0.1 M HCl. The pH of the solution after the addition of 10.0 mL and 25.0 mL were found to be 9.84 and 9.24, respectively. Calculate K_b of the base and pH at the equivalence point.
12. A weak acid (50.0 mL) is titrated aginst 0.1 M NaOH. The pH values when 10.0 mL and 25.0 mL of base have been added are found to be 4.16 and 4.76, respectively. Calculate K_a of the acid and pH at the equivalence point.
13. Determine the pH of a solution obtained by mixing 1.0 mol of sodium acetate and 1.0 mol of HCl in water to make one litre solution. $K_a(CH_3COOH) = 1.8 \times 10^{-5}$ M.
14. Calculate the solubility of magnesium phosphate in 500 mL of saturated solution. Given: $K_{sp}(Mg_3(PO_4)_2) = 1.0 \times 10^{-13}\ M^5$, M(Mg) = 24.3 g mol^{-1} and M(P) = 31.0 g mol^{-1}.
15. A solution is saturated with respect to $SrCO_3$ and SrF_2. the CO_3^{2-} was found to be 1.2×10^{-3} mol L^{-1}. Determine $[F^-]$.Given: $K_{sp}(SrCO_3) = 7.0 \times 10^{-10}\ M^2$ and $K_{sp}(SrF_2) = 7.9 \times 10^{-10}\ M^3$.
16. What is the maximum pH of 0.10 M solution in Mg^{2+} from which $Mg(OH)_2$ will not precipitate. Given: $K_{sp}(Mg(OH)_2) = 1.2 \times 10^{-11}\ M^3$.

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11. Which of the following reactions occurs at anode when the electrolysis of $CuSO_4$ solution is carried out by using copper electrodes?
(a) $Cu \rightarrow Cu^{2+} + 2e^-$ (b) $2SO_4^{2-} + 2H_2O \rightarrow 2H_2SO_4 + O_2 + 4e^-$
(c) $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ (d) $2Cu \rightarrow Cu_2^{2+} + 2e^-$

12. In an electrolytic cell, which of the following is **not** true?
(a) Anode is positive terminal (b) Anode is negative terminal
(c) Oxidation occurs at cathode (d) Reduction occurs at cathode

13. Which of the following statements is **not** correct?
(a) Electrons enter through cathode in an electrolytic cell
(b) Electrons leave through anode in an electrolytic cell
(c) Cations in the electrolytic cell move toward cathode and anions toward anode
(d) Cations are reduced at anode and anions are oxidized at cathode in an electrolytic cell

14. Which of the following statements is correct for an electrolytic cells?
(a) Electrons flow from cathode to anode through the external battery.
(b) Electrons flow from cathode to anode within the electrolytic solution.
(c) Migration of ions along with oxidation reaction at cathode and reduction reaction at anode.
(d) Migration of ions along with reduction reaction at cathode and oxidation reaction at anode. (2003)

15. The number of electrons carrying a total charge equivalent to one K^+ ion is equal to
(a) 6.02×10^{23} (b) 6.02×10^{21} (c) 6.20×10^{18} (d) 6.20×10^{16}

16. Which of the following statements regarding the variations of resistance with temperature occur during electrolytic and metallic conductions?
(a) increase in electrolytic, decrease in metallic (b) decrease in electrolytic, increase in metallic
(c) increase in both (d) decrease in both

17. Which of the following metals form a protective layer of oxide to prevent corrosion?
(a) Cu (b) Ag (c) Au (d) Al

Faraday Laws of Electrolysis

18. Faraday's law of electrolysis are related to the
(a) atomic number of the cation (b) atomic number of the anion
(c) equivalent mass of the electrolyte (d) speed of the cation (1983)

19. Which of the following expression is written correctly?
(a) $I = Qt$ (b) $I = Q/t$ (c) $I = 1/Qt$ (d) $I = t/Q$

20. Which of the following expressions regarding the electrolysis of an electrolytic solution is represented correctly?

(a) $m = \frac{I\,t\,F}{M\,|v_e|}$ (b) $m = \frac{I\,t\,|v_e|}{M\,F}$ (c) $m = \frac{Q\,F}{M\,|v_e|}$ (d) $m = \frac{Q\,M}{F\,|v_e|}$

21. The density of Cu is 8.94 g cm^{-3}. The quantity of electricity needed to plate an area 10 cm × 10 cm to a thickness of 10^{-2} cm using $CuSO_4$ solution is
(a) 13 586 C (b) 27 172 C (c) 40 758 C (d) 20 348 C

22. A current of 9.65 A is passed for 3 h between nickel electrodes in 0.5 L of a 2 M solution of $Ni(NO_3)_2$. The molarity of solution after electrolysis would be
(a) 0.46 M (b) 0.625 M (c) 0.92 M (d) 1.25 M

23. The time required to coat a metal surface of 80 cm^2 with 5×10^{-3} cm thick layer of silver (density 10.5 g cm^{-3}) with the passage of 3A current through a silver nitrate solution is
(a) 1150 s (b) 1250 s (c) 1350 s (d) 1450 s

24. In an electrolysis of an aqueous solution of sodium sulphate, 2.4 L of oxygen at STP was liberated at anode. The volume of hydrogen at STP liberated at cathode would be
(a) 1.2 L (b) 2.4 L (c) 2.6 L (d) 4.8 L

25. In the electrolysis of $CuCl_2$ solution using copper electrode, if 2.5 g of Cu is deposited at cathode, then at anode
(a) 890 mL of Cl_2 at STP is liberated (b) 445 mL of O_2 at STP is liberated
(c) 2.5 g of copper is deposited (d) a decrease of 2.5 g of mass takes place

26. On passing an electric current, the quantity of deposition of a metal on cathode depends on the
(a) shape of cathode (b) size of cathode
(c) concentration of electrolytic solution (d) quantity of charge and charge number of metal ion

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15. (c) **16.** (b) **17.** (d) **18.** (c) **19.** (b) **20.** (d) **21.** (b)
22. (c) **23.** (b) **24.** (d) **25.** (d) **26.** (d) **27.** (d) **28.** (d)
29. (c) **30.** (a) **31.** (b) **32.** (c) **33.** (d) **34.** (b) **35.** (a)
36. (b) **37.** (a) **38.** (c) **39.** (d) **40.** (a) **41.** (b) **42.** (b)
43. (c) **44.** (d) **45.** (b) **46.** (c) **47.** (c)

Multiple Correct Choice Type

1. (a), (b) **2.** (b), (c) **3.** (a), (d) **4.** (b), (c)
5. (a), (b), (c) **6.** (a), (c), (d) **7.** (b), (c), (d) **8.** (c), (d)
9. (b), (d)

Linked Comprehension Type

1. **(i)** (b) **(ii)** (d) **(iii)** (d)

Matrix Match Type

1. (a) – (s); (b) – (r); (c) – (q); (d) – (p)
2. (a) – (s); (b) – (p); (c) – (q); (d) – (r)
3. (a) – (r), (t); (b) – (s); (c) – (q); (d) – (p)

Hints and Solutions

Straight Objective Type

1. Molten sodium chloride conducts electricity due to the presence of free ions.
2. Electrolysis of a solution of sodium sulphate yields H_2 and O_2.
3. During the discharge of a lead storage battery, sulphuric acid is consumed.
4. Cathode is negative terminal.
5. While charging lead storage cell, sulphuric acid is formed.
6. Anodic reaction is $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$.
7. Same as Q.6.
8. In the electrolysis of dilute H_2SO_4 using Cu electrodes, the reaction occurring at anode is $Cu \longrightarrow Cu^{2+} + 2e^-$.
9. The products are O_2 and H_2.
10. Cl^- is oxidized in preference to H_2O

18. Faraday's law of electrolysis are related to the equivalent mass of the electrolyte.
19. By defination, $Q = It$.
20. Faraday's laws of electrolysis follow the expression $m = (Q/F)\ (M/|\nu_e|)$.
21. Amount of Cu deposited = mass of Cu deposited/molar mass of Cu
= (density × volume) of Cu deposited/molar mass of Cu
= $(8.94\ g\ cm^{-3})\ (10 \times 10 \times 10^{-2}\ cm^3)/(63\ g\ mol^{-1}) = 0.142\ mol$
Since 2 electrons are required to convert Cu^{2+} to Cu, the quantity of electricity needed is
$(2 \times 96500\ C\ mol^{-1})\ (0.142\ mol) = 27388\ C$.
22. We have $Q = It = (9.65\ A)\ (3 \times 60 \times 60\ s) = 104\ 220\ C$

$$\text{Amount of Ni deposited} = \frac{104\,220\ C}{2 \times 96\,500\ C\ mol^{-1}} = 0.54\ mol$$

Amount of Ni^{2+} left behind = 1 mol – 0.54 mol = 0.46 mol
Molarity of solution = 0.46 mol/0.5 L = 0.92 mol L^{-1}
23. Using the expression $m = (Q/F)\ (M/|\nu_e|)$, we get

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Solution We have

$$\text{Amount of gold deposited} = \frac{9.85\,\text{g}}{197\,\text{g mol}^{-1}} = 0.05 \text{ mol}$$

Based on the reaction $Au^{3+} + 3e^- \rightarrow Au$, it may be concluded that

$$\text{Amount of electrons passed} = 3 \times 0.05 \text{ mol} = 0.15 \text{ mol}$$

Now, the same quantity of electricity is passed through $CuSO_4$ solution causing the reaction $Cu^{2+} + 2e^- \rightarrow Cu$ at cathode. We will have

$$\text{Amount of Cu deposited} = \frac{0.15\,\text{mol}}{2} = 0.075 \text{ mol}$$

$$\text{Mass of Cu deposited} = (0.075 \text{ mol})\,(63.5 \text{ g mol}^{-1}) = 4.762\,5 \text{ g}$$

$$\text{Quantity of electricity passed} = (0.15 \text{ mol})\,(96\,500 \text{ C mol}^{-1}) = 14\,475 \text{ C}$$

$$\text{Quantity of current passed} = \frac{Q}{t} = \frac{14\,475\text{C}}{5 \times 60 \times 60\,\text{s}} = 0.804\,2 \text{ A}.$$

3. How long a current of 3 amperes has to be passed through a solution of silver nitrate to coat a metal surface of 80 cm^2 with a 0.005 mm thick layer? Density of silver is 10.5 g cm^{-3}. (1985)

Solution We have

$$\text{Volume of metal deposited} = (80 \text{ cm}^2)\,(0.000\,5 \text{ cm}) = 0.04 \text{ cm}^3$$

$$\text{Mass of metal deposited} = \rho V = (10.5 \text{ g cm}^{-3})\,(0.04 \text{ cm}^3) = 0.42 \text{ g}$$

$$\text{Amount of silver deposited} = \frac{0.42\,\text{g}}{108\,\text{g mol}^{-1}} = 3.889 \times 10^{-3} \text{ mol}$$

$$\text{Quantity of electricity passed} = (3.889 \times 10^{-3} \text{ mol})\,(96\,500 \text{ C mol}^{-1}) = 375.27 \text{ C}$$

$$\text{Time for which 3A current is passed} = \frac{375.27\text{C}}{3\text{A}} = 125.09 \text{ s}$$

4. During the discharge of a lead storage battery, the density of sulphuric acid fell from 1.294 to 1.139 g mL^{-1}. Sulphuric acid of density 1.294 g mL^{-1} is 39% H_2SO_4 by mass and that of density 1.139 g mL^{-1} is 20% H_2SO_4 by mass. The battery holds 3.5 L of the acid and the volume remained practically constant during the discharge. Calculate the number of ampere-hour for which the battery must have been used. The charging and discharging reactions are

$$Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^- \qquad \text{(charging)}$$

$$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O \quad \text{(discharging)} \qquad (1986)$$

Solution We have

$$\text{Mass of } H_2SO_4 \text{ solution to start with, } \rho V = (1.294 \text{ g mL}^{-1})\,(3.5 \times 10^3 \text{ mL}) = 4\,529 \text{ g}$$

$$\text{Actual mass of } H_2SO_4 \text{ in this solution} = \left(\frac{39}{100}\right)(4\,529 \text{ g}) = 1766.3 \text{ g}$$

$$\text{Mass of } H_2SO_4 \text{ solution at the end} = (1.139 \text{ g mL}^{-1})\,(3.5 \times 10^3 \text{ mL}) = 3986.5 \text{ g}$$

$$\text{Actual mass of } H_2SO_4 \text{ in this solution} = \left(\frac{20}{1000}\right)(3\,986.5 \text{ g}) = 797.3 \text{ g}$$

$$\text{Mass of } H_2SO_4 \text{ consumed} = (1\,766.3 - 91.3) \text{ g} = 969.0 \text{ g}$$

$$\text{Amount of } H_2SO_4 \text{ consumed} = \frac{969.0\,\text{g}}{98\,\text{g mol}^{-1}} = 9.888 \text{ mol}$$

$$\text{Amount of } H^+ \text{ consumed} = 2 \times 9.888 \text{ mol}$$

Since 4 mol of H^+ are consumed per 2 mol of electrons during discharge, we have

$$\text{Amount of electrons discharged} = \left(\frac{2\text{ mol}}{4\text{ mol}}\right)(2 \times 9.888 \text{ mol}) = 9.888 \text{ mol}$$

$$\text{Quantity of electricity discharged} = (9.888 \text{ mol})(96\,500 \text{ C mol}^{-1}) = 954\,192 \text{ C}$$

$$\text{Number of ampere-hour for which the battery has been used} = \frac{954192}{60 \times 60} = 265.05.$$

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16. In the electrolysis of a $CuSO_4$ solution, there are two possible reactions at the anode

(i) $Cu \rightarrow Cu^{2+} + 2e^-$ and (ii) $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

A current of 1.0 A is passed for 2.0 h. The loss in mass of the Cu anode was 1.50 g. How much volume of oxygen at STP was liberated? What fraction of current is used in the production of Cu^{2+} ions?

Solution Amount of Cu converted to Cu^{2+} ions $= \dfrac{1.50\,g}{63.5\,g\,mol^{-1}} = 0.02362$ mol

Amount of electrons involved $= 2 \times 0.02362$ mol $= 0.04724$ mol

Amount of electrons actually passed through solution $= \dfrac{It}{F} = \dfrac{(1.0\,A)(2 \times 60 \times 60\,s)}{(96500\,C\,mol^{-1})} = 0.07461$ mol

Amount of electrons involved in converting H_2O to $O_2 = (0.07461 - 0.04724)$ mol $= 0.02737$ mol

Amount of oxygen liberated $= \frac{1}{4} \times 0.02737$ mol $= 0.006843$ mol

Volume of oxygen liberated at STP $= (0.006843\ mol)\ (22414\ mL\ mol^{-1}) = 153.4$ mL

Fraction of current used in the production of Cu^{2+} ions $= \dfrac{0.04724}{0.07461} = 0.633.$

17. Electrolysis of a solution of $MnSO_4$ in aqueous sulphuric acid is a method for the preparation of MnO_2 as per the reaction $Mn^{2+}(aq) + 2H_2O \rightarrow MnO_2(s) + 2H^+(aq) + H_2(g)$

Passing a current of 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. (1997)

Solution The electrode reactions are

Anode	$Mn^{2+}(aq) + 2H_2O(l) \rightarrow MnO_2(s) + 4H^+(aq) + 2e^-$
Cathode	$2H^+(aq) + 2e^- \rightarrow H_2(g)$
Overall reaction	$Mn^{2+}(aq) + 2H_2O(l) \rightarrow MnO_2(s) + 2H^+(aq) + H_2(g)$

The actual current needed to deposit 1 kg MnO_2 is given by the expression

$$I = m\left(\frac{F}{t}\right)\left(\frac{z}{M}\right) = (1000\ g)\left(\frac{96500\,C\,mol^{-1}}{24 \times 60 \times 60\,s}\right)\left[\frac{2}{(54.9 + 2 \times 16)\,g\,mol^{-1}}\right] = 25.70\ A$$

$$\text{The current efficiency} = \left(\frac{25.70\ A}{27\ A}\right)(100) = 95.185\%$$

18. What mass 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 hours at a current of 8.46 amperes? What is the area of tray if the thickness of the silver plating is 0.00254 cm? Density of silver is 10.5 g/cm^3. (1997)

Solution Using the expression $m = \dfrac{It}{F}\dfrac{M}{|\nu_e|}$

we get $m = \dfrac{(8.46\ A)(8 \times 60 \times 60\ s)(107.8\ g\ mol^{-1})}{(96500\ C\ mol^{-1})\ \ (1)} = 272.18\ g$ (1)

Volume of silver plated out, $V = \dfrac{m}{\rho} = \dfrac{272.18\ g}{10.5\ g\ cm^{-3}} = 25.92\ cm^3$

$$\text{Area of the tray plated} = \frac{25.92\ cm^3}{0.00254\ cm} = 10204.7\ cm^2$$

19. Copper sulphate (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. (2000)

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Variation of Molar Conductivity with Concentration Both the conductivity and molar conductivity of a solution vary with concentration. The conductivity increases with increase in concentration, whereas the molar conductivity increases on dilution, i.e. decrease in concentration.

The conductivity of solution increases with increase in concentration because more ions are available for conduction.

The molar conductivity of a solution gives the conducting ability of all the ions produced by 1 mol of an electrolyte at any particular concentration. The increase in molar conductivity of a strong electrolyte on dilution is due to the increase in the number of ions caused by weakening of ion-ion interactions. The variation in molar conductivity for a strong electrolyte is almost linear in dilute solutions and is given by the expression

$$\Lambda_m = \Lambda_m^\infty - b\sqrt{c}$$

where Λ_m^∞ is molar conductivity at infinite dilution and b is constant.

The increase in molar conductivity of a weak electrolyte is due to increase in the degree of dissociation on dilution which causes increase in the number of ions. This fact is known as *Ostwald dilution law*.

The degree of dissociation of a weak electrolyte in a solution of known concentration can be computed by using Arrhenius equation:

$$\Lambda = \Lambda_c / \Lambda^\infty$$

where Λ_c is the molar conductivity of the solution at the given concentration.

Kohlrausch's Law of Independent Migration of Ions The molar conductivity at infinite dilution for a strong electrolyte can be determined by extrapolating the plot of Λ_c versus $\sqrt{c}$ to a value of $\sqrt{c} = 0$. This procedure cannot be adopted for a weak electrolyte as the variation of Λ_c with dilution is not linear. However, the value of Λ_m^∞ can be determined by the application of Kohlrausch's law of independent migration of ions. This law states that at infinite dilution, where dissociation of all electrolytes is complete (including weak electrolytes since degree of dissociation approaches one as the concentration approaches zero) and where all interionic effects disappear (because of larger distance between ions), each ion migrate independent of its co-ion and contributes to the total molar conductivity of an electrolyte a definite share which depends only on its own nature and not at all on the ion with which it is associated. Thus, we can write

$$\Lambda_m^\infty = \nu_+ \lambda_+^\infty + \nu_- \lambda_-^\infty$$

where ν_+ and ν_- are the respective stoichiometric numbers of cation and anion in one molecule of the electrolyte.

Exceptionally High Values of $\lambda^\infty(H^+)$ and $\lambda^\infty(OH^-)$ In aqueous solutions, the molar conductivities at infinite dilution for H^+ and OH^- are exceptionally larger than those of other ions. This was explained by von Grotthus and is known as Grotthus conduction. It was explained on the basis of transfer of a proton from one water molecule to another. The process of proton transfer results in a more rapid transfer of positive charge from one region of the solution to another, than would be possible if H_3O^+ ion has to push its way through the solution as other ions do.

Variation of Λ_m^∞ of Alkali Ions in Solution It is expected that the molar conductivity value should decrease with increase in the size of ion. However, the reverse is observed in alkali metal ions. This is due to decrease in extent of hydration of alkali metal ions with increasing size of ions. Thus, the effective size of hydrated ions in solution is $Na^+ > K^+ > Rb^+$ and hence the molar conductivities of these ions follow the trend $Rb^+ > K^+ > Na^+$

Transference Number The fraction of the total current carried by each ion in solution is known as the transference number of the ion. This may be computed by using the expression

$$t = \frac{\text{Conductivity of the ion in solution}}{\text{Total conductivity of the solution}}$$

Since $\lambda = \kappa/c$, we will have $t = \dfrac{c\lambda}{\Sigma_i c_i \lambda_i}$

Ionic Mobility The velocity of an ion in a solution is directly proportional to the potential gradient across the electrodes of a conductivity cell, i.e.

$$v \propto (d\phi/dl) \quad \text{or} \quad v = u\,(d\phi/dl)$$

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43. The molar conductivity of a weak electrolyte HA at infinite dilution can be determined by
(a) extrapolating Λ_m versus c plot to $c \to 0$.
(b) extrapolating Λ_m versus $\sqrt{c}$ plot to $c \to \infty$.
(c) using Kohlrausch law with the data on Λ_m^∞(HCl), Λ_m^∞(NaA) and Λ_m^∞(NaCl)
(d) Using Kohlrausch law with the data on Λ_m^∞(HA) and Λ_m^∞(NaA)

44. The conductivity of a saturated solution is 1.65×10^{-6} S cm^{-1}. If Λ_m^∞ (Co^{2+}) = 86 S cm^2 mol^{-1} and Λ_m^∞ ($Fe(CN)_6^{3-}$) = 444 S cm^2 mol^{-1}, the solubility of $Co_2[Fe(CN)_6]$ in water will be
(a) 2.7×10^{-4} mol dm^{-3} (b) 2.7×10^{-5} mol dm^{-3} (c) 2.7×10^{-6} mol dm^{-3} (d) 2.7×10^{-7} mol dm^{-3}

45. The conductivity of water at 298 K is 0.55×10^{-7} S cm^{-1}. If $\lambda_m(H^+)$ = 350 S cm^2 mol^{-1} and $\lambda(OH^-)$ = 200 S cm^2 mol^{-1}, the degree of dissociation of water will be
(a) 1.82×10^{-6} (b) 1.82×10^{-7} (c) 1.82×10^{-8} (d) 1.82×10^{-9}

46. If $\lambda_m(Na^+)$ = 50 S m^2 mol^{-1} and $\lambda_m(SO_4^{2-})$ = 160 S cm^2 mol^{-1}, then the transference number of Na^+ in 0.1 M Na_2SO_4 will be
(a) 5/21 (b) 10/26 (c) 5/8 (d) 2.5/16

47. If $\lambda_m(M^+)$ = 48 S cm^2 mol^{-1}, the ionic mobility of NH_4^+ ion will be
(a) 4.97×10^{-2} cm^2 V^{-1} s^{-1} (b) 4.8×10^{-3} cm^2 V^{-1} s^{-1}
(c) 4.97×10^{-4} cm^2 V^{-1} s^{-1} (d) 4.8×10^{-6} cm^2 V^{-1} s^{-1}

Linked Comprehension Type

1. Given are the following ionic molar conductivities.

$\lambda_m^\infty(Na^+)$ = 50.1 S cm^2 mol^{-1} and $\lambda_m^\infty\left(\frac{1}{2}\text{ Oxalate}^{2-}\right)$ = 74.1 S cm^2 mol^{-1}

Based on this information, answer the following three questions or for 0.1 M sodium oxalate.
(i) The molar ionic conductivity at infinite dilution for Na_2OX is
(a) 124.1 S cm^2 mol^{-1} (b) 174.3 S cm^2 mol^{-1} (c) 248.4 S cm^2 mol^{-1} (d) 62.1 S cm^2 mol^{-1}
(ii) The conductivity of 0.1 M solution of Na_2OX is
(a) 0.0124 S cm^{-1} (b) 0.0174 S cm^{-1} (c) 0.0248 S cm^{-1} (d) 6.21 S cm^2 mol^{-1}
(iii) The transference number of Na^+ ion in 0.1 M Na_2SO_4 solution is
(a) 0.7 (b) 0.6 (c) 0.5 (d) 0.4

2. Given are the following data.
Conductivity of a saturated solution of silver oxalate = 3.8×10^{-5} S cm^{-1}
K_{sp}° (silver oxalate) = 1.1×10^{-11} and $\lambda_m^\infty(Ag^+)$ = 62 S cm^2 mol^{-1}
Based on this information, answer the following three questions
(i) The solubility of silver oxalate in water is
(a) 3.31×10^{-6} M (b) 2.52×10^{-3} M (c) 1.4×10^{-4} M (d) 4.44×10^{-4} M
(ii) Molar conductivity at infinite dilution for silver oxalate is
(a) 284.6 S cm^2 mol^{-1} (b) 310.2 S cm^2 mol^{-1} (c) 271.4 S cm^2 mol^{-1} (d) 185.6 S cm^2 mol^{-1}
(iii) Equivalent conductivity of oxalate ion at infinite dilution is
(a) 160 S cm^2 mol^{-1} (b) 92.5 S cm^2 mol^{-1} (c) 60 S cm^2 mol^{-1} (d) 73.2 S cm^2 mol^{-1}

ANSWERS

Straight Objective Type

1. (d)	**2.** (a)	**3.** (a)	**4.** (b)	**5.** (a)	**6.** (b)	**7.** (b)
8. (b)	**9.** (a)	**10.** (d)	**11.** (b)	**12.** (c)	**13.** (d)	**14.** (d)
15. (c)	**16.** (a)	**17.** (d)	**18.** (a)	**19.** (b)	**20.** (a)	**21.** (d)
22. (a)	**23.** (d)	**24.** (d)	**25.** (b)	**26.** (c)	**27.** (a)	**28.** (d)
29. (c)	**30.** (b)	**31.** (d)	**32.** (c)	**33.** (a)	**34.** (a)	**35.** (c)
36. (b)	**37.** (c)	**38.** (a)	**39.** (b)	**40.** (c)	**41.** (c)	**42.** (b)
43. (c)	**44.** (c)	**45.** (d)	**46.** (b)	**47.** (c)		

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Solution Conductivity of acetic acid solution is $\kappa = \frac{K}{R} = \frac{2.0\ \text{cm}^{-1}}{3765\ \Omega} = 5.3 \times 10^{-4}\ \Omega^{-1}\ \text{cm}^{-1}$

Molar conductivity of 0.1 M acetic acid solution is

$$\Lambda_m = \frac{\kappa}{c} = \frac{5.3 \times 10^{-4}\ \Omega^{-1}\ \text{cm}^{-1}}{0.1\ \text{mol dm}^{-3}} = 5.3 \times 10^{-3}\ \Omega^{-1}\ \text{cm}^{-1}\text{dm}^3\ \text{mol}^{-1} = 5.3\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$$

Degree of dissociation of 0.1 M acetic acid is $\alpha = \frac{\Lambda_m}{\lambda_m(H^+) + \lambda_m^\infty(Ac^-)} = \frac{5.3}{(349.8 + 40.9)} = 0.0136$

The equilibrium constant of $\underset{c(1-\alpha)}{CH_3COOH} \rightleftharpoons \underset{c\alpha}{CH_3COO^-} + \underset{c\alpha}{H^+}$

is $K = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{(c\alpha)(c\alpha)}{c(1-\alpha)} \cong c\alpha^2$

Substituting the values, we get $K = (0.1\ \text{M})\ (0.0136)^2 = 1.84 \times 10^{-5}\ \text{M}$

2. The molar conductivity of 0.05 M solution of $MgCl_2$ is 194.2 $\Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$ at 25°C. A cell with electrodes that are 1.50 cm^2 in surface area and 0.50 cm apart is filled with 0.05 M $MgCl_2$ solution. How much current will flow when the potential difference between the two electrodes is 2.00 V?

Solution Conductivity of 0.05 M solution is

$$\kappa = \Lambda c = (194.2\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1})\ (0.05\ \text{mol dm}^{-3}) = 9.71\ \Omega^{-1}\ (\text{cm}^2\ \text{dm}^{-3}) = 9.71 \times 10^{-3}\ \Omega^{-1}\ \text{cm}^{-1}$$

Conductance of 0.05 M solution is $G = \kappa\left(\frac{A}{l}\right) = \left(9.71 \times 10^{-3}\ \Omega^{-1}\text{cm}^{-1}\right)\left(\frac{1.50\ \text{cm}^2}{0.50\ \text{cm}}\right) = 2.91 \times 10^{-2}\ \Omega^{-1}$

Resistance offered by the solution is $R = \frac{1}{G} = \frac{1}{2.91 \times 10^{-2}\ \Omega^{-1}} = 34.34\ \Omega$

Current flowing through the electrodes is $I = \frac{E}{R} = \frac{2.00\ \text{V}}{34.34\ \Omega} = 0.058\ \text{A}$

3. The conductivity of 0.1 M NaOH solution is 0.0221 $\Omega^{-1}\ \text{cm}^{-1}$. When an equal volume of 0.1 M HCl solution is added, the conductivity decreases to 0.0056 $\Omega^{-1}\ \text{cm}^{-1}$. A further addition of HCl solution, the volume of which is equal to that of the first portion added, the conductivity increases to 0.017 $\Omega^{-1}\ \text{cm}^{-1}$. Calculate (a) Λ_m(NaOH), (b) Λ_m(NaCl), (c) Λ_m(HCl), and $\Lambda_m(H^+, OH^-)$.

Solution Molar conductivity of 0.1 M NaOH is

$$\Lambda_m(\text{NaOH}) = \frac{\kappa}{c} = \frac{0.0221\ \Omega^{-1}\text{cm}^{-1}}{0.1\ \text{mol dm}^{-3}} = 0.221\ \Omega^{-1}(\text{cm}^{-1}\text{dm}^3)\ \text{mol}^{-1} = 221\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$$

On adding equal volume of 0.1 M HCl solution, the total volume becomes double and the concentration of the salt formed will be 0.05 M. Hence, molar conductivity of 0.05 M NaCl solution is

$$\Lambda_m(\text{NaCl}) = \frac{\kappa}{c} = \frac{0.0056\ \Omega^{-1}\ \text{cm}^{-1}}{0.05\ \text{mol dm}^{-3}} = 0.112\ \Omega^{-1}(\text{cm}^{-1}\text{dm}^3)\ \text{mol}^{-1} = 112\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$$

On further addition of equal volume of the acid, the solution will become 0.033 M in NaCl and 0.033 M in HCl. The conductivity of this solution will be given by the expression

$$\kappa = c(\text{NaCl})\ \Lambda_m(\text{NaCl}) + c(\text{HCl})\ \Lambda_m(\text{HCl})$$

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SECTION III | GALVANIC CELLS

In galvanic cells, current is generated as a result of a spontaneous chemical reaction that occurs in the cell. The main characteristics of galvanic cells are given in Table 8.2.

Table 8.2 Main Characteristics of Galvanic Cells

	Cathode	*Anode*
Sign	Positive as the electrons are consumed at this electrode	Negative as the electrons are released at this electrode
Half-reaction	Reduction	Oxidation
Direction of electron movement	Into the cell	Out of cell

Thus, electrons are generated at the anode because of the oxidation reaction. As the electrons are negatively charged species, the anode becomes the negative end of the cell. The generated electrons move through the external wire to the other electrode (cathode) where these are consumed due to the reduction reaction. This electrode is deficient in electrons and is, therefore, the positive terminal of the cell.

Cell Reaction A cell can be briefly represented by a cell diagram following the rules given below.

1. The separation of two phases is shown by a vertical line.
2. The various materials present in the same phase are shown together with the help of commas.
3. The two half-cells are joined with the help of double vertical lines.
4. The significant features of the substances such as pressure of the gas, concentration of ions, etc. are indicated in brackets, drawn immediately after writing the substance.

According to the recommended convention, if a cell is written in brief, known as cell diagram, the left half-cell (LHC) is considered as the negative terminal and the right half- cell (RHC) as the positive terminal. Thus, the oxidation reaction occurs at the left electrode and the reduction reaction at the right electrode.

A few examples of illustrating the above convention are described below.

1. $Zn \mid Zn^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu$

LHC: Oxidation $Zn \rightarrow Zn^{2+}(aq) + 2e^-$

RHC: Reducion $Cu^{2+}(aq) + 2e^- \rightarrow Cu$

Overall reaction $Zn + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu$

2. $Pt \mid H_2(g) \mid H^+(aq) \parallel Zn^{2+}(aq) \mid Zn$

LHC: Oxidation $H_2(g) \rightarrow 2H^+(aq) + 2e^-$

RHC: Reduction $Zn^{2+}(aq) + 2e^- \rightarrow Zn$

Overall reaction $H_2(g) + Zn^{2+}(aq) \rightarrow 2H^+(aq) + Zn$

A galvanic cell is made up of two half-cells. The electrodes used in a half-cell can be broadly classified into the following categories.

Gas-Ion Half-Cell In the gas-ion half-cell, an inert collector of electrons (platinum or graphite) is in contact with gas and a solution containing specified ion. A few examples of this type of half-cell are given below.

Half-Cell	*Half-Cell Reaction*
$H^+(aq) \mid H_2(g) \mid Pt$	$H^+(aq) + e^- \rightarrow \frac{1}{2} H_2(g)$
$OH^-(aq) \mid H_2(g) \mid Pt$	$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$
$OH^-(aq) \mid O_2(g) \mid Pt$	$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$
$H^+(aq) \mid O_2(g) \mid Pt$	$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$
$Cl^-(aq) \mid Cl_2(g) \mid Pt$	$\frac{1}{2} Cl_2(g) + e^- \rightarrow Cl^-(aq)$

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5. Which of the following statements is correct?
   (a) Oxidation occurs at anode in both galvanic and electrolytic cells
   (b) Reduction occurs at anode in both galvanic and electrolytic cells
   (c) Reduction occurs at anode in electrolytic cell whereas oxidation occurs at cathode in a galvanic cell
   (d) Oxidation occurs at anode in electrolytic cell whereas reduction occurs at anode in a galvanic cell.
6. Which of the following facts regarding the movements of cations in the solution is correct?
   (a) Towards cathode in an electrolytic cell and towards anode in a galvanic cell
   (b) Towards anode in an electrolytic cell and towards cathode in a galvanic cell
   (c) Towards cathode in both types of cells
   (d) Towards anode in both types of cells
7. Which of the following facts regarding the movement of anions in the solution is correct
   (a) Towards cathode in an electrolytic cell and towards anode in a galvanic cell
   (b) Towards anode in an electrolytic cell and towards cathode in a galvanic cell
   (c) Towards cathode in both types of cells
   (d) Towards anode in both types of cells
8. Two half cells have potentials -0.76 V and -0.13 V respectively. A galvanic cell is made from these two half-cells. Which of the following statements is correct?
   (a) Electrode of half-cell potential -0.76 V serves as cathode
   (b) Electrode of half-cell potential -0.76 V serves as anode
   (c) Electrode of half-cell potential -0.13 V serves as anode
   (d) Electrode of half-cell -0.76 V serves as positive electrode and -0.13 V as negative electrode
9. Which of the following is **not** correct for a galvanic cell when written in an abbreviated form?
   (a) Left half electrode is a negative terminal
   (b) Left half electrode is an anode
   (c) Electrons are given out in the external circuit from the anode
   (d) Electrons are given out in the external circuit from the cathode
10. Two half-cells have potentials -0.44 V and 0.799 V, respectively. These two are coupled to make a galvanic cell. Which of the following statements is true?
   (a) Electrode of half-cell potential -0.44 V acts as anode
   (b) Electrode of half-cell potential -0.44 V acts as cathode
   (c) Electrode of half-cell potential 0.799 V acts as anode
   (d) Electrode of half-cell potential -0.44 V acts as a positive terminal
11. Two half-cells have potentials -0.76 V and -0.13 V, respectively. A galvanic cell is made from these two half-cells. Which of the following statements is correct?
   (a) Electrode of half-cell potential -0.76 V serves as cathode
   (b) Electrode of half-cell potential -0.76 V serves as anode
   (c) Electrode of half-cell potential -0.13 serves as anode
   (d) The nature of electrodes cannot be determined.
12. In a galvanic cell,
   (a) Cations move towards cathode and anions move towards anode
   (b) Cations move towards anode and anions towards cathode
   (c) Both Cations move towards cathode
   (d) Both cations move towards anode
13. When a lead storage cell is discharged, there occurs
   (a) consumption of H_2SO_4
   (b) formation of $PbO_2(s)$
   (c) increase in the cell potential
   (d) consumption of $PbSO_4(s)$
14. In a lead-storage cell, the emf
   (a) increases with increase in the percentage of H_2SO_4
   (b) decreases with increase in the percentage of H_2SO_4
   (c) does not change with increase in the percentage of H_2SO_4
   (d) is not affected by the change in temperature of the cell

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	Statement–1	Statement–2
1.	Ionic molar conductivity at infinite dilution of Na^+ ion is smaller than that of K^+ ion.	Na^+ ion is more extensively hydrated as compared to K^+ ion.
2.	The ions Zn^{2+}, Na^+ and Mg^{2+} are not reducible with hydrogen gas under standard conditions.	The standard potential of hydrogen $H^+ \mid H_2$ is less than that of $M^{2+} \mid M$
3.	The reduction potential of mercurous/ mercury decreases by 0.0295 V on diluting the solution ten times at 298 K.	The mercurous ion in solution exists as Hg_2^{2+} ion and not as Hg^+ ion.
4.	In the titration between Fe^{2+} ions versus $Cr_2O_7^{2-}$ ions, diphenylbenzene is used as the indicator in the presence of phosphoric acid.	Phosphoric acid helps changing the potential of ferric-ferrous system.
5.	Potentiometric titrations involving acid and base can be carried out by using quinhydrone electrode as the reference electrode.	Quinhydrone is equimolar mixture of quinone (Q) and hydroquinone (H_2Q). In solution, it exists as $Q + 2H^+ \rightleftharpoons H_2Q$
6.	Potential of Calomel electrode is sensitive to the concentration of Cl^- in solution.	Calomel electrode is $Cl^-(aq) \mid Hg_2Cl_2(s) \mid Hg(Pt)$
7.	Oxidation and reduction reactions occur at anode and cathode, respectively, in electrolytic as well as galvanic cell.	The sign of anode and cathode are identical in electrolytic as well as galvanic cell.
8.	In the cell diagram, the left half cell acts as anode.	The reduction reaction occurs at anode of a galvanic cell.
9.	The cell potential is obtained by by subtracting half-cell potential of cathode from that of anode.	Anode involves oxidation and cathode involves reduction.
10.	The half-cell potential of $Na^+(aq)\mid Na$ is negative while that of $Cl^-(aq)\mid Cl_2(g)\mid Pt$ is positive.	The half-cell potential of an electrode is a measure of reduction tendency of the reaction occurring at this electrode relative to that occurring at $H^+(aq) \mid H_2(g) \mid Pt$ half cell. The latter acts as reference half-cell whose potential is taken to be zero at standard conditions.
11.	The compounds of active metals such as Zn, Na and Mg are not reduced by hydrogen but the metal itself oxidiable by H^+ to yield H_2.	The cell potential of a cell producing the reaction $M^{n+} + \frac{n}{2} H_2 \rightarrow M + nH^+$ is negative because the half-cell potential $M^{n+} + ne^- \rightarrow M$ is negative.
12.	The entropy of reaction occurring in a cell can be determined by cell potentials at different temperatures.	ΔS of the reaction is given by the expression $\Delta S = nF\left(\partial E / \partial T\right)_p$
13.	The glass electrode is sensitive to $[H^+]$ in the solution.	The expression of cell potential of glass electrode is given by $E_{glass} = E^\circ_{glass} + \frac{RT}{F}$ pH

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32. The smaller the value of reduction potential, lesser the reduction tendency of the ion and larger the oxidation tendency of the corresponding metal. Larger oxidation tendency implies stronger reducing agent.

33. Cu^{2+} has larger tendency to reduce than H^+ and Sn^{2+} has lesser tendency to reduce than H^+.
Hence, Cu^{2+} ion can be reduced by $H_2(g)$.

34. For depositing metal ions, the emf of external battery must exceed the reduction potential.

36. $E°(Cu^{2+}|Cu) > E°(Fe^{2+}|Fe)$. The reaction $Fe^{2+} + Cu \rightarrow Fe + Cu^{2+}$ is not feasible.

37. Larger the reduction potential, larger the oxidation tendency of the ion being reduced. Hence, the oxidizing tendency follows the order $Pb^{4+} > Hg^{2+} > Sn^{4+}$.
Lesser the reduction potential, larger the reduction tendency of the ion formed in the reduction reaction. Hence, the reducing tendency follows the order $Sn^{2+} > Hg^{2+} > Pb^{2+}$.

39. The cell reaction giving $E°_{cell}$ positive is $Hg_2^{2+} + Sn \rightarrow 2Hg + Sn^{2+}$. $E°_{cell} = E°_{Hg_2^{2+}|Hg} - E°_{Sn^{2+}|Sn}$
From this, it follows that Hg_2^{2+} can oxidize Sn to Sn^{2+}.

40. More positive potential means more easily ion is reducible and more difficult is the oxidation of the corresponding atom. Reducing power of the metal means more easily the metal should be oxidizable.

41. H_2 is oxidized to H^+ and thus it will occur at anode, i.e., left-side electrode Pt $|H_2(g)|$ HCl(aq)
AgCl is reduced to Ag and thus it will occur at cathode, i.e., right-side electrode HCl (aq)|AgCl(s)| Ag(s). Hence, the cell with these reactions is Pt | $H_2(g)$ | HCl(aq) | AgCl(s) | Ag

42. In the given reaction Zn is oxidised to Zn^{2+} and Fe^{2+} is reduced to Fe. Hence,

$$E_{cell} = E°_{Fe^{2+}|Fe} - E°_{Zn^{2+}|Zn} = -0.41\ V - (-0.76\ V) = 0.35\ V.$$

44. For the reaction $H^+(aq) + e^- \longrightarrow \frac{1}{2} H_2(g)$, the standard potential is given by $E = -\dfrac{RT}{nF} \ln \dfrac{(p_{H_2}/\text{bar})^{1/2}}{\left([H^+]/\text{mol dm}^{-3}\right)/c°}$

E will be negative if the numerical value of $p_{H_2}^{1/2}/[H^+] > 1$.

45. For the reaction $Cu^{2+} + 2e^- \rightarrow Cu$, Nernst equation is $E = E° - \dfrac{RT}{2F} \ln \dfrac{1}{[Cu^{2+}]/c°}$
If the solution is diluted 100 times, then we have

$$E_2 - E_1 = -\frac{RT}{2F} \ln \frac{[Cu^{2+}]}{(0.01)[Cu^{2+}]} = +\frac{RT}{2F} \ln (0.01) = -\frac{2 \times 0.059\ V}{2} = -0.059\ V$$

46. We have $E = -\dfrac{RT}{F} \ln \dfrac{\left(p_{H_2}^{1/2}/\text{bar}\right)}{\left([H^+]/\text{mol dm}^{-3}\right)}$

Since $E = 0$, we must have $(p_{H_2}/\text{bar})^{1/2}/([H^+]/\text{mol dm}^{-3}) = 1$. Thus $\dfrac{p_{H_2}}{\text{bar}} = \dfrac{[H^+]^2}{(\text{mol dm}^{-3})^2} = (10^{-7})^2$. Hence $p_{H_2} = 10^{-14}$ bar.

47. $E = -\dfrac{RT}{F} \ln \dfrac{\left(p_{H_2}/\text{bar}\right)^{1/2}}{[H^+]/\text{mol dm}^{-3}} = -(0.059\ V) \log \dfrac{1}{(10^{-7})} = -7 \times 0.059\ V = -0.413\ V$

48. The half cell reaction is $H^+ + e^- \rightarrow \frac{1}{2}H_2$. Its potential is given by $E = -(RT/nF) \ln \dfrac{(p_{H_2}/\text{atm})^{1/2}}{[H^+]/\text{mol dm}^{-3}}$.
In 1 M NaOH, $[H^+] = K_w/[OH^-] = 10^{-14}\ M^2 / 1\ M = 10^{-14}$ M. Hence, at 25 °C and 1 atm pressure
$E = -(0.059\ V) \log (1 / 10^{-14}) = -0.059 \times 14\ V = -0.826\ V$

49. For the reaction $H^+ + e^- \rightarrow (1/2)\ H_2$, we have $E = -\dfrac{RT}{F} \ln \dfrac{(p_{H_2}/\text{atm})^{1/2}}{([H^+]/\text{mol L}^{-1})}$

50. $E = -\dfrac{RT}{nF} \ln \dfrac{(p_{H_2}/\text{atm})^{1/2}}{[H^+]/\text{mol}^{-1}} = -(0.059\ V) \log \left(\dfrac{1}{10^{-7}}\right) = +0.413\ V$

51. $E_{H^+|H_2|Pt} = -\dfrac{RT}{F} \ln \dfrac{(p_{H_2}/\text{atm})^{1/2}}{[H^+]/\text{mol dm}^{-3}}$. The combination $p(H_2) = 1$ atm and $[H^+] = 2$ M will make $E_{H^+|H_2|Pt}$ positive

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Substituting the given data, we get $0.3495\ V = E^\circ - \frac{(0.059\,V)}{2} \log\left(\frac{0.001}{0.01}\right)$

This gives $E^\circ = 0.3495\ V - 0.0295\ V = 0.32\ V$. Since $\Delta G^\circ = -nFE^\circ = -RT \ln K^\circ_{eq}$, we get

$$\ln K^\circ_{eq} = \frac{nF}{RT} E^\circ$$

At 25 °C, we have $\log K^\circ_{eq} = \left(\frac{1}{0.0295\ V}\right)(0.32\ V) = \frac{0.32}{0.0295}$. Hence $K^\circ_{eq} = 10^{(0.32/0.0295)}$

76. From the given data, we have

$$2H^+(aq) + \tfrac{1}{2}\ O_2(g) + 2e^- \rightarrow H_2O(l);\quad E^\circ_1 = 1.23\ V$$

$$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s);\quad E^\circ_2 = -0.44\ V$$

Subtract

$$Fe(s) + 2H^+(aq) + \tfrac{1}{2}\ O_2(g) \rightarrow Fe^{2+}(aq) + H_2O(l)$$

$$E^\circ = E^\circ_1 - E^\circ_2 = (1.23 + 0.44)\ V = 1.67\ V$$

The given reaction is obtained by multiplying the above reaction by 2. Hence, in the given reaction, the number of electrons is 4. Thus

$$\Delta G^\circ = -nFE^\circ = -(4)\ (96\,500\ C\ mol^{-1})\ (1.67\ V) = -644\,620\ J\ mol^{-1} = -644.62\ kJ\ mol^{-1}$$

77. We have $Cd^{2+}(aq) + Fe(s) \rightleftharpoons Cd(s) + Fe^{2+}(aq)$

$1.0\ M - x$ $\qquad$ x

Hence $E = E^\circ - \frac{RT}{2F} \ln \frac{[Fe^{2+}]}{[Cd^{2+}]}$

At equilibrium $E = 0$. Hence

$$E^\circ = \frac{RT}{2F} \ln \frac{[Fe^{2+}]}{[Cd^{2+}]} \quad \text{i.e.} \quad \frac{x}{1.0\,M - x} = \text{antilog}\left(\frac{E^o}{RT/2F}\right)$$

or $$\frac{x}{1.0\,M - x} = \text{antilog}\left(\frac{0.037\ V}{0.0295\ V}\right) = 10^{1.254} \simeq 18 \quad \text{or} \quad x = \frac{18}{19}\ M = 0.95\ M$$

Thus, $[Fe^{2+}] = 0.95\ M$ and $Cd^{2+}(aq) = 0.05\ M$

78. The equilibrium constant of the reaction $H^+(aq) + OH^-(aq) \rightleftharpoons H_2O(l)$

is $$K_{eq} = \frac{[H_2O]}{[H^+][OH^-]} = \frac{55.56\,M}{10^{-14}\,M^2} = 55.56 \times 10^{14}\ M^{-1}$$

Since $\Delta G^\circ = -nFE^\circ = -RT \ln K^\circ$, we have

$$E^\circ = \frac{RT \ln K^\circ}{nF} = \left(\frac{2.303\,RT}{nF}\right) \log K^\circ = (0.059\ V) \log (55.56 \times 10^{-14}) = -0.723\ V$$

79. We have $Ag^+ + e^- = Ag$

$$E = E^\circ - \frac{RT}{F} \ln \frac{1}{[Ag^+]/M} = E^\circ - \frac{RT}{F} \ln \left(\frac{1}{[Ag^+]/M} \frac{[X^-]/M}{[X^-]/M}\right)$$

$$= [E^\circ + \frac{RT}{F} \ln K^\circ_{sp}(Ag\,X)] - \frac{RT}{F} \ln ([X^-]/M)$$

The last expression may be identified for the potential of $X^- \mid AgX(s) \mid Ag(s)$ half-cell.

Hence $E^\circ_{X^- \mid AgCl \mid Ag} = E^\circ_{Ag^+ \mid Ag} + \frac{RT}{F} \ln K^\circ_{sp}(AgX)$

Since $K_{sp}(AgCl) > K_{sp}(AgBr) > K_{sp}(AgI)$ It follows that $E^\circ_{Cl^- \mid AgCl \mid Ag} > E^\circ_{Br^- \mid AgBr \mid Ag} > E^\circ_{I^- \mid AgI \mid Ag}$

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The reaction (a) is obtained by adding reactions (b) and (c). Hence
$\Delta G_1^\circ = \Delta G_2^\circ + \Delta G_3^\circ = -F(4 \times 0.54 + 2 \times 0.17)\ V = -(2.5\ V)\ F$

(ii) $E^\circ = \dfrac{\Delta G_1^0}{nF} = -\dfrac{-(2.5\,V)}{6F} = 0.417\ V$

(iii) Only BrO^- can be oxidized as well as reduced. $3BrO^- \rightarrow BrO_3^- + 2Br^-$
The cell producing this reaction is $Pt \mid BrO_3^-, BrO^-, OH^- \mid\mid BrO^-, Br^-, OH^- \mid Pt$
$E^\circ_{cell} = E^\circ_R - E^\circ_L = E^\circ_{BrO^-,\ Br^-|Pt} - E^\circ_{BrO_3^-,\ BrO^-|Pt} = 0.17\ V - 0.54\ V = -0.37\ V$
Since E_{cell} is negative, the disproportionation of BrO^- is not possible.

10. (i) The given reactions are

(a) $Sn^{4+} + 2e^- \rightarrow Sn^{2+}$ $\qquad \Delta G_1^\circ = -(2)\ (F)\ (0.15\ V)$

(b) $Sn^{2+} + 2e^- \rightarrow Sn$ $\qquad \Delta G_2^\circ = -(2)\ (F)\ (-0.14\ V)$

The reaction $Sn^{4+} + 4e^- \rightarrow Sn$ can be produced by adding reactions (a) and (b). Hence
$\Delta G^\circ = \Delta G_1^\circ + \Delta G_2^\circ = (F)\ [0.30\ V - 0.28\ V) = -(F)\ (0.02\ V)$

(ii) $E^\circ = \dfrac{\Delta G^\circ}{nF} = -\dfrac{-(F)(0.02\,V)}{(4)\,(F)} = 0.005\ V$

(iii) Considering the disproportionation reaction $2Sn^{2+} \rightarrow Sn^{4+} + Sn$
The cell potential this reaction is

$$E^\circ = E^\circ_R - E^\circ_L = E^\circ_{Sn^{2+}/Sn} - E^\circ_{Sn^{4+},\ Sn^{2+}/Pt} = -0.14\ V - 0.15\ V = -0.29\ V$$

Since the cell potential is negative, the disproportionation reaction is not feasible.

11. (i) $ClO_4^- + 2H^+ + 2e^- \rightarrow ClO_3^- + H_2O$ $\qquad \Delta G_1^\circ = -2F\ (0.36\ V)$

$ClO_3^- + 2H^+ + 2e^- \rightarrow ClO_2^- + H_2O$ $\qquad \Delta G_2^\circ = -2F\ (0.33\ V)$

Add $ClO_4^- + 4H^+ + 4e^- \rightarrow ClO_2^- + 2H_2O$ $\qquad \Delta G = \Delta G_1^\circ + \Delta G_2^\circ = -4FE^\circ$

Hence $-4FE^\circ = -2F\ (0.36\ V) - 2F\ (0.33\ V)$ i.e. $E^\circ = (0.36\ V + 0.33\ V)/2 = 0.345\ V$

(ii) The reaction $2ClO_3^- \rightleftharpoons ClO_2^- + ClO_4^-$ involves the following half reactions

$ClO_3^- + 2H^+ + 2e^- \rightleftharpoons ClO_2^- + H_2O$

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

Hence $E^\circ_{cell} = E^\circ_R - E^\circ_L = E^\circ_{ClO_3^-,\ ClO_2^-,\ H^+|Pt} - E^\circ_{ClO_4^-,\ ClO_3^-,\ H^+|Pt} = 0.33\ V - 0.36\ V = -0.03\ V$

(iii) Since $\Delta G^\circ = -RT \ln K^\circ_{eq} = -nFE^\circ$, we have $RT \ln K^\circ_{eq} = nFE^\circ$

or $\qquad K^\circ_{eq} = \text{antilog}\left(\dfrac{E^\circ}{2.303\,RT/nF}\right) = \text{antilog}\left(\dfrac{-0.03\,V}{0.0295\,V}\right) = 10^{-1} = 0.1$

Now $2ClO_3^- \rightleftharpoons ClO_2^- + ClO_4^-$
$\qquad 0.1\ M - 2x \quad x \quad x$

Hence $K_{eq} = \dfrac{[ClO_2^-][ClO_4^-]}{[ClO_3^-]^2} = \dfrac{x^2}{(0.1\,M - 2x)^2}$ or $\dfrac{x}{1\,M - x} = \sqrt{K_{eq}} = \sqrt{0.1} = 0.32$

$x = \dfrac{0.32}{1.32}\ M = 0.24\ M.$ Thus $\dfrac{[ClO_4^-]}{[ClO_3^-]} = \dfrac{0.24\,M}{(1.0\,M - 0.24\,M)} = 0.32$

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Solution We have

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad E^\circ_{Cu^{2+}\,|\,Cu} = 0.337\ V$$
$$Ag^+ + e^- \rightarrow Ag \qquad E^\circ_{Ag^+\,|\,Ag} = 0.799\ V$$

Since $E^\circ_{Ag^+\,|\,Ag}$ is greater than $E^\circ_{Cu^{2+}|Cu}$, the half cell $Ag^+\,|Ag$ will constitute the cathode of the galvanic cell. Hence, the required cell is $Cu\,|\,Cu^{2+}\,||\,Ag^+\,|\,Ag$

Its standard emf is $E^\circ_{cell} = E^\circ_R - E^\circ_L = 0.799\ V - 0.337\ V = 0.462\ V$

The cell reaction may be obtained as follows.

Right half-cell	$2Ag^+ + 2e^- \rightarrow 2Ag$
Left half-cell	$Cu \rightarrow Cu^{2+} + 2e^-$
Add	$2\,Ag^+ + Cu \rightarrow 2Ag + Cu^{2+}$

Its Nernst equation is $E_{cell} = E^\circ_{cell} - \dfrac{RT}{2F} \ln \dfrac{[Cu^{2+}]}{[Ag^+]^2}$

For $E = 0$, we will have

$$0 = 0.462\ V - \left(\frac{0.059\,15\,V}{2}\right) \log \frac{0.01}{([Ag^+]/M)^2} \quad \text{or} \quad \log \frac{0.01}{([Ag^+]/M)^2} = \frac{2 \times 0.462}{0.059\,15} = 15.6345$$

or $$2 \log ([Ag^+]/M) = \log 0.01 - 15.6345 \quad \text{or} \quad \log ([Ag^+]/M) = \frac{-2 - 15.6345}{2} = -8.8173$$

or $$[Ag^+] = 1.523 \times 10^{-9}\ M.$$

6. Zinc granules are added in excess to 500 mL of 1.0 M nickel nitrate solution at 25 °C until equilibrium is reached. If the standard reduction potential of $Zn^{2+}\,|\,Zn$ and $Ni^{2+}\,|\,Ni$ are – 0.75 V and – 0.24 V, respectively, calculate the concentrations of Ni^{2+} in solution at equilibrium. (1991)

Solution The reaction to be considered is $Zn(s) + Ni^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Ni(s)$

The cell producing this reaction would be $Zn(s)\,|\,Zn^{2+}(aq)\,||\,Ni^{2+}(aq)\,|\,Ni(s)$

with standard cell potential as $E^\circ_{cell} = E^\circ_R - E^\circ_L = -0.24\ V - (-0.75\ V) = 0.51\ V$

The equilibrium constant of the reaction would be given as

$$\log K_{eq} = \frac{nFE^\circ}{2.303RT} = \frac{(2)\,(96\,500\,C\,mol^{-1})(0.51\,V)}{(2.303)\,(8.314\,J\,K^{-1}\,mol^{-1})\,(298\,K)} = 17.25$$

Hence $$K_{eq} = 1.78 \times 10^{-17}$$

Let x be the concentration of Ni^{2+} ions that have been reduced to Ni at equilibrium.

We will have $Zn(s) + \underset{1.0\ M - x}{Ni^{2+}(aq)} \rightleftharpoons \underset{x}{Zn^{2+}}(aq) + Ni(s)$

Thus $$K_{eq} = \frac{[Zn^{2+}]}{[Ni^{2+}]} = \frac{x}{1.0\,M - x}$$

Solving for x, we would get

$$x \simeq \frac{K_{eq} \times 1.0\,M}{1 + K_{eq}} \simeq 1.0\ M. \quad \text{Now} \quad [Ni^{2+}] = \frac{[Zn^{2+}]}{K_{eq}} = \frac{1.0\,M}{1.78 \times 10^{17}} = 5.6 \times 10^{-18}\ M.$$

7. 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 at 25 °C. Given: $K^\circ_{sp}(AgCl) = 2.8 \times 10^{-10}$ and $K^\circ_{sp}(AgBr) = 3.3 \times 10^{-13}$. (1992)

Solution The cell reaction and its potential may be determined as follows.

Half-cell	*Reduction reaction*	*Reduction potential*
(i) LHC	$AgCl + e^- \rightarrow Ag + Cl^-$	$E_{Cl^-\,|\,AgCl\,|\,Ag} = E^\circ_{Cl^-\,|\,AgCl\,|\,Ag} - \dfrac{RT}{F} \ln [Cl^-]$
(ii) RHC	$AgBr + e^- \rightarrow Ag + Br^-$	$E_{Br^-\,|\,AgBr\,|\,Ag} = E^\circ_{Br^-\,|\,AgBr\,|\,Ag} - \dfrac{RT}{F} \ln [Br^-]$

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15. A solution containing 1 M each of $AgNO_3$ and $Fe(NO_3)_2$ is allowed to come to equilibrium at 298 K. What are the values of $[Fe^{2+}]$, $[Fe^{3+}]$ and $[Ag^+]$ at this point? The reaction occurring is

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

Given: $E^\circ_{Fe^{3+},\,Fe^{2+}\,|\,Pt} = 0.770$ V and $E^\circ_{Ag^+\,|\,Ag} = 0.7996$ V.

Solution In the given reaction, Fe^{2+} is oxidized to Fe^{3+} and Ag^+ is reduced to Ag. The cell producing this reaction would be

$$Pt\,|\,Fe^{3+}(aq),\ Fe^{2+}(aq)\,||\,Ag^+(aq)\,|\,Ag$$

with $E^\circ_{cell} = E^\circ_{Ag^+\,|\,Ag} - E^\circ_{Fe^{3+},\,Fe^{2+}\,|\,Pt} = (0.7996 - 0.770)\text{V} = 0.0296$ V

The equilibrium constant of the reaction will be given as

$$\log K^\circ_{eq} = \frac{nFE^\circ}{2.303RT} = \frac{nE^\circ}{(2.303RT/F)} = \frac{0.0296\,\text{V}}{0.05915\,\text{V}} \simeq \frac{1}{2}$$

$$K^\circ_{eq} = 3.16$$

At equilibrium, the concentrations of various species involved in the reactions will be as follows.

Fe^{2+}	+	Ag^+	$\rightleftharpoons$	Fe^{3+}	+	Ag
$1.0\text{ M} - x$		$1.0\text{ M} - x$		x		x

Hence, $$K_{eq} = \frac{[Fe^{3+}]}{[Fe^{2+}][Ag^+]} = \frac{x}{(1.0\,\text{M} - x)^2}$$

Substituting the value of K_{eq} and solving for x, we get

$$x = 1.74\text{ M} \quad \text{and} \quad x = 0.574\text{ M}$$

As $x = 1.74$ M is greater than 1.0 M, it is a meaningless quantity. Hence,

$$x = 0.574\text{ M}$$

Thus $[Fe^{2+}] = 1.0\text{ M} - 0.574\text{ M} = 0.426\text{ M}$ $[Fe^{3+}] = 0.574$ M

$[Ag^+] = 1.0\text{ M} - 0.574\text{ M} = 0.426$ M.

16. Two cells are constructed in which the $Ni^{2+}\,|\,Ni$ is one of the half-cells. When the other half-cell is $Cu^{2+}\,|\,Cu$, the E° is measured as 0.570 V with the nickel electrode as anode. When the $Mg^{2+}\,|\,Mg$ electrode is the other half-cell, the E° is measured as 2.145 V with the magnesium electrode as the anode. Calculate E° for the cell made of the magnesium and copper electrodes and designate the anode and cathode.

Solution In the first case, since nickel electrode is anode, the cell would be

$$Ni\,|\,Ni^{2+}(aq)\,||\,Cu^{2+}(aq)\,|\,Cu \quad \text{with} \quad E^\circ_1 = E^\circ_{Cu^{2+}\,|\,Cu} - E^\circ_{Ni^{2+}\,|\,Ni} \tag{1}$$

In the second case, since magnesium electrode is anode, the cell would be

$$Mg\,|\,Mg^{2+}(aq)\,||\,Ni^{2+}(aq)\,|\,Ni \quad \text{with} \quad E^\circ_2 = E^\circ_{Ni^{2+}\,|\,Ni} - E^\circ_{Mg^{2+}\,|\,Mg} \tag{2}$$

Adding Eqs. (1) and (2), we get $E^\circ_1 + E^\circ_2 = E^\circ_{Cu^{2+}\,|\,Cu} - E^\circ_{Mg^{2+}\,|\,Mg}$

Substituting the values of E°_1 and E°_2, we get

$$E^\circ = E^\circ_{Cu^{2+}\,|\,Cu} - E^\circ_{Mg^{2+}\,|\,Mg} = E^\circ_1 + E^\circ_2 = (0.570 + 2.145)\text{ V} = 2.715\text{ V}$$

Since E° is positive, the cell made from $Cu^{2+}\,|\,Cu$ and $Mg^{2+}\,|\,Mg$ will have Cu electrode as cathode and magnesium electrode as anode.

17. Given that $K_{sp}(AgCl) > K_{sp}(AgBr) > K_{sp}(AgI)$, show that $E^\circ_{Cl^-\,|\,AgCl\,|\,Ag} > E^\circ_{Br^-\,|\,AgBr\,|\,Ag} > E^\circ_{I^-\,|\,AgI\,|\,Ag}$.

Solution Consider a half-cell assembly of silver dipped into a saturated solution of AgCl. This assembly may be viewed as $Ag^+\,|\,Ag$ half-cell or $Cl^-\,|\,AgCl\,|\,Ag$ half-cell. The potential of the half-cell calculated from the Nernst equation of either $Ag^+\,|\,Ag$ half-cell or $Cl^-\,|\,AgCl\,|\,Ag$ half-cell will come out to be identical. Hence, we have

$Ag^+\,\|\,Ag$ *half-cell*	$Ag^+(aq) + e^- \rightleftharpoons Ag$	$E = E^\circ_{Ag^+\,\|\,Ag} - \frac{RT}{F}\ln\frac{1}{[Ag^+]/M}$	(1)
$Cl^-\,\|\,AgCl\,\|\,Ag$ *half-cell*	$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq)$	$E = E^\circ_{Cl^-\,\|\,AgCl\,\|\,Ag} - \frac{RT}{F}\ln[Cl^-]/M$	(2)

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8. Show that $E^\circ_{Cl^- \mid AgCl \mid Ag} = E^\circ_{Ag^+ \mid Ag} + \dfrac{RT}{F} \ln K^\circ_{sp}(AgCl)$.

9. Show that at 298 K $E^\circ_{OH^- \mid H_2 \mid Pt} = -0.828$ V

10. Show that $E^\circ_{Fe^{3+},\, Fe^{2+} \mid Pt} = 3\, E^\circ_{Fe^{3+} \mid Fe} - 2\, E^\circ_{Fe^{2+} \mid Fe}$

Also calculate $E^\circ_{Fe^{3+},\, Fe^{2+} \mid Pt}$ if $E^\circ_{Fe^{3+} \mid Fe} = -0.036$ V and $E^\circ_{Fe^{2+} \mid Fe} = -0.439$ V.

11. Calculate the equilibrium constant at 298 K of the following reactions.

(a) $2\,MnO_4^- + 6H^+ + 5H_2 \rightarrow 2Mn^{2+} + 8H_2O$

(b) $2Cr^{3+} + 6\,Fe^{3+} + 7H_2O \rightarrow 6Fe^{2+} + Cr_2O_7^{2-} + 14\,H^+$

(c) $Hg_2Cl_2(s) \rightarrow 2Hg(l) + Cl_2(g)$

Given: $E^\circ_{MnO_4^-,\, Mn^{2+},\, H^+ \mid Pt} = 1.51$ V; $E^\circ_{Cr_2O_7^{2-},\, Cr^{3+},\, H^+ \mid Pt} = 1.33$ V

$E^\circ_{Fe^{3+},\, Fe^{2+} \mid Pt} = 0.77$ V; $E^\circ_{Cl^- \mid Cl_2 \mid Pt} = 1.3583$ V

$E^\circ_{Cl^- \mid Hg_2Cl_2 \mid Hg} = 0.2676$ V;

12. A sample of lead weighing 1.05 g was dissolved in a small quantity of nitric acid to produce an aqueous solution of Pb^{2+} and Ag^+ (which is present as impurity). The volume of the solution was increased to 350 mL by adding water, a pure silver electrode was immersed in the solution and the potential difference between this electrode and a standard hydrogen electrode was found to be 0.503 V. What was the percentage of silver in the lead metal?

13. The K_{sp} of CuI is $1.1 \times 10^{-12}\ M^2$. Determine E° for the cell $Cu(s) \mid CuI(s) \mid I^-(1M) \mid\mid Cu^+(1M) \mid Cu$.

14. Show that $E^\circ_{H^+ \mid O_2 \mid Pt} = 1.229$ V. Given: Half-cell reaction is $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$.

15. Compute E° for the following reactions at 298 K.

$Ag(NH_3)_2^+ + e^- \rightleftharpoons Ag + 2NH_3$

$Ag(CN)_2^- + e^- \rightleftharpoons Ag + 2CN^-$

Given: $E^\circ_{Ag^+ \mid Ag} = 0.799$ V

$Ag^+ + 2NH_3 \rightarrow Ag(NH_3)_2^+ \qquad K^\circ = 1.661 \times 10^7$

$Ag^+ + 2CN^- \rightarrow Ag(CN)_2^- \qquad K^\circ = 5.013 \times 10^{18}$

16. (a) The standard potentials of the two reactions

$M^{n+} + ne^- \rightarrow M$ and $M^{m+} + me^- \rightarrow M$

are $E^\circ_{M^{n+} \mid M}$ and $E^\circ_{M^{m+} \mid M}$, respectively. Assuming n to be greater than m, show that the standard potential of the reaction

$$M^{n+} + (n-m)\, e^- = M^{m+}$$

is given as $E^\circ_{M^{n+},\, M^{m+} \mid Pt} = \dfrac{n E^\circ_{M^{n+} \mid M} - m E^\circ_{M^{m+} \mid M}}{n-m}$

(b) If $E^\circ_{Cr^{3+} \mid Cr} = -0.74$ V and $E^\circ_{Cr^{3+},\, Cr^{2+} \mid Pt} = -0.40$ V, determine $E^\circ_{Cr^{2+} \mid Cr}$.

17. The emf of the cell $Pt \mid H_2(g, 1\ bar) \mid HA_1(0.1\ M) \mid\mid HA_2(0.1\ M) \mid H_2(g, 1\,bar) \mid Pt$ is found to be 0.032 V. Which of the two weak acids is stronger and how many times?

Unsolved Problems (Galvanic cells)

1. $2Cu^+ \rightarrow Cu^{2+} + Cu$ $\qquad E^\circ_{cell} = 0.38$ V

2. $Cl_2 + 2OH^- \rightarrow Cl_2 + ClO^- + H_2O$ $\qquad E^\circ_{cell} = 0.96$ V

3. 10^{-14} bar

4. 703.1

5. 0.0666 V

6. -0.70 V

7. 1.088 V

10. 0.770 V

11. (a) 2.4×10^{255} (b) 1.98×10^{-57} (c) 1.39×10^{-37}

12. 0.036% Ag

13. 0.71

15. 0.372 V, -0.307 V

16. -0.91 V

17. HA_2 is 3.5 time stronger than HA_1.

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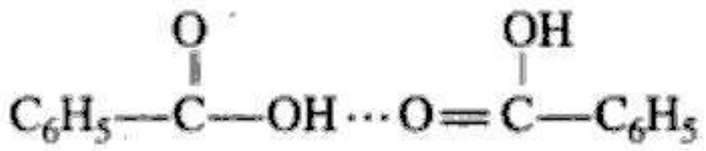
4. Which of the following expressions is/are correctly depicted?
(a) $x_2 = mx_1M_1$ (b) $x_2 = mM_1/(1 + mM_1)$
(c) $x_2 = MM_1/(M(M_1 - M_2) + \rho)$ (d) $x_2 = mM_2/M_1$

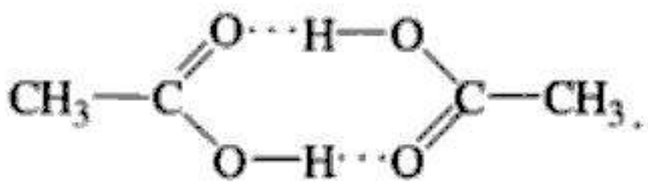
5. Which of the following expressions is/are correctly depicted?
(a) $m = n_2/n_1M_1$ (b) $M = n_2/V$ (c) $x_1 = n_1/n_2$ (d) $x_1 + x_2 = 1$

6. For an ideal binary liquid solution, which of the following statements is/are correct?
(a) The plot of $1/y_A$ (where y_A is the mole fraction of A in vapour phase) versus $1/x_A$ (where x_A is the mole fraction of A in liquid phase) is linear.
(b) The plot of $1/p_{total}$ versus y_A is linear.
(c) The plot of $1/p_{total}$ versus x_A is linear.
(d) y_A is greater than x_A if the component A is more volatile.

7. For an ideal binary liquid solution, which of the following statements is/are correct?
(a) The plot of temperature versus x_A (where x_A is the mole fraction of A in liquid phase) is linear.
(b) The plot of temperature versus y_A (where y_A is the mole fraction of A in vapour phase) is linear.
(c) The two components can be separated by the method of fractional distillation.
(d) The vapour phase is more rich in the more volatile component as compared to the liquid phase.

8. Which of the following statements are correct?
(a) Water has maximum density at 4 °C.
(b) The unit of K_f is K kg^{-1}.
(c) Isotonic solutions have identical osmotic pressures.
(d) Osmotic pressure of 0.1 molar sodium chloride solution is identical with that of 0.1 molar glucose solution.

9. Which of the following statements are not correct?
(a) The value of K_b for water is larger than that of K_f.
(b) The elevation of boiling point of a solvent when a nonvolatile solute is added to it is larger than its depression in freezing point.
(c) Osmotic pressure measurement is preferred over any other colligative properties in determining the molar mass of proteins and polymers.
(d) The dimerized form of benzoic acid in benzene is 

10. Which of the following statements are correct?
(a) The dimerized form of acetic acid in benzene is  .
(b) Lowering of vapour pressure is a colligative property.
(c) The value of K_b or K_f depends only on the type of solvent and not solute dissolved in it.
(d) For a very dilute solution, mole fraction of a solute is directly proportional to the molality of the solution.

11. Which of the following statements are correct?
(a) The increasing order of osmotic pressure of 0.1 M aqueous solution containing different electrolyte is as follows. 0.1 M Glucose < 0.1 M Sodium chloride < 0.1 M Magnesium chloride.
(b) Density of a solution is independent of temperature.
(c) Camphor has comparatively larger value of K_f as compared to other common solvents.
(d) Limiting value of van't Hoff factor of $K_4Fe(CN)_6$ is 11.

12. Which of the following statements are correct?
(a) A solution contains two non-volatile solutes. The molar mass of such a solution determined through colligative property is the mass average molar mass.
(b) The vapour pressure of an ideal solution may be predicted by using Raoult's law.
(c) The molarity of a solution is independent of temperature
(d) The relative lowering of vapour pressure of a solution containing nonvolatile solutes is a colligative property.

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Thus $K_{eq} = \dfrac{(1-\Delta T_b / K_b m)}{m[(2\Delta T_b / K_b m)-1]^2} = \dfrac{K_b (K_b m - \Delta T_b)}{(2\Delta T_b - K_b m)^2}$

61. Since $\Delta T_b = K_b\, m = K_b \left(\dfrac{n_2}{m_1}\right)$, we have $0.15\ \text{K} = K_b \left(\dfrac{n_2}{0.05\ \text{kg}}\right)$ and $0.375\ \text{K} = K_b \left(\dfrac{n_2}{m_1}\right)$

Thus $\dfrac{0.15\ \text{K}}{0.375\ \text{K}} = \dfrac{m_1}{0.05\ \text{kg}}$ or $m_1 = \left(\dfrac{0.15\ \text{K}}{0.375\ \text{K}}\right)(0.05\ \text{kg}) = 0.02\ \text{kg}$

Mass of water evaporated = 50 g – 20 g = 30 g.

62. Since $K_b = (M_1 R T_b^{*2} / \Delta_{vap} H_m)$, we have

$$\Delta_{vap} H_m = \frac{M_1 R T_b^{*2}}{K_b} = \frac{(0.082\ \text{kg mol}^{-1})(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(354.55\ \text{K})^2}{(2.79\ \text{K kg mol}^{-1})} = 30717\ \text{J mol}^{-1} = 30.72\ \text{kJ mol}^{-1}$$

63. $K_b = \dfrac{M_1 R T_b^{*2}}{\Delta_{vap} H_m} = \dfrac{(0.076\ \text{kg mol}^{-1})(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(320\ \text{K})^2}{(352\ \text{J g}^{-1})(76\ \text{g mol}^{-1})} = 2.42\ \text{K kg mol}^{-1}$

64. $0.4\ \text{K} = K_b \dfrac{(0.5\ \text{g})/(130\ \text{g mol}^{-1})}{(50\ \text{g})}$ and $0.65\ \text{K} = K_b \dfrac{(0.6\ \text{g})/M}{(50\ \text{g})}$

From these, we get $\dfrac{0.4}{0.65} = \dfrac{0.5/(130\ \text{g mol}^{-1})}{0.6/M} \Rightarrow M = \dfrac{0.4 \times 0.6 \times 130}{0.65 \times 0.5}\ \text{g mol}^{-1} = 96\ \text{g mol}^{-1}$

65. A semipermeable membrane allows the passage of solvent molecules only

66. Concentration of glucose $= \dfrac{(50/180)\ \text{mol}}{(1.05\ \text{kg}/1.02\ \text{kg L}^{-1})} = 0.27\ \text{mol L}^{-1}$

Osmotic pressure, $\Pi = cRT = (0.27\ \text{mol L}^{-1})\ (8.314\ \text{kPa L}^{-1}\ \text{K}^{-1}\ \text{mol}^{-1})\ (300\ \text{K}) = 673.85\ \text{kPa}$

67. Osmotic pressure, $\Pi = cRT = (2 \times 0.1\ \text{mol L}^{-1})\ (0.082\ \text{atm L K}^{-1}\ \text{mol}^{-1})\ (300\ \text{K}) = 4.92\ \text{atm}.$

69. Isotonic solutions have the same osmotic pressures. The same osmotic pressures implies the same concentrations. 0.1 M $Ca(NO_3)_2$ produces 0.3 M species (0.1 M Ca^{2+} + 0.2 M NO_3^-) and also 0.1 M Na_2SO_4 produces 0.3 M species (0.2 M Na^+ and 0.1 M SO_4^{2-}).

70. The dissociation of K_2SO_4 may be written as

$$\underset{c(1-\alpha)}{K_2SO_4} \rightleftharpoons \underset{c(2\alpha)}{2K^+} + \underset{c\alpha}{SO_4^{2-}}$$

The concentration of species in the solution is $c(1 - \alpha) + c(2\alpha) + c\alpha = c(1 + 2\alpha)$, (where $c = 0.004$ M).

Hence $c(1 + 2\alpha) = 0.01\ \text{M}$ or $\alpha = \dfrac{1}{2}\left(\dfrac{0.01}{0.004} - 1\right) = 0.75$

The per cent dissociation is 0.75×100, i.e. 75%

71. The correct expression is $\alpha = \dfrac{i-1}{(x+y-1)}$

72. Benzoic acid dimerizes in benzene. Its van't Hoff factor will be 1/2.

73. $K_3[Fe(CN)_6]$ and $Al(NO_3)_3$ produce the same number of species.

74. $\alpha = \dfrac{i-1}{(x+y)-1} = \dfrac{2.74-1}{3-1} = 0.87$

75. Acetic acid ionizes as $\underset{1-\alpha}{CH_3COOH} \rightleftharpoons \underset{\alpha}{CH_3COO^-} + \underset{\alpha}{H^+}$

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(iii) Mole fraction of methanol in vapour phase $y_1 = \dfrac{p_1}{p_1 + p_2} = \dfrac{36.37}{36.37 + 26.26} = \dfrac{36.37}{62.63} = 0.58$

5. **(i)** The composition of A in vapour phase is $y_A = \dfrac{p_A}{p_{total}} = \dfrac{x_A p_A^*}{x_A p_A^* + x_B p_B^*} = \dfrac{x_A p_A^*}{p_B^* + (p_A^* - p_B^*) x_A}$

Hence, $y_A - x_A = \dfrac{x_A p_A^*}{p_B^* + (p_A^* - p_B^*) x_A} - x_A$

For the maximum value of $y_A - x_A$, we set $d(y_A - x_A)/dx_A = 0$. This gives

$$\frac{p_A^*}{p_B^* + (p_A^* - p_B^*) x_A} - \frac{x_A p_A^* (p_A^* - p_B^*)}{[p_B^* + (p_A^* - p_B^*)]^2} - 1 = 0$$

Solving for x_A, we get $x_A = \dfrac{\sqrt{p_A^* p_B^*} - p_B^*}{p_A^* - p_B^*}$

(ii) $p_{total} = p_B^* + (p_A^* - p_B^*) x_A = p_B^* + \left(\sqrt{p_A^* p_B^*} - p_B^*\right) = \sqrt{p_A^* p_B^*}$

(iii) $y_A = \dfrac{p_A}{p_{total}} = \dfrac{x_A p_A^*}{\sqrt{p_A^* p_B^*}} = \left(\dfrac{\sqrt{p_A^* p_B^*} - p_B^*}{p_A^* p_B^*}\right)\left(\dfrac{p_A^*}{p_B^*}\right)^{1/2} = \left(\dfrac{\sqrt{p_A^*} - \sqrt{p_B^*}}{p_A^* - p_B^*}\right)\sqrt{p_A^*}$

6. **(i)** Total pressure of the first bubble of vapour is

$$p_{total} = x_A p_A^* + x_B p_B^* = (0.6 \times 300 + 0.4 \times 800)\ \text{Torr} = 500\ \text{Torr}$$

$$y_A = \frac{p_A}{p_{total}} = \frac{x_A p_A^*}{p_{total}} = \frac{0.6 \times 300\ \text{Torr}}{500\ \text{Torr}} = 0.36$$

(ii) When the last drop of liquid remains the composition of A in vapour phase will be equal to 0.60 as most of the liquid has vapourized. Hence

$$y_A = \frac{p_A}{p_{total}} = \frac{x_A p_A^*}{x_A p_A^* + x_B p_B^*} = \frac{x_A p_A^*}{p_B^* + (p_A^* - p_B^*) x_A} \quad \text{i.e } 0.60 = \frac{x_A (300\ \text{Torr})}{800\ \text{Torr} - (300\ \text{Torr} - 800\ \text{Torr})\, x_A}$$

Solving for x_A, we get $x_A = 0.80$.

(iii) The pressure of the vapour when the last liquid remains would be

$$p = x_A p_A^* + x_B p_B^* = (0.8 \times 300 + 0.2 \times 800)\ \text{Torr} = 400\ \text{Torr}.$$

ANNEXURE

Subjective Problems for Practice

SOLVED PROBLEMS

1. The vapour pressure of pure benzene at 25 °C is 639.7 mmHg and the vapour pressure of a solution of a solute in benzene at the same temperature is 631.9 mmHg. Calculate the molality of the solution. (1981)

Solution Using Raoult's law ($p_1 = x_1 p_1^*$), we get

$$x_1 = \frac{p_1}{p_1^*} = \frac{631.9\ \text{mmHg}}{639.7\ \text{mmHg}} = 0.988$$

Now molality of the solution is given as

$$m = \frac{n_2}{n_1 M_1} = \frac{x_2}{x_1}\frac{1}{M_1} = \frac{0.012}{0.988} \times \frac{1}{0.078\ \text{kg mol}^{-1}} = 0.156\ \text{mol kg}^{-1}.$$

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$$\text{Volume of 100 g solution} = \frac{100\ \text{g}}{1.198\ \text{g cm}^{-3}} = 83.47\ \text{cm}^3$$

$$\text{Molarity of solution} = \frac{0.276\ \text{mol}}{(83.47/1000)\ \text{dm}^3} = 3.307\ \text{mol dm}^{-3}$$

$$\text{Molality of solution} = \frac{0.276\ \text{mol}}{(73/1000)\ \text{kg}} = 3.78\ \text{mol kg}^{-1}$$

Since sulphuric acid contains 2 replaceable H^+ ions, we will have Normality of solution = 6.614 eq dm^{-3}
Applying normality equation, we get

$$(100\ \text{mL})\ (6.614\ \text{N}) = V\ (1.5\ \text{N}) \quad \text{or} \quad V = \frac{100 \times 6.614}{1.5}\ \text{mL} = 440.9\ \text{mL}.$$

14. What volume of 1.0 M HCl must be added to 50.0 mL of 0.50 M HCl to give a solution whose concentration is 0.6 M?

Solution Let V be the volume of 1.0 M HCl that has been added to 50.0 mL of 0.50 M HCl to give a solution whose concentration is 0.6 M. We will have

$$(V)\ (1.0\ \text{M}) + (50.0\ \text{mL})\ (0.50\ \text{M}) = (V + 50.0\ \text{mL})\ (0.6\ \text{M})$$

Solving for V, we get $(V)\ (1.0\ \text{M} - 0.6\ \text{M}) = (50.0\ \text{mL})\ (0.6\ \text{M} - 0.50\ \text{M})$

or $V = (0.1/0.4) \times 50.0\ \text{mL} = 12.5\ \text{mL}.$

15. To what volume must 250 mL of 1.40 M H_2SO_4 be diluted to give a solution, 25.0 mL of which is able to completely react with 15.0 mL of 0.75 M NaOH solution?

Solution Let M be the molarity of diluted sulphuric acid solution. We will have

$$(25.0\ \text{mL})\ (2\ M) = (15.0\ \text{mL})\ (0.75\ \text{M}) \quad \text{or} \quad M = \frac{15.0 \times 0.75}{25.0 \times 2}\ \text{M}$$

If V is the volume to which the original sulphuric acid is diluted, we will have

$$(V)\left(\frac{15.0 \times 0.75}{25.0 \times 2}\ \text{M}\right) = (250\ \text{mL})\ (1.40\ \text{M}) \quad \text{or} \quad V = (250 \times 1.40)\left(\frac{25.0 \times 2}{15.0 \times 0.75}\right)\ \text{mL} = 1555.56\ \text{mL}.$$

16. Determine the volume of dilute nitric acid (density 1.11 g cm^{-3}, 19 mass % HNO_3) that can be prepared by diluting 50.0 cm^3 of concentrated acid (density 1.42 g cm^{-3}, 69.8 mass % HNO_3). Calculate the molarities and molalities of concentrated and dilute acids.

Solution *Concentrated Acid*

69.8 mass % HNO_3 implies that 69.8 g of HNO_3 is present in 100 g of total solution. Thus, we have

$$\text{Mass of } HNO_3 = 69.8\ \text{g} \qquad \text{Amount of } HNO_3 = \frac{69.8\ \text{g}}{63\ \text{g mol}^{-1}} = 1.1075\ \text{mol}$$

$$\text{Mass of solution} = 100\ \text{g} \qquad \text{Volume of solution} = \frac{100\ \text{g}}{1.42\ \text{g cm}^{-3}} = 70.42\ \text{cm}^3$$

$$\text{Mass of water} = 100\ \text{g} - 69.8\ \text{g} = 30.2\ \text{g}$$

Hence, $$\text{Molarity of solution} = \frac{1.1075\ \text{mol}}{70.42 \times 10^{-3}\ \text{dm}^3} = 15.73\ \text{mol dm}^{-3}$$

$$\text{Molality of solution} = \frac{1.1075\ \text{mol}}{30.2 \times 10^{-3}\ \text{kg}} = 36.67\ \text{mol kg}^{-1}$$

Dilute Acid

Here, we have

$$\text{Mass of } HNO_3 = 19\ \text{g} \qquad \text{Amount of } HNO_3 = \frac{19\ \text{g}}{63\ \text{g mol}^{-1}} = 0.3016\ \text{mol}$$

$$\text{Mass of solution} = 100\ \text{g} \qquad \text{Volume of solution} = \frac{100\ \text{g}}{1.11\ \text{g cm}^{-3}} = 90.05\ \text{cm}^3$$

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Total concentration of species in solution = $c(1 + \alpha) = (0.1\ \text{M})(1 + \alpha)$

Now, Osmotic pressure of NaCl solution = $(0.1\ \text{M})\ (1 + \alpha)\ RT$

Osmotic pressure of urea solution = $\dfrac{(1/60)\ \text{mol}}{0.1\ \text{L}}\ RT$

Since the two solutions are isotonic, we will have

$$(0.1\ \text{M})(1 + \alpha)RT = \left(\frac{1}{60 \times 0.1}\ \text{mol L}^{-1}\right)\ RT \quad \text{or} \quad \alpha = \frac{1}{60 \times 0.1 \times 0.1} - 1 = 1.667 - 1 = 0.667$$

Now, van't Hoff factor = $\dfrac{c(1+\alpha)}{c} = 1.667$

28. The freezing point depression of a 0.109 M aqueous solution of formic acid is –0.21 °C. Calculate the equilibrium constant for the equation $\text{HCOOH(aq)} \rightleftharpoons \text{H}^+\text{(aq)} + \text{HCOO}^-\text{(aq)}$

The molality of the solution is 0.110 mol kg^{-1} and K_f(water) = 1.86 K kg mol^{-1}.

Solution If α is the degree of dissociation of HCOOH, we will have

$$\underset{m(1-\alpha)}{\text{HCOOH}} \rightleftharpoons \underset{m\alpha}{\text{H}^+} + \underset{m\alpha}{\text{HCOO}^-} \qquad \text{Total molality of the solution} = m(1 + \alpha)$$

Hence, $0.21\ \text{K} = m(1 + \alpha)(1.86\ \text{K kg mol}^{-1})$ which gives $\alpha = \dfrac{0.21}{0.11 \times 1.86} - 1 = 0.0264$

Thus $K = \dfrac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]} = \dfrac{(c\alpha)(c\alpha)}{c(1-\alpha)} = \dfrac{c\alpha^2}{1-\alpha} = \dfrac{(0.109\,\text{M})\,(0.026\,4)^2}{(1-0.026\,4)} = 7.8 \times 10^{-5}\,\text{M}.$

29. When 2 g of a nonvolatile hydrocarbon containing 94.4 per cent carbon is dissolved in 100 g benzene, the vapour pressure of benzene is lowered from 74.66 Torr to 74.01 Torr. Determine the molecular formula of the hydrocarbon.

Solution According to Raoult's law, $\dfrac{-\Delta p}{p^*} = x_2$ where $-\Delta p = (74.01 - 74.66)$ Torr and $p^* = 74.66$ Torr.

If M is the molar mass of hydrocarbon, then

$$x_2 = \frac{n_2}{n_1 + n_2} = \frac{(2\,\text{g}/M)}{(100\,\text{g}/78\,\text{g mol}^{-1}) + (2\,\text{g}/M)} \quad \text{Hence,} \quad \frac{(74.66 - 74.01)\,\text{Torr}}{74.66\,\text{Torr}} = \frac{(2\,\text{g}/M)}{(100\,\text{mol}/78) + (2\,\text{g}/M)}$$

Solving for M, we get $M = 177.6\ \text{g mol}^{-1}$

Thus atomic ratio is $N_C : N_H :: \dfrac{94.4}{12} : \dfrac{5.6}{1} \Rightarrow 7.87 : 5.6 \Rightarrow 1.4 : 1 \Rightarrow 7 : 5$

Hence, Empirical formula is C_7H_5. Molar empirical mass = 89 g mol^{-1}

$$\text{Number of } C_7H_5 \text{ unit in the given molecule} = \frac{\text{Molar mass}}{\text{Molar empirical mass}} = \frac{177.6}{89} \simeq 2$$

Thus, molecular formula is $C_{14}H_{10}$.

30. The addition of 3 g of a substance to 100 g CCl_4 (M = 154 g mol^{-1}) raises the boiling point of CCl_4 by 0.60 °C. If $K_b(CCl_4)$ is 5.03 K mol^{-1} kg, calculate (a) the freezing point depression, (b) the relative lowering of vapour pressure, (c) the osmotic pressure at 298 K and (d) the molar mass of the substance. Given: $K_f(CCl_4)$ = 31.8 K kg mol^{-1} and ρ(solution) = 1.64 g cm^{-3}.

Solution The molality of the given solution is $m = \dfrac{\Delta T_b}{K_b} = \dfrac{0.60\,\text{K}}{5.03\,\text{K kg mol}^{-1}} = 0.12\ \text{mol kg}^{-1}$

(a) $-\Delta T_f = K_f\, m = (31.8\ \text{K kg mol}^{-1})\ (0.12\ \text{mol kg}^{-1}) = 3.816\ \text{K}$

(b) If M_2 is the molar mass of the substance, then

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Solution Let M be the molar mass of benzoic acid in the solution. The molality of the solution is

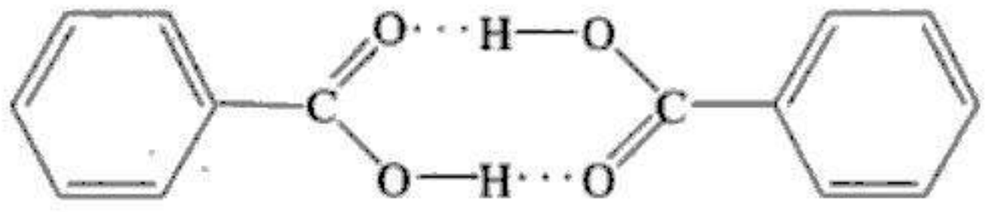
$$m = \frac{n}{m_1} = \frac{(12.2\text{ g})/M}{1\text{ kg}}$$

Since $\Delta T_b = K_b\, m$, we get

(a) *Acetone solution* $0.17\text{ K} = (1.7\text{ K kg mol}^{-1})\left[\dfrac{12.2\text{ g}/M_1}{1\text{ kg}}\right]$; $M_1 = \dfrac{1.7\times12.2}{0.17}\text{ g mol}^{-1} = 122\text{ g mol}^{-1}$

Benzene solution $0.13\text{ K} = (2.6\text{ K kg mol}^{-1})\left[\dfrac{12.2\text{ g}/M_2}{1\text{ kg}}\right]$; $M_2 = \dfrac{2.6\times12.2}{0.13}\text{ g mol}^{-1} = 244\text{ g mol}^{-1}$

(b) The actual molar mass of benzoic acid (C_6H_5COOH) is 122 g mol^{-1}. This means benzoic acid is present as monomer in acetone solution while it dimerises in benzene solution. The structure of dimerised benzoic acid is



39. In 1 kg of a solvent ($K_f = 14\text{ K kg}^{-1}$ mol), 75.2 g of phenol was dissolved. The depression in freezing point of the solvent was found to be 7 K. Determine the degree of dimerization of phenol. (2006)

Solution We have

$$\underset{m(1-\alpha)}{2\,\text{PhOH}} \rightleftharpoons \underset{m\alpha/2}{(\text{PhOH})_2}$$

where $m = \dfrac{n_2}{m_1} = \dfrac{75.2\text{ g}/(94\text{ g mol}^{-1})}{1\text{ kg}} = 0.8\text{ mol kg}^{-1}$

Molality of solution $= m(1-\alpha) + m\,\alpha/2 = m(1-\alpha/2)$

Since $\Delta T_f = K_f\, m$, we get

$7\text{ K} = (14\text{ K kg}^{-1}\text{ mol})\,(0.8\text{ mol kg}^{-1})\,(1-\alpha/2)$ This gives $\alpha = 2\left[1-\dfrac{1}{2\times0.8}\right] = 0.75$

Unsolved Problems

1. What volume of 95 mass per cent of alcohol (density 0.809 g cm^{-3}) must be used to prepare 150 cm^3 of 30 mass per cent alcohol (density 0.987 g cm^{-3})?
2. Concentrated HNO_3 has a specific gravity of 1.42 and is 69 mass % in HNO_3. What mass of HNO_3 is contained in 500 mL of this reagent? What volume of this concentrated HNO_3 be diluted to obtain 800 mL of 0.20 M HNO_3?
3. What would be the molality of a solution made by mixing equal volumes of 30 mass % H_2SO_4 (density 1.218 g cm^{-3}) and 70 mass % H_2SO_4 (density 1.610 g cm^{-3})? If the density of the resulting solution is 1.425 g cm^{-3}, what is its molarity?
4. The molality of a 1 M solution of sodium nitrate is 0.858 mol kg^{-1}. Determine the density of the solution.
5. The molarity of NH_3 in an aqueous solution is 11.8 mol dm^{-3}. The density of the solution is 0.916 g cm^{-3}. Determine : (a) molality, (b) mass per cent and (c) mole fraction of NH_3.
6. What is the mole fraction of benzene in a benzene-toluene solution that is in equilibrium with a vapour phase containing 60.0 mol % C_6H_6? Given: p^* (benzene) = 95.1 mmHg and p^* (toluene) = 28.4 mmHg.
7. *n*-Butane and *n*-pentane form a nearly ideal solution. At 25 °C, the vapour pressure of *n*-butane is 1823 Torr and that of *n*-pentane is 521 Torr.
   (a) Find the vapour pressure at 25°C of a liquid solution containing 10 mass % of *n*-butane.
   (b) Find the mole fraction of *n*-butane of a solution having vapour pressure of 760 Torr at 25°C.
   (c) What is the mass percentage of *n*-butane in the vapour phase in (b)?

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General Expression For a reaction A → products following n^{th} order ($n \neq 1$), we have

$$\frac{dx}{dt} = k_n ([A]_0 - x)^n; \qquad \frac{1}{(n-1)}\left[\frac{1}{[A]_t^{n-1}} - \frac{1}{[A]_0^{n-1}}\right] = k_n t$$

$$t_{0.5} = \frac{1}{k_n(n-1)} \frac{2^{n-1}-1}{[A]_0^{n-1}}$$

The reaction of the type $aA + bB + cC \rightarrow$ products with $\frac{[A]_0}{a} = \frac{[B]_0}{b} = \frac{[C]_0}{c}$ also belongs to this category. The integrated rate expression is

$$\frac{1}{(n-1)}\left[\frac{1}{[A]_t^{n-1}} - \frac{1}{[A]_0^{n-1}}\right] = k\frac{b^\beta c^\gamma}{a^{n-\alpha-1}} t; \qquad \text{where } n = \alpha + \beta + \gamma$$

The half-life time is

$$t_{0.5} = \frac{1}{k(n-1)} \frac{a^{n-\alpha-1}}{b^\beta c^\gamma} \frac{2^{n-1}-1}{[A]_0^{n-1}}$$

Ostwald Isolation Method In a reaction A + B → products following the rate law $r = k[A]^\alpha [B]^\beta$ if one of the reacting species (say, A) has very large concentrations in comparing to the other species, its concentration virtually remains constant (or the charge is negligible), the rate expression can be written as

$$r = k'[B]^\beta \qquad \text{where } k' = k[A]^\alpha = \text{constant}$$

This method reduces the order of a reaction. One of the examples is the acid hydrolysis of an ester which follows the rate law

$$r = k\,[\text{ester}]\,[H_2O]\,[H^+]$$

here H^+ ions act as a catalyst (its concentration remains constant throughout the hydrolysis) and H_2O is present in excess. Hence, the rate law is reduced to

$$r = k'\,[\text{ester}] \qquad \text{where } k' = k\,[H_2O]\,[H^+]$$

Variation of Rate Constant with Temperature The rate of a reaction depends on the temperature of the system. The Arrhenius equation describing the temperature dependence is

$$k = A \exp(-E_a/RT)$$

where A is known as pre-exponential term and E_a is the energy of activation. The latter is definied as the difference between the minimum energy required to bring about molecular rearrangement and the average energy of the reactant species. The logarithmic form of Arrhenius equation is

$$\log \frac{k_2}{k_1} = -\frac{E_a}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where k_2 and k_1 are the rate constants at temperatures T_2 and T_1, respectively.

Effect of a Catalyst on a Reaction Sometimes, the rate of a chemical reaction is altered in the presence of a substance called the catalyst. Though the catalyst is involved in the reaction, it does not appear in the overall reaction.

Broadly, two types of catalysts are known, namely, *homogeneous* and *heterogeneous* catalysts. A homogeneous catalyst is present in the same phase as the reaction and a heterogeneous catalyst exists in different phase from the reaction it catalyzes. The rate of catalytic reaction is usually proportional to the concentration of the homogeneous catalyst or the surface area of the heterogeneous catalyst. It is because of this reason, the latter is usually taken in a finally divided form.

For a reversible reaction, the rates of forward as well as reverse directions are increased with the result that the equilibrium stage is reached more quickly. The catalyst has no effect on the equilibrium amounts of reactants and products. Thus, the equilibrium constant of the reaction is not affected in the presence of a catalyst.

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which of the following facts is true?
(a) $k = k'$ (b) $k > k'$ (c) $k > 2k'$ (d) $2k = k'$

38. The gaseous reaction $A(g) \rightarrow 2\ B(g) + C(g)$ is found to be first-order with respect to A. If the reaction is started with $p_A = 90$ mmHg, the pressure after 10 min is found to be 180 mmHg. The rate constant of the reaction is
(a) $1.15 \times 10^{-3}\ s^{-1}$ (b) $2.30 \times 10^{-3}\ s^{-1}$ (c) $3.45 \times 10^{-3}\ s^{-1}$ (d) $4.60 \times 10^{-3}\ s^{-1}$

39. A substance A reacts according to a first-order rate law with rate constant equal to $5.0 \times 10^{-5}\ s^{-1}$. The rate of the reaction $A \rightarrow B$ after 3.85 h when the reaction is started with 1.0 M of A will be
(a) 4.0×10^{-5} mol $L^{-1}\ s^{-1}$ (b) 3.0×10^{-5} mol $L^{-1}\ s^{-1}$
(c) 2.5×10^{-5} mol $L^{-1}\ s^{-1}$ (d) 2.0×10^{-5} mol $L^{-1}\ s^{-1}$

40. For a first-order reaction, the time taken to reduce initial concentration by a factor of 1/4 is 10 min. The time required to reduce initial concentration by a factor of 1/16 will be
(a) 10 min (b) 20 min (c) 30 min (d) 40 min

41. For a first-order reaction $A \rightarrow B$, the ratio of times to complete 99.9% and half of the reaction is
(a) 8 (b) 9 (c) 10 (d) 12

42. The reaction $\nu_1 A + \nu_2 B \rightarrow$ products is first-order with respect to A and zero-order with respect to B. If the reaction is started with $[A]_0$ and $[B]_0$, the integrated rate expression of this reaction would be
(a) $\ln \dfrac{[A]_0}{[A]_0 - x} = k_1 t$ (b) $\ln \dfrac{[A]_0}{[A]_0 - \nu_1 x} = k_1 t$
(c) $\ln \dfrac{[A]_0}{[A]_0 - \nu_1 x} = \nu_1 k_1 t$ (d) $\ln \dfrac{[A]_0}{[A]_0 - \nu_1 x} = -\nu_1 k_1 t$

43. The radioactive decay follows
(a) first-order kinetics
(b) second-order kinetics
(c) a complicated kinetics with temperature dependence behaviour
(d) zero-order kinetics

44. A first order reaction is 20% complete in 10 min. The rate constant of the reaction $A \rightarrow B$ is
(a) $0.223\ min^{-1}$ (b) $0.0223\ min^{-1}$ (c) $2.23\ min^{-1}$ (d) $22.3\ min^{-1}$

45. The half-life of a radioactive isotope is 3 h. What mass out of 100 g is left after 15 h?
(a) 12.5 g (b) 6.25 g (c) 3.125 g (d) 1.562 g

46. For a first order reaction $2N_2O_5 \xrightarrow{k} 4NO_2 + O_2$, the half-life period is given by
(a) $2.303/k$ (b) $0.693/k$ (c) $2.303/2k$ (d) $0.693/2k$

47. If the concentration of a reactant decreases from 800 mol dm^{-3} to 50 mol dm^{-3} in 2×10^5 s in a first order reaction $A \rightarrow B$, the rate constant of the reaction would be
(a) 2×10^{-5} s (b) 1.386×10^{-5} s (c) 3.45×10^{-5} s (d) 2×10^5 s (2003)

48. The reaction, $A \rightarrow$ products, follows first order kinetics. In 45 min, the concentration of A changes from 0.1 M to 0.0125 M. The rate of reaction when [A] = 0.001 M is
(a) 2.31×10^{-5} mol $L^{-1}\ min^{-1}$ (b) 4.62×10^{-5} mol $L^{-1}\ min^{-1}$
(c) 2.31×10^{-4} mol $L^{-1}\ min^{-1}$ (d) 4.62×10^{-4} mol $L^{-1}\ min^{-1}$ (2004)

49. Under the same reaction condition of $A \rightarrow B$, initial concentration of 1.386 mol dm^{-3} of a substance becomes half in 40 seconds and 20 seconds through first order and zero order kinetics, respectively. Ratio (k_1/k_0) of the rate constants for first order (k_1) and zero order (k_0) of the reactions is
(a) 0.5 $mol^{-1}\ dm^3$ (b) 1.0 mol dm^{-3} (c) 1.5 mol dm^{-3} (d) 2.0 $mol^{-1}\ dm^3$ (2008)

50. 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 $L^{-1}\ s^{-1}$, then the concentration of N_2O_5 (in mol L^{-1}) is
(a) 1.4 (b) 1.2 (c) 0.04 (d) 0.8 (2000)

51. The hydrolysis of an ester was carried out separately with 0.05 M HCl and 0.05 M H_2SO_4. Which of the following will be true?
(a) $k_{HCl} > k_{H_2SO_4}$ (b) $k_{HCl} < k_{H_2SO_4}$ (c) $k_{HCl} = k_{H_2SO_4}$ (d) $k_{H_2SO_4} = 2k_{HCl}$

52. The hydrolysis of an ester was carried out separately with 0.05 N HCl and 0.05 N H_2SO_4. Which of the following will be true?
(a) $k_{HCl} > k_{H_2SO_4}$ (b) $k_{HCl} < k_{H_2SO_4}$ (c) $k_{HCl} = k_{H_2SO_4}$ (d) $k_{H_2SO_4} = 2k_{HCl}$

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84. Given are the information: Reaction 1; $k = A\ e^{-E_1/RT}$ and Reaction 2; $k' = A\ e^{-E_2/RT}$
If $E_1 = 2E_2$, then the ratio $\ln(k_{T+10K}/k_T)$ for the reaction 1 will be
(a) equal to that of reaction 2
(b) greater than that of reaction 2
(c) lesser than that of reaction 2
(d) may be greater or lesser than reaction 2 depending upon the temperature T.

Catalyst

85. A catalyst is a substance which
(a) increases the equilibrium concentration of the product
(b) changes the equilibrium constant of the reaction
(c) shortens the time to reach equilibrium
(d) supplies energy to the reaction (1983)

86. A catalyst is a substance which
(a) increases the equilibrium constant of the reaction
(b) increases the equilibrium concentrations of the products
(c) does not alter the reaction mechanism
(d) changes the activation energy of the reaction

87. A catalyst lowers the activation energy of the forward reaction by 20 kJ mol^{-1}. It also changes the activation energy of the backward reaction by an amount
(a) equal to that of the forward reaction
(b) equal to twice that of the forward reaction
(c) which is determined only by the average energy of products
(d) which is determined by the average energy of products relative to that of reactants

88. The use of a catalyst helps in increasing the
(a) rate of forward direction only
(b) rate of backward direction only
(c) rates of both forward as well as backward directions
(d) relative amounts of products

89. Which of the following statements is **not** true?
(a) Catalyst is not involved in the reaction
(b) The concentration of a catalyst remains constant throughout the progress of chemical reaction
(c) The mechanism of catalytic reaction may vary from reaction to reaction
(d) Nitric oxide acts as a homogeneous catalyst in the oxidation of SO_2 into SO_3

90. Which of the following statements is **not** correct?
(a) The efficiency of a solid catalyst depends upon its surface area
(b) Catalyst operates by providing alternate path for the reaction that involves a lower activation energy
(c) Catalyst lowers the energy of activation of the forward direction without affecting the energy of activation of the backward direction
(d) Catalyst does not affect the overall enthalpy change of the reaction

91. Which of the following statements is **not** correct?
(a) The catalyst changes not only the rate of forward direction but also that of backward direction
(b) The catalyst changes the value of equilibrium constant of the reaction
(c) The mechanism of a catalytic reaction depends on the type of catalyst, i.e. whether it is homogeneous or heterogeneous
(d) Enzymes are essentially proteins which catalyze reaction occurring in living matter

92. Which of the following statements is **not** correct?
(a) Most heterogeneous catalytic reactions involve the solid surface of the catalyst
(b) Heterogeneous catalysts primarily function by lowering the activation energy of the reaction
(c) A solid catalyst present in the powder form is more effective as it has larger surface area
(d) The catalyst may be deactivated by heating it to high temperature

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24. Which of the following statements are **not** correct?
(a) For a reaction $(1/2)A \rightarrow 2B$, the rate of reaction in terms of disappearance of A is $-d[A]/dt$.
(b) For a reaction $(1/2)A_2 \rightarrow 2B$, the rate of disappearance of A_2 is related to the rate of appearance of B through an expression $-d[A_2]/dt = 4\ d[B]/dt$.
(c) Reactions with small activation energies slow a lesser increase in rate with rise in temperature as compared to that having high activation energy.
(d) The half-life for a given reaction is doubled as the initial concentration of a reactant was doubled. The order of the reaction would be zero.

25. Which of the following statements are **not** correct?
(a) A reaction has $k = 1.2 \times 10^{-4}\ mol^{-1}\ L\ s^{-1}$. Its order is two.
(b) The average rate of appearance of concentration of a product increases with the progress of a chemical reaction.
(c) The rate constant and order of a reaction are experimentally determined quantities.
(d) The rate constant of a zero order gaseous reaction is dependent of the gaseous pressure.

26. Which of the following statements are correct?
(a) A plot of $\log K_p^\circ$ versus $1/T$ is linear
(b) A plot of $\log \{[X]/M\}$ versus time is linear for a first order reaction, $X \rightarrow P$
(c) A plot of $\log (p/p^\circ)$ versus $1/T$ is linear at constant volume
(d) A plot of p versus $1/V$ is linear at constant temperature

Linked Comprehension Type

1. The reaction $2NO(g) + H_2(g) = N_2O(g) + H_2O(g)$ follows the rate law

$$\frac{dp(N_2O)}{dt} = k\,(p_{NO})^2\,p_{H_2}$$

The following data have been obtained.

Expt. No.	$(p_{NO})_0$ / mmHg	$(p_{H_2})_0$ / mmHg	*Half-life time* / *s*	*Temperature* / °C
1.	600	10	19.2	827
2.	600	20	?	827
3.	10	600	830	827
4.	20	600	?	827
5.	600	10	9.6	847

Based on these informations, answer the following three questions.
(i) The values of half-life time not shown above in the run 2 and 4, respectively, are
(a) 19.2 s, 8.30 s (b) 19.2 s, 415 s (c) 38.4 s, 830 s (d) 38.4 s, 415 s
(ii) The rate constant of the reaction is
(a) $10^{-5}\ mmHg^{-2}\ s^{-1}$ (b) $10^{-6}\ mmHg^{-2}\ s^{-1}$ (c) $10^{-7}\ mmHg^{-2}\ s^{-1}$ (d) $10^{-8}\ mmHg^{-2}\ s^{-1}$
(iii) The energy of activation of the reaction is about
(a) 250 kJ mol^{-1} (b) 280 kJ mol^{-1} (c) 315 kJ mol^{-1} (d) 355 kJ mol^{-1}

2. The following data were obtained for the decomposition of dimethyl ether:

$$CH_3OCH_3(g) \rightarrow CH_4(g) + CO(g) + H_2(g)$$

t/s	0	1600	3200
$p_{total/Torr}$	300	600	750

Based on this information, answer the following three questions.
(i) The order of the reaction is
(a) 0 (b) 1 (c) 2 (d) 3
(ii) The rate constant of the reaction is
(a) $4.33 \times 10^{-2}\ s^{-1}$ (b) $4.33 \times 10^{-3}\ s$ (c) $4.33 \times 10^{-4}\ s$ (d) $4.33 \times 10^{-5}\ s$

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57. (a)	**58.** (d)	**59.** (b)	**60.** (a)	**61.** (d)	**62.** (c)	**63.** (c)
64. (b)	**65.** (c)	**66.** (d)	**67.** (c)	**68.** (d)	**69.** (b)	**70.** (b)
71. (a)	**72.** (d)	**73.** (b)	**74.** (b)	**75.** (d)	**76.** (a)	**77.** (b)
78. (c)	**79.** (b)	**80.** (d)	**81.** (b)	**82.** (b)	**83.** (c)	**84.** (b)
85. (c)	**86.** (d)	**87.** (a)	**88.** (c)	**89.** (a)	**90.** (c)	**91.** (b)
92. (d)	**93.** (c)	**94.** (b)	**95.** (b)	**96.** (b)		

Multiple Correct Choice Type

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

Linked Comprehension Type

1. (i) (b)	(ii) (c)	(iii) (d)	**2.** (i) (b)	(ii) (c)	(iii) (c)
3. (i) (c)	(ii) (b)	(iii) (a)	**4.** (i) (c)	(ii) (b)	(iii) (b)
5. (i) (c)	(ii) (b)	(iii) (d)	**6.** (i) (b)	(ii) (c)	(iii) (d)
7. (i) (a)	(ii) (b)	(iii) (d)			

Reason and Assertion Type

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

Matrix Match Type

1. (a)-(r), (u)	(b)-(r), (s), (t)	(c)-(p), (r)	(d)-(q), (r)
2. (a)-(s)	(b)-(p), (u), (v)	(c)-(q), (t)	(d)-(r)

Hints and Solutions

Straight Objective Type

1. The rate constant of a reaction depends on temperature.

2. Same answer as Q.1.

3. The rate of reaction and rate of appearance (or disappearance) of a reactant (or product) are different quantities unless its stoichiometric number in chemical equation is one.

4. For the reaction $2A + 3B \rightarrow 4C$, the rate of reaction is represented as

$$-\frac{1}{2}\frac{d[A]}{dt} = -\frac{1}{3}\frac{d[B]}{dt} = \frac{1}{4}\frac{d[C]}{dt}$$

5. The unit of rate of reaction is mol L^{-1} s^{-1}.

6. The order of a reaction is an experimentally determined quantity.

7. The units of rate of reaction and rate constant are identical for a zero-order reaction.

8. For an elementary reaction, order is equal to the molecularity (i.e. sum of stoichiometric number of reactants).

9. The species OH^- with order -1 is an inhibitor.

10. $1.837 = (1.5)^{1.5}$

11. We have $K_{eq} = k_1/k_{-1}$.

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4. (i) The Arrhenius equation is $k = A\ e^{-E_a/RT}$. This gives $\log k = \log A - \dfrac{E_a}{2.303R}\dfrac{1}{T}$

$$\text{Thus } E_{a(f)} = (2.303\ R)\left(\frac{26000\text{K}}{4.58}\right) = (2.303)\ (8.314\ \text{J K}^{-1}\ \text{mol}^{-1})\left(\frac{26000\ \text{K}}{4.157}\right)$$

$$= 119756\ \text{J mol}^{-1} = 120\ \text{kJ mol}^{-1}$$

$$E_{a(b)} = (2.303\ R)\left(\frac{52400\text{K}}{4.375}\right) = (2.303)\ (8.314\ \text{J K}^{-1}\ \text{mol}^{-1})\left(\frac{52500\text{K}}{4.375}\right)$$

$$= 229766\ \text{J mol}^{-1} \simeq 230\ \text{kJ mol}^{-1}$$

(ii) The value of $\Delta_r H$ is $\Delta_r H = E_{a(f)} - E_{a(b)} = (120 - 230)\ \text{kJ mol}^{-1} = -110\ \text{kJ mol}^{-1}$

(iii) The standard equilibrium constant of the reaction is

$$K^\circ_{eq} = \frac{k_b/\text{s}^{-1}}{k_f/\text{M}^{-1}\,\text{s}^{-1}} = \frac{\text{antilog}\,[30.0 - 52500/(4.375\times 300)]}{\text{antilog}\,[8.848 - (26000)/(4.157\times 300)]} = \frac{1\times 10^{-10}}{1\times 10^{-12}} = 10^2$$

5. (i) In experiments 1 and 2, the $[OCl^-]$ is changed while those of I^- and OH^- are constant. Since the $[OCl^-]$ and $d[IO_3^-]/dt$ are doubled in experiment 2 as compared to experiment 1, it is concluded that the order of OCl^- is reaction with respect to 1. The same conclusion is drawn from experiments 1 and 3 where the concentration of I^- is changed, i.e. the order of reaction with respect to I^- is 1.
From experiments 1 and 4, it is obvious that on decreasing the concentration of OH^- to a half value, the rate of reaction is doubled. Hence, it may be concluded that the order of the reaction with respect to OH^- is – 1.

Hence, the rate law is $\dfrac{d[IO_3^-]}{dt} = k\dfrac{[OCl^-][I^-]}{[OH^-]}$

(ii) Taking data from experiment 1, we get

$$1.75\times 10^{-4}\ \text{mol dm}^{-3}\ \text{s}^{-1} = k\frac{(0.0017\,\text{M})(0.0017\,\text{M})}{(1\,\text{M})} \quad \Rightarrow \quad k = \frac{1.75\times 10^{-4}}{(0.0017)^2}\ \text{s}^{-1} = 60.55\ \text{s}^{-1}$$

(iii) $\dfrac{d[IO_3^-]}{dt} = (60.55\ \text{s}^{-1})\ \dfrac{(0.004\,\text{M})(0.002\,\text{M})}{(0.5\,\text{M})} = 9.7\times 10^{-4}\ \text{M}^{-1}\ \text{s}^{-1}$

6. (i) From the chemical equation $A(g) \rightarrow 2B(g) + C(g)$ we find that the decomposition of one gaseous molecule gives three molecules of gaseous products. Therefore, the initial pressure of A will be one third of the pressure obtained after very long time from the initiation of reaction. Hence

$$p_A = 270\ \text{mmHg}/3 = 90\ \text{mmHg}.$$

(ii) If p is the partial pressure of A that has decomposed after 10 min, we will have

i.e. $p_A + p_B + p_C = 176\ \text{mmHg}$ i.e. $(p_A)_0 - p + 2p + p = (p_A)_0 + 2p = 176\ \text{mmHg}$

Hence $p = \dfrac{176\ \text{mmHg} - (p_A)_0}{2} = \dfrac{176\ \text{mmHg} - 90\ \text{mmHg}}{2} = 43\ \text{mmHg}$

The partial pressure of A at this stage will be

$$p_A = (p_A)_0 - p = 90\ \text{mmHg} - 43\ \text{mmHg} = 47\ \text{mmHg}$$

(iii) The rate constant of the reaction will be

$$k = \frac{2.303\log[p_A/(p_A)_0]}{t} = \frac{2.303\log[47/90]}{(10\times 60\,\text{s})} = 1.1\times 10^{-3}\ \text{s}^{-1}$$

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in 20 min at 25 °C. Hence, at this temperature, the rate constant is given as

$$k = \left(\frac{1}{t}\right)\left(2.303 \ \log \frac{[A]_0}{[A]}\right) = \left(\frac{1}{20\,\text{min}}\right)\left(2.303 \ \log \ \frac{100}{75}\right) = 1.439 \times 10^{-2}\ \text{min}^{-1}$$

Now using Arrhenius equation, we calculate the rate constant at 40 °C.

We have $\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

or $\log k_2 - \log (1.439 \times 10^{-2}) = -\frac{(70 \times 10^3\ \text{J mol}^{-1})}{(2.303)\,(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})}\left(\frac{1}{313.15\text{K}} - \frac{1}{298.15\text{K}}\right)$

or $\log k_2 + 1.842 = \frac{70 \times 10^3 \times 15}{2.303 \times 8.314 \times 313.15 \times 298.15} = 0.587$

or $\log k_2 = 0.587 - 1.842 = -1.255$

or $k_2 = 5.56 \times 10^{-2}\ \text{min}^{-1}$

Finally $\log \frac{[A]}{[A]_0} = -\left(\frac{k_2}{2.303}\right) t = -\left(\frac{5.56 \times 10^{-2}\ \text{min}^{-1}}{2.303}\right)(20\ \text{min}) = -0.482\,8$ or $\frac{[A]}{[A]_0} = 0.33$

Per cent of A remaining = 33% and Per cent of A decomposed = 67%.

9. The gas phase decomposition of dimethyl ether follows first-order kinetics

$$CH_3OCH_3(g) \rightarrow CH_4(g) + H_2(g) + CO(g)$$

The reaction is carried out at constant volume container at 500 °C and has a half-life of 14.5 minutes. Initially only dimethyl ether is present at a pressure of 0.40 atmosphere. What is the total pressure of the system after 12 minutes? Assume ideal gas behaviour. **(1993)**

Solution We have

$$CH_3OCH_3(g) \rightarrow CH_4(g) + H_2(g) + CO(g)$$

$t = 0$	p_0	0	0	0
t	$p_0 - p$	p	p	p

Total pressure of the system at time $t = p_0 + 2p$

The rate expression for first order kinetics is

$$\log \frac{[A]}{[A]_0} = -\left(\frac{k}{2.303}\right) t$$

In the present case, we get

$$\log \frac{p_0 - p}{p_0} = -\frac{(0.693/t_{0.5})}{2.303}\, t = \frac{(-0.693/14.5\ \text{min})}{2.303}\,(12\ \text{min}) = -0.249 \quad \text{or} \quad \frac{p_0 - p}{p_0} = 0.564$$

$$p = p_0 - 0.564\, p_0 = p_0\,(1 - 0.564) = (0.40\ \text{atm})\ (0.436) = 0.174\,4\ \text{atm}$$

Hence, Total pressure of the system is $p_0 + 2p = (0.40 + 2 \times 0.174\,4)\ \text{atm} = 0.748\,8\ \text{atm}$.

10. From the following data for the reaction between A and B, 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.

[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^{-2}	1.6×10^{-2}	–

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$$\log \frac{[A]_t}{[A]_0} = -\left(\frac{k}{2.303}\right) t \quad \text{gives} \quad \log \frac{1}{m^n} = -\left(\frac{k}{2.303}\right) t$$

or $\quad t = \dfrac{2.303\, n \log m}{k}$ which is independent of the initial concentration of A.

16. For the first-order decomposition reaction $(CH_3)_3COOC(CH_3)_3 \rightarrow 2CH_3COCH_3 + C_2H_6$ in the gaseous phase, the pressures of the system at $t = 0$ and $t = 15$ min were found to be 169.3 Torr and 256.0 Torr, respectively. Calculate (a) the rate constant of the reaction, (b) half-life period and (c) the pressure of the system at 9 min.

Solution For the given reaction, we have

	$(CH_3)_3COOC(CH_3)_3$	$\rightarrow$	$2CH_3COCH_3$	+	C_2H_6
$t = 0$	p_0		0		0
t	$p_0 - p$		$2p$		p

Total pressure at time t, $p_t = p_0 + 2p$

Thus from the given data at $t = 0$ and $t = 15$ min, we get $\quad 256.0 \text{ Torr} = 169.3 \text{ Torr} + 2p$

or $\quad p = \dfrac{(256 - 169.3)\text{ Torr}}{2} = 43.35 \text{ Torr}$. Hence, $p_0 - p = (169.3 - 43.35)\text{ Torr} = 125.95 \text{ Torr}$

(a) Now using the integrated expression, $\log \dfrac{p_0 - p}{p_0} = -\dfrac{k}{2.303}\, t$, we get (1)

$$k = -\frac{2.303}{(15 \text{ min})} \log \left(\frac{125.95}{169.3}\right) = -\frac{2.303}{(15 \text{ min})}(-0.1285) = 0.019\,7 \text{ min}^{-1}$$

(b) The half-life period is $\quad t_{1/2} = \dfrac{0.693}{k} \log \dfrac{0.693}{(0.019\,7 \text{ min}^{-1})} = 35.18 \text{ min}$

(c) Substituting the data in Eq. (1), we get

$$\log \left(\frac{169.3 \text{ Torr} - p}{169.3 \text{ Torr}}\right) = -\frac{(0.019\,7 \text{ min}^{-1})}{(2.303)} (9 \text{ min}) = -0.076 \quad \text{or} \quad \frac{169.3 \text{ Torr} - p}{169.3 \text{ Torr}} = 0.837$$

This gives $\quad p = 27.50$ Torr. $\quad$ Hence, $p_{\text{total}} = p_0 + 2p = (169.3 + 2 \times 27.50)$ Torr $= 224.3$ Torr.

17. Azomethane decomposes according to the equation $(CH_3)_2N_2(g) \rightarrow C_2H_6(g) + N_2(g)$ The reaction was studied in a 200-mL flask at 300 °C. The data obtained were as follows.

t/min	0	15	30	48	75
p_{total}/Torr	36.2	42.4	46.5	53.1	59.3

Calculate the rate constant and the half-life for this reaction

Solution we have

	$(CH_3)_2N_2(g)$	$\rightarrow$	$C_2H_6(g)$	+	$N_2(g)$
$t = 0$	p_0		0		0
t	$p_0 - p$		p		p

Total pressure at time t, $p_{\text{total}} = p_0 + p$

The partial pressure of $(CH_3)_2N_2(g)$ at any time will be given as

$$p_{(CH_3)_2N_2} = p_0 - p = p_0 - (p_{\text{total}} - p_0) = 2p_0 - p_{\text{total}}$$

Hence, we have

t/min	0	15	30	48	75
$p_{(CH_3)_2N_2}$/Torr	36.2	30.0	25.9	19.3	13.1

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Hence, at 318 K we get

$$k = (3.56 \times 10^9\ s^{-1}) \exp\left[\frac{-76.57 \times 10^3\ J\ mol^{-1}}{(8.314\ J\ K^{-1}mol^{-1})(318\ K)}\right] = (3.56 \times 10^9\ s^{-1}) \exp(-28.96)$$

$$= (3.56 \times 10^9\ s^{-1})\ (2.65 \times 10^{-13}) = 9.43 \times 10^{-4}\ s^{-1}$$

25. The rate constant for the first order decomposition of a certain reaction is described by the equation

$$\log\ (k/s^{-1}) = 14.34 - (1.25 \times 10^4\ K)/T$$

(i) What is the energy of activation of this reaction?
(ii) At what temperature will its half-life be 256 minutes? (1997)

Solution The Arrehenius equation is

$$k = A \exp(-E_a/RT) \quad \text{or} \quad \log\ (k/s^{-1}) = \log\ (A/s^{-1}) - \frac{E_a}{2.303\ R}\frac{1}{T}$$

Comparing this expression with the given one, we get

$$\frac{E_a}{2.303\ R} = 1.25 \times 10^4\ K$$

Hence, $E_a = (1.25 \times 10^4\ K)\ (2.303)\ (8.314\ J\ K^{-1}\ mol^{-1}) = 2.39 \times 10^5\ J\ mol^{-1} = 239\ kJ\ mol^{-1}$

(ii) The reaction is first order as the unit of rate constant is s^{-1}. For a first-order reaction

$$t_{1/2} = 0.693/k$$

Hence, $k = \dfrac{0.693}{256 \times 60 s} = 4.51 \times 10^{-5}\ s$

Substituting this in the given expression, we get

$$\log\ (4.51 \times 10^{-5}) = 14.34 - \frac{1.25 \times 10^{-5} K}{T}$$

Solving for T, we get $T = 669$ K.

26. 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. (1998)

Solution The Arrhenius equation is $k = A \exp(-E_a/RT)$

For the two temperatures, we get

$$\log \frac{k_2}{k_1} = -\frac{E_a}{2.303}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Substituting the given data, we get

$$\log \frac{4.5 \times 10^7}{1.5 \times 10^7} = -\frac{E_a}{(2.303)(8.314\ J\ K^{-1}mol^{-1})}\left[\frac{1}{373\ K} - \frac{1}{323\ K}\right]$$

or $$E_a = \frac{(2.303)(8.314)(373)(323)}{50} \log\ (3.0) = 22012.7\ J\ mol^{-1}$$

The value of A would be

$$A = k \exp(E_a/RT) = (1.5 \times 10^7\ s^{-1}) \exp\left[\frac{22012.7\ J\ mol^{-1}}{(8.314\ J\ K^{-1}\ mol^{-1})(323\ K)}\right]$$

$$= (1.5 \times 10^7\ s^{-1})\ (3630.44) = 5.45 \times 10^{10}\ s^{-1}$$

27. The rate constant for an isomerization reaction A → B is $4.5 \times 10^{-3}\ min^{-1}$. If the initial concentration of A is 1 M, calculate the rate of the reaction after 1 h. (1999)

Solution From the unit of rate constant, it follows that the given isomerisation reaction is a first order reaction.

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8. For the reaction $H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow I_2(aq) + 2H_2O$ the following data are obtained

$\frac{[H_2O_2]}{\text{mol L}^{-1}}$	$\frac{[I^-]}{\text{mol L}^{-1}}$	$\frac{[H^+]}{\text{mol L}^{-1}}$	$\frac{d[I_2]/dt}{\text{mol L}^{-1}\text{ s}^{-1}}$
0.01	0.01	0.10	1.75×10^{-6}
0.03	0.01	0.10	5.25×10^{-6}
0.03	0.02	0.10	1.05×10^{-5}
0.03	0.02	0.20	1.05×10^{-5}

Determine the expression of rate law along with the value of rate constant.

9. At 300 K, a first-order reaction is 50% complete in 20 min. At 350 K, the same reaction is 50% complete in 5.0 min. Calculate the activation energy of the reaction.

10. The half-life of a first-order reaction at 298 K is 21 833 s. If the value of pre-exponential factor in Arrhenius equation is $1.97 \times 10^{12}\ s^{-1}$, calculate its activation energy.

11. The activation energy of the reaction $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$ is 132.0 kJ mol^{-1} and the rate constant at 500 K is 2.02×10^{-6} L mol^{-1} s^{-1}. Find the rate constant at 550 K.

12. A substance A was found to undergo two parallel first-order rearrangements $A \rightarrow B$ and $A \rightarrow C$ with rate constants $1.26 \times 10^{-4}\ s^{-1}$ and $3.8 \times 10^{-5}\ s^{-1}$, respectively. What were the percentage distribution of B and C?

13. The first-order gaseous decomposition of N_2O_4 into NO_2 has a k value of $4.5 \times 10^3\ s^{-1}$ at 1°C and an energy of activation of 58 kJ mol^{-1}. At what temperature its half-life would be 6.93×10^{-5} s?

14. H_2O and O react bimolecularly to form two OH radicals. ΔH for this reaction is 72 kJ mol^{-1} at 500 K and energy of activation equal to 77 kJ mol^{-1}. Estimate energy of activation for the bimolecular combination of two OH radicals to form H_2O and O.

15. The rate constant for the forward reaction is $1.2 \times 10^{-3}\ mm^{-1}$ at 30 °C. The enthalpies of activation and reaction are 85.48 kJ mol^{-1} and −107.1 kJ mol^{-1}, respectively. The rate constant for the reverse reaction is $1.2 \times 10^{-4}\ min^{-1}$ at 50 °C. What is its value at 40 °C?

16. The total pressure of the system for the equation $SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$ was observed as a function of time :

t/s	204	942	1686	2466	4944	7500	∞
p_{total}/Torr	325	335	345	355	385	415	594.2

Determine the order of the reaction and its rate constant.

17. The optical rotation of sucrose in 0.9 M HCl at 300 K at various times were found to be as follows.

t/min	0	15	30	45	60	∞
θ	+32.4°	+28.8°	+25.5°	+22.4°	+9.4°	−11.0°

Determine the order of reaction and its rate constant.

18. From the following data at a certain temperature show that the decomposition of H_2O_2 in aqueous solution is first-order reaction.

t/s	0	300	600	900	1200
V_{KMnO_4}/mL	22.8	17.7	13.8	10.6	8.2

Determine its rate constant.

19. The following data are obtained for the hydrolysis of ethyl acetate in the presence of HCl.

t/min	0	25	40	60	∞
V_{NaOH}/mL	19.2	24.2	26.6	29.5	42.1

where V_{NaOH} is the volume of NaOH solution used to neutralize acid present in certain volume of reacting mixture. Find the value of rate constant.

20. Two reactions of same order have equal pre-exponential factors but their activation energies differ by 24.9 kJ mol^{-1}. Calculate the ratio of the rate constants of these reactions at 300 K.

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Straight Objective Type

Adsorption

1. Which of the following statements about physical adsorption is **not** correct?
   (a) It is usually monolayer
   (b) It is reversible in nature
   (c) It involves van der Waals interactions between adsorbent and adsorbate
   (d) It involves small value of heat of adsorption
2. Which of the following statements about chemisorption is **not** applicable?
   (a) It involves chemical forces between adsorbent and adsorbate
   (b) It is irreversible in nature
   (c) It involves high heat of adsorption
   (d) It involves low activation energy
3. Which of the following statements regarding adsorption is **not** correct?
   (a) Extent of adsorption of gases on charcoal increases with increase in pressure of the gas
   (b) Extent of adsorption is independent of temperature
   (c) Extent of adsorption by a given mass of adsorbent has an upper limit
   (d) Extent of adsorption is dependent on the nature of adsorbate and adsorbent
4. Physical adsorption
   (a) involves the weak attractive interactions between the adsorbent and adsorbate
   (b) involves the chemical interactions between the adsorbent and adsorbate
   (c) is irreversible in nature
   (d) increases with increase in temperature
5. Chemisorption
   (a) involves the weak attractive interactions between the adsorbent and adsorbate
   (b) is irreversible in nature
   (c) decreases with increase in temperature
   (d) involves multilayer adsorption
6. Which of the following is **not** correct?
   (a) The extent of adsorption depends on the nature of the adsorbent and adsorbate
   (b) The extent of adsorption depends on the pressure of the gas
   (c) The extent of adsorption depends on the temperature
   (d) The extent of adsorption has no upper limit
7. Which of the following statements regarding adsorption is **not** true?
   (a) The phenomenon of adsorption implies the presence of excess concentration of adsorbate at the surface of adsorbent
   (b) The phenomenon of adsorption is due to the presence of residual forces at the surface of the body
   (c) During adsorption, there occurs a decrease in free energy of the system
   (d) During adsorption, there occurs an increase in entropy of the system
8. Which of the following statements regarding adsorption is **not** correct?
   (a) The process of adsorption is an exothermic process
   (b) The substances being adsorbed is known as adsorbate
   (c) The substance on which adsorption occurs is known as adsorbent
   (d) The activation energy in chemisorption is smaller as compared to that of physisorption
9. Which of the following statements is **not** correct?
   (a) Physical adsorption is monolayer
   (b) Physical adsorption is reversible in nature
   (c) Physical adsorption involves low activation energy
   (d) The extent of physical adsorption decreases with increase in temperature
10. Which of the following statements is **not** correct?
    (a) Chemisorption is monolayer
    (b) Chemisorption is irreversible in nature
    (c) Chemisorption involves larger activation energy
    (d) The extent of chemisorption initially decreases with increase in temperature

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56. Which of the following enzymes converts starch into maltose?
(a) Maltase (b) Diastase (c) Zymase (d) Invertase

57. Which of the following enzymes converts maltose into glucose?
(a) Maltase (b) Diastase (c) Zymase (d) Invertase

58. Which of the following enzymes converts glucose into alcohol?
(a) Maltase (b) Diastase (c) Zymase (d) Invertase

59. Which of the following statements is **not** correct?
(a) Most heterogeneous catalytic reactions involve the solid surface of the catalyst
(b) Heterogeneous catalysts primarily function by lowering the activation energy of the reaction
(c) A solid catalyst present in the powder form is more effective as it has larger surface area
(d) The catalyst may be deactivated by heating it to a high temperature in vacuum

60. Which of the following statements is **not** correct?
(a) Zeolite contains aluminosilicate framework
(b) The general formula of zeolite is $M^{n+}_{x/n}\,[(AlO_2)_x\,(SiO_2)_y]^{x-} \cdot z\,H_2O$
(c) Zeolites are characterized by their open structures that permit the exchange of anions and water molecules
(d) Sodalite cage is formed by linking 24 SiO_4 tetrahedra

61. Which of the following statements is **not** correct?
(a) Zeolite A is formed by linking sodalite cages through double four-membered rings
(b) Faujasite zeolite is formed by linking the sodalite cages through double six-membered rings
(c) Zeolite structures contain tunnels or systems of interconnected cavaties which have precisely defined dimensions on the atomic scales
(d) Zeolites are anion exchanger

ANSWERS

Straight Objective Type

1. (a)	**2.** (d)	**3.** (b)	**4.** (a)	**5.** (b)	**6.** (d)	**7.** (d)
8. (d)	**9.** (a)	**10.** (d)	**11.** (a)	**12.** (c)	**13.** (c)	**14.** (b)
15. (c)	**16.** (a)	**17.** (d)	**18.** (c)	**19.** (d)	**20.** (b)	**21.** (a)
22. (d)	**23.** (b)	**24.** (c)	**25.** (a)	**26.** (a)	**27.** (d)	**28.** (b)
29. (a)	**30.** (c)	**31.** (a)	**32.** (a)	**33.** (c)	**34.** (b)	**35.** (b)
36. (c)	**37.** (c)	**38.** (d)	**39.** (a)	**40.** (b)	**41.** (c)	**42.** (c)
43. (d)	**44.** (d)	**45.** (a)	**46.** (d)	**47.** (d)	**48.** (a)	**49.** (d)
50. (d)	**51.** (a)	**52.** (c)	**53.** (a)	**54.** (c)	**55.** (b)	**56.** (b)
57. (a)	**58.** (c)	**59.** (d)	**60.** (c)	**61.** (d)		

Hints and Solutions

Straight Objective Type

1. Physical adsorption is usually multilayer (and not monolayer).
2. Chemisorption involves high activation energy.
3. Extent of adsorption depends on temperature. It decreases with increase in temperature.
15. Adsorption is accompanied with decrease in entropy as the adsorbed molecules become more ordered.
16. Lyophobic sol is solvent hatered sol. Thus, it is not easily solvated.
17. Lyophilic sol is quite stable in a solvent.
18. Liquid-liquid sol is known as emulsion.
19. Liquid adsorbate dispersed in solid adsorbent is known as gel.
20. Silver sol in water is an example of lyophobic sol.

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KINETICS OF RADIOACTIVE DECAY

The radioactive decays follow the first-order kinetics. The integrated rate expression is

$$\log N = \log N_0 - \frac{\lambda}{2.303} t$$

where N and N_0 are the number of radioactive atoms present at time t and 0, respectively, and λ is the decay constant. The time required to reduce the initial number of atoms of a radioactive element to half value is known as *half-life period* and is given by the expression

$$t_{1/2} = \frac{0.693}{\lambda}.$$

Straight Objective Type

General Characteristics

1. The radiations from a naturally occurring radioactive substance as seen after deflection by a magnetic field in one direction are
(a) definitely alpha rays (b) definitely beta rays
(c) both alpha and beta rays (d) either alpha or beta rays (1984)

2. The increasing order for the values of *e/m* (charge/mass) for electron (*e*), proton (*p*), neutron (*n*) and alpha particle (α) is
(a) e, p, n, α (b) n, p, e, α (c) n, p, α, e (d) n, α, p, e (1984)

3. Nuclear reaction(s) accompanied with emission of neutron(*s*) is/are
(a) $^{27}_{13}Al + {}^{4}_{2}He \rightarrow {}^{30}_{15}P$ (b) $^{12}_{6}C + {}^{1}_{1}H \rightarrow {}^{13}_{7}N$
(c) $^{30}_{15}P \rightarrow {}^{30}_{14}Si + {}^{0}_{1}e$ (d) $^{241}_{96}Am + {}^{4}_{2}He \rightarrow {}^{245}_{97}Bk + {}^{0}_{1}e$ (1988)

4. Which of the following is not deflected in an electric field?
(a) Alpha particles (b) Beta particles (c) Gamma rays (d) Positrons

5. The emission of beta particles is from
(a) the valence shell of an atom
(b) the inner shell of an atom
(c) the nucleus due to the nuclear conversion proton $\rightarrow$ neutron + electron
(d) the nucleus due to the nuclear conversion neutron $\rightarrow$ proton + electron

6. The instability of a nucleus is due to
(a) high proton : electron ratio (b) high proton : neutron ratio
(c) low proton : electron ratio (d) low proton : neutron ratio

7. Which of the following has a negative charge?
(a) Neutrino (b) Neutron (c) Positron (d) Antiproton

8. Mesons are responsible for
(a) disintegration of the nucleus (b) repulsion between the protons within the nucleus
(c) attraction between nucleus and electrons (d) attraction between nucleons

9. Which of the following isotopes is used in establishing the reaction mechanism of photosynthesis in plants?
(a) $^{12}_{6}C$ (b) $^{13}_{6}C$ (c) $^{14}_{6}C$ (d) $^{2}_{1}H$

10. Which of the following is the man-made radioactive disintegration series ?
(a) Thorium series (b) Neptunium series (c) Uranium series (d) Actinium series

11. The density of a nucleus is of the order of
(a) 10^5 kg m^{-3} (b) 10^{10} kg m^{-3} (c) 10^{17} kg m^{-3} (d) 10^{25} kg m^{-3}

12. One Curie of radioactivity is equal to
(a) 3.7×10^8 disintegrations/s (c) 3.7×10^9 disintegrations/s
(c) 3.7×10^{10} disintegrations/s (d) 3.7×10^{11} disintegrations/s

13. One becquerel of radioactivity is equal to
(a) one disintegration/s (b) two disinte grations/s
(c) 6.023×10^{23} disintegrations/s (d) three disintegrations/s

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68. The binding energy per nucleon of ^{16}O is 7.97 MeV and that of ^{17}O is 7.75 MeV. The energy in MeV required to remove a neutron from ^{17}O is
(a) 3.52 (b) 3.64 (c) 4.23 (d) 7.86

69. When a β^+ particle encounters an electron, they cancel each other and both disappear. This annihilation of matter produces two photons, each having an energy approximately
(a) 0.466 MeV (b) 0.511 MeV (c) 0.869 MeV (d) 1.15 MeV

70. The binding energy per nucleon for ^4_2He whose mass difference from 2p and 2n is 3.0308×10^{-2}u is approximately
(a) 7.06 MeV (b) 7.59 MeV (c) 8.02 MeV (d) 8.21 MeV

Nuclear Reactions

71. Which one of the following is an (α, n) type nucleus transformation?
(a) $^{75}_{33}As + {}^4_2He \rightarrow {}^{78}_{35}Br + {}^1_0n$
(b) $^7_3Li + {}^1_1He \rightarrow {}^7_4Be + {}^1_0n$
(c) $^{45}_{21}Sc + {}^1_0n \rightarrow {}^{45}_{20}Ca + {}^1_1H$
(d) $^{14}_7N + {}^1_1H \rightarrow {}^{15}_8O + \gamma$

72. In the nuclear reaction $^{14}_7N + {}^4_2He \longrightarrow {}^{17}_8O + {}^1_1H$ the projectile is
(a) $^{14}_7N$ (b) ^4_2H (c) $^{17}_8O$ (d) ^1_1H

73. Atom bombs are based on
(a) natural radioactivity
(b) nuclear fission
(c) nuclear fusion
(d) spontaneous chemical reaction

74. Hydrogen bomb is based on
(a) natural radioactivity
(b) nuclear fission
(c) nuclear fusion
(d) spontaneous chemical reaction

75. The material used for absorbing neutrons in a nuclear reactor is
(a) cadmium (b) radium (c) uranium (d) zinc

76. Which of the following is a capture reaction?
(a) $^{19}_9F + {}^1_1H \longrightarrow {}^{16}_8O + {}^4_2He$
(b) $^7_3Li + {}^4_2He \longrightarrow {}^{11}_5B + \gamma$
(c) $^{32}_{16}S + {}^3_1H \longrightarrow {}^{34}_{17}Cl + {}^1_0n$
(d) $^9_4Be + \gamma \longrightarrow {}^8_4Be + {}^1_0n$

77. Which of the following is a fission reaction?
(a) $^{16}_8O + {}^2_1H \longrightarrow {}^{14}_7N + {}^4_2He$
(b) $^{25}_{12}Mg + \gamma \longrightarrow {}^{24}_{11}Na + {}^1_1H$
(c) $^{75}_{33}As + {}^4_2He \longrightarrow {}^{78}_{35}Br + {}^1_0n$
(d) $^{235}_{92}U + {}^1_0n \longrightarrow {}^{140}_{56}Ba + {}^{94}_{36}Kr + 2{}^1_0n$

78. Which of the following is a spallation reaction?
(a) $^{16}_8O + {}^2_1H \longrightarrow {}^{14}_7N + {}^4_2He$
(b) $^{63}_{29}Cu + {}^4_2He \longrightarrow {}^{37}_{17}Cl + 16{}^1_0n + 14{}^1_1H$
(c) $^2_1H + {}^2_1H \longrightarrow {}^4_2He + \gamma$
(d) $^{238}_{92}U + {}^1_0n \longrightarrow {}^{239}_{92}U + \gamma$

79. The expression of mass-energy conversion is
(a) $E = m^2c$ (b) $E = mc^2$ (c) $E^2 = mc$ (d) $E^2 = mc^2$

80. Which of the following reactions represents a fusion reaction?
(a) $^{238}_{92}U + {}^1_0n \longrightarrow {}^{239}_{92}U$
(b) $^3_1H + {}^2_1H \longrightarrow {}^4_2He + {}^1_0n$
(c) $^{75}_{33}As + {}^4_2He \longrightarrow {}^{78}_{35}Br + {}^1_0n$
(d) $^{32}_{16}S + {}^3_1H \longrightarrow {}^{34}_{17}Cl + {}^1_0n$

81. In a nuclear reactor, the speed of neutrons is slowed down by
(a) ordinary water (b) heavy water (c) zinc rod (d) mercury

82. The $^{14}_6C$ in upper atmosphere is generated by the nuclear reaction
(a) $^{14}_7N + {}^1_1H \longrightarrow {}^{14}_6C + {}^0_1e + {}^1_1H$
(b) $^{14}_7N \longrightarrow {}^{14}_6C + {}^0_1e$
(c) $^{14}_7N + {}^1_0n \longrightarrow {}^{14}_6C + {}^1_1H$
(d) $^{14}_7N + {}^1_1H \longrightarrow {}^{11}_6C + {}^4_2He$

83. In nuclear reactors, cadmium is used to
(a) slow down neutron
(b) absorb neutron
(c) activate neutron
(d) absorbed energy released during nuclear reaction.

84. Which of the following isotopes of uranium is a fissionable isotope?
(a) ^{234}U (b) ^{235}U (c) ^{238}U (d) ^{239}U

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3.	Larger the binding energy per nucleon, the greater the stability of nuclide.	Binding energy per nucleon is a measure of strength of nuclear bonding.
4.	The region of greatest stability of nucleus occurs for atomic numbers from 50 to 80.	For low and high atomic number, binding energy per nucleon is lesser than that exists for nuclides from atomic number 50 to 80.
5.	Nuclei containing even numbers of neutrons and protons are more stable than the other nuclei.	Nucleus containing even numbers of neutrons and protons involve complete spin pairing of nucleons.
6.	The proportion of ^{14}C remains constant in the atmosphere.	^{14}C is a non-radioactive nuclide.
7.	The nuclear fusion reactions is accompanied with decrease in binding energy per nucleon.	There occurs a loss of mass in nuclear fusion reactions.
8.	For transmutation experiments, α-particles and protons are accelerated but neutrons have to be slowed down.	α-particles and proton carry positive charge while neutrons are uncharged particles.
9.	The radius of a nucleus is given as $R = R_o A^{1/3}$, where R_o is a constant and A is the mass number of the nucleus.	All neuclei have the same density and thus volume of the nucleus is directly proportional to A.
10.	Alpha decay occurs much more frequently than the release of two neutrons and two protons separately.	Helium ion is an usually stable entity with high binding energy.
11.	The large amount of energy (approximately 200 MeV) is released per fissioning nucleus.	The difference in the masses of the fission fragments is less than the mass of the fission nucleus by an amount corresponding to about 200 MeV.
12.	Lead obtained from uranium series has the same atomic mass as obtained from thorium series.	Uranium and thorium decays belong to different series.
13.	^{238}U decay via α-emission and not via β-emission.	In this case, α-emission is an exothermic process while β-emission is an endothermic process.
14.	Even-even nuclear type nuclides are most stable nuclides while odd-odd nuclear type nuclides are least stable nuclides.	Two nucleons of the same type in a nucleus can interact with each other more strongly than two nucleons of different type.

Matrix Match Type

1. Column I lists the type of artificial transmutation reactions and Column II includes incomplete reactions with target and product elements. Match each entry of Column I with those given in Column II.

Column I	**Column II**
(a) (p, α)	(p) $^{10}_{5}B \longrightarrow {}^{7}_{3}Li$
(b) (α, n)	(q) $^{19}_{9}F \longrightarrow {}^{16}_{8}O$
(c) (T, p)	(r) $^{75}_{33}As \longrightarrow {}^{78}_{35}Br$
(d) (n, a)	(s) $^{59}_{27}Co \longrightarrow {}^{61}_{27}Co$

2. Column I lists the type of artificial transmutation reactions and Column II includes incomplete reactions with target and product elements. Match each entry of Column I with those given in Column II.

Column I	**Column II**
(a) (p, γ)	(p) $^{31}_{15}P \longrightarrow {}^{30}_{15}P$
(b) (D, T)	(q) $^{32}_{16}S \longrightarrow {}^{34}_{17}Cl$
(c) (γ, n)	(r) $^{14}_{7}N \longrightarrow {}^{15}_{8}O$
(d) (T, n)	(s) $^{9}_{4}Be \longrightarrow {}^{8}_{4}Be$

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45. The expression of decay constant is $\lambda = (2.303/t) \log (N_0/N)$.

46. The radioisotope $^{13}_{6}C$ is used to determine the age of dead plants and animals.

47. 10,000 disintegrations $\xrightarrow[t_{0.5}]{}$ 5000 disintegrations $\xrightarrow[t_{0.5}]{}$ 2500 disintegrations

Obviously, $2t_{0.5} = 50$ days. Hence $t_{0.5} = 25$ days

48. $\lambda = \dfrac{0.693}{5000\ \text{y}}$; $t = -\dfrac{2.303}{\lambda} \log \dfrac{[A]}{[A]_0} = -\dfrac{2.303 \times 5000\ \text{y}}{0.693} \log (0.4) = \dfrac{2.303 \times 5000}{0.693} \times 0.401\ \text{y} = 6667\ \text{y}.$

49. 50% of ^{14}C means half of ^{14}C has disappeared. Therefore, $t = t_{0.5} = 5760$ y.

50. One fourth implies two half lives. Hence, $t = 2t_{0\cdot5}$.

51. Average life time is reciprocal of decay constant.

52. The rate of decay for the material is

$$\frac{dN}{dt} = -\lambda_1 N - \lambda_2 N = -N(\lambda_1 + \lambda_2) \quad \text{or} \quad N = N_0 e^{-(\lambda_1 + \lambda_2)t} \quad \text{or} \quad \ln N = \ln N_0 - (\lambda_1 + \lambda_2)t$$

$$\text{or} \qquad \ln\left(\frac{N}{N_0}\right) = -\left[\frac{\ln 2}{(t_{0.5})_1} + \frac{\ln 2}{(t_{0.5})_2}\right] t = -(\ln 2)\left[\frac{(t_{0.5})_1 + (t_{0.5})_2}{(t_{0.5})_1 (t_{0.5})_2}\right] t$$

$$\text{or} \qquad t = \left[\frac{\ln(N_0/N)}{\ln 2}\right]\left[\frac{(t_{0.5})_1 (t_{0.5})_2}{(t_{0.5})_1 + (t_{0.5})_2}\right] = (2)\left[\frac{(1620)(810)}{1620 + 810}\right] y = 1080\ y$$

53. The number of radioactive particles at any instant will be given by $N = N_0 e^{-\lambda t}$ where $\lambda = 0.693/t_{1/2}$
A given nucleus may decay at any time after $t = 0$ but the number of radioactive particles will be given by the above expression.

54. By definition $t_{1/2} = 0.693/\lambda$ and $t_m = 1/\lambda$
It is given that $(t_{1/2})_X = (t_m)_Y$, that is

$$\frac{0.693}{\lambda_X} = \frac{1}{\lambda_Y} \Rightarrow \lambda_Y > \lambda_X$$

The expression of rate law is

$$-\frac{dN}{N} = \lambda N.$$

Since $\lambda_Y > \lambda_X$, it follows that $\left(-\dfrac{dN}{N}\right)_Y > \left(-\dfrac{dN}{N}\right)_X$

55. $N_1 = N_0 e^{-\lambda_1 t}$ and $N_2 = N_0 e^{-\lambda_2 t}$ Thus $\dfrac{N_1}{N_2} = \dfrac{e^{-\lambda_1 t}}{e^{-\lambda_2 t}} = e^{-(\lambda_1 - \lambda_2)t} = e^{-9\lambda t}$

It is given that $N_1/N_2 = e^{-1}$. Hence $-9\lambda t = -1 \Rightarrow t = 1/(9\lambda)$

56. Since $\dfrac{1}{16} = \dfrac{1}{2^4}$. $t = 4t_{1/2} = 4(100\ \mu s) = 400\ \mu s$

57. $\ln\left(\dfrac{0.9}{1}\right) = -\lambda\,(5\ \text{d})$ and $\ln\left(\dfrac{N}{N_0}\right) = -\lambda\,(20\ \text{d})$.

Thus $\ln\left(\dfrac{N}{N_0}\right) = \left(\dfrac{1}{5} \ln 0.9\right)(20) = 4 \ln (0.9)$

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Now, the rate constant of radioactive decay is $\lambda = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{66.6\text{ h}} = 0.010404\text{ h}^{-1}$

Now using the integrated rate expression $\log \dfrac{n_0 - n_{\text{consumed}}}{n_0} = -\dfrac{\lambda t}{2.303}$, we get

$$\log \frac{n_0 - 2.3818\times10^{-19}\text{ mol}}{n_0} = -\frac{(0.010404\text{ h}^{-1})(6.909\text{ h})}{2.303} = -0.03121 \quad \text{or} \quad \frac{n_0 - 2.3818\times10^{-19}\text{ mol}}{n_0} = 0.9306$$

Solving for n_0, we get

$$n_0 = \frac{2.3818\times10^{-19}\text{ mol}}{1-0.9306} = 3.43\times10^{-18}\text{ mol.}$$

5. One of the hazards of nuclear explosion is the generation of ^{90}Sr and its subsequent incorporation in bones. This nuclide has a half-life of 28.1 years. Suppose one microgram was absorbed by a new-born child, how much ^{90}Sr will remain in his bones after 20 years? (1995)

Solution For the half-life $t_{1/2} = 28.1$ y, the decay constant is $\lambda = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{28.1\text{ y}}$

Since the radioactivity decay follows the first order kinetics, we have $\log \dfrac{[A]}{[A]_0} = -\dfrac{\lambda}{2.303}t$

Thus $\log \dfrac{[A]}{1.0\,\mu g} = -\dfrac{0.693}{28.1\text{ y}} \times \dfrac{20\text{ y}}{2.303}$ or $\log [A]/\mu g = -0.2142$ or $[A] = 0.6107\ \mu g$.

6. Calculate the mass of ^{14}C (half-life period = 5720 y) atom which gives 3.70×10^7 disintegrations per second.

Solution Since the radioactive decay is first order, we will have

$$-\frac{d\,n(^{14}C)}{dt} = \lambda\, n(^{14}C) \quad \text{where} \quad -\frac{d\,n(^{14}C)}{dt} = \frac{3.70\times10^7\text{ s}^{-1}}{6.023\times10^{23}\text{ mol}^{-1}} = 6.143\times10^{-17}\text{ mol s}^{-1}$$

Now $\lambda = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{5720\times365\times24\times60\times60\text{ s}} = 3.842\times10^{-12}\text{ s}^{-1}$

Hence, $n(^{14}C) = \left(-\dfrac{d\,n(^{14}C)}{dt}\right)\left(\dfrac{1}{\lambda}\right) = \dfrac{6.143\times10^{-17}\text{ mol s}^{-1}}{3.842\times10^{-12}\text{ s}^{-1}} = 1.599\times10^{-5}\text{ mol}$

$$m(^{14}C) = (1.599\times10^{-5}\text{ mol})\,(14\text{ g mol}^{-1}) = 2.340\times10^{-4}\text{ g.}$$

7. An analysis of the rock shows that the relative number of ^{87}Sr and ^{87}Rb atoms is $^{87}Sr/^{87}Rb = 0.052$. Determine age of the rock. Given that the half-life period of β-decay of Rb to Sr is 4.7×10^{10} y.

Solution We have

$$\frac{\text{Atoms of Sr}}{\text{Atoms of Pb}} = 0.052$$

Adding one on both sides, we get

$$\frac{\text{Atoms of (Sr + Pb)}}{\text{Atoms of Pb}} = 1.052 \quad \text{or} \quad \frac{\text{Initial atoms of Pb}}{\text{Present atoms of Pb}} = 1.052$$

Now $t = \dfrac{2.303}{k}\log\dfrac{[Pb]_0}{[Pb]} = \dfrac{2.303}{(0.693/t_{1/2})}\log\dfrac{[Pb]_0}{[Pb]} = \dfrac{2.303(4.7\times10^{10}\text{ y})}{0.693}\log 1.052 = 3.725\times10^9\text{ y}$

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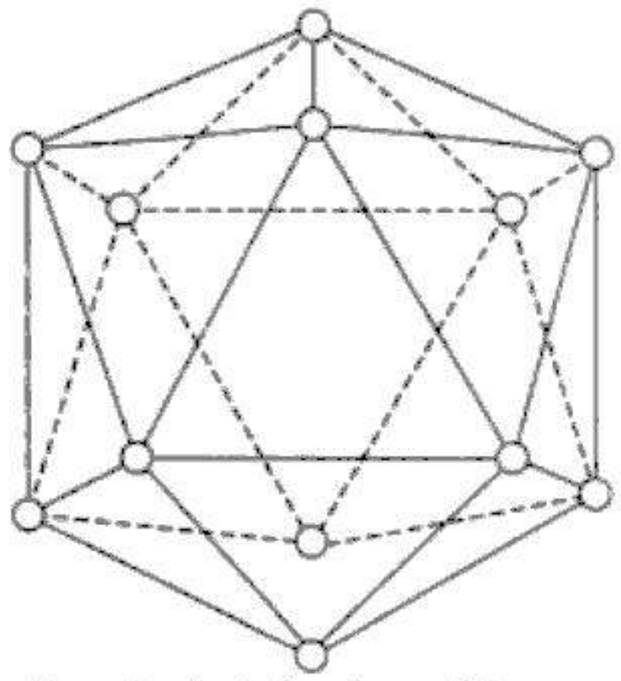
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CHAPTER 13

NON-METALS

BORON

Boron belongs to Group 13. It is a nonmetal and has a very high melting point (2453 K). The structure of crystalline boron is icosahedral (20-faced) with boron atoms at all 12 corners.



Icosahedral structure of boron

Boron is extracted from its mineral borax $Na_2B_4O_7$ or colemanite $Ca_2B_6O_{11}$. The latter is converted into borax by boiling with a solution of sodium carbonate in the requisite proportions.

$$2Ca_2B_6O_{11} + 3Na_2CO_3 + H_2O \rightarrow 3Na_2B_4O_7 + 3CaCO_3 + Ca(OH)_2$$

From the above solution, borax is crystallized from the mother liquor.

Borax is firstly converted into boron trioxide by treating it with hot concentrated hydrochloric acid followed by strongly heating the precipitated boric acid.

$$Na_2B_4O_7 + 2HCl \rightarrow 2NaCl + H_2B_4O_7; \qquad H_2B_4O_7 + 5H_2O \rightarrow \underset{\text{Boric acid}}{4H_3BO_3}$$

$$2H_3BO_3 \xrightarrow{\Delta} B_2O_3 + 3H_2O$$

The obtained boron trioxide is reduced to boron by heating with Na, K or Mg pieces.

$$B_2O_3 + 6K \rightarrow 2B + 3K_2O; \qquad B_2O_3 + 3Mg \rightarrow 2B + 3MgO$$

The above method results into amorphous form of boron. Its crystalline form is obtained by passing a mixture of boron tribromide vapours and hydrogen over electrically heated filament of tungsten at 1200°C. It may also be obtained by reducing boron trioxide or boron halide with excess of aluminium

$$B_2O_3 + 2Al \rightarrow Al_2O_3 + 2B; \qquad KBF_4 + Al \rightarrow AlF_3 + KF + B$$

Boron is unaffected by air at room temperature, but when heated to about 700°C, it forms protective layers of boron trioxide and boron nitride

$$4B + 3O_2 \rightarrow 2B_2O_3; \qquad 2B + N_2 \rightarrow 2BN$$

With hot concentrated HNO_3 and H_2SO_4, amorphous boron reacts to form boric acid.

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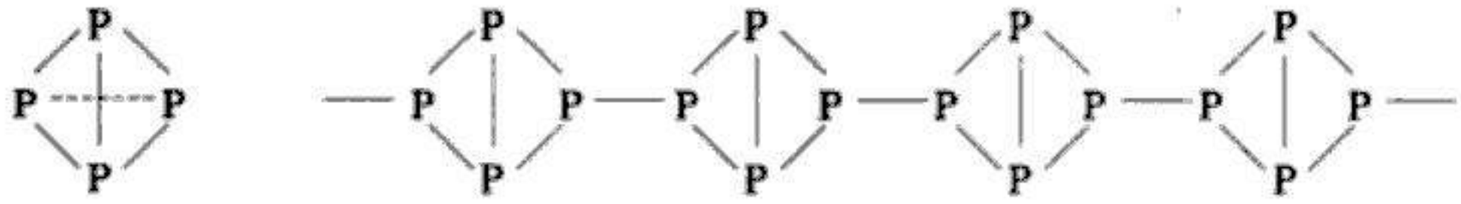


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The four atoms in white phosphorus are arranged tetrahedrally. Red phosphorus is believed to be polymeric and consists of chains of P_4 tetrahedrally linked together as shown in Fig. 13.3.



White Red

Fig. 13.3 Structures of white and red phosphorus

In the liquid and in solid white phosphorus exists as tetrahedral P_4 molecule with P—P distance 221 pm and bond angle P—P—P equal to 60°. The low angle indicates considerable strain. The total energy of the six P—P bonds in P_4 molecule is much smaller than the total energy expected for six P—P bonds of the same length with normal bond angles. Because of the strain in P_4 molecule, phosphorus is very reactive.

White P_4 is stored under water to protect it from the air, whereas the red and black are stable in air. White P_4 inflames in air and is soluble in organic solvents such as CS_2 and benzene.

Phosphorus does not have a structure like nitrogen (N ≡ N). This can be understood from the following bond enthalpy data.

$\varepsilon(N \equiv N) = 946\ kJ\ mol^{-1}$ $\varepsilon(P \equiv P) = 490\ kJ\ mol^{-1}$

$\varepsilon(>N - N<) = 160\ kJ\ mol^{-1}$ $\varepsilon(>P - P<) = 200\ kJ\ mol^{-1}$

The species N ≡ N is more stable than three N – N bonds whereas P ≡ P is less stable than three P – P bonds. It is because of this factor, phosphorus atoms are liked through single bonds.

Oxygen

Atmosphere contains about 20% of oxygen by volume. In the combined form, it is present in water (89% by mass), earth's crust (about 50%), plants and animal tissues (50.7%).

Oxygen can be conveniently prepared as follows.

1. By heating chlorates, nitrates and permanganate. $2KClO_3 \xrightarrow{heat} 2KCl + 3O_2$
2. By heating metallic oxide such as HgO, PbO, Ag_2O, MnO_2 and BaO_2. $2HgO \xrightarrow{liquid} 2Hg + O_2$
3. By the action of water on peroxides. $2Na_2O_2 + 2H_2O \rightarrow 2NaOH + O_2$
4. By the decomposition of peroxides or hypochlorites.

$$2H_2O_2 \rightarrow 2H_2O + O_2; \qquad 2CaOCl_2 \xrightarrow{COCl_2} 2CaCl_2 + O_2$$

5. By the action of concentrated H_2SO_4 on $KMnO_4$, $K_2Cr_2O_7$ or MnO_2

$$2K_2Cr_2O_7 + 8H_2SO_4 \rightarrow 2K_2SO_4 + 2Cr_2(SO_4)_3 + 8H_2O + 3O_2$$

Commercially, oxygen is obtained by fractional evaporation of liquid air or by electrolysis of acidic or alkaline solution of water.

Oxygen combines with a large number of elements and compounds under different conditions. It is a paramagnetic with two unpaired electrons. This behaviour has been explained on the basis of molecular orbital theory. Its electronic configuration is

$$KK(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2\ (\pi 2p_x)^2(\pi 2p_y)^2(\pi^* 2p_x)^1(\pi^* 2p_y)^1$$

Ozone Ozone is an allotropic modification of oxygen. It is prepared by the passage of silent electric discharge through pure and dry oxygen or air. The silent discharge is carried out by packing insulating materials in the space between electrodes through which discharge passes. This prevents any local rise in temperature, which would lead to the decomposition of ozone. The reaction

$$3O_2 \rightleftharpoons 2O_3$$

is endothermic ($\Delta H = +284.5\ kJ\ mol^{-1}$).

Ozone is a pale-blue gas with a characteristic strong smell. When inhaled in small amount, it causes headache and nausea. In larger quantities, it is poisonous. The main reactions of ozone are the oxidation reactions.

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48. Oxygen and sulphur belong to
(a) alkaline earth metals (b) s block element
(c) chalcogens (d) halogens

49. Common allotropic forms of sulphur are represented as
(a) S_2 (b) S_4 (c) S_6 (d) S_8

50. The bond angle O—O—O in ozone is about
(a) 180° (b) 90° (c) 116° 5′ (d) 135°

51. The bond order of O—O bonds in ozone is
(a) 1 (b) 1.5 (c) 2 (d) 2.5

Halogens

52. Chlorine acts as a bleaching agent only in presence of
(a) dry air (b) moisture (c) sunlight (d) pure oxygen (1983)

53. Bromine can be liberated from potassium bromide solution by action of
(a) iodine solution (b) chlorine solution (c) sodium chloride (d) potassium iodide (1987)

54. Concentrated HNO_3 reacts with iodine to give
(a) HI (b) HOI (c) $HOIO_2$ (d) $HOIO_3$ (1989)

55. The gaseous flourine is pale yellow in colour. The light absorbed by fluorine in the visible region would be
(a) violet light (b) red light (c) green light (d) orange light

56. The gaseous iodine molecules absorb yellow light from the visible region. Its colour would be
(a) yellow (b) red (c) green (d) violet

57. Which of the following sequences of electron affinity regarding halogens is correct?
(a) F < Cl < Br (b) F > Cl > Br (c) F < Cl > Br (d) F > Cl < Br

58. Which of the following characteristics regarding halogens is not correct?
(a) Ionization energy decreases with increase of atomic number.
(b) Electronegativity decreases with increase of atomic number.
(c) Electron affinity decreases with increase of atomic number.
(d) Enthalpy of fusion increases with increase of atomic number.

59. The halogen exhibiting no positive oxidation state is
(a) fluorine (b) chlorine (c) bromine (d) iodine

60. Which of the following reactions is not observed?
(a) $2F_2 + \underset{\text{(dilute)}}{2OH^-} \rightarrow 2F^- + H_2O + OF_2$
(b) $2F_2 + \underset{\text{(conc.)}}{4OH^-} \xrightarrow[\text{hot}]{} 4F^- + 2H_2O + O_2$
(c) $\underset{(F_2, Cl_2, I_2)}{X_2} + \underset{\text{(conc.)}}{2OH^-} \xrightarrow[\text{hot}]{} H_2O + X^- + XO^-$
(d) $Xe + F_2 \xrightarrow{\text{(light)}} XeF_2$

61. Which of the following reactions would not proceed to right hand side?
(a) $F_2 + Cl^- \rightarrow$ (b) $Cl_2 + Br^- \rightarrow$ (c) $Br_2 + I^- \rightarrow$ (d) $I_2 + Cl^- \rightarrow$

62. Amongst the halogens, the strongest oxidizing agent is
(a) fluorine (b) chlorine (c) bromine (d) iodine

63. The products obtained when chlorine reacts with cold and dilute solution of sodium hydroxide are
(a) $Cl^- + ClO^-$ (b) $Cl^- + ClO_2^-$ (c) $Cl^- + ClO_3^-$ (d) $Cl^- + ClO_4^-$

64. The products obtained when iodine reacts with hot and concentrated solution of sodium hydroxide are
(a) $I^- + IO^-$ (b) $I^- + IO_3^-$ (c) $I^- + IO_4^-$ (d) $I^- + I_2O_9^{4-}$

65. With excess of Cl_2, ammonia forms
(a) NH_4Cl (b) N_2 (c) NCl_3 (d) $NCl_3 \cdot NH_3$

66. Which of the following compounds undergoes hydrolysis?
(a) SF_6 (b) NF_3 (c) SF_4 (d) CCl_4

67. The highest bond enthalpy is shown by the halogen
(a) F_2 (b) Cl_2 (c) Br_2 (d) I_2

68. I_2 reacts with NH_3 giving
(a) NI_3 (b) $NI_3 \cdot NH_3$ (c) N_2 (d) NH_4I

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28. Which of the following statements are **not** correct?
(a) The coal containing maximum carbon content is bituminous.
(b) The coal containing minimum carbon content is anthracite.
(c) Silicon exists in the two allotropic forms.
(d) Silicon crystallizes in face-centred cubic lattice.

29. Which of the following statements are **not** correct?
(a) Treatment of urea or ammonium salt with an alkaline solution of sodium hypobromite produces N_2 gas.
(b) The mineral phosphorite is $Ca_3(PO_4)_2$.
(c) Phosphorus is manufactured by reducing calcium phosphate by Al in the presence of SiO_2.
(d) Phosphorus has five allotropic modifications.

30. Which of the following statements are not correct?
(a) White phosphorus on boiling with caustic soda produces PH_3 gas.
(b) Four phosphorus atoms in white variety are arranged tetrahedrally.
(c) The meniscus of mercury disappears when it comes in contact with ozone. This is due to the formation of HgO.
(d) The central oxygen atom in ozone is sp hybridized.

31. Which of the following statements are correct?
(a) In elemental form, sulphur exists as S_8 molecule.
(b) The stablest variety of sulphur is rhombic sulphur.
(c) The transition temperature of rhomic sulphur into monoclinic sulphur is 95°C – 96°C at 1 atm pressure.
(d) Passing H_2S through dilute nitric acid produces colloidal form of sulphur.

32. Which of the following statements are **not** correct?
(a) The reactivity of halogens towards metals increases on descending the group.
(b) Of halogens, the halogen having low enthalpy of dissociation is iodine.
(c) Fluorspar is CaF_2
(d) Cryolite is Na_3AlF_6

33. Which of the following statements are **not** correct?
(a) Fluorapatite is $CaF_2 \cdot 3Ca_3(PO_4)_2$.
(b) Fluorine reacts with water forming HF and O_2.
(c) With slaked lime, chlorine forms $CaCl_2$.
(d) With excess of ammonia, chlorine forms N_2 and HCl.

34. Which of the following statements are correct?
(a) With excess of chlorine, ammonia forms NCl_3 which is explosive in nature.
(b) The ultimate product of the hydrolysis of NCl_3 are NH_3 and HOCl.
(c) Iodine oxidizes thiosulphate to tetrathionate.
(d) The equivalent mass of sodium thiosulphate in its reaction with iodine is equal to its molar mass divided by two.

35. Which of the following statements are **not** correct?
(a) *Ortho* hydrogen molecule have antiparallel spins of nuclei.
(b) *Para* hydrogen molecule has parallel spins of nuclei.
(c) The *para* hydrogen molecule has energy higher than *ortho* isomer.
(d) At low temperatures, the predominant isomer of hydrogen molecule is *para*.
(e) At higher temperatures, the predominant isomer of hydrogen molecule is *ortho*.

36. The crystalline form of boron may be obtained by
(a) heating B_2O_3 with Mg.
(b) reducing B_2O_3 with excess of Al
(c) passing a mixture of boron tribmode vapours and hydrogen over electrically heated filament of tungsten at about 1500 K
(d) strong heating of B_2O_3.

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42. The reaction is $2O_3 \rightarrow 3O_2$. This reaction is accompanied with $\Delta\nu_g = +1$, hence, increase in volume at constant temperature and pressure.
43. Floropatite is $[Ca_3(PO_4)_2 \cdot CaF_2]$; Fool's gold is FeS_2; Sphaelerite is ZnS; Chalcopyrite is $CuFeS_2$
44. Rhombic sulphur is stable at room temperature.
47. The reaction is $S + 6HNO_3 \rightarrow H_2SO_4 + 6NO_2 + 2H_2O$
50. The bond angle is near to 120° as oxygens are sp^2 hybridized.
51. The bond order is 1.5; one from sigma bond and 0.5 from four-electron three-centred π bond.
54. The reaction is $I_2 + 2HNO_3 \rightarrow 2HIO_3 + N_2$
55. Light absorbed is of complimentary colour of yellow which is violet light. **56.** See, Q.55.
57. Chlorine has larger electron affinity as compared to fluorine and bromine. **58.** See Q.57.
59. Fluorine being most electronegative, it does not show positive oxidation state. It has only 0 and – 1 oxidation states.
60. The reaction is $6OH^- + 3X_2 \rightarrow 5X^- + XO_3^- + 3H_2O$.
61. I_2 is least reactive.
62. Fluorine is the strongest oxidation agent.
63. The reaction is $2OH^- + Cl_2 \rightarrow Cl^- + ClO^- + H_2O$ **64.** See, Q.60.
65. The reaction is $NH_3 + \underset{\text{(excess)}}{3Cl_2} \rightarrow NCl_3 + 3HCl$
66. SF_4 undergoes hydrolysis due to d orbitals in S.
67. Cl–Cl bond energy is maximum due to double bond-one σ bond and one π bond due to back bonding.
68. The reaction is $2NH_3 + I_2 \rightarrow NI_3 \cdot NH_3 + 3HI$
70. The reaction is $I_2 + OH^- \underset{\text{cold}}{\rightarrow} HIO + I^-$
72. The energy levels become closer. The promotion energy from ground state to the first excited state decreases and thus wavelength of energy becomes larger. This is supported by the colour of halogens. Gaseous F_2 is light yellow, Cl_2 gas is yellow-green, Br_2 gas and liquid are dark red-brown and I_2 gas is violet.

Multiple Correct Choice Type

13. (a) Red phosphorus has polymeric structure and not a tetrahedral, due to which red phosphorus is less volatile than white phosphorus.
(c) The lubricating properties of graphite depend not only on the slippage between the planes, but also on a film of moisture or gas molecules adsorbed on the surface of the graphite layers. The adsorbed substance decreases the friction as the layers in graphite slide past each other. Dry graphite in vacuum is not slippery.
(d) The correct order is F < Cl > Br. The larger electronic repulsion in F due to smaller size makes its electron affinity less than that of Cl.
14. (a) In diamond, all the four valencies of carbon are involved in stronger σ bonding whereas in graphite, three are involved in σ bonding whereas the fourth one is involved in weak π bonding.
(b) The tendency for catenation is related to the strength of C—C bond. The C—C bond is much stronger than Si—Si.
(d) It is a bad conductor of electricity. Graphite is a conductor of electricity.
15. (b) Each carbon in diamond is sp^3 hybridized.
(c) It is anthracite which contains maximum carbon content.
(d) Coke is obtained when coal is subjected to destructive distillation in the absence of air.
16. (a) The amorphous carbon is obtained by this method.
(b) It is a metalloid.
17. (a) The Si —O single bond is the strongest of all silicon bonds.
(b) Heating of ammonium dichromate produces nitrogen gas according to the reaction

$$(NH_4)_2Cr_2O_7 \rightarrow N_2 + 4H_2O + Cr_2O_3.$$

(c) White phosphorus is poisonous in nature, while red phosphorus is nonpoisonous.
18. (a) The products are phosphoric acid and nitrogen dioxide:

$$P_4 + 20HNO_3 \rightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$

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Sodium carbonate is known as *washing soda* and is used in the manufacture of soap, glass, caustic soda and borax. Sodium bicarbonate is known as *baking soda* and is used as leavening agent in cooking. It is also used as antacid to neutralize acidity in the stomach.

In general, carbonates of alkali metals are soluble in water except Li_2CO_3 which is sparingly soluble. Bicarbonates are very much less soluble than the corresponding carbonates.

Chlorides Sodium chloride is known as *common salt* and is manufactured from seawater and water of certain lakes by evaporation. The salt obtained is slightly hygroscopic due to traces of $MgCl_2$ and $CaCl_2$ present in it. Potassium chloride is extracted from the mineral carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$). It is a good substituent for NaCl for patients with high blood pressure.

Sulphates The hydrated salt $Na_2SO_4 \cdot 10H_2O$ is known as *Glauber's salt*. Sodium sulphate is manufactured by heating sodium chloride with sodium bisulphate.

$$NaCl + NaHSO_4 \rightarrow Na_2SO_4 + HCl$$

Cooling of the saturated solution of decahydrate below 285 K results into the formation of heptahydrate, $Na_2SO_4 \cdot 7H_2O$.

Potassium sulphate is manufactured from the mineral schonite, $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$ by a process of crystallization after treating with sylvine (KCl).

$$K_2SO_4 \cdot MgSO_4 \cdot 6H_2O + 2KCl \rightarrow 2K_2SO_4 + MgCl_2 + 6H_2O$$

Magnesium and Calcium

Oxides These can be obtained by heating either carbonate or hydroxide of the metal. Magnesium oxide is a white powder and is very resistant to change at high temperatures. It is used as a refractory material for lining electric furnaces. Calcium oxide is also known as *quicklime*. On adding water it gives a hissing sound and becomes very hot. The product obtained is $Ca(OH)_2$ and is known as *slaked lime*. This process is known as slaking of lime. The paste of lime in water is known as *milk of lime* whereas the filtered and clear solution is known as *lime water*. Moist Cl_2, CO_2, SO_2 and HCl gives $CaOCl_2 \cdot H_2O$ (bleaching powder), $CaCO_3$, $CaSO_3$ and $CaCl_2$ respectively when reacted with CaO.

Both the oxides are basic. These are less basic than the oxides of alkali metals. The basic properties increase with descent of the group.

Moistening of MgO with a saturated solution of magnesium chloride results in the formation of a firm hard cement known as *Sorel's cement*. It is used as a stopping for teeth.

Peroxides The addition of hydrogen peroxide (or sodium peroxide) to cold alkaline solutions of magnesium and calcium salt results into the formation of peroxides. For example

$$Ca^{2+} + H_2O_2 + 8H_2O \rightarrow \underset{\text{crystallizes out}}{CaO_2 \cdot 8H_2O} + 2H^+$$

CaO_2 is less stable than MgO_2. Both react with acid producing H_2O_2 and O_2.

In general, Be forms only the monoxide, all other elements of Group 2 form monoxides and peroxides. BeO is predominantly covalent. All oxides are thermally very stable. BeO and MgO are insoluble in water, rest react with water giving hydroxides. BeO is amphoteric while others are basic in nature. The thermal stability of peroxides increases with increasing cation size on descending the group.

Hydroxides The addition of alkali to magnesium salts solution precipitates out magnesium hydroxides. In qualitative analysis, magnesium is not percipitated out by adding ammonium hydroxide in the presence of ammonium chloride. An aqueous suspension of $Mg(OH)_2$ is known as *milk of magnesia* and is used as a digestive antacid.

In general, the hydroxides of Group 2 are less basic than alkali metal hydroxides. The basic character increases on moving down the group. Their solubility also increases on moving down the group, $Be(OH)_2$ is least soluble while $Ba(OH)_2$ is most soluble.

Carbonates and Bicarbonates Carbonates of magnesium and calcium can be obtained by adding sodium carbonate in the aqueous solution of respective salt. When carbon dioxide is passed through the suspension of carbonates, the latter dissolve forming bicarbonate.

$$\underset{\text{(insoluble)}}{MgCO_3} + H_2O + CO_2 \rightarrow \underset{\text{(soluble)}}{Mg(HCO_3)_2}$$

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Alkaline hypochlorite can also be used for the oxidation.

$$PbCl_2 + NaOCl + 2NaOH \rightarrow PbO_2 + 3NaCl + H_2O$$

Fusion of monoxide with $KClO_3$ or KNO_3 also produces PbO_2.

It is a chocolate brown powder and is a powerful oxidizing agent. It dissolves in concentrated HCl as well as in concentrated NaOH.

$$PbO_2 + 4HCl \rightarrow PbCl_4 + 2H_2O; \qquad PbO_2 + 2NaOH \rightarrow \underset{\text{sodium plumbate}}{Na_2PbO_3} + H_2O$$

A few reactions showing oxidizing nature of PbO_2 are as under.

$$PbO_2 + SO_2 \rightarrow PbSO_4; \qquad PbO_2 + 4HCl \rightarrow PbCl_2 + 2H_2O + Cl_2$$

$$2Mn^{2+} + 5\ PbO_2 + 6H^+ \rightarrow \underset{\text{pink colour}}{2HMnO_4} + 5\ Pb^{2+} + 2H_2O$$

Red lead (Pb_3O_4) is, in fact, a mixed oxides ($2PbO \cdot PbO_2$). This has a orange-red colour and is obtained by heating PbO in air at 575 K–850 K.

$$6PbO + O_2 \underset{\text{above 850K}}{\overset{\text{575K–850 K}}{\rightleftharpoons}} 2Pb_3O_4$$

It oxidizes HCl to Cl_2 and gives oxygen with hot concentrated H_2SO_4.

$$Pb_3O_4 + 8HCl \rightarrow 3PbCl_2 + 4H_2O + Cl_2; \qquad 2Pb_3O_4 + 6H_2SO_4 \rightarrow 6PbSO_4 + 6H_2O + O_2$$

With nitric acid, PbO gives $Pb(NO_3)_2$ while PbO_2 remains as such.

$$Pb_3O_4 + 4HNO_3 \rightarrow PbO_2 + 2Pb(NO_3)_2 + 2H_2O$$

Red lead is used as a protective paint for iron and steel and as an oxidizing agent in a laboratory.

Lead suboxide (Pb_2O) is obtained when lead oxalate is heated in absence of air.

$$2PbC_2O_4 \rightarrow Pb_2O + 3CO_2 + CO$$

Lead sesquioxide (Pb_2O_3) is obtaind when lead monoxide is heated in air up to 775 K.

$$4PbO + O_2 \rightarrow 2Pb_2O_3$$

Chlorides Tin forms two chlorides—stannous and stannic chlorides. Of these, the former is more ionic than the latter.

Stannous chloride is formed when tin is dissolved in concentrated HCl followed by evaporation when $SnCl_2 \cdot 2H_2O$ is deposited. Anhydrous chloride cannot be prepared by dehydrating the hydrated salt as it undergoes hydrolysis to give basic chloride, Sn(OH)Cl. However, this can be prepared by heating tin in a current of dry hydrochloric acid gas. Also, distillation of excess of tin with Hg_2Cl_2 gives $SnCl_2$ as the residue.

Stannous chloride is soluble in water. However on standing, the precipitates of Sn(OH)Cl are obtained. In the presence of HCl, this hydrolysis is prevented.

Stannous chloride in concentrated HCl is a powerful reducing agent. A few examples are

(a) $2Hg^{2+} + 2Cl^- + Sn^{2+} \rightarrow Hg_2Cl_2 + Sn^{4+}$
$Hg_2Cl_2 + Sn^{2+} \rightarrow 2Hg + Sn^{4+} + 2Cl^-$

(b) $2Fe^{3+} + Sn^{2+} \rightarrow 2Fe^{2+} + Sn^{4+}$

(c) $2Cu^{2+} + 2Cl^- + Sn^{2+} \rightarrow 2\ CuCl + Sn^{4+}$

(d) $2Au^{3+} + 3Sn^{2+} \rightarrow 2Au + 3Sn^{4+}$

(e) $I_2 + Sn^{2+} \rightarrow 2I^- + Sn^{4+}$

(f) $C_6H_5NO_2 + 6H^+ + 3Sn^{2+} \rightarrow C_6H_5NH_2 + 2H_2O + 3Sn^{4+}$

(g) $2MnO_4^- + 5Sn^{2+} + 16H^+ \rightarrow 2Mn^{2+} + 5Sn^{4+} + 8H_2O$

(h) $Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 3Sn^{4+} + 7H_2O$

With ammonia, $SnCl_2$ forms a number of double salts ($SnCl_2 \cdot NH_3$, $SnCl_2 \cdot 2NH_3$ and $3SnCl_2 \cdot 2NH_3$).

Anhydrous stannous chloride is an angular covalent molecule because of the repulsion between a lone pair of electrons on Sn and the two bonding pair of electrons.

Stannic chloride is a colourless fuming liquid. It is a covalent compound as it is soluble in benzene. With limited water, it forms a series of hydrated salts ($SnCl_4 \cdot 3H_2O$, $SnCl_4 \cdot 5H_2O$, $SnCl_4 \cdot 6H_2O$ and $SnCl_4 \cdot 8H_2O$). With excess water, it is hydrolysed.

$$SnCl_4 + H_2O \rightleftharpoons Sn(OH)Cl_3 + HCl; \qquad Sn(OH)Cl_3 + 3H_2O \rightleftharpoons Sn(OH)_4 + 3HCl$$

The crystals of hydrochlorostannic acid, $H_2[SnCl_6] \cdot 6H_2O$ are obtained when $SnCl_4$ is evaporated with hydrochloric acid. Similarly, salts of $(NH_4)_2\ [SnCl_6]$ and $K_2[SnCl_6]$ are obtained when $SnCl_4$ is crystallized in the presence of NH_4Cl and KCl, respectively. Stannic chloride also forms double salt with ammonia, $SnCl_4 \cdot 4NH_3$.

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The solution is treated with potassium chloride to get less soluble potassium dichromate which crystallizes as orange crystals.

$$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$$

Potassium dichromate is a powerful oxidizing agent:

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

It can oxidise Fe^{2+} to Fe^{3+}, I^- to I_2, SO_3^{2-} to SO_4^{2-} and S^{2-} to S.

Potassium dichromate reacts with chloride ions in the presence of concentrated sulphuric acid to give red vapours of chromyl chloride.

$$K_2Cr_2O_7 + 2H_2SO_4 \rightarrow 2KHSO_4 + H_2Cr_2O_7$$

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl] \times 4$$

$$H_2Cr_2O_7 + 4HCl \rightarrow 2CrO_2Cl_2 + 3H_2O$$

$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \rightarrow 2KHSO_4 + 4NaHSO_4 + 2CrO_2Cl_2 + 3H_2O$$

When the vapours of CrO_2Cl_2 are passed through water or alkaline solution, a yellow solution of H_2CrO_4 is obtained.

$$CrO_2Cl_2 + 2H_2O \rightarrow H_2CrO_4 + 2HCl; \qquad CrO_2Cl_2 + 2OH^- \rightarrow H_2CrO_4 + 2Cl^-$$

The addition of lead acetate in this solution gives yellow precipitate of $PbCrO_4$.

$$Pb^{2+} + H_2CrO_4 \rightarrow PbCrO_4 + 2H^+$$

The above entire procedure is used to test Cl^- ions in a laboratory.

On heating, potassium dichromate decomposes to green chromic oxide and oxygen.

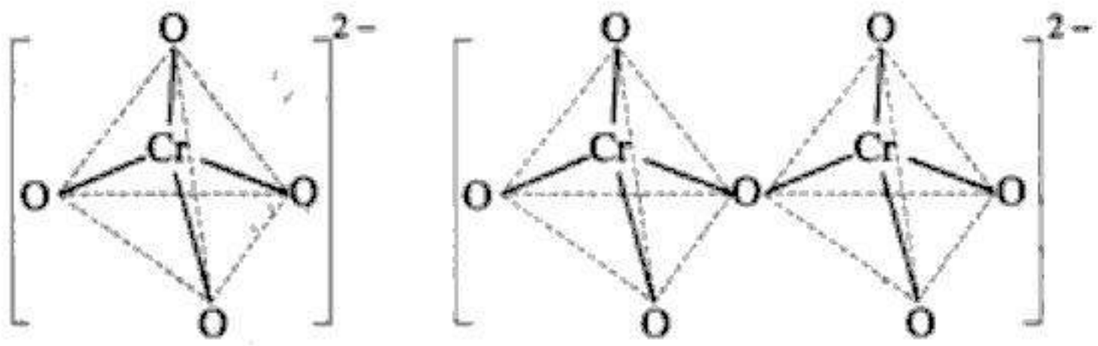
$$4K_2Cr_2O_7 \rightarrow 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$$

In a solution, dichromate and chromate ions exist in equilibrium with each other

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

In acidic medium, solution contains $Cr_2O_7^{2-}$ ions whereas in alkaline medium, solution contains CrO_4^{2-} ions.

The structure of CrO_4^{2-} and $Cr_2O_7^{2-}$ are as follows.



Potassium dichromate is used in dyeing, chrome tanning, calico printing and photography.

Straight Objective Type

Sodium and Potassium

1. The oxide that gives hydrogen peroxide on treatment with a dilute acid is
(a) PbO_2 (b) Na_2O_2 (c) MnO_2 (d) TiO_2 (1985)

2. The molecular formula of Glauber's salt is
(a) $MgSO_4 \cdot 7H_2O$ (b) $CuSO_4 \cdot 5H_2O$ (c) $FeSO_4 \cdot 7H_2O$ (d) $Na_2SO_4 \cdot 10H_2O$ (1985)

3. Solvay process is used for the manufacture of
(a) NaOH (b) $NaCO_3 \cdot 10H_2O$ (c) K_2CO_3 (d) Na_2O_2

4. Which of the following statements is **not** correct?
(a) The main raw materials required in Solvay process are NaCl and NH_4Cl
(b) $NaHCO_3$ is less soluble in water as compared to NH_4Cl

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56. The basic strength of hydroxides of alkaline earth elements follows the order
(a) $Mg(OH)_2 > Ca(OH)_2 > Sr(OH)_2$ (b) $Mg(OH)_2 > Sr(OH)_2 > Ca(OH)_2$
(c) $Ca(OH)_2 > Sr(OH)_2 > Mg(OH)_2$ (d) $Ca(OH)_2 > Mg(OH)_2 > Sr(OH)_2$

57. Which of the following salts is used as mild laxative?
(a) $MgSO_4 \cdot 7H_2O$ (b) anhydrous $MgSO_4$ (c) $CaSO_4 \cdot 2H_2O$ (d) anhydrous $CaSO_4$

58. The thermal stability of sulphates of alkaline earth elements follows the order
(a) $MgSO_4 > CaSO_4 > SrSO_4$ (b) $MgSO_4 > SrSO_4 > CaSO_4$
(c) $SrSO_4 > MgSO_4 > CaSO_4$ (d) $SrSO_4 > CaSO_4 > MgSO_4$

59. The formula of basic beryllium nitrate is
(a) $[Be_4O(NO_3)_4]$ (b) $[Be_4O_2(NO_3)_4]$ (c) $[Be_4O(NO_3)_6]$ (d) $[Be_4O_3(NO_3)_3]$

60. The least stable hydride of alkaline earth elements is
(a) BeH_2 (b) MgH_2 (c) CaH_2 (d) SrH_2

61. Which of the following hydrides is covalent and exists as polymeric form?
(a) BeH_2 (b) MgH_2 (c) CaH_2 (d) SrH_2

62. In the polymeric BeH_2 structure, each beryllium is bound to
(a) 2 hydrogen atoms (b) 3 hydrogen atoms
(c) 4 hydrogen atoms (d) alternatively to 2 and 4 hydrogen atoms

Aluminium

63. Which of the following statements about anhydrous aluminium chloride is correct?
(a) It exists as $AlCl_3$ molecules. (b) It is not easily hydrolysed.
(c) It sublimes at 100 °C under vacuum. (d) It is a strong Lewis base. (1981)

64. Hydrogen gas will not reduce
(a) heated cupric oxide (b) heated ferric oxide
(c) heated stannic oxide (d) heated aluminium oxide (1985)

65. Which of the following statements regarding aluminium chloride is **not** correct?
(a) Fused aluminium chloride does not conduct electricity.
(b) Aluminium chloride exists as dimer in organic solvents such as benzene and ether.
(c) Aluminium chloride exists as monomer in organic solvents such as benzene and ether.
(d) Aluminium chloride forms double salt $AlCl_3 \cdot 6NH_3$ with ammonia.

66. Which of the following characteristics of aluminium chloride dimer is correct?
(a) All bond lengths are identical.
(b) All bond angles are identical.
(c) All bond lengths and angles are different.
(d) The terminal Al—Cl bond length and the terminal bond angle Cl—Al—Cl are different from those involving bridged atoms.

67. Which of the following statements is **not** correct?
(a) Anhydrous aluminium chloride cannot be prepared by heating hydrated salt.
(b) Aluminium chloride solution is acidic.
(c) In the temperature range (420K-480 K) aluminium chloride exists as monomer in the vapour phase.
(d) At very high temperature, aluminium chloride exists as monomer.

68. The general formula of aluminium alums is
(a) $[M^I (H_2O)_4] [Al(H_2O)_4] (SO_4)_2$ (b) $[M^I (H_2O)_6] [Al(H_2O)_6] (SO_4)_2$
(c) $[M^I (H_2O)_5] [Al(H_2O)_5] (SO_4)_2$ (d) $M^I Al^{III} (SO_4)_2$ in nonpolar solvents

69. Anhydrous aluminium chloride in nonpolar solvents exists as
(a) monomer (b) dimer (c) ionic form (d) polymer

70. Which of the following hydroxide is amphoteric in nature?
(a) $B(OH)_3$ (b) $Al(OH)_3$ (c) $Ga(OH)_3$ (d) Tl(OH)

Tin and Lead

71. Which of the following oxides is amphoteric?
(a) Na_2O (b) CaO (c) K_2O (d) SnO_2 (1993)

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(c) remove undecomposed AgBr as a soluble silver thiosulphate complex
(d) remove reduced silver

122. Which of the following dissolves in hot concentrated solution of NaOH?
(a) Fe (b) Zn (c) Cu (d) Ag (1980)

123. Which of the following is the weakest base?
(a) NaOH (b) $Ca(OH)_2$ (c) KOH (d) $Zn(OH)_2$ (1980)

124. Identify the correct order of acidic strengths of CO_2, CuO, CaO and H_2O.
(a) $CaO < CuO < H_2O < CO_2$ (b) $H_2O < CuO < CaO < CO_2$
(c) $CaO < H_2O < CuO < CO_2$ (d) $H_2O < CO_2 < CaO < CuO$ (2002)

Potassium Permanganate and Potassium Dichromate

125. The oxidation state of Mn in $KMnO_4$ is
(a) +2 (b) +6 (c) +7 (d) +8

126. In acidic medium, $KMnO_4$ acts as a strong oxidizing agent. Its equivalent mass is molar mass divided by
(a) 2 (b) 3 (c) 4 (d) 5

127. The oxidation state of Mn in K_2MnO_4 is
(a) +2 (b) +6 (c) +7 (d) +8

128. In a reaction MnO_4^- is changed to MnO_2. The change in oxidation state of Mn is
(a) −3 (b) +3 (c) −1 (d) +1

129. The oxidation state of Cr in $K_2Cr_2O_7$ is
(a) +2 (b) +4 (c) +6 (d) +8

130. Chromyl chloride is represented by the formula
(a) CrOCl (b) $CrOCl_2$ (c) CrO_2Cl_2 (d) Cr_2OCl_2

131. Ammonium dichromate is used in some fireworks. The green coloured powder blown in air is
(a) CrO_3 (b) Cr_2O_3 (c) Cr (d) $CrO(O_3)$ (1997)

132. In the dichromate dianion,
(a) four Cr—O bonds are equivalent (b) six Cr—O bonds are equivalent
(c) all Cr—O bonds are equivalent (d) all Cr—O bonds are nonequivalent (1999)

133. On heating ammonium dichromate, the gas evolved is
(a) oxygen (b) ammonia (c) nitrous oxide (d) nitrogen (1999)

134. In alkaline medium, MnO_4^- oxidises I^- to
(a) IO_3^- (b) I_2 (c) IO_4^- (d) IO^- (2004)

135. In alkaline medium, MnO_4^- in oxidation reaction is converted into
(a) MnO_4^{2-} (b) Mn^{2+} (c) MnO_2 (d) MnO_3^+

136. The equivalent mass of $KmnO_4$ in its oxidation reaction in alkaline medium is equal to
(a) molar mass (b) molar mass/3 (c) molar mass/4 (d) molar mass/5

137. In acidic medium $K_2Cr_2O_7$ acts as a strong oxidizing agent. Its equivalent mass is molar mass divided by
(a) 2 (b) 3 (c) 4 (d) 6

138. On adding NaOH in $K_2Cr_2O_7$ solution, the $Cr_2O_7^{2-}$ species is changed to
(a) Cr^{3+} (b) Cr_2O_3 (c) CrO_4^{2-} (d) Cr_2O_5

Multiple Correct Choice Type

1. Which of the following statement(s) is are correct when a mixture of NaCl and $K_2Cr_2O_7$ is gently warmed with concentrated H_2SO_4?
(a) A deep red vapour is evolved
(b) The vapour when passed into NaOH solution gives a yellow solution of Na_2CrO_4
(c) Chlorine gas is evolved
(d) Chromyl chloride is formed (1998)

2. Sodium nitrate decomposes above ~ 800 °C to give
(a) N_2 (b) O_2 (c) NO_2 (d) Na_2O (1998)

3. The pair(s) of compounds which can exist together in aqueous solution is/are
(a) Na_2CO_3 and $NaHCO_3$ (b) Na_2CO_3 and NaOH (c) $NaHCO_3$ and NaOH (d) $K_2Cr_2O_7$ and NaOH

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35. Which of the following statements are
(a) The solubility of the hydroxides of elements of Group 2 decreases on descending the group.
(b) The basic character of hydroxides of elements of Group 2 decreases on descending the group.
(c) Anhydrous calcium chloride melts at a temperature higher than that of anhydrous magnesium chloride because the charge: radius ratio is higher for Mg^{2+} as compared to Ca^{2+} ions.
(d) Epsom salt is $CaSO_4 \cdot 2H_2O$

36. Which of the following statements are **not** correct?
(a) Plaster of paris is $2CaSO_4 \cdot H_2O$
(b) The solubility of sulphates of alkaline earth metals increases on descending the group.
(c) The salt of magnesium which is used as a refractory material for lining electric furnaces is MgO.
(d) Sorel's cement contains CaO and MgO.

37. Which of the following statements are correct?
(a) Calcium peroxide is crystallized with the molecular formula $CaO_2 \cdot 8H_2O$.
(b) An aqueous suspension of $Mg(OH)_2$ is known as milk of magnesia.
(c) Magnesium chloride is crystallized with molecular formula $MgCl_2 \cdot 7H_2O$
(d) Calcium sulphate is crystallized with the molecular formula $CaSO_4 \cdot 2H_2O$

38. Which of the following statements are **not** correct?
(a) Aluminium chloride is crystallized with molecular formula $AlCl_3 \cdot 6H_2O$
(b) The molecular formula of potash alum is $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 12H_2O$
(c) In concentrated HNO_3, aluminium gets a coating of Al_2O_3 and becomes passive.
(d) The slaked lime is CaO.

39. Which of the following statements are **not** correct?
(a) Tin(II) oxide on dissolution in NaOH produces sodium stannate.
(b) Stannite ion is a powerful reducing agent.
(c) Tin(IV) oxide on dissolution in NaOH produces sodium stannite.
(d) In acidic medium, $SnCl_2$ reduces nitrobenzene to aniline.

40. Which of the following statements are **not** correct?
(a) Litharage is crystalline mass having molecular composition PbO.
(b) Pb_3O_4 is known as red lead.
(c) The molecular formula of lead suboxide is PbO.
(d) The molecular formula of lead sesquioxide is Pb_2O.

41. Which of the following statements are **not** correct?
(a) Lunar Caustic is $AgNO_3$
(b) With an excess of $SnCl_2$, $HgCl_2$ gives black precipitate due to the formation of mercurous chloride.
(c) Chemical composition of white lead is $Pb(OH)_2$
(d) Chrome yellow is $PbCrO_4$.

42. Which of the following statements are **not** correct?
(a) Green vitriol is ferrous sulphate.
(b) Ferrous sulphate crystallized with seven water of crystallization.
(c) The basic ferric sulphate is $Fe(OH)_2SO_4$
(d) The venetian red is FeO.

43. Which of the following statements are **not** correct?
(a) Philospher's wool is ZnO.
(b) White vitriol is $ZnSO_4$.
(c) Zinc sulphate crystallizes with six water of crystallization.
(d) A lead compound which is used as an antiknocking agent is $Pb(CH_3)_4$.

44. Which of the following statements are correct?
(a) In medicine, $MgSO_4 \cdot 7H_2O$ is used as purgative.
(b) Fusion of solid KNO_3 with solid K produces K_2O and N_2.
(c) KNO_3 is commonly known as salt petre.
(d) $NaNO_3$ is commonly known as chile salt peter.

45. Which of the following statements are **not** correct?
(a) The water of crystallization associated with ferric chloride is six.

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Column I lists the labeling A, B, ..., and Column II mentiones their chemical formula. Match each entry of Column I with those given in Column II.

Column I	**Column II**
(a) A	(p) $Ca(OH)_2$
(b) B	(q) NH_4Cl
(c) C	(r) NaCl
(d) D	(s) CaO
(e) E	(t) $CaCO_3$
(f) F	(u) NH_4HCO_3

ANSWERS

Straight Objective Type

1. (b)	**2.** (d)	**3.** (b)	**4.** (a)	**5.** (a)	**6.** (d)	**7.** (d)
8. (b)	**9.** (a)	**10.** (c)	**11.** (d)	**12.** (b)	**13.** (a)	**14.** (d)
15. (c)	**16.** (d)	**17.** (b)	**18.** (c)	**19.** (c)	**20.** (a)	**21.** (d)
22. (b)	**23.** (b)	**24.** (c)	**25.** (a)	**26.** (a)	**27.** (c)	**28.** (a)
29. (b)	**30.** (d)	**31.** (c)	**32.** (b)	**33.** (c)	**34.** (d)	**35.** (c)
36. (a)	**37.** (b)	**38.** (b)	**39.** (b)	**40.** (c)	**41.** (a)	**42.** (c)
43. (a)	**44.** (b)	**45.** (b)	**46.** (c)	**47.** (b)	**48.** (d)	**49.** (b)
50. (a)	**51.** (c)	**52.** (d)	**53.** (a)	**54.** (c)	**55.** (a)	**56.** (c)
57. (a)	**58.** (d)	**59.** (c)	**60.** (a)	**61.** (a)	**62.** (c)	**63.** (c)
64. (d)	**65.** (c)	**66.** (d)	**67.** (c)	**68.** (b)	**69.** (b)	**70.** (b)
71. (d)	**72.** (a)	**73.** (d)	**74.** (c)	**75.** (d)	**76.** (b)	**77.** (d)
78. (d)	**79.** (d)	**80.** (b)	**81.** (c)	**82.** (c)	**83.** (c)	**84.** (a)
85. (c)	**86.** (b)	**87.** (a)	**88.** (d)	**89.** (b)	**90.** (b)	**91.** (d)
92. (a)	**93.** (b)	**94.** (c)	**95.** (d)	**96.** (c)	**97.** (a)	**98.** (d)
99. (a)	**100.** (c)	**101.** (b)	**102.** (a)	**103.** (b)	**104.** (c)	**105.** (b)
106. (c)	**107.** (b)	**108.** (b)	**109.** (b)	**110.** (d)	**111.** (d)	**112.** (a)
113. (c)	**114.** (d)	**115.** (a)	**116.** (a)	**117.** (c)	**118.** (c)	**119.** (b)
120. (c)	**121.** (c)	**122.** (b)	**123.** (d)	**124.** (a)	**125.** (c)	**126.** (d)
127. (b)	**128.** (a)	**129.** (c)	**130.** (c)	**131.** (b)	**132.** (b)	**133.** (d)
134. (a)	**135.** (c)	**136.** (b)	**137.** (d)	**138.** (c)		

Multiple Correct Choice Type

1. (a), (b), (d)	**2.** (a), (b), (d)	**3.** (a), (b)	**4.** (a), (b), (c)
5. (a), (d)	**6.** (a), (b)	**7.** (c), (d)	**8.** (b), (c), (d)
9. (b), (c)	**10.** (a), (b), (c), (d)	**11.** (c), (d)	**12.** (a) (b), (c)
13. (c), (d)	**14.** (a), (b), (c), (d)	**15.** (b), (c), (d)	**16.** (a), (b), (d)
17. (a), (b), (c), (d)	**18.** (a), (b)	**19.** (b), (c)	**20.** (a), (c), (d)
21. (a), (c)	**22.** (a), (b), (c), (d)	**23.** (a), (b), (c)	**24.** (a), (b), (d)
25. (a), (c), (d)	**26.** (b), (c)	**27.** (b), (c), (d)	**28.** (a), (b), (c)
29. (a), (b), (c), (d)	**30.** (b), (c)	**31.** (a), (b)	**32.** (c), (d)
33. (b), (c)	**34.** (a), (d)	**35.** (a), (b)	**36.** (b), (d)
37. (a), (b), (d)	**38.** (b), (d)	**39.** (a), (c)	**40.** (c), (d)
41. (b), (c)	**42.** (c), (d)	**43.** (b), (c)	**44.** (a), (b), (c), (d)
45. (c), (d)	**46.** (a), (b)	**47.** (b), (d)	**48.** (c), (d)
49. (a), (b)	**50.** (a), (b)	**51.** (a), (b), (d)	

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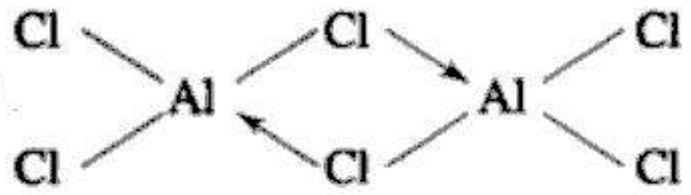


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15. (a) A paste of lime in water is known as milk of lime whereas clear solution is known as lime water.

16. (a) $AlCl_3$ is a Lewis acid because it accepts rather than donating electrons.

(b) The structure of Al_2Cl_6 is



The terminal bonds are different from the bridge Al—Cl bonds.

17. (a) It exists as a dimer.
(b) It is a covalent compound and is thus soluble in alcohol, ether and benzene.
(d) It as Lewis base.

19. (a) PbO_2 is a dioxide and not peroxide.
(b) This is due to inert-pair effect.
(d) It is a yellow powder.

20. (b) It is lead dioxide.
(c) It is due to the formation of H_2PbCl_4.

21. (d) Sodium stannite is known only in aqueous solution. It is readily oxidized by atmospheric oxygen to sodium stannate.

22. (a) On heating hydrated salt, basic chloride, Sn(OH)Cl, is formed.
(b) It is an angular covalent molecule because of repulsion between a lone pair of electrons on Sn and two bonding pairs of electrons.
(c) It is a covalent molecule soluble in benzene.
(d) Stannic chloride forms a series of hydrated salts ($SnCl_4 \cdot 3H_2O$, $SnCl_4 \cdot 5H_2O$, $SnCl_4 \cdot 6H_2O$ and $SnCl_4 \cdot 8H_2O$).

23. (a) It is an ampoteric oxide.
(c) It is a reducing agent due to the reaction $Sn^{2+} \rightarrow Sn^{4+} + 2e^-$

24. (a) It produces ferric oxide, SO_2 and SO_3.
(b) It is susceptible to aerial oxidation and dehydration.
(d) Heating upto 430 K produces FeO, CO and CO_2. Only in the presence of air, ferric oxide is formed.

25. (a) The reaction $2Cu^+ \rightarrow Cu^{2+} + Cu$ is possible as $E^\circ_{Cu^+|Cu} > E^\circ_{Cu^{2+}|Cu}$
(b) The products are CuO and SO_3.

26. (b) Copper(II) oxidizes I^- to I_2. The reaction is $2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2$

27. (a) The solubility of halides of silver varies as AgF > AgCl > AgBr > AgI.
(b) Silver nitrate decomposes as $2AgNO_3 \rightarrow 2Ag + 2NO_2 + O_2$ on heating.
(c) There does occur change in colour but the final product is Ag_2S and not Ag.
(d) With concentrated solution of sodium thiosulphate, no precipitate is obtained. Instead, a complex ion $[Ag(S_2O_3)_2]^{3-}$ is obtained.

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$$B_2H_6 + 3O_2 \rightarrow 2B_2O_3 + 3H_2O; \qquad B_2H_6 + 6H_2O \rightarrow 2H_3BO_3 + 3H_2$$

Higher boranes are obtained by heating diborane in a sealed tube. The compounds formed are B_4H_{10}, B_5H_{11}, B_6H_{12} and $B_{10}H_{14}$.

One of the important reactions shown by B_2H_6 is the process of *hydroboration*. This involves the following steps.

1. Reaction of B_2H_6 with an alkene or alkyne

$$B_2H_6 + 6RCH{=}CH_2 \rightarrow 2B(CH_2CH_2R)_3; \qquad B_2H_6 + 6RC{\equiv}CR \rightarrow 2B(RC{=}CHR)_3$$

The reaction is carried out in the atmosphere of nitrogen as the product is very reactive.

The net reaction is a *cis*-addition reaction across a double or triple bond. The reactions follow anti-Markovnikov rule, that B attaches to the least substituted C atom.

2. Conversion of alkylborane into other stable products.

(a) Treatment with carboxylic acids yields a hydrocarbon

$$B(CH_2CH_2R)_3 + 3CH_3COOH \rightarrow 3RCH_2CH_3 + B(CH_3COO)_3$$

(b) Treatment with alkaline H_2O_2 yields an alcohol

$$B(CH_2CH_2R)_3 + 3H_2O_2 \rightarrow 3RCH_2CH_2OH + H_3BO_3$$

(c) Oxidation with chromic acid yields a ketone or a carboxylic acid.

$$B(CH(R)R')_3 \xrightarrow{H_2CrO_4} RCOR'; \qquad B(CH_2CH_3)_3 \xrightarrow{H_2CrO_4} CH_3COOH$$

All the boranes are electron-deficient compounds. They form simple adducts with amines

$$B_2H_6 + 2(CH_3)_3N: \rightarrow 2[(CH_3)_3N \rightarrow BH_3]$$

Their reactions with ammonia depend on the experimental conditions.

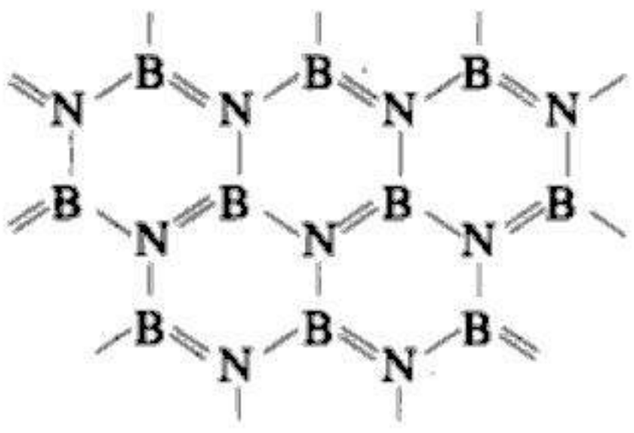
$$B_2H_6 + NH_3 \xrightarrow[\text{excess}]{\text{low temperature}} B_2H_6 \cdot 2NH_3 \quad \text{or} \quad 2\,BH_3 \cdot NH_3$$

$$\xrightarrow{\text{higher temperature}} (BN)_x$$

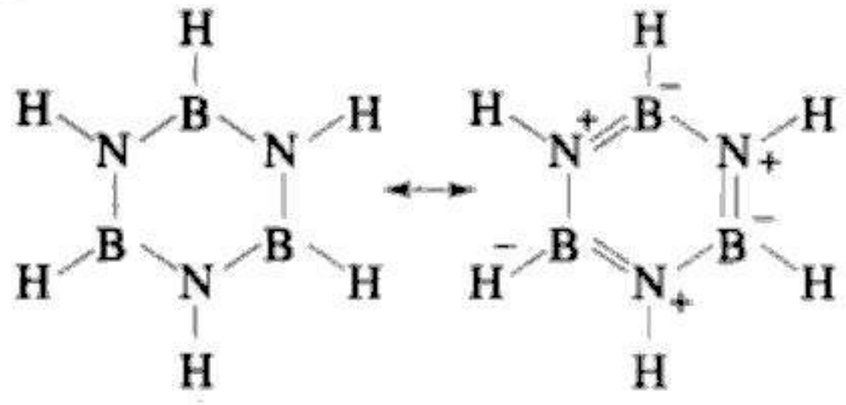
Boron nitride

If the ratio of B_2H_6 and NH_3 is 1:2, the product obtained at higher temperature is borazine ($B_3N_3H_6$).

The structure of boron nitride is very similar to graphite (as the sum of valence electrons of B and N is equal to that of two C atoms). Borazine is known as inorganic benzene.



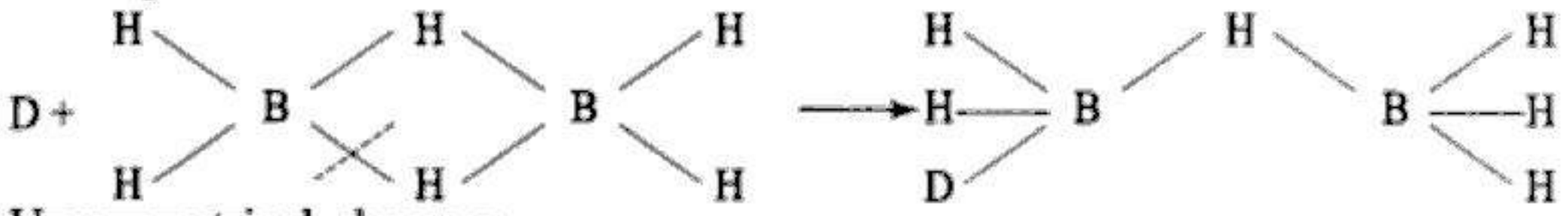
Boron nitride



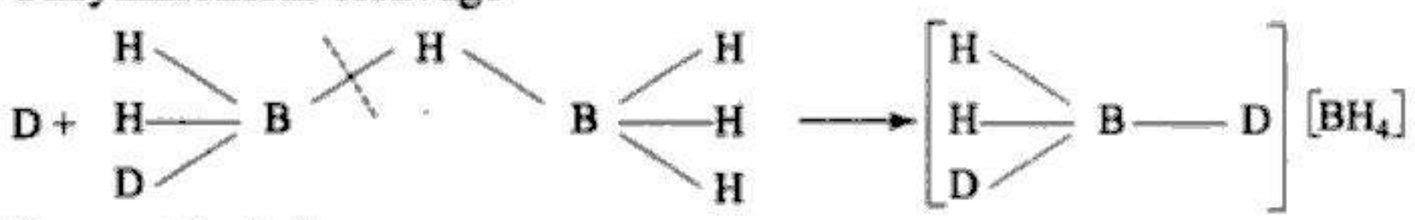
Borazine

The reaction between B_2H_6 and electron-donor compound D (such as ammonia or alkylamines) at low temperatures proceeds in two steps.

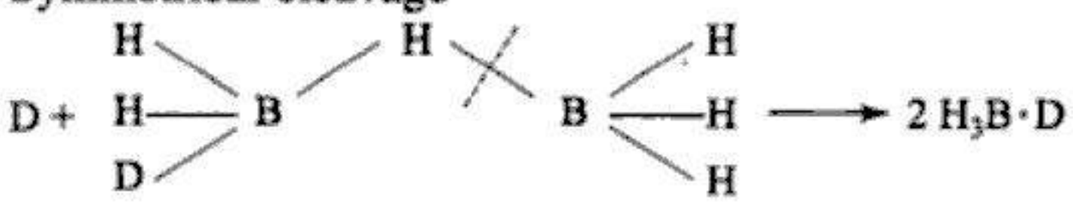
Step 1



Step 2 Unsymmetrical cleavage



or Symmetrical cleavage



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$$2RCl + Si(Cu) \rightarrow R_2SiCl_2$$

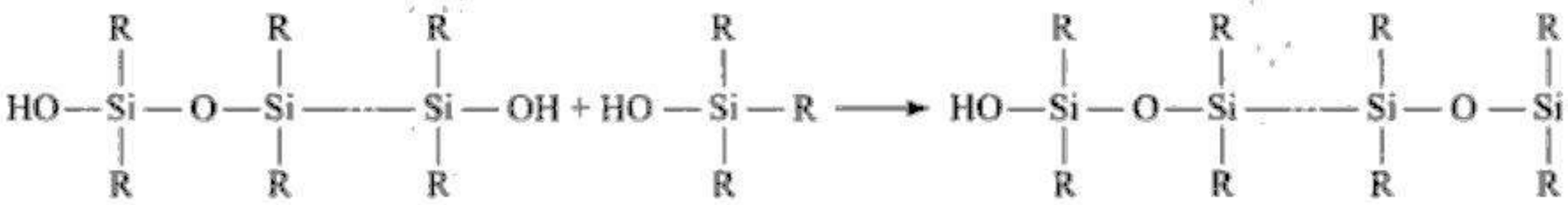
reacts with water producing dialkyldihydrosilane. This, in turn, may be dehydrated to give a linear polymer.

$$R_2SiCl_2 + 2H_2O \rightarrow R_2Si(OH)_2 + 2HCl$$

$$nR_2Si(OH)_2 \xrightarrow[-H_2O]{} (R_2SiO)_n, \text{ i.e. } [O - R_2Si - O]_n$$

silicone

Polymerization of $R_2Si(OH)_2$ is due to the active hydroxyl groups which exist at the two ends of the straight chain. However, if some trialkylchlorosilane, R_3SiCl, is mixed with R_2SiCl_2 and hydrolysed, the R_3SiCl helps blocking the end of straight chain produced by R_2SiCl_2.



The hydrolysis of $RSiCl_3$ produces a complex cross-linked polymer.

Silicones have good thermal and oxidative stability. These are excellent water repellants, good electrical insulators, and chemically inert substances. Silicon rubber is not attacked by ozone. Liquid silicones are used as excellent lubricants. These are mixed with paints and enamels to increase the resistance to the effects of high temperatures, sunlight and chemicals.

Silicates Silicon forms a very large number of compounds containing SiO_4^{4-} anion as the basic unit. The structure of this basic unit is a tetrahedron in which oxygen atoms are arranged tetrahedrally around a silicon atom. Depending on the number of corners (0, 1, 2, 3 or 4) of SiO_4^{4-} tetrahedron shared with other tetrahedra, a variety of silicates are obtained.

Orthosilicates These contain individual discrete SiO_4^{4-} tetrahedra. Examples are phenacite (Be_2SiO_4), willemite (Zn_2SiO_4), and zircon ($ZnSiO_4$) minerals.

Pyrosilicates These contain discrete $Si_2O_7^{6-}$ ions formed by the sharing of one oxygen atom between the two SiO_4^{4-} tetrahedra. The structure is known as an island structure. Examples include thortveitite ($Sc_2Si_2O_7$) and hemimorphite ($Zn_4(OH)_2\,Si_2O_7$).

Chain and Cyclic Silicates These silicates are formed when two oxygen atoms of SiO_4^{4-} tetrahedron are shared with two other tetrahedra. The resulting structure may be the chain type or the cyclic type. The general formula of these silicates is $(SiO_3)_n^{2n-}$. Examples of cyclic silicates are benitoite ($BaTiSi_3O_9$), catapleite ($Na_2ZrSi_3O_9 \cdot 2H_2O$), dioptase ($Cu_6Si_6O_{18} \cdot 6H_2O$) and beryl ($Be_3Al_2Si_6O_{18}$).

Infinite chain are formed when two oxygen atoms of SiO_4^{4-} tetrahedron are shared with the adjacent tetrahedra. If further sharing of oxygen atoms occurs by half of the silicon atoms, a double chain or band structure is formed. Examples of the former include enstatite $MgSiO_3$ and diopside $CaMg(SiO_3)_2$. Asbestos also contains silicate chains. The band structure contains the basic $Si_4O_{11}^{6-}$ repeating unit. An example is $Ca_2Mg_5(OH)_2(Si_4O_{11})_2$.

Layer and Sheet Silicates These are formed by sharing of three oxygen atoms by each tetrahedron giving an infinite two-dimensional sheet of the empirical formula $(Si_2O_5)_n^{2n-}$. Examples include kaolin [$Al_2(OH)_4Si_2O_5$], talc [$Mg_3(OH)_2Si_4O_{10}$] and the micas.

Three-Dimensional Silicates In these silicates, all the four oxygen atoms of a SiO_4^{4-} tetrahedron are shared with other tetrahedra resulting in a three-dimensional lattice. The formula of such a silicate is SiO_2(quartz).

Carbide Silicon carbide, also known as *carborundum*, is a very hard substance. It is made by heating sand and coke in an electric furnace at very high temperature of 2000–2500 °C.

$$SiO_2 + 2C \rightarrow Si + 2CO$$

$$Si + C \rightarrow SiC$$

Chemically, silicon carbide is extremely inert and is not attacked by even hydrofluoric acid. When fused with alkalis, it is decomposed to give silicate and carbonate.

$$SiC + 4NaOH + 2O_2 \rightarrow Na_2SiO_3 + 2H_2O + Na_2CO_3.$$

It is used as an abrasive for cutting and grinding glass.

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Phosphorus tetroxide Liquid phosphorus trioxide when heated in a sealed tube at 440°C, changes into tetroxide.

$$4P_4O_6 \rightarrow 3P_4O_8 + 4P$$

Phosphorus tetroxide is a mixed anhydride as it gives both phosphorous and phosphoric acids with water.

$$P_4O_8 + 6H_2O \rightarrow 2H_3PO_3 + 2H_3PO_4$$

The structure of P_4O_8 is shown in Fig. 15.3.

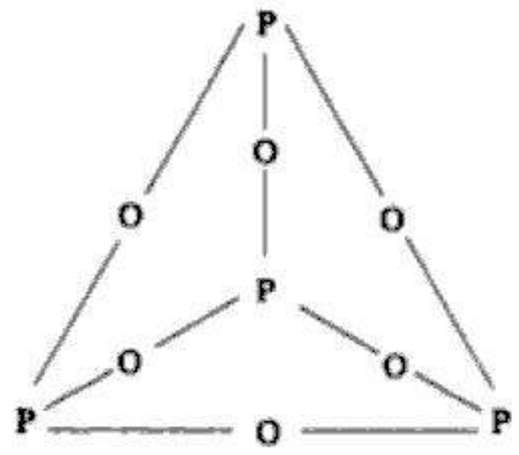


Fig. 15.2 Structure of P_4O_6

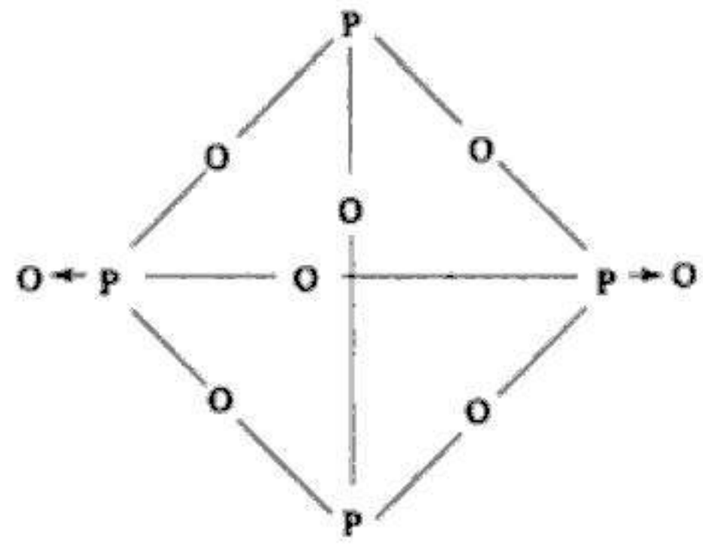


Fig. 15.3 Structure of P_4O_8

Phosphorus pentoxide Burning of phosphorus in an excess of dried air or oxygen gives phosphorus pentoxide. It is a white solid which sublimes on heating. It is odourless when pure. It dissolves in cold water giving metaphosphoric acid.

$$P_4O_{10} + 2H_2O \xrightarrow[\text{hot}]{} 4HPO_3$$

With hot water, orthophosphoric acid is formed. $P_4O_{10} + 6H_2O \xrightarrow[\text{hot}]{} 4H_3PO_4$

It is a strong dehydrating agent. For example, H_2SO_4 and HNO_3 are converted into corresponding anhydride.

$$2H_2SO_4 + P_4O_{10} \rightarrow 2SO_3 + 4HPO_3; \qquad 4HNO_3 + P_4O_{10} \rightarrow 2N_2O_5 + 4HPO_3$$

Acetamide gives acetonitrile. $2CH_3CONH_2 + P_4O_{10} \rightarrow 2CH_3CN + 4HPO_3$

On heating with carbon, it is reduced to phosphorus. $P_4O_{10} + 10C \rightarrow P_4 + 10CO$

In the structure of P_4O_{10}, each P atom forms three bonds to oxygen atoms and also an additional coordinate bond with an oxygen atom (Fig. 15.4). Terminal coordinate P—O bond is 143 pm which is much shorter than the expected bond length of 162 pm. This shows the presence of considerable $p\pi$-$d\pi$ back bonding because of the lateral overlap of full p orbitals on oxygen with empty d orbitals on phosphorus.

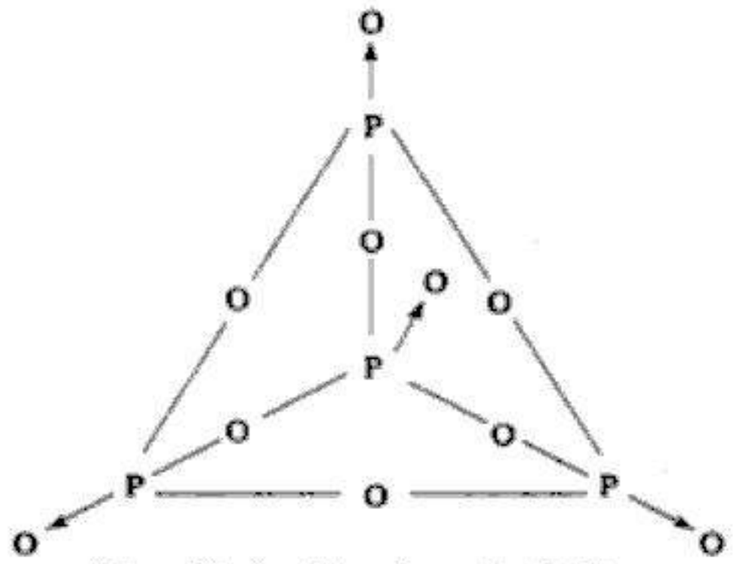


Fig. 15.4 Structure fo P_4O_{10}

Oxoacids Six important oxoacids are described in the following.

Hypophosphorous Acid (H_3PO_2) Heating of phosphorus with barium hydroxide solution forms barium hypophosphite in the solution. Excess of barium hydroxide is removed by passing carbon dioxide in the solution. It is filtered and the filtrate is evaporated to give crystals of barium hypophosphite. The latter is treated with the calculated quantity of H_2SO_4 when the acid is set free.

$$2P_4 + 3Ba(OH)_2 + 6H_2O \rightarrow 2PH_3\uparrow + 3Ba(H_2PO_2)_2$$

$$Ba(H_2PO_2)_2 + H_2SO_4 \rightarrow BaSO_4 + 2H_3PO_2$$

The acid and its salt decomposes on heating.

$$2H_3PO_2 \rightarrow H_3PO_4 + PH_3; \qquad 3NaH_2PO_2 \rightarrow NaH_2PO_3 + Na_2HPO_3 + PH_3$$

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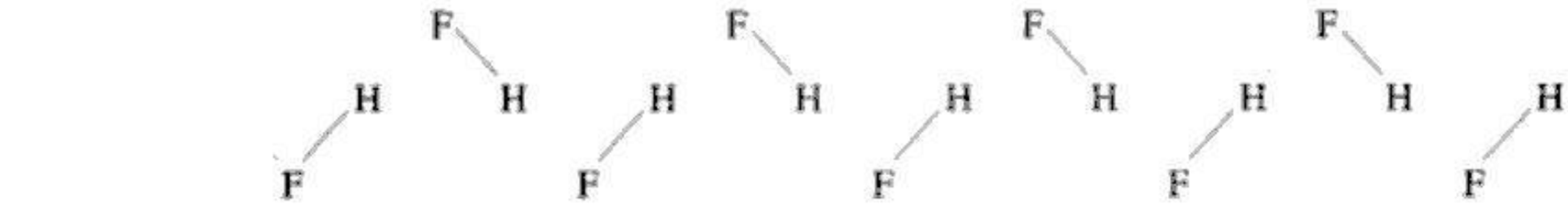
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In water, HCl, HBr, and HI ionize almost completely and are therefore strong acids. HF only ionizes slightly and is therefore a weak acid.

The aqueous solutions form azeotropic mixtures with maximum boiling points, because of a negative deviation from Raoult's law. In lesser ionic solvent, the acid strength of hydrohalic acids follows the order

$$HI > HBr > HCl > HF$$

Of the four hydrogen halides, HF has the highest boiling point due to the hydrogen bonds which persist even in the gaseous phase. In liquid and solid, HF forms zig-zag chains as shown in the following figure.



In the gaseous phase, a mixture of cyclic $(HF)_6$ polymers, dimeric $(HF)_2$, and monomeric HF are formed. HCl, HBr and HI are not hydrogen bonded in the gas and liquid, though HCl and HBr are weakly hydrogen bonded in the solid.

Liquid HF has been used as a non-aqueous solvent. It undergoes self ionization.

$$2HF \rightleftharpoons [H_2F]^+ + F^-$$

Acid-base reactions occur in this solvent system. Mineral acids HNO_3, H_2SO_4 and HCl behave as bases in HF solvent. Perchloric acid behaves as an acid in HF. The fluoride acceptors compounds (SbF_5, NbF_5, AsF_5 and BF_3) also act as acids in HF.

Oxides of Chlorine

1. **Dichlorine monoxide, Cl_2O**

   This is prepared by heating freshly precipitated mercuric oxide with halogen gas diluted with dry air.

   $$2\,Cl_2 + 2\,HgO \xrightarrow{575\ K} HgCl_2{\cdot}HgO + Cl_2O$$

   It is a yellow-brown gas which explodes in the presence of reducing agent or NH_3, on heating

   $$3\,Cl_2O + 10\,NH_3 \rightarrow 6\,NH_4Cl + 2\,N_2 + 3\,H_2O$$

   Cl_2O is acidic anhydride of hypochlorous acid.

   $$Cl_2O + H_2O \rightleftharpoons 2\,HOCl$$

   Cl_2O is angular shape with bond angle ClOCl equal to 111°. The bond length Cl—O is 170 pm. Oxygen in Cl_2O is sp^3 hybridized with two lone pairs of electrons. The increase in bond angle from 109°28′ to 111° is due to the removal of steric crowding of the larger chlorine atoms.

2. **Chlorine dioxide, ClO_2**

   This is prepared in situ and is used after diluting with air or CO_2.

   Laboratory preparation

   $$2\,NaClO_3 + 2(COOH)_2 \xrightarrow[90^\circ C]{H_2O} 2\,ClO_2 + 2\,CO_2 + (COONa)_2 + 2\,H_2O$$

   Commercial Preparation

   $$2\ NaClO_3 + SO_2 + H_2SO_4 \xrightarrow[NaCl]{\text{trace of}} 2ClO_2 + NaHSO_4$$

   $$2\ HClO_3 + 2\ HCl \rightarrow ClO_2 + Cl_2 + 2H_2O$$

   ClO_2 is a powerful oxidizing, bleaching and chlorinating agent. It is used for the purification of water and for bleaching purposes.

   The ClO_2 is an old electron molecule and is thus paramagnetic. The odd electron is delocalized over the entire molecule and thus ClO_2 does not show any tendency for dimerization.

   The bond length Cl—O is 147 pm and it is shorter than for a single bond. This indicates the delocalization of odd electron on the entire molecule.

Dichloro Hexoxide, Cl_2O_6

This oxide exists in equilibrium with ClO_3. $\quad Cl_2O_6 \rightleftharpoons 2\ ClO_3$

Cl_2O_6 is made from ClO_2 and O_3. It is a strong oxidizing agent. It undergoes hydrolysis:

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100. The number of hydrogen atoms attached to each phosphorus atoms in pyrophosphorous acid is
(a) one (b) two (c) three (d) none

101. Pyrophosphorous acid has the molecular formula
(a) H_3PO_3 (b) H_3PO_4 (c) $H_4P_2O_5$ (d) $H_4P_2O_7$

102. Pyrophosphorous acid is
(a) monobasic (b) dibasic (c) tribasic (d) tetrabasic

103. Hypophosphoric acid is
(a) monobasic (b) dibasic (c) tribasic (d) tetrabasic

104. The number of hydrogen atoms attached to each phosphorus atom in hypophosphoric acid is
(a) zero (b) one (c) two (d) three

105. Orthophosphoric acid is
(a) monobasic (b) dibasic (c) tribasic (d) tetrabasic

106. The number of hydrogen atoms attached to phosphorus atom in orthophosphoric acid is
(a) zero (b) one (c) two (d) three

107. Which of the following equations is **not** correctly formulated?
(a) $P_4O_{10} + 6H_2O \underset{\text{cold}}{\rightarrow} 4H_3PO_3 + 2O_2$
(b) $P_4 + 20HNO_3 \xrightarrow{I_2} 4H_3PO_4 + 20NO_2 + 4H_2O$
(c) $PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$
(d) $Ca_3(PO_4)_2 + 3H_2SO_4 \xrightarrow[\text{heat}]{} 3CaSO_4 + 2H_3PO_4$

108. The formula of pyrophosphoric acid is
(a) H_3PO_3 (b) H_3PO_4 (c) $H_4P_2O_5$ (d) $H_4P_2O_7$

109. Pyrophosphoric acid is
(a) monobasic (b) dibasic (c) tribasic (d) tetrabasic

110. Which of the following statements regarding pyrophosphoric acid is **not** correct?
(a) It is obtained by heating equimolar mixture of ortho- and meta-phosphoric acid at 100 °C
(b) On boiling with water, it produces orthophosphoric acid
(c) On strong heating, it produces metaphosphoric acid
(d) It forms four series of salts, e.g. $NaH_3P_2O_7$, $Na_2H_2P_2O_7$, $Na_3HP_4O_7$ and $Na_4P_2O_7$

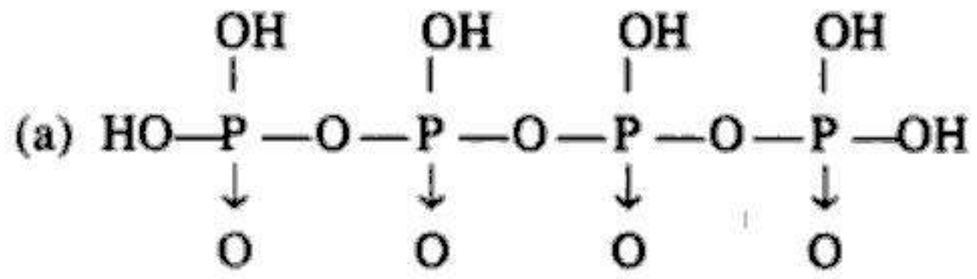
111. The number of hydrogen atoms attached to each phosphorus atom in pyrophosphoric acid is
(a) zero (b) one (c) two (d) three

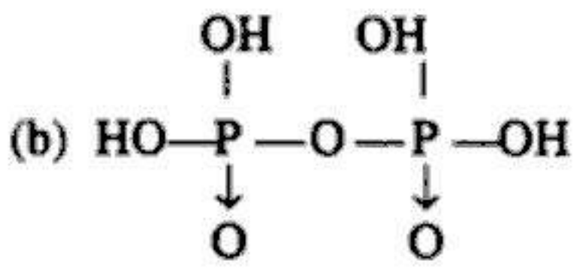
112. Which of the following statements regarding metaphosphoric acid is **not** correct?
(a) It is also known as glacial phosphoric acid
(b) It is a transparent liquid
(c) It is a monobasic acid
(d) It produces orthophosphoric acid on treating with water

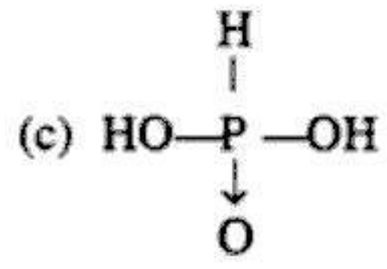
113. Which of the following represents metaphosphoric acid?
(a) HPO_3 (b) H_3PO_3 (c) H_3PO_4 (d) $H_4P_2O_7$

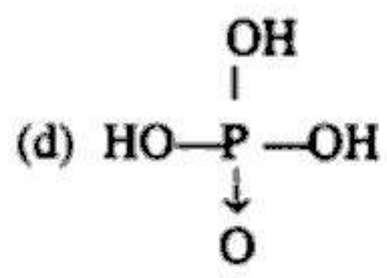
114. The anhydride of orthophosphorous acid is
(a) P_4O_6 (b) P_4O_8 (c) P_4O_{10} (d) P_2O_4

115. Which of the following oxoacids of phosphorus is reducing in character?

(a)


(b)


(c)


(d)


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Hints and Solutions

Straight Objective Type

1. The formula of nido-boranes is B_nH_{n+4}.

2. The formula of arachno-boranes ins B_nH_{n+6}.

3. Diborane is highly reactive.

4. Diborane reacts with NH_3 as follows.

$$(BN)_x \xleftarrow[\text{higher temperature}]{\text{excess } NH_3} B_2H_6 \xrightarrow[\text{low temperature}]{\text{excess } NH_3} B_2H_6 \cdot 2NH_3$$

$$B_2H_6 \downarrow 2NH_3$$

$$B_3N_3H_6$$

5. See. Q. 4.

6. See Q. 4.

7. B in B_2H_6 is sp^3 hybridized.

8. Boric acid is weak acid. it does not give H^+ but accepts OH^-. It is Lewis acid.

9. The reaction is $Na_2B_4O_7 \cdot 10H_2O + 2HCl \rightarrow 2NaCl + 4H_3BO_3 + 5H_2O$
Due to the formation of H_3BO_3, methyl orange is used as the indicator.

10. In B_2H_6, bridge B---H---B is 3c-2e bond.

12. The neutralization reaction is $B(OH)_3 + NaOH \rightleftharpoons Na[B(OH)_4] + NaBO_2 + 2H_2O$ *cis*-diol forms a stable complex with the $[B(OH_4]^-$ and thus the neutralization reaction proceeds in the forward direction. Thus $B(OH)_3$ in the presence of *cis*-diol acts as a strong acid.

14. BF_3 hydrolyses incompletely and forms fluoborates.

$$4BF_3 + 12H_2O \rightarrow 4H_3BO_3 + 12HF$$
$$12HF + 3H_3BO_3 \rightarrow 3H^+ + 3[BF_4]^- + 9H_2O$$
$$\overline{4BF_3 + 3H_2O \rightarrow H_3BO_3 + 3H^+ + 3[BF_4]^-}$$

The other halides undergo complete hydrolysis $BCl_3 + 3H_2O \rightarrow H_3BO_3 + 3HCl$

15. Besides σ bond between boron and halogen atoms, there exist additional $p\pi$-$p\pi$ bond between the two atoms resulting from back-donation of electrons from halide to boron (back bonding). The tendency to form back bonding is maximum in BF_3 and falls rapidly on passing to BCl_3 and BBr_3. The tendency to accept electron pair, therefore, increases from BF_3 to BBr_3.

16. Due to back bonding, B—F bond acquires some double bond character due to which its bond length is lesser than in the complex $F_3B \leftarrow NH_3$ where back bonding is not present.

17. Borazine has structure similar to that of benzene.

18. The hefty and crowded electron donor species involves symmetrical breaking of B_2H_6.

19. CO_2 is linear molecule while the other three are bent molecules.

20. The compound formed is $Ni(CO)_4$.

21. CO involves sp orbitals of carbon. It has lone pair of electrons on both C and O. The lone pair of C has more directional characteristics and is thus it binds to metals via carbon end.

22. Al_4C_3 is an ionic carbide. SiC is a covalent carbide, MoC and Cr_3C are metallic (or interstitial) carbides.

23. See Q. 22.

24. See Q. 22.

25. Be_2C and Al_4C_3 are methanides as they yield methane on reacting with water. CaC_2 is acetylides as it forms acetylene. Mg_2C_3 yields $CH_3—C \equiv CH$.

26. See Q. 25.

27. See. Q. 26.

28. Carborundum is SiC.

29. In CaC_2, the carbide ion is $(—C \equiv C—)^{2-}$.

30. Silicones are polymeric organosilicon compounds $\left[O—Si(R_2)—O\right]_n$.

31. Silicon rubber is chemically inert straight-chain polymers. Methyl silicones can be used as light duty lubricating oil.

32. Orthosilicates contain discrete $(SiO_4)^{4-}$ tetrahedra unit.

33. Pyrosilicates involve sharing of one oxygen atom between two SiO_4^{4-} tetrahedral.

34. The sharing of two oxygen atoms of one SiO_4^{4-} tetrahedron with two other tetrahedra forms chain and cyclic silicates.

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6. Complex positive ions and neutral molecules have no special ending but complex negative ions end in '-ate'.
7. If the complex contains two or more metal atoms, the bridging ligands are indicated by the prefix μ.
8. Sometimes a ligand may be attached through different atoms. For example, M—NO_2 is called a nitro and M—ONO is called nitrito; M—SCN is called thiocyanato and M—NCS isothiocyanto.
9. Water or solvent of crystallization are indicated after the name of the complex. Arabic numerals are used to indicate the number of such molecules.

A few examples of naming the complex compounds are given in the following.

$[Co(NH_3)_6]Cl_3$	Hexaamminecobalt(III) chloride	$Na_2[ZnCl_4]$	Sodium tetrachlorozincate(II)
$[CoCl(NH_3)_5]^{2+}$	Pentaamminechlorocobalt(III) ion	$K_3[Fe(CN)_5(NO)]$	Potassium pentacyanonitrosoylferrate(II)
$[CoSO_4(NH_3)_4]NO_3$	Tetramminesulphatocobalt(III) nitrate	$Fe(C_2H_5)_2$	Bis(cyclopentadienyel)iron(II)
$[Co(NO_2)_3(NH_3)_3]$	Triamminetrinitrocobalt(III)	$Cr(C_6H_6)_2$	Bis(benzene)chromium(0)

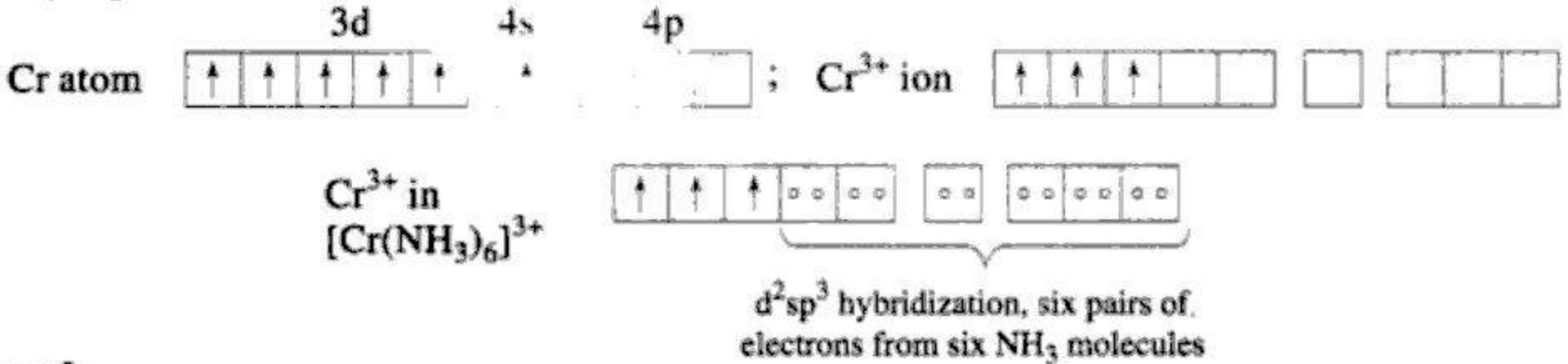
The simplest theory to explain bonding in complex compounds is the valence bond theory as developed by Linus Pauling. The salient features of the theory are as follows.

1. The central metal loses a requisite number of electrons to form the ion. The number of electrons lost is the valence of the resulting cation.
2. The cation makes available a number of orbitals equal to its coordination number, for the formation of covalent bonds with the ligands.
3. The cation orbitals hybridize to form a new set of equivalent hybrid orbitals with definite directional characteristics.
4. The nonbonding metal electrons occupy the inner d orbitals and do not participate in the hybridization.
5. Each ligand contains a lone pair of electrons. A covalent bond is formed by the overlap of a vacant hybrid metallic orbital and a filled orbital of the ligand.

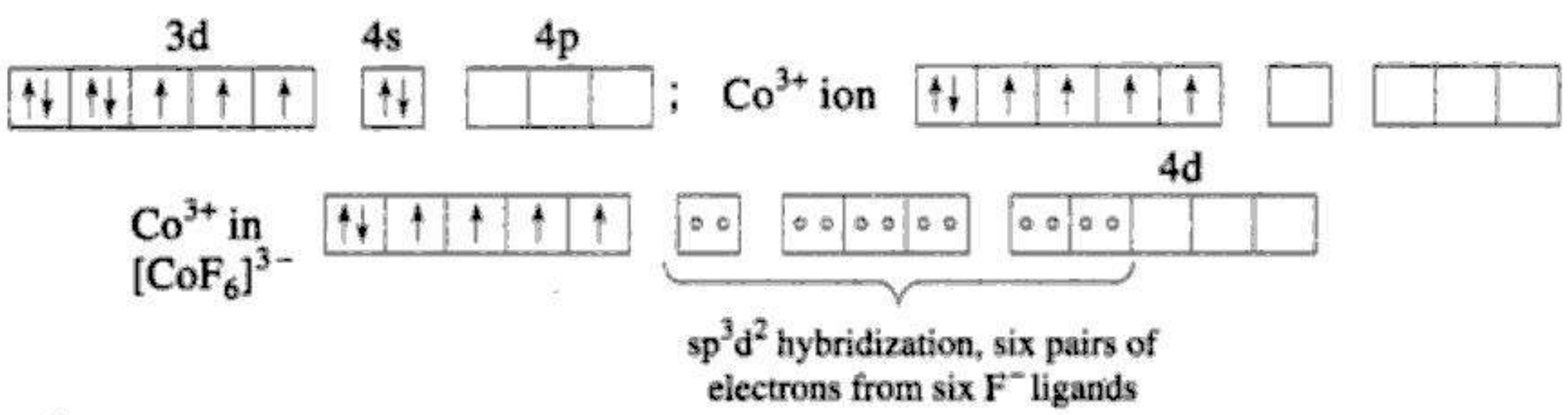
The above rules are illustrated with the following typical examples.

(i) $[Cr(NH_3)_6]^{3+}$

The outer electronic configuration of Cr is $(3d)^5(4s)^1$. Chromium in the above complex is in +3 oxidation state, hence, Cr(III) has the configuration of $(3d)^3$. There are six ligands, so six empty orbitals of chromium are required. These include two 3d orbitals, one 4s orbital and three 4p orbitals. These orbitals hybridize to give d^2sp^3 hybrid orbitals directed towards the corners of an octahedron. The final configuration of the complex will contain three unpaired electrons in three 3d orbitals of chromium. Hence, the complex will be paramagnetic. The above description is diagrametically represented as follows.



(ii) $[CoF_6]^{3-}$



The complex $[CoF_6]^{3-}$ is octahedral and is strongly paramagnetic.

Inner and Outer Orbital Octahedral Complexes

In the inner orbital octahedral complexes, d^2sp^3 hybridization in the central metal occurs while in the outer orbital complexes, sp^3d^2 hybridization is involved.

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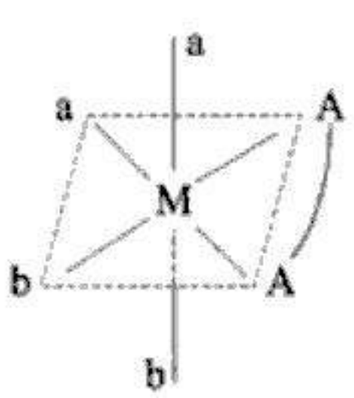
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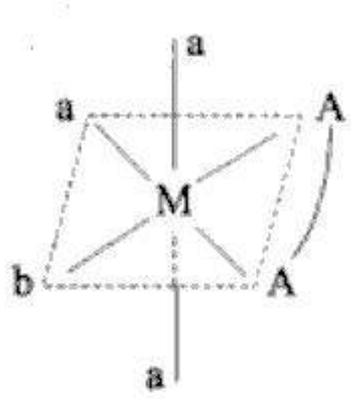
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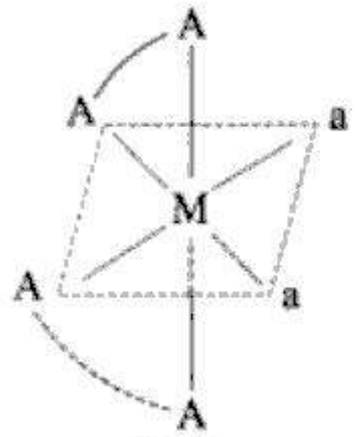
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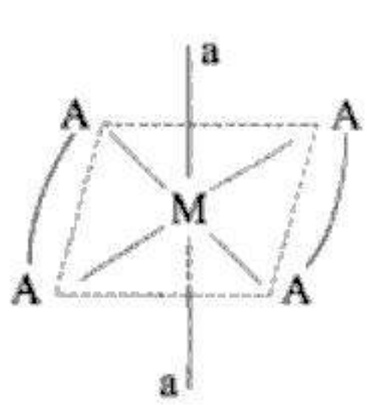
Cis-form
(and its enantiomer)



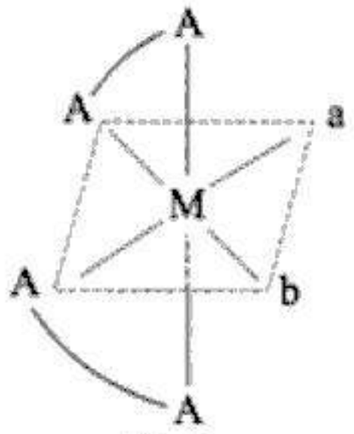
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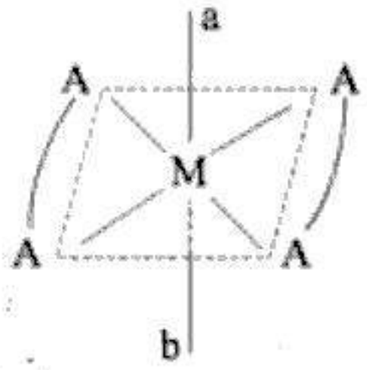
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(and its enantiomer)



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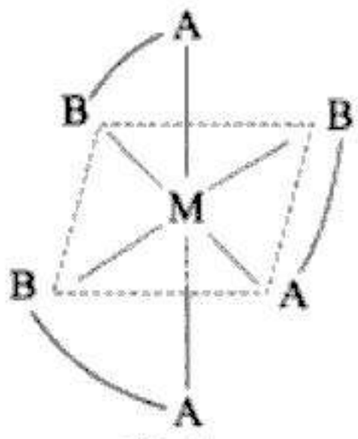


Cis-form
(and its enantiomer)

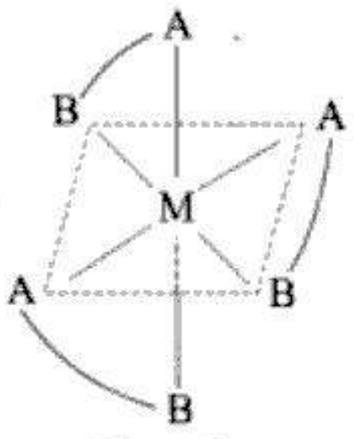


(*Trans*-form)

- The complex $[M(AB)_3]$, where AB is unsymmetrical bidentate ligand in which A and B are two different donor atoms, exists in *cis*– and *trans*–forms. Each of the two also has its enantiomer.



Cis-form
(and its enantiomer)



Trans-form
(and its enantiomer)

Stability of Coordination Compounds

The stability of a complex compound depends on the nature of the metal and that of the ligand. In general, the higher the oxidation state of the metal, the more stable the complex. The cynao complexes are far more stable than those formed by halide ions. The stability of halide complexes increases in the order $Cl^- < Br^- < I^-$.

The stability of complexes also decreases with increase in the ionic size of the central metallic ion having the same charge number. For example, the stability of complexes formed from the same ligands increases from Mn^{2+} to Cu^{2+} and then decreases at Zn^{2+}, that is, the order of stability is

Mn^{2+}	$<$	Fe^{2+}	$<$	Co^{2+}	$<$	Ni^{2+}	$<$	Cu^{2+}	$>$	Zn^{2+}
91 pm		83 pm		82 pm		78 pm		69 pm		74 pm

This sequence is known as *Iriving-William order of stability* of complexes of M^{2+} ions.
The increasing order of influence of ligands (known as spectrochemical series) on the electronic configuration of central metal atom or ion is

$$I^- < Br^- < Cl^- < F^- < OH^- < H_2O < NH_3 < NO^-_2 < CN^-$$

Thus, halogens are said to be weak ligands while NO^-_2, CN^- are said to be strong ligands.

3. Size of Atoms The covalent radii of the elements decrease from left to right across a row in the transition series, until near the end when the size increases slightly. The decrease is due to the increase in the effective nuclear charge. The exception at the end of the series is due to the more electronic repulsion amongst the electrons.

The elements of the first group in the d-block series show the expected increase in size Sc → Y → La. However, in the subsequent group there is an increase in the radius of 10 to 20 pm between the first and second member, but hardly any increase between the second and third elements. This is due to the lanthanide contraction which is interposed between

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61. The IUPAC name of $[Ni(NH_3)_4]$ $[NiCl_4]$ is
(a) Tetrachloronickel(II)–tetraamminenickel(II)
(b) Tetraamminenickel(II)–tetrachloronickel(II)
(c) Tetraamminenickel(II)–tetrachloronickelate(II)
(d) Tetrachloronickel(II)–tetraamminenickelate(0)
(2008)

Geomety of Complexes

62. Which of the following statements about the complex $[CoF_6]^{3-}$ which is paramagnetic in nature is correct?
(a) Cobalt involves d^2sp^3 hybridization
(b) Cobalt involves sp^3d^2 hybridization
(c) F is in zero oxidation state
(d) Co is in +2 oxidation state

63. Which of the following statements is not correct?
(a) The complexes $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ differ in the state of hybridization of nickel
(b) The complexes $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ differ in the magnetic properties
(c) The complexes $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ differ in the geometry
(d) The complexes $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ differ in primary valencies of nickel

64. Which of the following statements is **not** correct?
(a) The complexes $[Ni(CO)_4]$ and $[NiCl_4]^{2-}$differ in the state of hybridization
(b) The complexes $[Ni(CO)_4]$ and $[NiCl_4]^{2-}$ differ in the magnetic properties
(c) The complexes $[Ni(CO)_4]$ and $[NiCl_4]^{2-}$ differ in the primary valencies of nickel
(d) The complexes $[Ni(CO)_4]$ and $[NiCl_4]^{2-}$ have nickel in the different oxidation states

65. The geometry of $Ni(CO)_4$ and $Ni(PPh_3)_2Cl_2$ are
(a) both square planar
(b) tetrahedral and square planar, respectively
(c) both tetrahedral
(d) square planar and tetrahedral, respectively.
(1999)

66. A complex involving dsp^2 hybridization has
(a) a square planar geometry
(b) a tetrahedral geometry
(c) an octahedral geometry
(d) trigonal planar geometry

67. A complex involving d^2sp^3 hybridization is
(a) a square planar geometry
(b) a tetrahedral geometry
(c) an octahedral geometry
(d) trigonal planar geometry

68. Which of the following complex ions possesses d^2sp^3 hybridization?
(a) $[Ni(NH_3)_6]^{2+}$ (b) $[CoF_6]^{3-}$ (c) $[Co(NH_3)_6]^{3+}$ (d) $[FeF_6]^{3-}$

69. Which of the following complexes ions possesses dsp^2 hybridization?
(a) $[Ni(CN)_4]^{2-}$ (b) $[Ni(CO)_4]$ (c) $[NiCl_4]^{2-}$ (d) $[Ni(PF_3)_4]$

70. Which of the following complexes has magnetic moment of 2.83 Bohr magneton?
(a) $[Co(H_2O)_6]Cl_3$ (b) $[Ni(H_2O)_6]Cl_2$ (c) $[Cu(NH_3)_6]Cl_2$ (d) $[Mn(H_2O)_6]Cl_2$

71. Which of the following complex ions possesses sp^3d^2 hybridization?
(a) $[Cr(NH_3)_6]^{3+}$ (b) $[FeF_6]^{3-}$ (c) $[Co(NO_2)_6]^{3-}$ (d) $[TiF_6]^{3-}$

72. Which of the following is not a tetrahedral complex?
(a) $Ni(CO)_4$ (b) $K_2[Ni(CN)_4]$ (c) $K_3[Cu(CN)_4]$ (d) $[NiCl_4]^{2-}$

73. The species having tetrahedral shape is
(a) $Ni(CO)_4$ (b) $[Ni(CN)_4]^{2-}$ (c) $[PdCl_4]^{2-}$ (d) $[Pd(CN)_4]^{2-}$ (2004)

74. Both $[Ni(CO)_4]$ and $[Ni(CN)_4]^{2-}$ are diamagnetic. The hybridizations of nickel in these complexes, respectively, are
(a) sp^3, sp^3 (b) sp^3, dsp^2 (c) dsp^2, sp^3 (d) dsp^2,dsp^2 (2008)

Magnetism of Complexes

75. Among the following, the lowest degree of paramagnetism per mole of the compound at 298 K will be shown by
(a) $MnSO_4 \cdot 4H_2O$ (b) $FeSO_4 \cdot 6H_2O$ (c) $CuSO_4 \cdot 5H_2O$ (d) $NiSO_4 \cdot 6H_2O$ (1988)

76. Amongst $Ni(CO)_4$, $[Ni(CN)_4]^{2-}$ and $NiCl_4^{2-}$
(a) $Ni(CO)_4$ and $NiCl_4^{2-}$ are diamagnetic and $[Ni(CN)_4]^{2-}$ is paramagnetic
(b) $NiCl_4^{2-}$ and $[Ni(CN)_4]^{2-}$ are diamagnetic and $Ni(CO)_4$ is paramagnetic

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(c) V_2O_5 is used as a catalyst in the contact process to convert SO_2 into SO_3.
(d) In the Haber process for the manufacture of NH_3, Mn is used as a catalyst

12. Which of the following statements are correct?
(a) $[Cu(NCCH_3)_4]^+ BF_4^-$ is a coloured compound.
(b) $Ti(NO_3)_4$ is a colourless compound.
(c) $K_3[VF_6]$ is a coloured compound.
(d) CuSCN is a yellow coloured compound

13. Which of the following statements are correct?
(a) The formula of the deep red liquid formed on warming dichromate with KCl in concentrated sulphuric acid is CrO_2Cl_2.
(b) The atomic radii of the transition elements of 5d series are very nearly the same as the corresponding element of 4d series. This is due to lanthanide contraction.
(c) The outer electronic configuration of chromium (atomic number 24) is $(3d)^4(4s)^2$.
(d) The outer electronic configuration of copper (atomic number 29) is $(3d)^{10}(4s)^1$.

14. Which of the following statements are **not** correct?
(a) The atomic radius of Zn is smaller than that of Cu.
(b) Copper(I) salts are colourless as there are no electrons in 3d orbitals.
(c) The value of Bohr magneton is 9.273×10^{-24} J T^{-1}.
(d) The magnetic moment of transition element containing two unpaired electrons would be nearly $\sqrt{8}$ Bohr magneton.

15. Which of the following statements are correct?
(a) The colour of the solution of a complex absorbing violet radiation would be yellow.
(b) A solution of a complex compound absorbs orange radiation. Its colour would be blue.
(c) The expression of magnetic moment in terms of number of unpaired electrons is $n(n+2)$ bohr magneton.
(d) The Natta catalyst is $TiCl_4$.

16. Which of the following statements are correct?
(a) The reaction between $KMnO_4$ and oxalic acid is catalysed by Mn^{2+} which is known as autocatalyst.
(b) The colour of compounds of transition elements is due to d–d electronic excitation.
(c) The atomic volumes of the transition elements are larger as compared to the elements in the nearby Groups 1 and 2.
(d) The maximum paramagnetic character in the 3d series elements is possessed by manangese atom.

17. Which of the following statements are correct?
(a) Amongst the bivalent metal ions of 3d series transition elements, the maximum paramagnetism is shown by the ion Mn^{2+}.
(b) The IUPAC name of $K[Ag(CN)_2]$ is potassium dicyanoargentate(I)
(c) The IUPAC name of $K_4[Fe(CN)_6]$ is potassium hexacyanoferrous
(d) The IUPAC name of $Na_2[Fe(CN)_5(NO)]$ is sodium nitrosylpentacyanoferrate(II)

18. Which of the following statements are correct?
(a) The complex ion $[Fe(CN)_6]^{4-}$ is diamagnetic. The state of hybridization of iron is d^2sp^3.
(b) The complex ion $[Fe(H_2O)_6]^{2+}$ is paramagnetic. The state of hybridization of iron is sp^3d^2.
(c) The magnetic moment of the $[Fe(H_2O)_6]^{2+}$ would be $\sqrt{20}$ bohr magneton.
(d) The complex ion $[Ni(CO)_4]$ is paramagnetic. The state of hybridization of Ni is sp^3.

19. Which of the following statements are correct?
(a) The complex ion $[CuCl_4]^{2-}$ is paramagnetic. The state of hybridization of Cu is dsp^2.
(b) Of the ions Co^{2+} and Co^{3+}, the ion having lower magnetic moment is Co^{3+}.
(c) Of the two elements Fe and Zn, the element having higher melting point is Zn.
(d) Of the two elements Sc and Mn, the element having more oxidation state is Mn.

20. Which of the following statements are **not** correct?
(a) Of the two ions Cu^{2+} or Zn^{2+}, the diamagnetic ion is Cu^{2+}.
(b) Of the two ions Fe^{2+} or Fe^{3+}, the ion having higher magnetic moment is Fe^{2+}.
(c) The type of magnetism exhibited by $[Mn(H_2O)_6]^{2+}$ ion is paramagnetism.
(d) The magnetic moment of Fe^{2+} is identical to that of Co^{3+}.

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113. The electronic configurations of Ti^{3+}, Ti^{4+}, Fe^{2+} and Fe^{3+} are $(3d)^1$, $(3d)^0$, $(3d)^6$ and $(3d)^5$, respectively. The hydrated transition metal ion Ti^{4+} contains no unpaired electron, hence, colourless.

114. The electronic configurations of Ti^{4+}, Cu^+, Cr^{3+} and V^{3+} are $(3d)^0$, $(3d)^{10}$, $(3d)^3$ and $(3d)^2$, respectively. Hence, $K_3[VF_6]$ is a coloured compound as it contains two unpaired electrons.

115. CuF_2 is expected to be coloured as Cu^{2+} contains one unpaired electron.

116. The colour of a transition metal ion may be related to its number of unpaired d electrons. We have $V^{4+}$and Cu^{2+} ($n = 1$), blue; Fe^{2+} ($n = 4$), green and Mn^{2+} ($n = 5$), pink.
Hence, $CuCl_2$ and $VOCl_2$ are expected to have the same colour.

117. The electronic configuration of $_{71}Lu^{3+}$ is $[Xe](4f)^{14}$. Hence, it is expected to be colourless.

118. The electronic configuration of $_{57}La^{3+}$ is that of Xe. Hence, there is no f electrons. The species La^{3+} is expected to be colourless.

119. The electronic configuration of $_{62}Sm^{3+}$ is $(4f)^5$ and that of $_{66}Dy^{3+}$ is $(4f)^9$. The colour of f^n and f^{14-n} are often identical.

120. We have $4\Delta_O = 9\,\Delta t$

121. The colour of the complex compound is due to d – d electronic transition.

122. t_{2g} orbitals (d_{xy}, d_{xz}, d_{yz}) have lower energy by $(2/5)\Delta_O$

123. t_{2g} orbitals have higher energy by $(2/5)\Delta_t$.

124. e_g orbitals (d_{z2}, d_{x2-y2}) have higher energies by $(3/5)\Delta_O$.

125. e_g orbitals have lower energies by $(3/5)\Delta_t$.

126. The order is $SCN^- < F^- < CN^-$.

127. The spectrochemical series of ligands is

$$I^- < Br^- < Cl^- < F^- < OH^- < H_2O < NH_3 < NO_2^- < CN^-$$

128. F^- and Cl^- are weak ligands. These have small tendency of pairing metal electrons. Thus, these form high-spin complexes. The spacing of splitted orbitals of metal ions is small.
CN^- a strong ligand. It has high tendency of pairing metal electrons. Thus, it forms low-spin complexes. CO is a strong ligand and thus it forms low-spin complexes.

129. See Q.128

130. Only in CuF_2, copper exists as Cu^{2+} with one unpaired electron. Its colour is blue. In other choices, copper exists as Cu^+ with no unpaired electrons and thus are colourless.

131. F is a weak ligand and thus forms a high spin complex. NH_3 is a strong ligand and thus forms a low spin complex

132. $Pt(Cl_2)(CN)_2^{2-}$ will show *cis-trans* isomerism.

133. *cis*-$CrCl_2en_2^+$ exists as a pair of enantiomers.

134. The remaining three complexes have plane of symmetry. Hence, they are optically inactive.

135. There are only two isomers, *cis*-and *trans*-forms.

136. There are only two isomers, *cis*-and *trans*-forms.

137. There are three geometric isomers; one isomer of *cis*-dichloro and two isomers of *trans*-dichloro. All the three are optically active. Hence, there are six isomers.

138. There is exchange of ligand in the coordination sphere and the anion present outside the coordination sphere. Thus, the given complexes are ionization isomers.

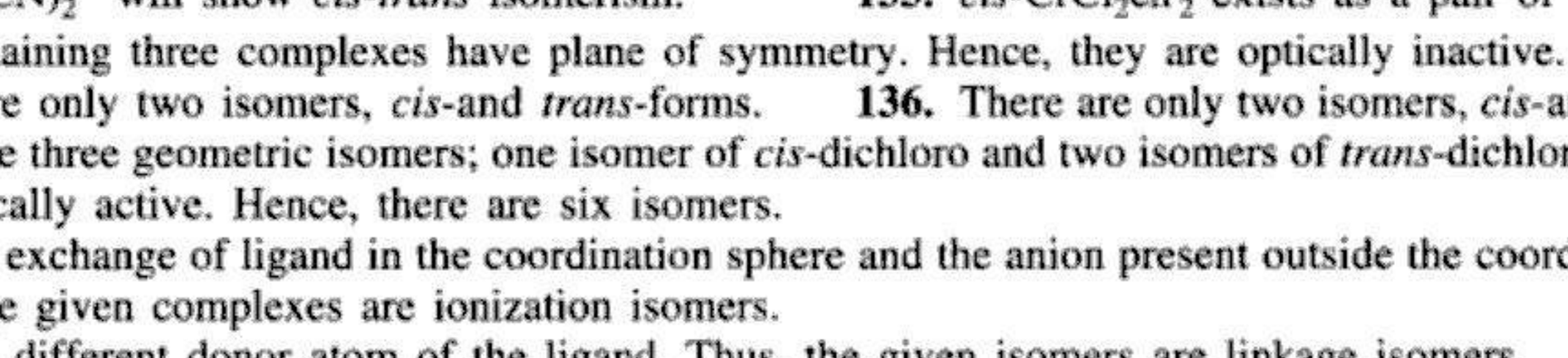
139. There is different donor atom of the ligand. Thus, the given isomers are linkage isomers.

140. There is a exchange of ligands between the complex cation and complex anion. Thus, the given isomers are coordination isomers;

141. $[PtCl_2(NH_3)_2]$ is square planar. The arrangement of two Cl or two NH_3 may be *cis* or trans. Thus, the given isomer forms geometrical isomers.

142. The compound $[CoCl_2(NH_3)_2(en)]$ has octahedral arrangement of ligands. It can form optical isomers.

143. The complex $[Ma_2b_2c_2]$ can exist in five geometrical isomers. These are (i) all ligands occupy *cis* positions, (ii) all ligands occupy *trans* positions and (iii) three isomers in which one of the ligands occupy *trans* position. These are depicted below.



Cis-isomer exists in two optical (mirror image) isomers. Only this compound is asymmetrical.

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Extraction of Iron Iron is extracted from its principal ore, haematite. After the preliminary washing, concentration and roasting, the ore is smelted in the presence of coke and limestone in a blast furnace (Fig. 17.1).

Roasted ore (8 parts) with desulphurized coke (4 parts) and limestone pieces (1 part) is fed into the blast furnace from the top. Preheated air is blown in through water-jacketed pipes called tuyeres fixed in the lower part of the furnace. There is a temperature gradient as we move from the bottom (temperature about 2000 K) to the top (temperature about 500 K) of the blast furnace. The blast furnace may be broadly divided into three main parts as described in the following.

1. Zone of fusion The lower portion where coke burns and produce carbon dioxide and a lot of heating is known as zone of fusion :

$$C + O_2 \rightarrow CO_2 \qquad \Delta H = -406 \text{ kJ mol}^{-1}$$

Here the temperature is about 1775 K. A little above this, where temperature is about 1475 K – 1575K, iron coming from above melts.

2. Zone of heat absorption The middle portion (temperature 1075 K – 1275 K), CO_2 rising up is reduced to CO with the absorption of heat:

$$CO_2 + C \rightarrow 2CO \qquad \Delta H = 163 \text{ kJ mol}^{-1}$$

In this portion, limestone coming from above is decomposed and the resultant lime (CaO), which acts as flux, combines with silica (present as impurity-gangue) to form calcium silicate (fusible slag):

$$CaCO_3 \rightarrow CaO + CO_2; \qquad CaO + SiO_2 \rightarrow CaSiO_3$$

3. Zone of reduction The upper portion (675 K – 975 K) where iron oxide is reduced to spongy iron by carbon monoxide rising up the furnace:

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$$

The reduction is believed to take place in stages:

$$3Fe_2O_3 + CO \rightarrow 2\,Fe_3O_4 + CO_2; \qquad Fe_3O_4 + CO \rightarrow 3FeO + CO_2$$

$$FeO + CO \rightarrow Fe + CO_2$$

At the bottom of the furnace the molten iron sinks down while above this floats the fusible slag which protects the molten iron from oxidation. These two can be removed from different holes (Fig. 17.1). Waste gases escaping at the top consists of about 30% CO, 10% CO_2 and the rest nitrogen.

Iron obtained from the blast furnace is known as pig iron.

Pig iron contains about 2–5% carbon as well as other impurities (usually Si, Mn, S and P). Pig iron is converted into cast iron by remelting in a vertical furnace heated by coke. Cast iron expands on solidification and is used for casting various articles. Wrought iron, which is the purest form of iron, can be obtained by heating cast iron in a reverberatory furnace lined with iron oxide. Wrought iron contains about 0.2% carbon.

Extraction of Tin Metallic tin is extracted from tin stone which contains about 10% of the metal as SnO_2, the rest being siliceous matter, tungstates of Fe, Cu and As. After crushing, the ore is concentrated by washing in a current of water (Gravity process to remove lighter gangue particles) and by magnetic separator to remove tungstates of Fe and Mn. The ore is roasted to remove S and As as their oxides. The ore then may be washed to remove sulphates of Cu and Fe. Finally, the ore is smelted in a reverberatory furnace or in a blast furnace at 1475–1575 K. The ore is mixed with one-fifth of its mass of powdered anthracite and little of lime or fluorspar which is used as flux. Tin oxide is reduced to tin:

$$SnO_2 + 2C \rightarrow Sn + 2CO$$

The molten metal collected from the bottom of furnace contains impurities such as Fe, Pb, S and As. The metal may be purified electrolytically (electrolyte; tin sulphate, sulphuric acid and hydrofluosilicic acid. anode; impure tin and cathode; pure tin).

Copper and Lead

Copper occurs in the native state as well as in the compound form. The natural ores of copper are

Copper pyrites, $CuFeS_2$ — Malachite, $Cu(OH)_2 \cdot CuCO_3$ — Azurite, $Cu(OH)_2 \cdot 2CuCO_3$ — Cuprite or ruby copper, Cu_2O — Copper glance, Cu_2S

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(c) Ore purification
(d) Production of nitric acid
(r) Ostwald process
(s) Cyanamide (1981)

4. Match the entries on the left with those given on the right

(a) Al
(b) Cu
(c) Mg
(d) Zn
(p) Calamine
(q) Cryolite
(r) Malachite
(s) Carnallite (1983)

5. Match the entries on the left with those given on the right

(a) Haber
(b) Graham
(c) Arrhenius
(d) Lewis
(p) Activation energy
(q) Diffusion of gases
(r) Oclet rule
(s) Ammonia synthesis (1983)

6. Match the entries on the left with those given on the right.

(a) Spinel
(b) Felspar
(c) Cerussite
(d) Malachite
(e) Kisserite
(p) $Mg\ Al_2O_4$
(q) $PbCO_3$
(r) $KAlSi_2O_3$
(s) $MgSO_4 \cdot H_2O$
(t) $Cu(OH)_2 \cdot CuCO_3$ (1985)

7. Match the entries on the left with those given on the right.

(a) Self reduction
(b) Carbon reduction
(c) Reduction by heating its trihalide
(s) Complex formation followed by precipitation
(p) Copper extraction
(q) Lead extraction
(r) Silver extraction
(s) Boron extraction (2006)

8. Match the conversions in Column I with the type(s) of reaction(s) given in Column II.

Column I	**Column II**
(a) $PbS \longrightarrow PbO$	(p) roasting
(b) $CaCO_3 \longrightarrow CaO$	(q) calcination
(c) $ZnS \longrightarrow Zn$	(r) carbon reduction
(d) $Cu_2S \longrightarrow Cu$	(s) self reduction (2008)

Straight Objective Type

1. (a)	**2.** (b)	**3.** (a)	**4.** (b)	**5.** (a)	**6.** (a)	**7.** (a)
8. (d)	**9.** (b)	**10.** (d)	**11.** (c)	**12.** (b)	**13.** (c)	**14.** (d)
15. (b)	**16.** (c)	**17.** (b)	**18.** (b)	**19.** (b)	**20.** (c)	**21.** (c)
22. (b)	**23.** (b)	**24.** (c)	**25.** (d)	**26.** (c)	**27.** (a)	**28.** (c)
29. (d)	**30.** (b)	**31.** (a)	**32.** (a)	**33.** (d)	**34.** (c)	**35.** (a)
36. (d)	**37.** (c)	**38.** (a)	**39.** (c)	**40.** (c)	**41.** (a)	**42.** (d)
43. (a)	**44.** (d)	**45.** (a)	**46.** (b)			

ANSWERS

1. (a), (b)	**2.** (b), (d)	**3.** (c), (d)
4. (a), (c), (d)	**5.** (a), (c)	**6.** (a), (b), (c), (d)
7. (a), (c)	**8.** (a), (c), (d)	**9.** (a), (b)
10. (a), (b), (c), (d)	**11.** (b), (d)	**12.** (a), (b), (c), (d)
13. (c), (d)	**14.** (a), (b)	**15.** (b), (d)
16. (b), (c)	**17.** (a), (c)	**18.** (a), (b), (c)

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Borate Heating a borate salt in a test tube with concentrated H_2SO_4 and C_2H_5OH produces vapours of ethylborate which burns with green flame.

$$2BO_3^{3-} + 3H_2SO_4 \rightarrow 3SO_4^{2-} + 2H_3BO_3; \qquad H_3BO_3 + 3C_2H_5OH \rightarrow \underset{\text{(Ethyl borate)}}{B(OC_2H_5)_3} + 3H_2O$$

Analysis of Cations

In a solution containing more than one cation, the scheme shown in Fig. 18.1 for the identification of cations may be adopted.

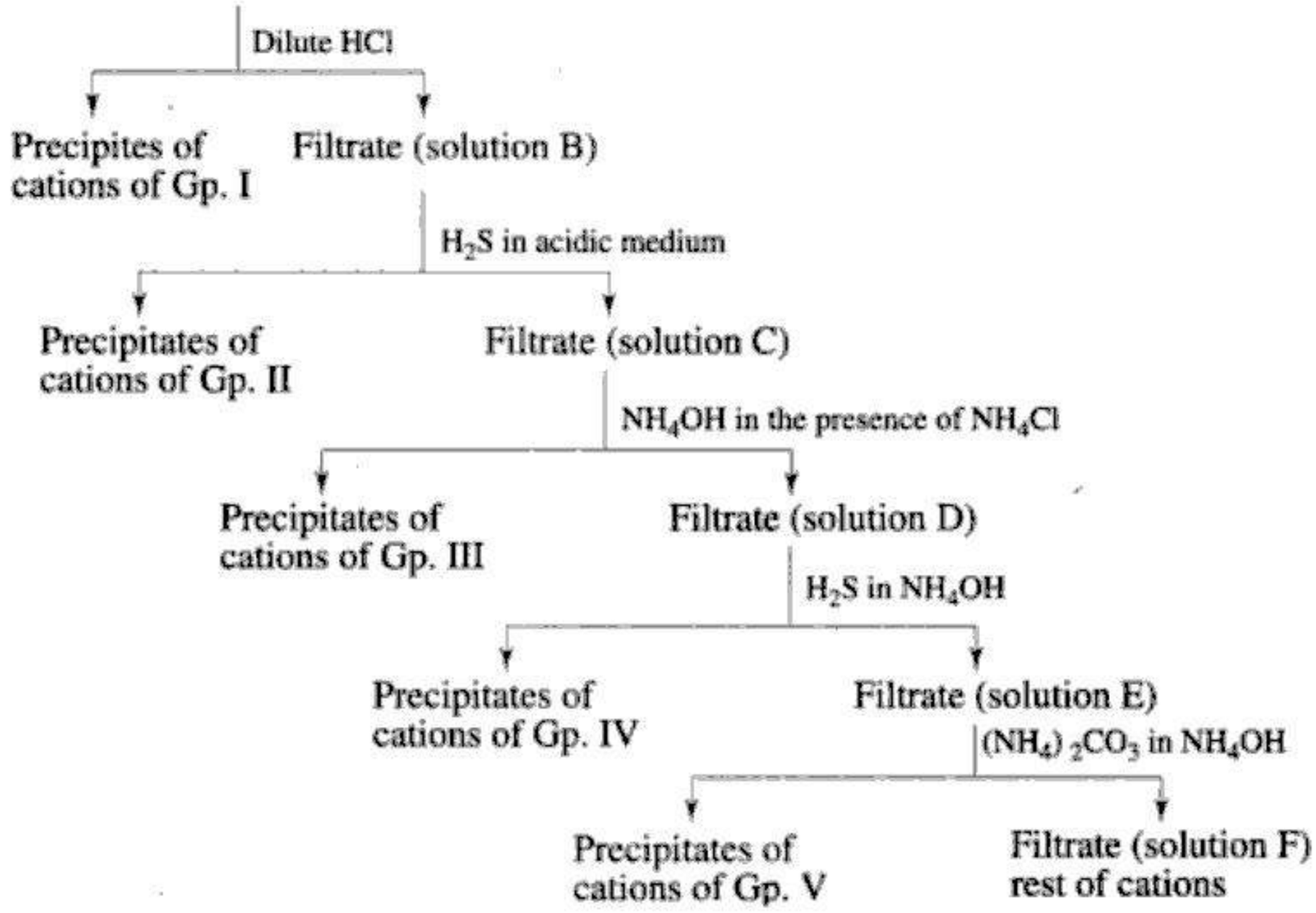


Fig. 18.1 Scheme for the analysis of cations

Details of Scheme

Cations of Group I These include the precipitates of AgCl, Hg_2Cl_2 and $PbCl_2$. From these $PbCl_2$ may be separated by boiling the precipitates with water and filtering the hot solution. In the fitrate, $PbCl_2$ may be tested by adding potassium chromate solution or potassium iodide:

$$PbCl_2(aq) + K_2CrO_4 \rightarrow \underset{\text{(yellow ppt.)}}{PbCrO_4} + 2KCl; \qquad PbCl_2(aq) + KI \rightarrow \underset{\text{(yellow ppt.)}}{PbI_2} + 2KCl$$

In the remaining precipitates, AgCl may be separated by additing ammonium hydroxide solution.

$$AgCl + 2NH_4OH \rightarrow \underset{\text{(soluble)}}{[Ag(NH_3)_2]Cl} + 2H_2O$$

Mercurous chloride forms black precipitates with NH_4OH.

$$Hg_2Cl_2 + 2NH_4OH \rightarrow \underset{\text{(black ppt.)}}{2[Hg(NH_3)]Cl} + 2H_2O$$

In solution, silver ions if present can be tested by adding KI solution:

$$[Ag(NH_3)_2]Cl + KI \rightarrow \underset{\text{(yellow ppt.)}}{AgI} + 2NH_3 + KCl$$

The black precipitates of $[Hg(NH_3)]Cl$ is soluble in aqua regia. To this solution, if $SnCl_2$ is added a white precipitate turning to black is obtained.

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17. Which of the following oxidizing agents are used to convert Mn^{2+} to MnO_4^-?
(a) Conc. HNO_3 (b) PbO_2 + Conc. HNO_3
(c) Sodium bismuthate ($NaBiO_3$) (d) BaO_2 + dil. HNO_3

18. Which of the following ions form white precipitate with saturated sodium hydrogen tartrate solution?
(a) NH_4^+ (b) K^+ (c) Na^+ (d) Mg^{2+}

19. Which of the following ions form white precipitate with silver nitrate solution?
(a) Cl^- (b) CN^- (c) OCN^- (d) SCN^-

20. Which of the following ions must be removed before proceeding to Group III of salt analysis?
(a) NO_3^- (b) F^- (c) Borate (d) SO_3^{2-}

21. Which of the following ions give yellow precipitate with hexachloroplatinic acid?
(a) Na^+ (b) K^+ (c) Mg^{2+} (d) NH_4^+

22. Which of the following ions form a precipitate with $K_4[Fe(CN)_6]$?
(a) Ca^{2+} (b) Zn^{2+} (c) Fe^{3+} (d) Fe^{2+}

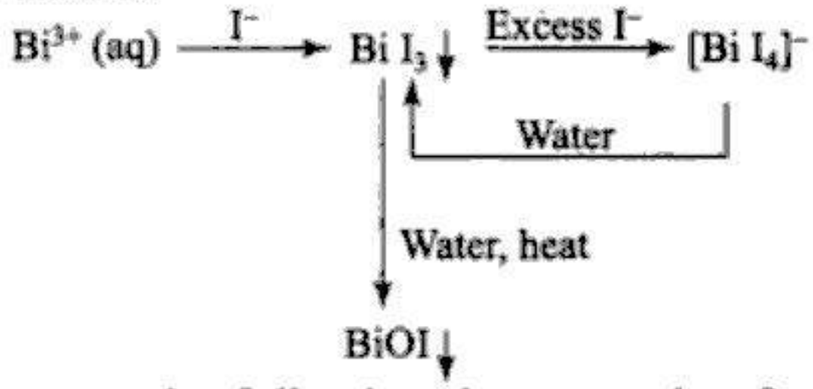
23. Which of the following ions form a precipitate with Na_2HPO_4 in ammoniacal medium?
(a) Fe^{2+} (b) Mn^{2+} (c) Al^{3+} (d) Mg^{2+}

24. Which of the following statements regarding $Ni^{2+}(aq)$ are correct?
(a) This gives green precipitate of $Ni(OH)_2$ with NaOH solution which is insoluble in excess of NaOH.
(b) This gives green precipitate of $Ni(OH)_2$ with NH_4OH which is solution in excess of ammonium hydroxide.
(c) This does not give green precipitate with NaOH in the presence of tartrate or citrate ions.
(d) This gives green precipitate $Ni(CN)_2$ with potassium cyanide solution which is soluble in excess of KCN giving complex $[Ni(CN)_4]^{2-}$.

25. Which of the following statements is correct for cobalt(II) nitrate solution?
(a) In excess of NaOH solution, pink precipitates of $Co(OH)_2$ appears
(b) With the excess of NH_4OH, blue coloured basic salt, $Co(OH)NO_3$, appears.
(c) With KCN, reddish-brown precipitates appear which is soluble in excess of KCN.
(d) With NH_4SCN, a red precipitates of $[Co(SCN)_4]^{2-}$.

Linked Comprehension Type

1. Given are the following observations:



Based on these observations, answer the following three questions?
(i) The colour of BiI_3 precipitates is
(a) orange (b) red (c) white (d) black
(ii) The colour the solution containing $[BiI_4]^-$ is
(a) orange (b) red (c) white (d) black
(iii) The colour of BiO precipitates is
(a) orange (b) red (c) white (d) black

2. Given are the following observations.

$$Cu^{2+}(aq) \xrightarrow{CN^-} A\downarrow \xrightarrow{\text{on standing}} B\downarrow \xrightarrow[CN^-]{\text{excuss of}} C$$

Based on these observations, answer the following three questions.

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3. Match the entries on the left with most appropriate choice(s) given on the right.

Column I	**Column II**
(a) $Bi_2O_3 \rightarrow BiO^+$	(p) Hydrolysis
(b) $AlO_2^- \rightarrow Al(OH)_3$	(q) Dilution with water
(c) $SiO_4^{4-} \rightarrow Si_2O_7^{2-}$	(r) Acidification
(d) $B4O_7^{2-} \rightarrow B(OH)_3$	(s) Heating (2006)

4. Match the reactions given in Column I with nature of the reactions/type of the products given in Column II.

Column I	**Column II**
(a) $O_2^- \rightarrow O_2 + O_2^{2-}$	(p) redox reaction
(b) $CrO_4^{2-} + H^+ \rightarrow \cdots$	(q) one of the products has trigonal planar structure
(c) $MnO_4^- + NO_2^- + H^+ \rightarrow \cdots$ metal ion	(r) dimeric bridged tetrahedral
(d) $NO_3^- + H_2SO_4 + Fe^{2+} \rightarrow \cdots$	(s) disproportionation (2008)

5. Column II lists some of the gases evolved when the compounds mentioned in column I are heated. Match each entry of column I with those given in Column II.

Column I	**Column II**
(a) $Pb(NO_3)_2$	(p) N_2
(b) $Mg(NO_3)_2$	(q) O_2
(c) $(COO)_2Fe$	(r) CO_2
(d) $FeSO_4$	(s) NO_2
	(t) SO_2
	(u) CO

ANSWERS

Straight Objective Type

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

Multiple Correct Choice Type

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

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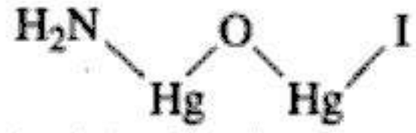


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Solution From the given information, it appears that A is HgI_2 and B is KI. The given reactions are as follows.

(a) $HgI_2 + H_2S \rightarrow \underset{\text{(black)}}{\underset{\text{(C)}}{HgS}} + 2HI$

(b) $HgS \xrightarrow{\text{aqua regia}} HgCl_2$
$HgCl_2 + SnCl_2 \rightarrow Hg_2Cl_2 + SnCl_4$
$HgCl_2 + SnCl_2 \rightarrow 2Hg + SnCl_4$

(c) $2HgI_4^{2-} + NH_3 + 3OH^- \rightarrow$  $+ 7I^- + 2H_2$

(iodide of Millon's base)

(d) I_2 is absorbed in CCl_4 giving violet colour. (e) $I^- + Ag^+ \rightarrow AgI\downarrow$ insoluble in NH_4OH.

28. There are two ores A_1 and A_2 of a metal M. (i) When the ore A_1 is calcined a black solid S is obtained alongwith the evolution of CO_2 and H_2O. (ii) The ore A_1 on treatment with HCl and KI gives a precipitate P and iodine is liberated. (iii) The ore A_2 on roasting gives a gas G and metal M is free. (iv) When the gas G is passed through $K_2Cr_2O_7$ it turns green. Identify M, A_1, A_2, S, P and G. (2004)

Solution Metal M is copper and its two ores are

A_1 : Malachite, $CuCO_3 \cdot Cu(OH)_2$ A_2 : Copper glance, Cu_2S

The given reactions are as follows.

(i) $\underset{(A_1)}{CuCO_3 \cdot Cu(OH)_2} \xrightarrow{\text{calcination}} \underset{\text{black}}{\underset{(S)}{2CuO}} + CO_2 + H_2O$

(ii) $CuCO_3 \cdot Cu(OH)_2 + 4HCl \rightarrow 2CuCl_2 + CO_2 + 3H_2O$; $2CuCl_2 + 4KI \rightarrow \underset{(P)}{Cu_2I_2} + 4KCl + I_2$

(iii) $\underset{(A_2)}{2Cu_2S} + 3O_2 \xrightarrow{\text{roasting}} \underset{(G)}{2Cu_2O} + 2SO_2$; $Cu_2S + 2Cu_2O \rightarrow \underset{(M)}{6Cu} + SO_2$

(iv) $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$
$SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^- \times 3$

$Cr_2O_7^{2-} + 2H^+ + 3SO_2 \rightarrow \underset{\text{(green)}}{2Cr^{3+}} + 3SO_4^{2-} + H_2O$

Unsolved Problems

1. One gram of an alloy of magnesium and aluminium reacts with excess of hydrochloric acid. The hydrogen collected was found to occupy a volume of 1.2 L at 699 mmHg and 273 K. Calculate the mass composition of the alloy.
2. When a mixture of sodium chloride and sodium bromide is repeatedly digested with sulphuric acid, sodium sulphate is formed. If the mass of sodium sulphate obtained is equal to the mass of the mixture, calculate the massper cents of NaBr and NaCl in the mixture.
3. 25.4 g of iodine and 14.2 g of chlorine are made to react completely to form a mixture of ICl and ICl_3. Calculate the masses of the products formed.
4. 1.0 g of a mixture of equal amounts (i.e. number of moles) of carbonates of two alkali metals required 44.4 mL of 0.5 M hydrochloric acid for complete reaction. The atomic mass of one of the metals is 7.0 amu. Find the atomic mass of the second metal. Calculate the masses of sulphates formed on quantitative conversion of 1.0 g of the mixture into sulphates.
5. 1.0 g of a moist sample of a mixture of potassium chlorate and potassium chloride was dissolved in water and made upto 250 mL. 25 mL of this solution was treated with SO_2 to reduce the chlorate and the excess of SO_2 was removed by boiling. The total chloride was precipitated as silver chloride whose mass was found to be 0.1435 g. In another experiment, 25 mL of the original solution was heated with 30 mL of 0.2 M solution of ferrous sulphate and the unreacted ferrous sulphate required 37.5 mL of 0.08 N solution of an oxidizing agent for complete oxidation. Calculate the mass per cents of chlorate and chloride in the given mixture. The reaction between ClO_3^- and Fe^{2+} is $ClO_3^- + 6Fe^{2+} + 6H^+ \rightarrow Cl^- + 6Fe^{3+} + 3H_2O$

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53. Sodium thiosulphate added to AgBr.
54. Sodium thiosulphate added to silver nitrate.
55. To cupric chloride, sodium thiosulphate is added slowly till it is in excess.
56. Sodium thiosulphate is added slowly to auric chloride solution.
57. Carbon dioxide is passed through a suspension of calcium sulphate in aqueous ammonia.
58. Magnesium is treated with dilute nitric acid.
59. Sulphur dioxide is passed through colemanite ($Ca_2B_6O_{11}$) in boiling water.
60. Passing $SiCl_4$ vapour over molten aluminium.
61. Heating a fluoride salt with sand in the presence of concentrated sulphuric acid followed by exposure of th vapours to water.
62. Stannous chloride is added to mercuric chloride.
63. Iodine is treated with cold caustic soda solution.
64. Iodine is treated with hot caustic soda solution.
65. Chlorine is passed through hot milk of lime.
66. Iodine treated with concentrated nitric acid.
67. Iodine is treated with hot concentrated $KClO_3$ solution.
68. Chromium chloride treated with an alkaline solution of hypochlorous acid followed by the addition of aceti acid and lead acetate.
69. Ferrous sulphate is added to potassium ferricyanide.
70. Ferric sulphate is added to potassium ferrocyanide.
71. Red lead is treated with concentrated sulphuric acid.
72. Red lead is treated with concentrated hydrochloric acid.
73. Ammonia is treated with excess of chlorine.
74. Nitric oxide is passed through cold solution of ferrous sulphate followed by heating.
75. Nitric oxide is passed through acidified potassium permanganate.
76. Dilute nitric acid is added to zinc.
77. Heating of hydrated aluminium chloride.
78. Heating of lead nitrate.
79. Heating of hydrated ferrous sulphate.
80. Heating of potassium permanganate.
81. Chloride is passed through sodium thiosulphate solution.
82. Carbon monoxide is passed through sodium hydroxide solution.
83. Fluorine is passed through dilute sodium hydroxide solution.
84. Fluorine is passed through concentrated sodium hydroxide solution.
85. Bromine is added to sodium thiosulphate solution.
86. Ozone is passed through potassium ferrocyanide solution.
87. Magnesium is burnt in the atmosphere of ammonia.
88. Carbon dioxide is passed over heated potassium superoxide.
89. Sodium nitrite is added to acidified potassium permanganate solution.
90. A mixture of nitric oxide and oxygen is passed through sodium carbonate solution.
91. Phosphorous acid is added to silver nitrate solution.
92. Concentrated nitric acid is mixed with concentrated sulphuric acid.
93. Silver oxide is added to hydrogen peroxide solution.
94. Copper is treated with concentrated hydrochloric acid.
95. Stannous sulphite is treated with sodium hydroxide solution.
96. Aluminium oxide is heated with amorphous carbon.
97. Potassium iodide is added to $Na_3[Ag(S_2O_3)_2]$ solution.
98. Heating of $ZnCl_2 \cdot 2H_2O$.
99. Mercuric chloride is treated with phosphorous acid.
100. Ozone is passed through potassium ferrocyanide solution.

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35. This produces chromyl chloride.

$$K_2Cr_2O_7 + 2H_2SO_4 \rightarrow 2KHSO_4 + 2CrO_3 + H_2O$$
$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl] \times 4$$
$$2CrO_3 + 4HCl \rightarrow 2CrO_2Cl_2 + 2H_2O$$
$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \rightarrow 2CrO_2Cl_2 + 2KHSO_4 + 3H_2O + 4NaHSO_4$$

36. Nitrate is reduced to ammonia. $NaNO_3 + 4Zn + 7NaOH \rightarrow 4Na_2ZnO_2 + NH_3 + 2H_2O$

37. Same as reaction (2).

38. With cold dilute acid, iron produces ferrous nitrate and ammonium nitrate.

$$4Fe + 10HNO_3 \rightarrow 4Fe(NO_3)_2 + NH_4NO_3 + 3H_2O$$

39. MnO_4^- oxidizes Mn^{2+} to MnO_2 and is itself reduced to MnO_2.

$$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O] \times 2$$
$$Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e^-] \times 3$$
$$2MnO_4^- + 3Mn^{2+} + 2H_2O \rightarrow 5MnO_2 + 4H^+$$

or $2KMnO_4 + 3MnSO_4 + 2H_2O \rightarrow 5MnO_2 + K_2SO_4 + 2H_2SO_4$

40. $NO + NO_2 + H_2O \rightleftharpoons 2HNO_2$

$$Na_2CO_3 + H_2O \rightleftharpoons NaHCO_3 + NaOH$$
$$NaOH + HNO_2 \rightarrow NaNO_2 + H_2O$$
$$NaHCO_3 + HNO_2 \rightarrow NaNO_2 + CO_2 + H_2O$$
$$Na_2CO_3 + NO + NO_2 \rightarrow 2NaNO_2 + CO_2$$

41. $MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-] \times 2$

$$2NH_3 + 6OH^- \rightarrow N_2 + 6H_2O + 6e^-$$
$$2MnO_4^- + 2NH_3 \rightarrow 2MnO_2 + 2OH^- + 2H_2O + N_2$$

or $2KMnO_4 + 2NH_3 \rightarrow 2MnO_2 + 2KOH + 2H_2O + N_2$

42. $NO_3^- + 2H^+ + e^- \rightarrow NO_2 + H_2O] \times 20$

$$P_4 + 10H_2O \rightarrow 2P_2O_5 + 20H^+ + 20e^-$$
$$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4] \times 2$$
$$20NO_3^- + 20H^+ + P_4 \rightarrow 20NO_2 + 4H_2O + 4H_3PO_4$$

43. $MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-] \times 2$

$$C_2H_4 + 2OH^- \rightarrow HOCH_2CH_2OH + 2e^-] \times 3$$
$$2MnO_4^- + 3C_2H_4 + 4H_2O \rightarrow 2MnO_2 + 2OH^- + 3HOCH_2CH_2OH$$

44. $2NaHSO_3 \rightarrow Na_2SO_3 + H_2O + SO_2$

$$SO_2 + 2H_2S \rightarrow 3S + 2H_2O$$
$$2NaHSO_3 + 2H_2S \rightarrow Na_2SO_3 + 3H_2O + 3S$$

45. $CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$

46. $Cu \rightarrow Cu^{2+} + 2e^-] \times 7$

$$HNO_3 + H^+ + 2e^- \rightarrow NO_2 + H_2O] \times 2$$
$$HNO_3 + 3H^+ + 3e^- \rightarrow 2H_2O + NO] \times 4$$
$$7Cu + 6HNO_3 + 14H^+ \rightarrow 7Cu^{2+} + 2NO_2 + 4NO + 10H_2O$$

or $7Cu + 20HNO_3 \rightarrow 7Cu(NO_3)_2 + 2NO_2 + 4NO + 10\ H_2O$

47. On adding Na_2CO_3 to copper sulphate solution, the solution becomes alkaline and thus $Cu(OH)_2$ is precipitated. The net reaction is

$$CuSO_4 + Na_2CO_3 + H_2O \rightarrow Cu(OH)_2 + Na_2SO_4 + CO_2$$

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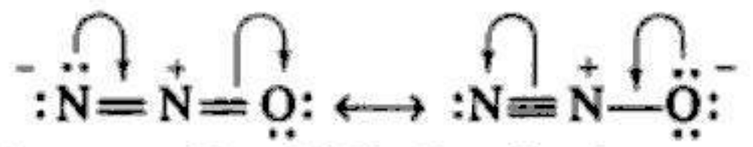


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Molecule	CH_4		C_2H_4		C_2H_2
Order of electronegativity of hybrid orbital of C	sp^3	<	sp^2	<	sp
Bond length	110 pm		108 pm		106 pm

RESONANCE

For some molecules, more than one Lewis structures having fixed arrangement of atomic nuclei and differing in the arrangement of electrons can be written. Such a molecule is said to possess different *resonating* or *canonical structures*. None of the individual structures explains adequately the characteristics of the molecule. The resonance theory postulates that the actual state of the molecule is hybrid of all canonical structures. For example, for dinitrogen oxide, we can write



The observed bond length of 112 pm between N and N is found to be greater than the calculated triple bond length (110 pm) and smaller than double bond length (120 pm). The same is the situation between N and O atoms. The observed value is 119 pm, calculated double and single bond lengths are 115 pm and 147 pm, respectively. These observations indicate that the resonance hybrid has some double-bond character between N and O and some triple-bond character between N and N.

The energy of the hybrid is always less than the calculated energy of any canonical structure. The *resonance energy* is defined as the difference between the enthalpy of formation of the molecule and that of resonating structure having the lowest energy (obtained theoretically). The resonance energy depends on the two main factors listed below.

1. Number of resonating structures
2. Energies of resonating structures

In organic molecules, benzene constitutes an excellent example of resonance. The canonical structures of benzene are shown in Fig. 19.6.

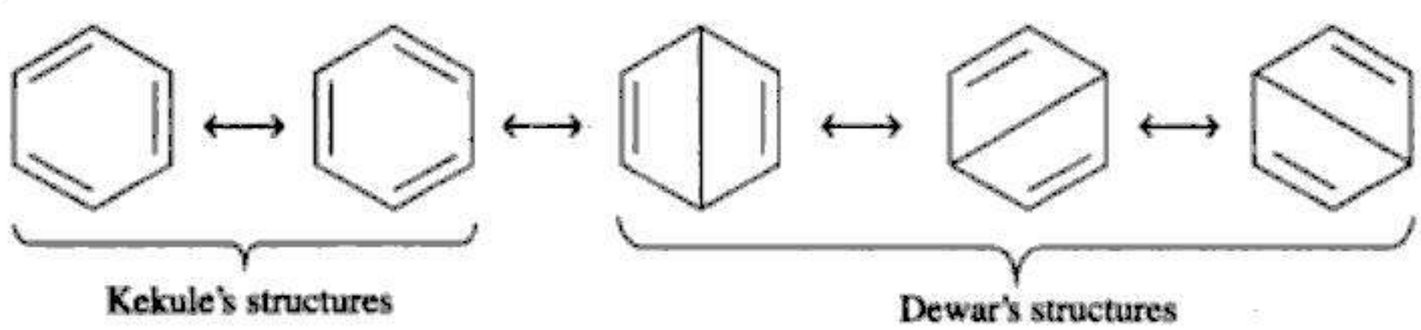


Fig. 19.6

The actual molecule of benzene involves 39% contribution from each of Kekule's structure and 7.3% from each of Dewar's structures. All the C and C bond lengths are identical and have bond length equal to 139 pm. This value is greater than C=C bond length (134 pm) and smaller than C—C bond length (154 pm).

Hyperconjugation π-Orbitals can overlap with other π-Orbitals to produce conjugation. π-Orbitals, however, can also overlap to certain extent with the adjacent σ-orbitals to form extended orbitals. This phenomenon, known as hyperconjugation, is displayed by methyl group attached to an unsaturated carbon atom; as shown in Fig. 19.7.

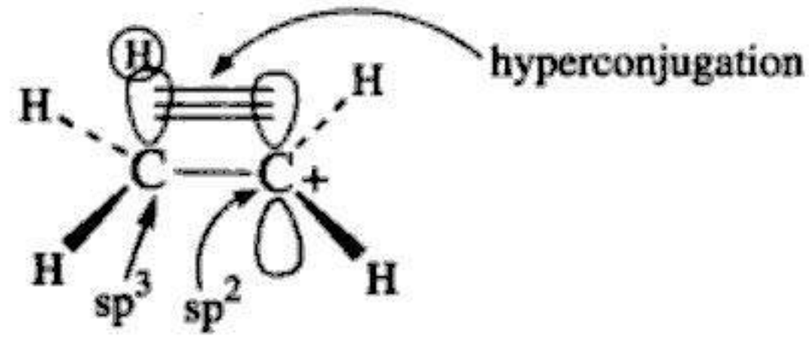


Fig. 19.7

The effect of hyperconjugation is to increase ionic character of the C—H bond, the electrons of which become partially delocalised through conjugation. Hyperconjugation is also known as no bond resonance.

HOMOLOGOUS SERIES

In organic chemistry, a series of compounds having same functional group but differing in CH_2 group can be written. Such a series is known as homologous series and the members of such a series is known as homologues. The physical properties of the members of a homologous series exhibit gradual variation with increase in the molecular mass.

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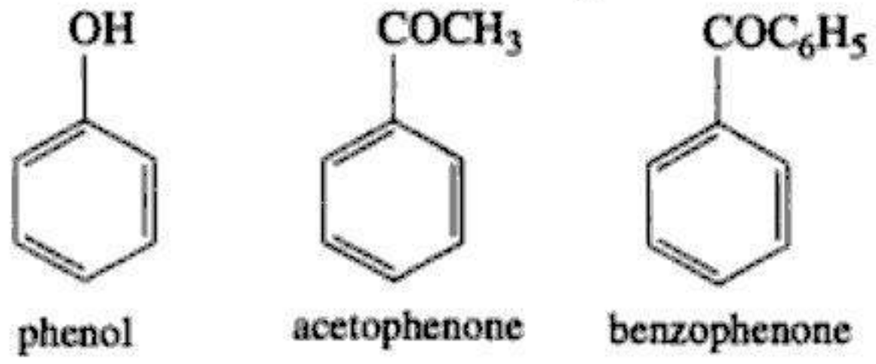


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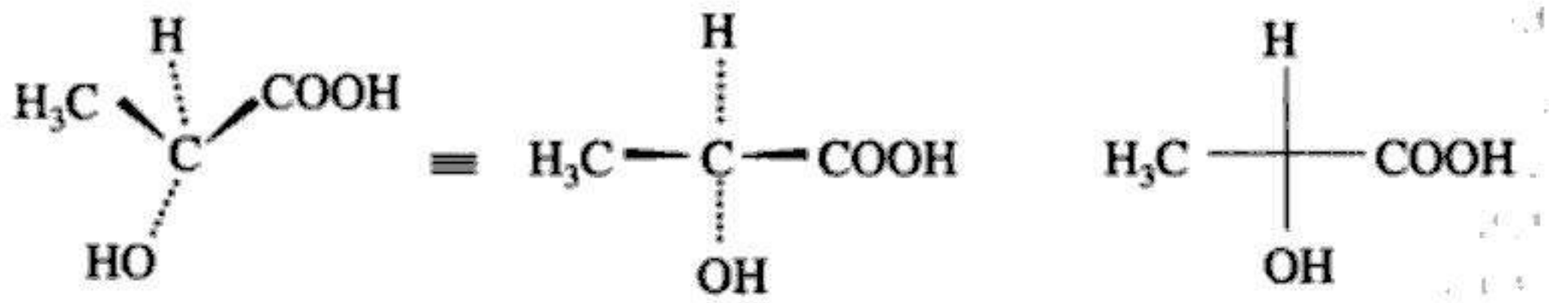
(c) *Some derivatives are named as per their common names.* For example,



phenol acetophenone benzophenone

Supplementary Material

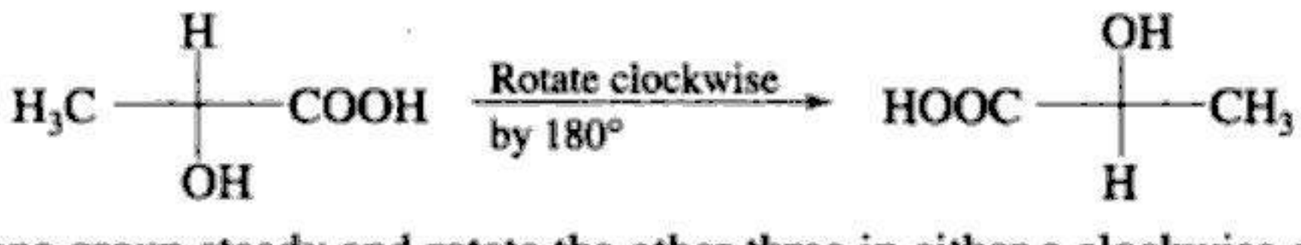
Fischer Projections Fischer projection is a standard method to depict a three-dimensional arrangement of atoms on a flat page. In this method, a tetrahedral carbon is represented by two crossed lines. The horizontal lines represent bonds coming out of the page, and the vertical lines represent bonds going into the page. For example,



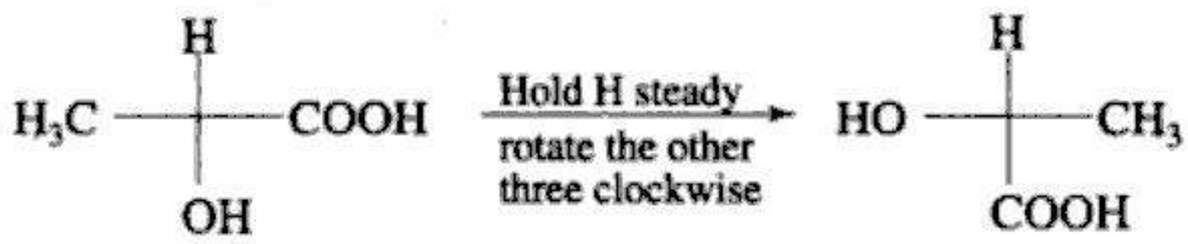
(+)-Lactic acid

Many different Fischer projections can be drawn for a given molecule. Quite often, it is necessary to compare two different projections to see if they represent the same or different enantiomers. To test this, a Fischer projection may be moved in the following two ways without changing the meaning of the projection.

1. Rotating the Fischer projection by 180° (and not by 90° or 270°).



2. Hold any one group steady and rotate the other three in either a clockwise or a counterclockwise direction.



Sawhorse Projections In a sawhorse projection, C—C bond in the two adjacent carbon atoms is displayed by a larger diagonal line which is taken to be the plane of the paper and the substituents attached to these carbon atoms are projected above and below the plane by small lines. For example, the sawhorse projection of $\overset{1}{C}H_3\overset{2}{C}H_2\overset{3}{C}H_2\overset{4}{C}H_3$ is shown in Fig. 19.8a

Since there is a free rotation about $\overset{2}{C}-\overset{3}{C}$ bond, one can draw other conformations of the molecule by rotating the substituents of one of the carbon atoms clockwise or anticlockwise. The conformation shown in Fig. 19.8a is the staggered form of butane, its eclipsed form will be represented as shown in Fig. 19.8b.

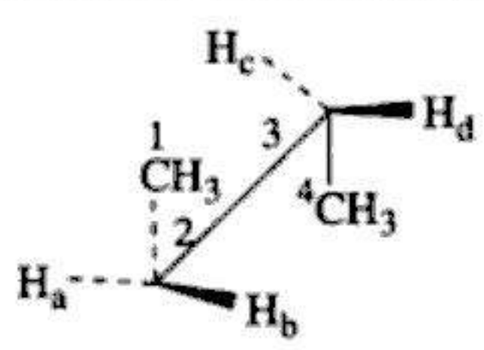


Fig. 19.8a

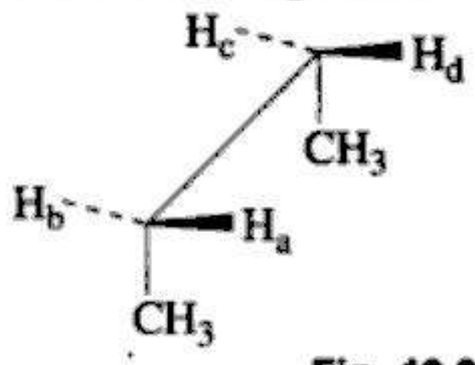


Fig. 19.8b

Newman Projections In a Newman projection, the two C atoms in the molecule CH_3—CH_3 (or a molecule in which H atom(s) is(are) replaced by any other substituent(s)) are represented by the superimposed circles (in fact, only one of the circles will be visible). The centre of the circle represent the front carbon atom and the circumference of the circle represents the back carbon atom. The substituents attached to these carbon atoms are projected into a vertical plane,

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(a) I and II are identical (b) I and II are diastereomers
(c) I and III are enantiomers (d) I and II are enantiomers (1997)

57. How many optically active stereoisomers are possible for butane-2, 3-diol?
(a) 1 (b) 2 (c) 3 (d) 4 (1997)

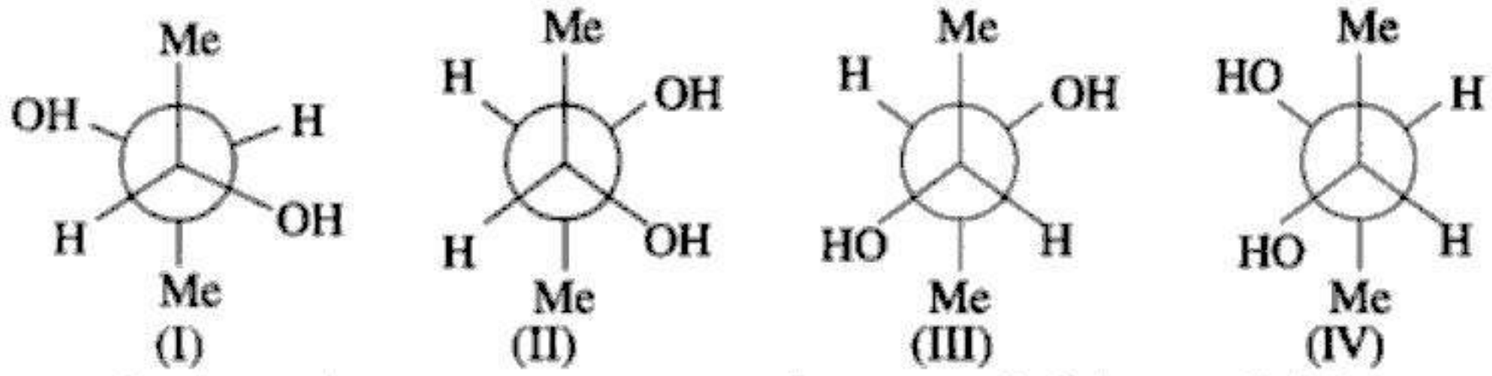
58. The optically active tartaric acid is named as D-(+)-tartaric acid because it has a positive
(a) optical rotation and is derived from D-glucose
(b) pH in organic solvent
(c) optical rotation is derived from D-(+)-glyceraldehyde
(d) optical rotation when substituted by deuterium (1999)

59. A solution of (+)-2-chloro-2-phenylethane in toluene racemises slowly in the presence of small amount of $SbCl_5$, due to the formation of
(a) carbanion (b) carbene (c) free-radical (d) carbocation (1999)

60. Which of the following compounds will exhibit geometrical isomerism?
(a) 1-Phenyl-2-butene (b) 3-Phenyl-1-butene (c) 2-Phenyl-1-butene (d) 1,1-Diphenyl-1-propene (2000)

61. The compounds $CH_2 = CHOH$ and CH_3CHO are
(a) metamers (b) chain isomers (c) tautomers (d) functional isomers

62. Given are the four Newmann projections of 2, 3-butandiol.



Amongst these projections, the structures representing meso-2, 3-butanediol is/are
(a) (I) and (II) (b) (I) and (III) (c) (II) and (III) (d) (II) and (IV)

63. The number of stereoisomers of methylcyclopropane is
(a) zero (b) one (c) two (d) three

64. The number of stereoisomers of 1,2-dimethylcyclopropane is
(a) one (b) two (c) three (d) four

Supplementary Materials

65. The correct decreasing priority of ligands —$CH(OH)CH_3$, —OH, —COOH and—CH_2OH in absolute configuration of an enantiomer is
(a) $CH(OH)CH_3 > OH > COOH > CH_2OH$ (b) $OH > CH(OH)CH_3 > CH_2OH > COOH$
(c) $OH > COOH > CH(OH)CH_3 > CH_2OH$ (d) $COOH > OH > CH(OH)CH_3 > CH_2OH$

66. The correct decreasing priority of ligands —NO_2, —C≡N, —NH_2 and —CH_2NH_2 in absolute configuration of an enantiomer is
(a) $NO_2 > NH_2 > C{\equiv}N > CH_2NH_2$ (b) $NO_2 > C{\equiv}N > NH_2 > CH_2NH_2$
(c) $NH_2 > NO_2 > C{\equiv}N > CH_2NH_2$ (d) $NH_2 > NO_2 > CH_2NH_2 > C{\equiv}N$

67. Which of the following operations on the Fischer formula does not change its absolute configuration?

(a) Exchanging ligands across the horizontal bond
(b) Exchanging ligands across the vertical bond
(c) Exchanging ligands across the horizontal bond and also across the vertical bond
(d) Exchanging a vertical and horizontal ligand.

68. Which of the following switching ligands or rotating Fischer structures changes its absolute configuration?
(a) An even number of switches
(b) An odd number of switches

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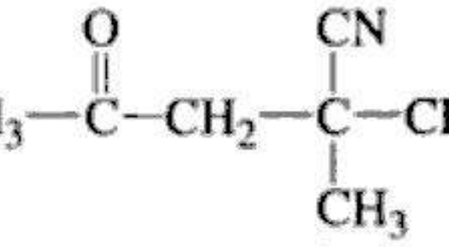
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98. The IUPAC name of the compound $CH_3CH{=}CHCH{=}CHC{\equiv}CCH_3$ is

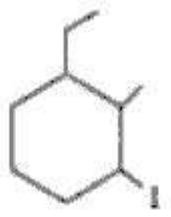
(a) 4, 6 - octadien - 2 - yne
(b) 2, 4 - octadien - 6 - yne
(c) 2 - octyn - 4, 6 - diene
(d) 6 - octyn - 2, 4 - diene

99. The IUPAC name of the compound  is

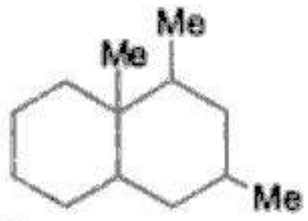
(a) 4–cyano–4–methyl–2–oxopentane
(b) 2–cyano–2–methyl–4–oxopentane
(c) 2, 2–dimethyl–4–oxopentanenitrile
(d) 4–cyano–4–methyl–2–pentanone

100. The IUPAC name of $(C_2H_5)_2NCH_2CHClCOOH$ is

(a) 2–chloro–4–*N*–ethylpentanoic acid
(b) 2–chloro–3–(*N*, *N*–diethylaminopropanoic acid)
(c) 2–chloro–2–oxodiethylamine
(d) 2–chloro–2–carboxy–*N*–ethylethane

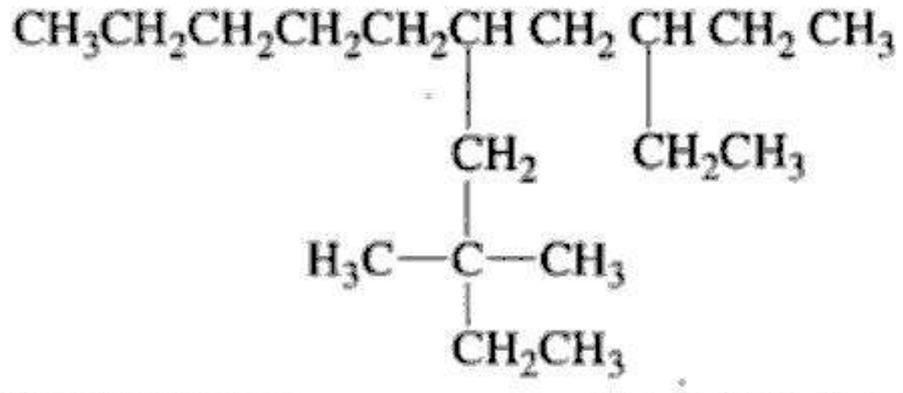
101. The IUPAC name of the compound  is

(a) 1-Iode-2-methyl-3-ethylcyclohexane
(b) 1-methyl-2-ethyl-6-iodocyclohexane
(c) 1-Ethyl-2-methyl-3-iodocyclohexane
(d) 1-Iodo-2-methyl-1-ethylcyclohexane

102. The IUPAC name of the compound  is

(a) 1,2,3-Trimethylbicyclo [4.4.0] decane
(b) 1,8,10-Trimethylbicyclo [4.4.0] decane
(c) 1,3,9-Trimethylbicyclo [4.4.0] decane
(d) 1,3,10-Trimethylbicyclo[4.4.0]decane

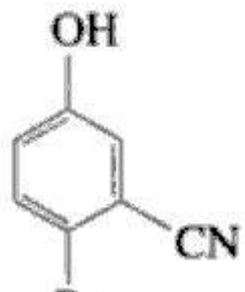
103. The IUPAC name of the compound



(a) 5-(2-ethylbutyl)-3,3-dimethyldecane
(b) 5-(2,2-dimethylbutyl)-3-3-ethyldecane
(c) 6-(2,2-dimethylbutyl)-8-ethyldecane
(d) 3,3-dimethyl-5-(2-ethylbutyl)decane

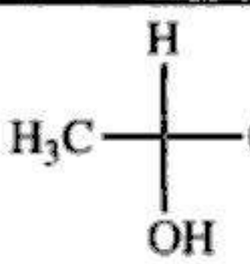
104. The IUPAC name of C_6H_5COCl is

(a) Benzal chloride
(b) Benzyl chloride
(c) Benzoyl chloride
(d) Phenylchloro ketone (2006)

105. The IUPAC name of the compound  is

(a) 4-Bromo-3-cyanophenol
(b) 2-Bromo-5-hydroxybenzonitrile
(c) 2-cyano-4-hydroxybromobenzene
(d) 6-Bromo-3-hydroxybenzonitrile (2009)

Multiple Correct Choice Type

1. Three dimensional structure of (+)-lactic acid is represented as  . In this structure

(a) CH_3 and COOH groups are coming out of the page.
(b) H and OH groups are coming out of the page.

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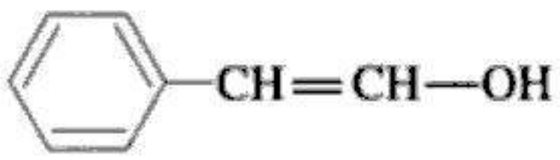
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18. Which of the following statements is/are **not** correct for D-(+)-glyceraldehyde?
(a) The symbol D indicates the dextrorotatory nature of the compound
(b) The sign (+) indicates the dextrorotatory nature of the compound
(c) The symbol D indicates that hydrogen atom lies left to the chiral centre in the Fischer projection diagram
(d) The symbol D indicates that hydrogen atom lies right to the chiral centre in the Fisher projection diagram

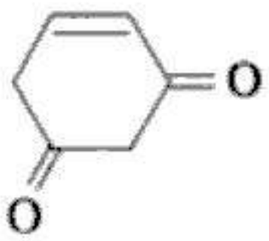
19. Which of the following statements is/are **not** correct?
(a) A compound whose molecule has D configuration will always be dextrorotatory
(b) A compound whose molecule has D configuration may be dextrotatory or laevorotatory
(c) A compound whose molecule has L configuration will always be laevorotatory
(d) A compound whose molecule has L configuration may be dextrorotatory or laevorotatory

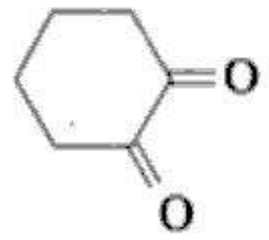
20. Which of the following compounds will show geometrical isomerism?
(a) 2-Butene (b) Propene (c) 1-Phenylpropene (d) 2-Methyl-2-butene
(1998)

21. Tautomerism is exhibited by

(a) 

(b) 

(c) 

(d) 

(1998)

22. Which of the following statements is/are **not** correct?
(a) Metamerism belongs to the category of structural isomerism
(b) Tautomeric structures are the resonating structures of a molecule
(c) The violet colouration produced by a molecule with neutral ferric chloride solution indicates the presence of enolic group in the molecule
(d) Geometrical isomerism is shown only by alkenes

23. Which of the following statements regarding diastereomers is/are **not** correct?
(a) They have different physical properties.
(b) They cannot be separated from each other by fractional crystallization.
(c) They can be separated from each other by chromatographic methods.
(d) They have identical chemical properties towards both chiral and achiral reagents.

24. Which of the following statements are correct?
(a) sp hybrid orbital is more electronegative than sp^2 hybrid orbital.
(b) The size of sp^3 hybrid orbital of carbon is smaller than that of sp hybrid orbital.
(c) Amongst CH_4, C_2H_4 and C_2H_2, the carbon-hydrogen bond length is maximum in methane.
(d) The resonating structures differ in the number of unpaired electrons.

25. Which of the following statements are correct?
(a) The resonance energy is defined as the difference between the enthalpy of formation of the molecule and that of resonating structure having the largest energy.
(b) Benzene has about 78 per cent contribution from Kekule's structures.
(c) Metamerism is due to the different arrangement of groups attached to a functional group.
(d) Tautomers of a compound are in equilibrium with each other.

26. Which of the following statements are **not** correct?
(a) *Cis-* and *trans-* structures can be written for the substituted cyclopropane.
(b) Diastereomers are observed in a molecule containing one chiral carbon atom
(c) Mesotartaric acid has a centre of symmetry.
(d) In the compound D-(+)-glyceraldehyde, D stands for the dextrorotatory nature of the molecule.

27. Which of the following statements are correct?
(a) Chain isomers are possible for alkanes having four or more carbon atoms.
(b) Enantiomorphs possess the same physical properties.
(c) Maleic acid has zero dipole moment.
(d) Only organic molecules can be optically active.

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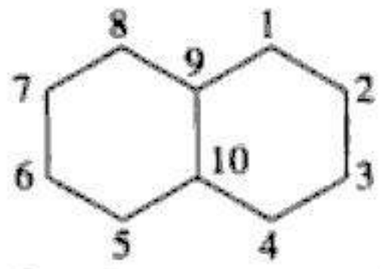
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99. The compound is name as nitrile. The correct name is 2,2-dimethyl-4-oxopentanenitrile.

100. The IUPAC name of $(C_2H_5)_2\overset{3}{N}\overset{2}{C}H_2\overset{1}{C}HClCOOH$ is 2-choloro-3-(N, N-diethylamino)propanoic acid.

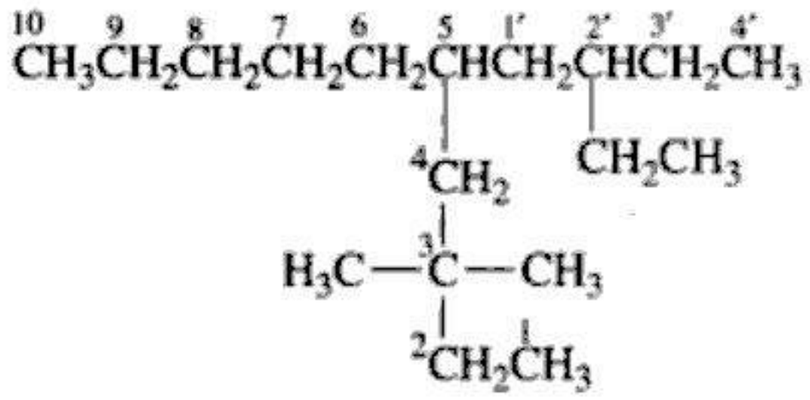
101. Substituted cycloalkanes are named in the same way as alkanes. The name of the given compound is 3-Iodo-2-methyl-1-ethylcyclohexane.

102. The numbering in the given compound goes as follows:



The name of the given compound is 1,3,9-trimethylbycyclo[4.4.0]decane. The numbers within the brackets indicate number of carbon in each cycle. They are inserted in decreasing order.

103. The numbering goes as follows.

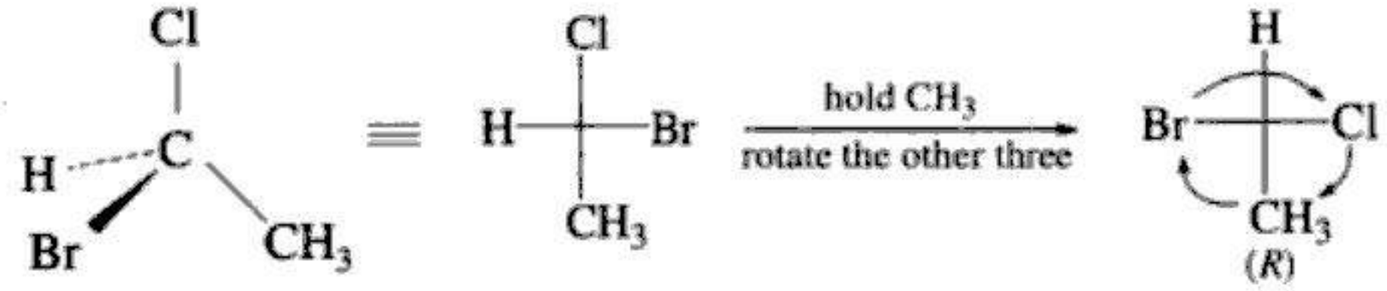


Its IUPAC name is 5-(2-ethylbutyl)-3, 3-dimethyldecane.

105. The order of preference of principal functional group is as follows.
Carboyxlic acid, sulphonic acid, ester, acid halide, amide, nitrile, aldehyde, ketone, alcohol, amine, ether, alkene.
The given compound contains —OH, —CN and —Br groups. Of these, —CN group gets the preference and thus the compound is named as nitrile. Hence, its name is 2-Bromo-5-hydroxybenzonitrile.

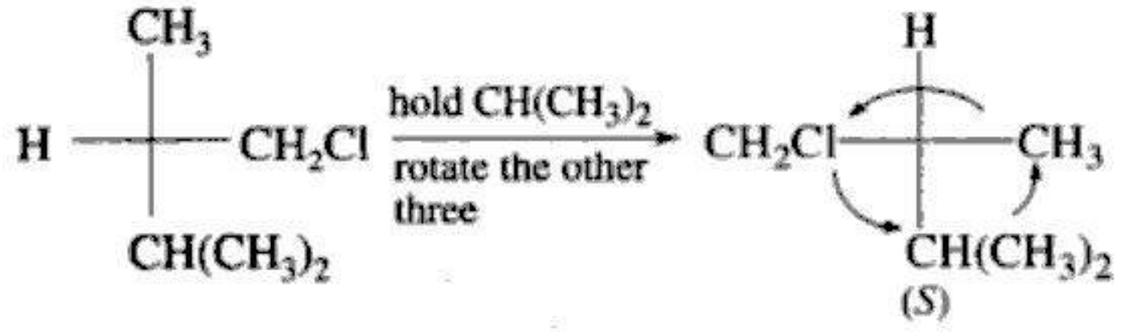
Multiple Correct Choice Type

5. (a) In the given molecule, the priority sequence is Br > Cl > CH_3 > H. The given molecule is to be visualised as under:

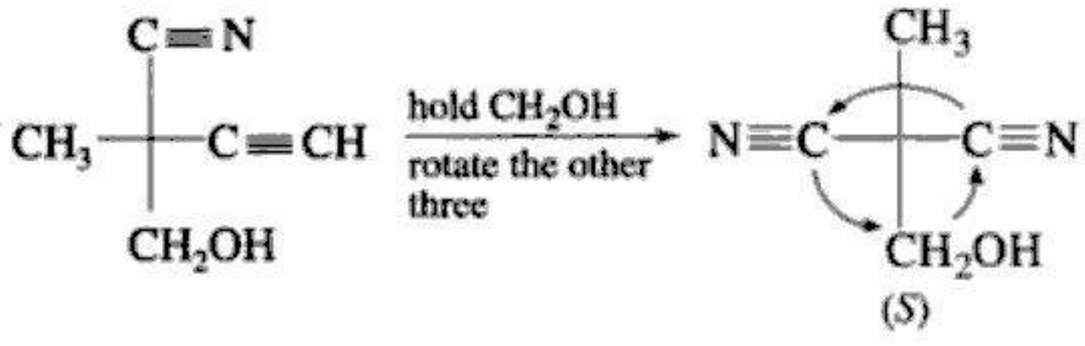


Since the priority sequence follows clockwise, the molecule is designated as *R*.

(b) The priority order is CH_2Cl > $CH(CH_3)_2$ > CH_3 > H. The molecule may be visualised as follows:



(c) The priority order is CH_2OH > CN > C≡CH > CH_3.



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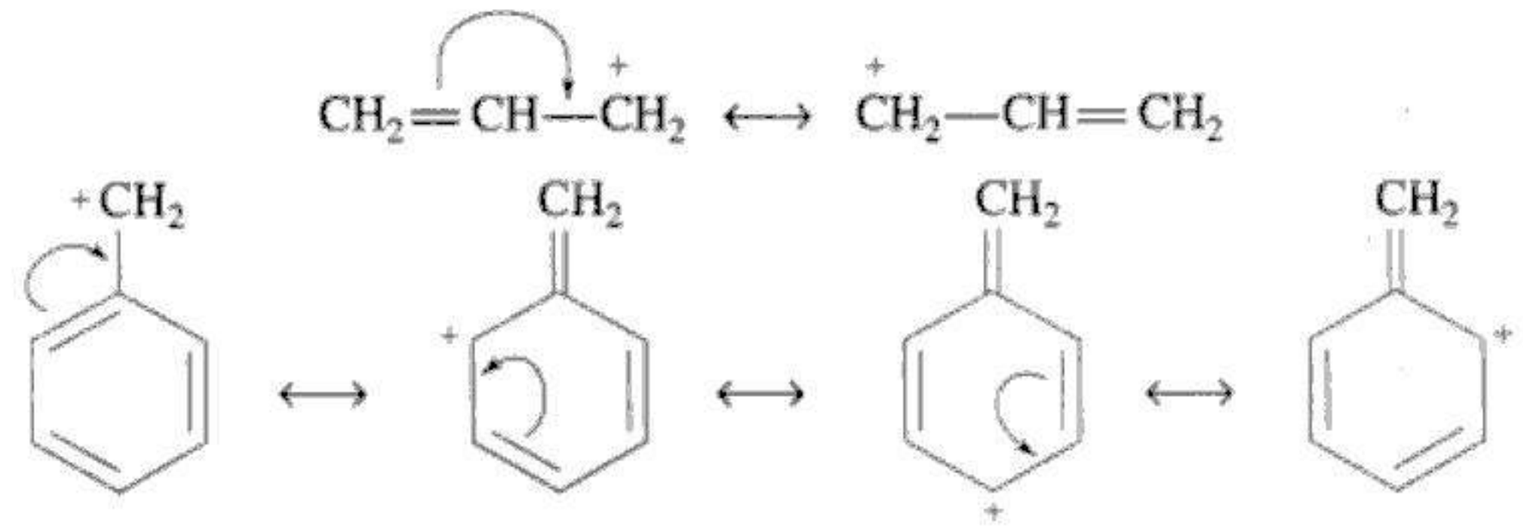
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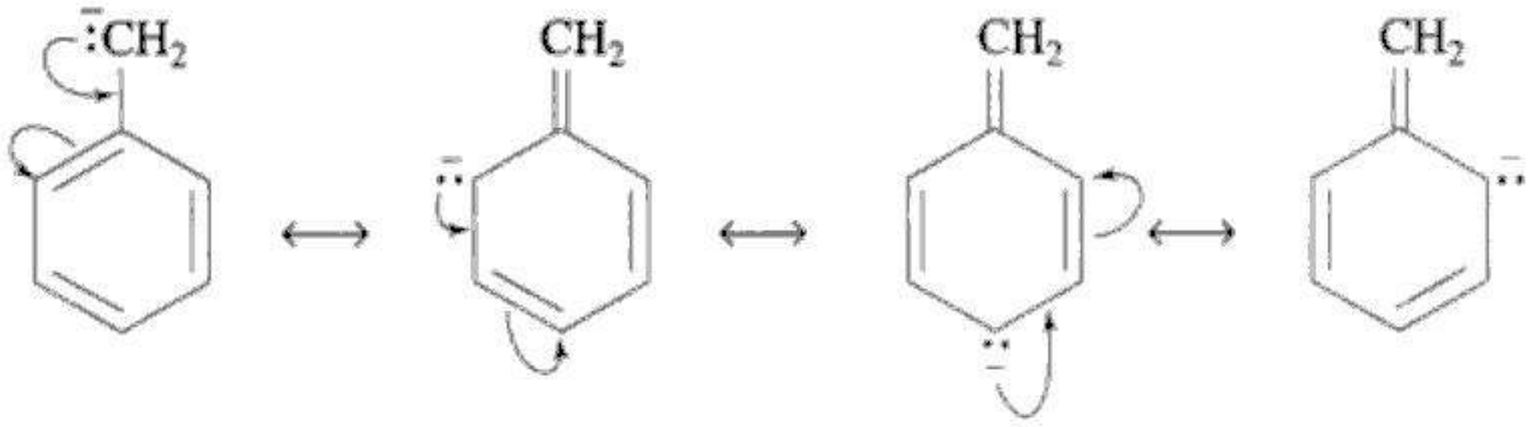
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Similarly, benzyl carbanion is more stable than propyl carbanion:



Classification of Carbonium ion The carbonium ion has been classified into primary (or 1°), secondary (or 2°) and tertiary (or 3°) depending upon one, two and three carbon atoms to which C^+ is attached with. For example,

$CH_3\overset{+}{C}H_2$	$(CH_3)_2C^+H$	$(CH_3)_3\overset{+}{C}$
primary (or 1°)	secondary (or 2°)	tertiary (or 3°)

Classification of Reagents Two types of reagents may be distinguished on the basis of their centre of attack. These are given below.

Electrophiles or Electrophilic Reagents The reagents which attack region of high electron density (negative centres) are knwon as electrophiles (meaning electron loving). These include positive ions (such as carbonium ion) and neutral molecules with electron-deficient centres. Examples are

$$H^+,\ Cl^+,\ Br^+,\ I^+,\ NO_2^+,\ R_3C^+,\ RN_2^+,\ AlCl_3,\ BF_3,\ ZnCl_2,\ FeCl_3,\ ICl,\ NOCl$$

Nucleophiles or Nucleophilic Reagents The reagents which attack region of high positive charge density are known as nucleophiles (meaning nucleus loving). These include negative ions (such as carbanion) and neutral molecules with free electron pairs. Examples are

$$Cl^-,\ Br^-,\ I^-,\ CN^-,\ OH^-,\ R\bar{C}H_2,\ NH_3,\ H_2O,\ ROH$$

Types of Organic Reactions

The common organic reactions may be classified into three categories, viz., substitution reactions, addition reactions and elimination reactions. A brief description of these is in order.

1. Substitution Reactions In these reactions, an atom attached to carbon atom of a molecule is replaced by another atom. These reactions may be initiated by free radical, electrophile or nucleophile.

Free-radical substitution One of the common examples is the reaction between CH_4 and Cl_2. The reaction is initiated by the homolytic cleavage of Cl_2 by sunlight. The mechanism of the reaction is as follows.

(a) *Initiation step*

$$Cl : Cl \rightarrow 2^\bullet Cl$$

(b) *Propagation steps*

$$CH_4 + {}^\bullet Cl \rightarrow CH_3^\bullet + HCl$$
$$CH_3^\bullet + Cl_2 \rightarrow CH_3Cl + Cl^\bullet$$
....
....

(c) *Termination steps*

$$Cl^\bullet + {}^\bullet Cl \rightarrow Cl_2$$
$$CH_3^\bullet + {}^\bullet Cl \rightarrow CH_3Cl$$

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28. Which of the following is the most stable carbocation?
(a) $\overset{+}{C}H_3$ (b) $R\overset{+}{C}H_2$ (c) $R_2\overset{+}{C}H$ (d) $R_3\overset{+}{C}$

29. An electrophilic reagent must have
(a) a vacant orbital (b) an orbital containing one electron
(c) an orbital containing two electrons (d) all completely filled atomic orbitals

30. Which of the following is an electrophile?
(a) Na^+ (b) Li^+ (c) H^+ (d) Ca^{2+}

31. Which of the following is the most stable radical?
(a) $CH_3^{\bullet}$ (b) $RCH_2^{\bullet}$ (c) $R_2CH^{\bullet}$ (d) $R_3C^{\bullet}$

32. Which of the foilowing statements is correct?
(a) $+I$ Group stabilises a carbocation (b) $+I$ Group stabilises a carbanion
(c) $-I$ Group stabilises a carbocation (d) $-I$ Group destabilises a carbanion

33. The relative order of stability of carbocations $R\overset{+}{C}{=}CH_2$, $R\overset{+}{C}H_2$ and $RCH{=}\overset{+}{C}H$ is
(a) $R\overset{+}{C}{=}CH_2 > R\overset{+}{C}H_2 > RCH{=}\overset{+}{C}H$ (b) $R\overset{+}{C}{=}CH_2 < R\overset{+}{C}H_2 < RCH{=}\overset{+}{C}H$
(c) $R\overset{+}{C}{=}CH_2 > R\overset{+}{C}H_2 < RCH{=}\overset{+}{C}H$ (d) $R\overset{+}{C}{=}CH_2 < R\overset{+}{C}H_2 > RCH{=}\overset{+}{C}H$

34. In CH_3CH_2OH, the bond that undergoes heterolytic cleavage most readily is
(A) C—C (B) C—H (C) C—O (D) O—H (1988)

35. For the following reactions

$CH_3Cl \rightarrow CH_3^+ + Cl^-$ ΔH_1° $(CH_3)_2CHCl \rightarrow (CH_3)_2CH^+ + Cl^-$ ΔH_3°

$CH_3CH_2Cl \rightarrow CH_3CH_2^+ + Cl^-$ ΔH_2° $(CH_3)_3CCl \rightarrow (CH_3)_3C^+ + Cl^-$ ΔH_4°

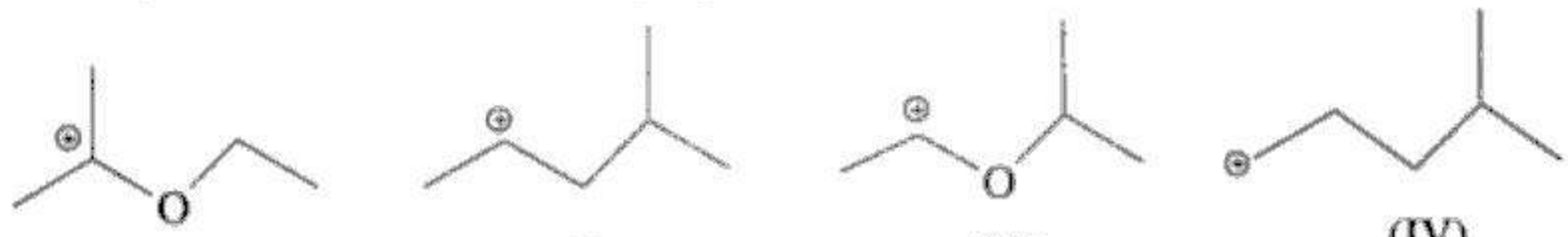
the correct order of enthalpies of ionization is
(a) $\Delta H_1^\circ > \Delta H_2^\circ > \Delta H_3^\circ > \Delta H_4^\circ$ (b) $\Delta H_1^\circ < \Delta H_2^\circ < \Delta H_3^\circ < \Delta H_4^\circ$
(c) $\Delta H_1^\circ > \Delta H_2^\circ > \Delta H_3^\circ < \Delta H_4^\circ$ (d) $\Delta H_1^\circ > \Delta H_2^\circ < \Delta H_3^\circ < \Delta H_4^\circ$

36. The order of stability of allyl, 3° and vinyl radicals is
(a) allyl > 3° > vinyl (b) 3° > allyl > vinyl (c) 3° > vinyl > allyl (d) vinyl > 3° > allyl

37. Which of the following has the highest nucleophilicity?
(a) F^- (b) OH^- (c) CH_3^- (d) NH_2^- (2000)

38. The correct order of reactivity of the following types of H atom towards radical substitution is
(a) allylic > vinylic > 1° H (b) allylic > 1° H > vinylic
(c) 1° H > allylic > vinylic (d) vinylic > allylic > 1° H

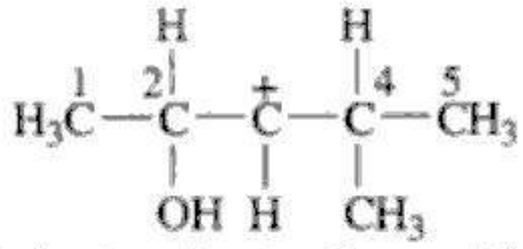
39. The correct stability order for the following species is



(I) (II) (III) (IV)

(a) (II) > (IV) > (I) > (III) (b) (I) > (II) > (III) > (IV)
(c) (II) > (I) > (IV) > (III) (d) (I) > (III) > (II) > (IV) (2008)

40. In the carbocation



(2009)

the species H/CH_3 that is most likely to migrate the positively charged carbon is
(a) CH_3 at C—4 (b) H at C—4 (c) CH_3 at C—2 (d) H at C—2

41. The order of stability of the given carbocations is
(a) $(CH_3)_3\overset{+}{C} > (CH_3)_2\overset{+}{C}H > CH_3\overset{+}{C}H_2$ (b) $(CH_3)_3\overset{+}{C} > CH_3\overset{+}{C}H_2 > (CH_3)_2\overset{+}{C}H$
(c) $(CH_3)_2\overset{+}{C}H > (CH_3)_3\overset{+}{C} > CH_3\overset{+}{C}H_2$ (d) $(CH_3)_2\overset{+}{C}H > CH_3\overset{+}{C}H_2 > (CH_3)_3\overset{+}{C}$

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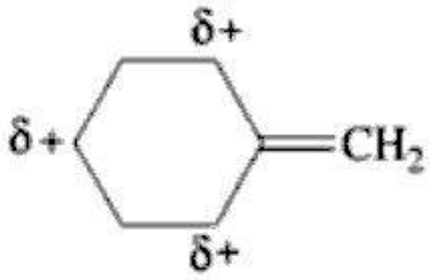
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Resonance stabilization makes a more dominating role than the inductive effect, making Cl_3C^- a weaker base than F_3C^-. In F, there is no d orbitals, hence, no stabilization occurs in F_3C^-.

2. Benzylic radical is most stable due to extensive π-electron delocalization



Allylic radical is also more stable due to resonance $H_2C{=}CH{-}\dot{C}H_2 \longleftrightarrow H_2\dot{C}{-}CH{=}CH_2$

In general, the stability follows the order 3° > 2° > 1°.

5. (a) A group pushing electrons away from the carbon atom to which it is attached is said to have *–I* effect. An alkyl group pushes electrons towards carbon to which it is attached and thus belongs to *+I* group.

(c) Resonance involves rearrangement of electrons only whereas tautomerism is the shift of active hydrogen from one atom to another in the molecule.

(d) Both inductive and resonance effect operate, but the latter is more predominating over the former.

6. (a) BF_3 can accept a pair of electrons and is thus behave as a Lewis acid.

7. (a) Electron-withdrawing group stabilizes the carboxylate anion, hence increases the acidity of carboxylic acid.

(b) *+I* group is electron-releasing group and it destabilizes the carboxylate anion, hence decreases the acidity of carboxylic acid.

(c) Inductive effect is distance dependent.

8. (a) The correct order is $(CH_3)_3C^+ > (CH_3)_2CH^+ > CH_3CH_2^+ > CH_3^+$.

(b) In S_N1 mechanism, a planar carbocation is formed. Attack of a nuclephile may occur from either sides of planar geometry. Thus, it may or may not lead to inversion. In fact, S_N1 produces both types of configuration, inverted and noninverted.

9. (a) Since 3° carbocation is most stable, the reaction proceeds via the formation of 3° carbocation, i.e. S_N1.

(b) Since 1° carbocation is least stable, the reaction does not proceed via the formation of carbocation, i.e. S_N2.

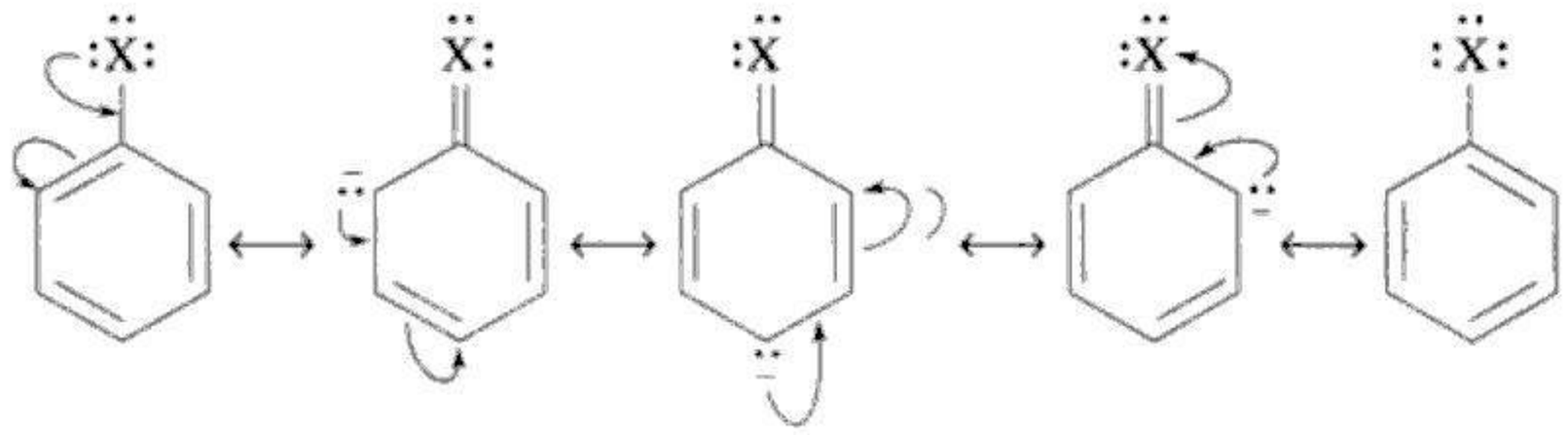
(c) Since there is inversion in optical rotation, the reaction must have proceeded via S_N2 mechanism.

(d) Since there is no inversion in optical rotation, the reaction must have proceeded by S_N1 mechanism as in S_N2 there occurs inversion of configuration of carbon atom.

10. (a) The addition across C=O group is a nucleophilic addition reaction.

(b) This is due to the following two factors.

(i) *Delocalization of electrons*



The delocalization imparts a partial double bond character to C—X bond making it stronger than C—X bond in alkyl halide.

(ii) *Difference in hybridization of carbon*

In alkyl halides, the carbon to which the halogen is attached is sp^3 hybridized while in aryl halide it is sp^2 hybridized. Therefore, the C—X bond in latter is shorter than in former.

(c) The acylium ion $R{-}{-}C{\equiv}\overset{+}{O}:$ is more stable than $R{-}\overset{+}{C}{=}O$, the ordinary carbonium ion. In the former the octet of every atom is complete while in the latter it is not so, as in the case of C atom which has only 6 electrons.

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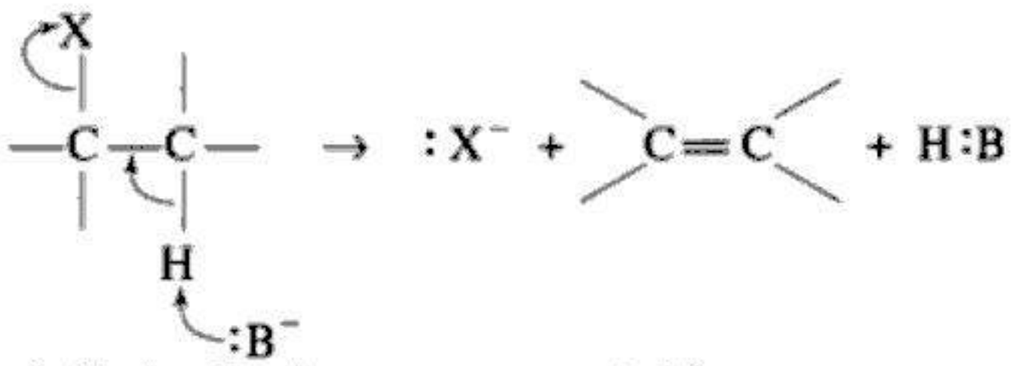
For example,



The more substituted product is known as *Saytzeff product* and the least substituted product is known as *Hofmann product*.

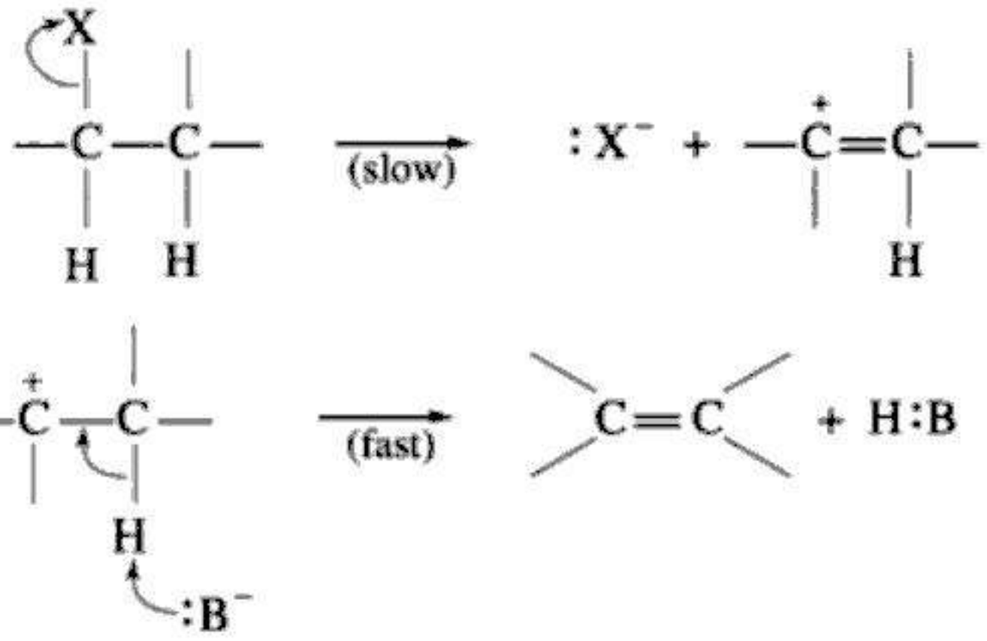
Mechanism of Dehydrohalogenation

E2 *mechanism* The base : B^- (such as $\ddot{:}OC_2H_5$) pulls a proton away from carbon, simultaneously a halide ion departs and the double bond is formed.

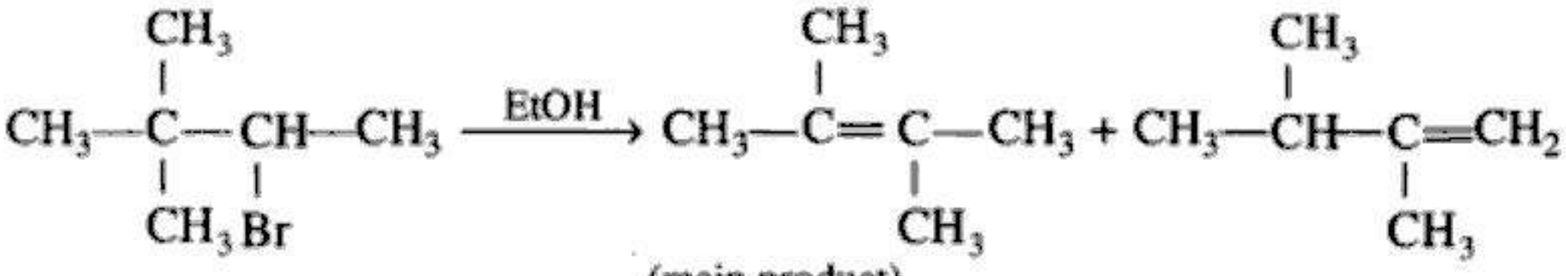


This mechanism of elimination is not accompanied by rearrangement.

E1 *mechanism* Two steps involved in this mechanism are:

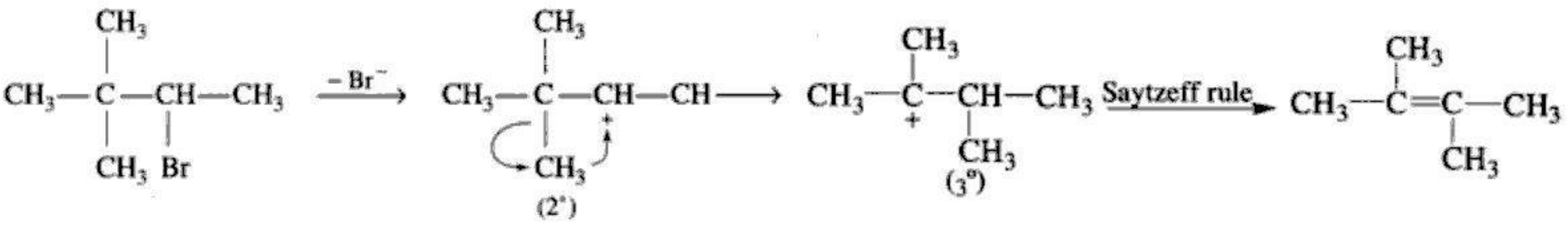


A carbocation formed as an intermediate is particularly prone to rearrangement. For example, the following reaction involves rearrangement.



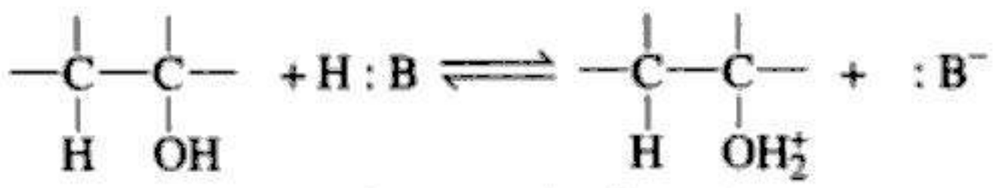
(main product)

This arrangement is due to the formation of more stable 3° carbocation from the lesser stable 2° carbocation:



Mechanism of dehydration The steps involved are as follows.

1. Acid-base reaction between the alcohol and catalyzing acid.



The role of acid is to convert —OH to $—OH_2^+$ so that very good leaving group H_2O (a very weak base) is eliminated

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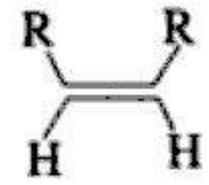
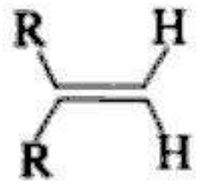
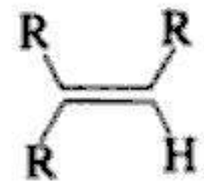
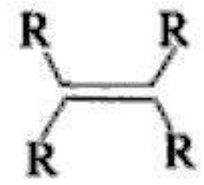


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27. Which one of the following alkenes will react fastest with H_2 under catalytic hydrogenation condition

(a)  (b)  (c)  (d)  (2000)

28. The electrophilic addition of 1,4-butadiene produces
- (a) 1,2–addition product only
- (b) 1,4–addition product
- (c) both 1,2– and 1,4– addition products which are not at equilibrium with each other
- (d) both 1,2– and 1,4-addition products which are at equilibrium with each other

29. The addition reactions shown by alkenes are the example of
- (a) electrophilic addition reactions
- (b) nucleophilic addition reactions
- (c) free radical addition reactions
- (d) the formation of carbanion as the intermediate

30. The addition of Br_2 to cyclohexene in the presence of NaCl gives
- (a) only *trans*-1,2-dibromocyclohexane
- (b) only *cis*-1,2-dibromocyclohexane
- (c) *trans*-1,2-dibromocyclohexane and *trans*-1-bromo-2-chlorocyclohexane
- (d) *cis*-1,2-dibromocyclohexane and *cis*-1-bromo-2-chlorocyclohexane

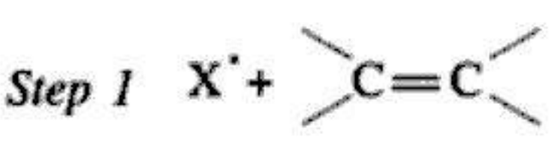
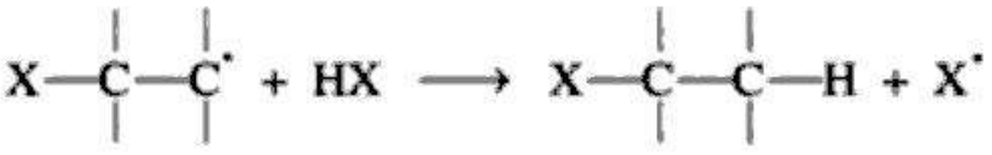
31. The addition of Br_2 dissolved in CH_3OH to cyclohexene gives
- (a) a mixture of *trans*-and *cis*-dibromocyclohexane
- (b) a mixture of *trans*-1-bromo-2-methoxycyclohexane and *trans*-dibromocyclohexane
- (c) a mixture of *cis*-1-bromo-2-methoxycyclohexane and *trans*-1-bromo-2-methyoxycyclohexane
- (d) only dibromocyclohexane.

32. The addition of Br_2 to *cis*-2-butene gives
- (a) (*R*,*R*)-2,3-dibromobutane only.
- (b) (*S*,*S*)-2,3-dibromobutane only.
- (c) (*R*,*S*)-dibromobutane.
- (d) a mixture of (*R*,*R*) and (*S*,*S*)-dibromobutane.

33. The addition of Br_2 to *trans*-2-butene gives
- (a) (*R*,*R*)-2,3-dibromobutane
- (b) (*S*,*S*)-2,3-dibromobutane
- (c) (*R*,*S*)-dibromobutane
- (d) a mixture of (*R*,*R*) and (*S*,*S*)-dibromobutane.

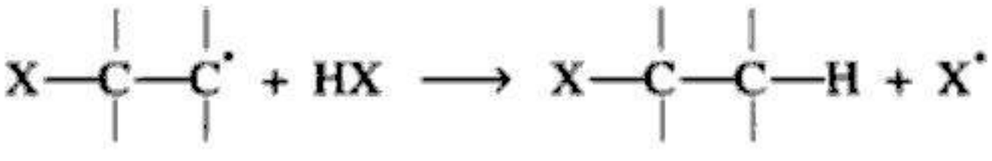
34. Which one of the following has the smallest heat of hydrogenation per mole?
(a) 1-Butene (b) *trans*-2-Butene (c) *cis*-2-Butene (d) 1,3-Butadiene (1993)

35. The propagation steps involved in the free radical addition of HX across a double bond are

Step 1  *Step 2* 

HCl does not follow free-radical addition because
- (a) Step 1 is exothermic and step 2 is endothermic
- (b) Step 1 is endothermic and step 2 is exothermic
- (c) Steps 1 and 2 are exothermic
- (d) Steps 1 and 2 are endothermic

36. The propagation steps involved in the free radical addition of HX across a double bond are

Step 1  *Step 2* 

HI does not follow free-radical addition because
- (a) Step 1 is exothermic and Step 2 is endothermic
- (b) Step 1 is endothermic and Step 2 is exothermic
- (c) Both steps are exothermic
- (d) Both steps are endothermic

37. The treatment of ethene with cold alkaline potassium permanganate produces
- (a) ethylene glycol
- (b) formaldehyde
- (c) formic acid
- (d) carbon dioxide and water

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(d) The treatment of 3,3-dimethyl-1-butene with hydrogen chloride gives products $CH_3C(CH_3)_2CH(Cl)\ CH_3$ and $CH_3\underset{\displaystyle Cl}{\underset{|}{C}}(CH_3)CH(CH_3)_2$.

36. Which of the following statements are **not** correct?

(a) Of the compounds 1-butene, *cis*-2-butene and *trans*-2-butene, the compound having the lowest enthalpy of combustion is *cis*-2-butene and that having the highest value is 1-butene.

(b) The treatment of $CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_3$ with $KMnO_4$ and $NaIO_4$ gives $CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=O$ and

$HOOC-\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_3$.

(c) The treatment of $CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_3$ with $KMnO_4$ and $NaIO_4$ gives HCHO and

$O=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_3$.

(d) The treatment of $CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$ with $KMnO_4$ and $NaIO_4$ gives CH_3COCH_3 and

$(CH_3)_2CHCOOH$.

37. Which of the following statements are correct?

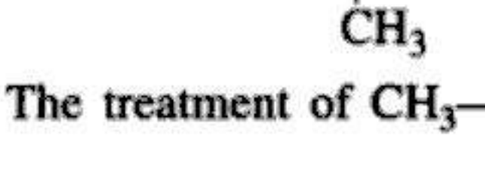
(a) An alkene on treating with $KMnO_4$ and $NaIO_4$ gave CH_3COOH and CH_3CH_2COOH. The alkene is $CH_3CH=CHCH_2CH_3$.

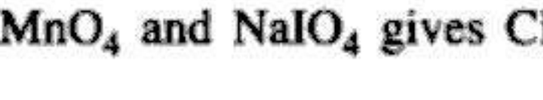
(b) A diene on treating with $KMnO_4$ and $NaIO_4$ gave CO_2, $(COOH)_2$ and CH_3COOH. The diene is $CH_2=CH-CH=CH-CH_3$.

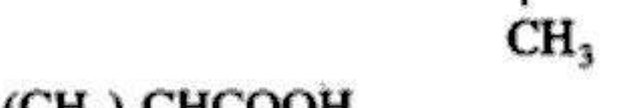
(c) The relative reactivities in radical substitution of the H in C—H bond in the given type of H is allyl > 3° > 2° > 1° Me > vinyl.

(d) 3,3-Dimethyl-1-butene gives only one addition product.

38. Which of the following alkenes have Z configuration?

(a) 

(b) 

(c) 

(d)

39. The addition of HBr to 3,3-dimethyl-1-butene results in the formation of

(a) 3-bromo-2,2-dimethylbutane
(b) 2-bromo-2,3-dimethylbutane
(c) 1-bromo-2-methyl-3,3-dimethylbutane
(d) 4-bromo-3-methyl-2,2-dimethylbutane

Linked Comprehension Type

1. Water can be added across a double bond through the following two methods.

Method- I	Oxymercuration and demercuration
Method-II	Hydroboration–oxidation

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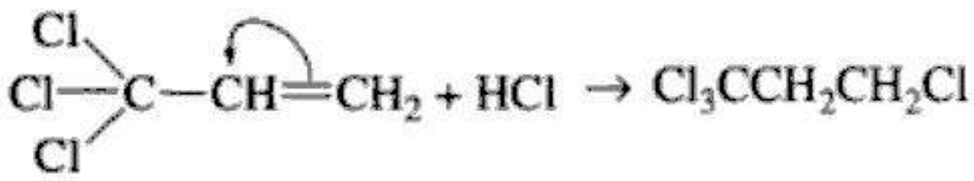


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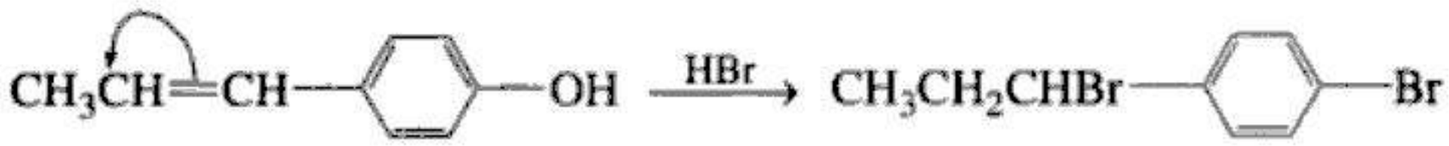
13. The dehydration involves rearrangement of double bond



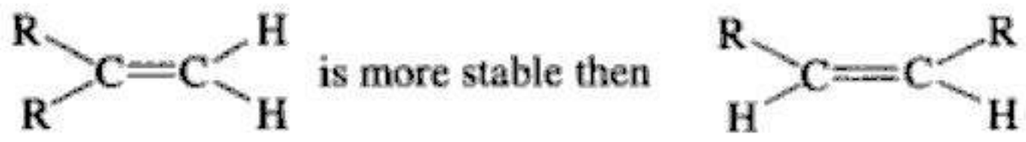
14. Debromination of *meso*-dibromobutane, produces *trans*-2-butene as the major product.
15. 2-Butene is $CH_3CH{=}CHCH_3$. The addition of HBr gives the same product whether it occurs via Markovnikov or anti-Markovnikov rule.
16. The addition of HBr across a double bond in the presence of peroxide involves free radical addition.
17. The addition of HI in the presence of peroxide does not follow anti-Markovnikov's rule because I atom is not reactive enough to add on a double bond.
18. The addition of HCl in the presence of peroxide does not follow anti-Markovnikov's rule because HCl bond is too strong to be broken homolytically.
19. The peroxide effect involves free-radical mechanism.

20. 

21. The addition of HCl proceeds via the formation of carbocation $CH_3\overset{+}{C}HCH_3$. The peroxide is not able to produce radicals from HCl as the bond H—Cl cannot be broken into radicals.

22. 

23. The addition of halogen to an alkene involves the formation of halonium ion as the intermediate.
24. The addition of Br_2 to *cis*-2-butene produces *rac*-2, 3-dibromobutane.
25. The addition of Br_2 to *trans*-2-butene produces *meso*-2, 3-dibromobutane.
26. The products are ethylene dibromide and 1-bromo-2-chloroethane.

27.  is more stable then

28. The electrophilic addition of 1, 3-butadiene gives both 1,2-and 1,4-addition products which are at equilibrium with each other.
29. Addition across a double bond proceeds via electrophilic addition.
30. The addition of halogen to a double bond is stereoselective and stereospecific. The first step is the formation of a bridged cation, called a bromonium ion. In the second step, the nucleophile (Br^- or another anion) adds to the face away from the bridging group to yield the *anti* addition product. So, the products are *trans*-1, 2-dibromocyclohexane and *trans*-1-bromo-2-chlorocyclohexane.
31. A mixture of *trans*-1, 2-dibromocyclohexane and *trans*-1-bromo-2-methoxycyclohexane is obtained.
32. The addition of Br_2 to *cis*-2-butene gives a mixture of (*R*, *R*) and (*S*, *S*)-dibromobutane
33. The addition of Br_2 to *trans*-2-butene gives (*R*, *S*)-dibromobutane
34. The more stable the compound, the smallest is the heat of hydrogenation per mole.
35. For Step I. $\Delta H = \varepsilon(C{=}C) - \varepsilon(C{-}C) - \varepsilon(C{-}Cl) = [612 - (348 + 338)]$ kJ mol^{-1} = negative
Step II. $\Delta H = \varepsilon(H{-}Cl) - \varepsilon(C{-}H) = (431 - 412)$ kJ mol^{-1} = positive
Thus, step 1 is exothermic and step 2 is endothermic.
36. For Step I. $\Delta H = \varepsilon(C{=}C) - \varepsilon(C{-}C) - \varepsilon(C{-}I) = [612 - (348 + 238)]$ kJ mol^{-1} = positive
For Step II. $\Delta H = \varepsilon(HI) - \varepsilon(C{-}H) = (299 - 412)$ kJ mol^{-1} = negative
Thus, step 1 is endothermic and step 2 is exothermic.
37. The treatment of ethene with cold alkaline potassium permanganate produces ethylene glycol.
38. There is *syn* addition of the two —OH groups. The product is (2*R*, 3*S*)-dihydroxybutane for *cis*-2-butene.
39. The product is a mixture of (2*S*, 3*S*) and (2*R*, 3*R*)-2, 3-dihydroxybutane for *trans*-2-butenen.
40. The addition involves the electrophilic attack by Cl^+ as the first step.
41. In the propagation steps, one of the two steps is endothermic in case of HCl and HI.

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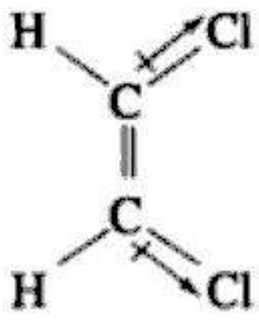


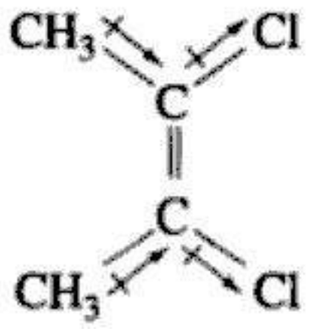
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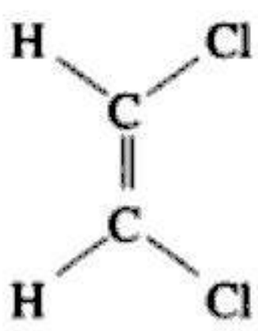
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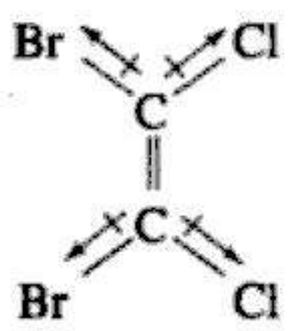




The dipole moment of *cis*-2,3-dichloro-2-butene is greater than that of *cis*–1, 2–dichloroethene because the two methyl groups in the $C_4C_6Cl_2$ compound releases electron in the same direrction of C—Cl dipoles.

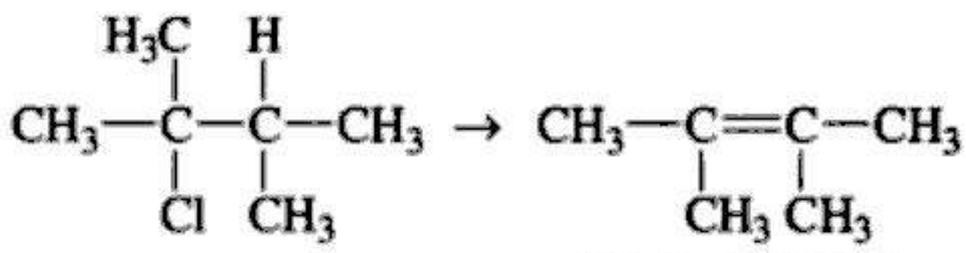
(d)





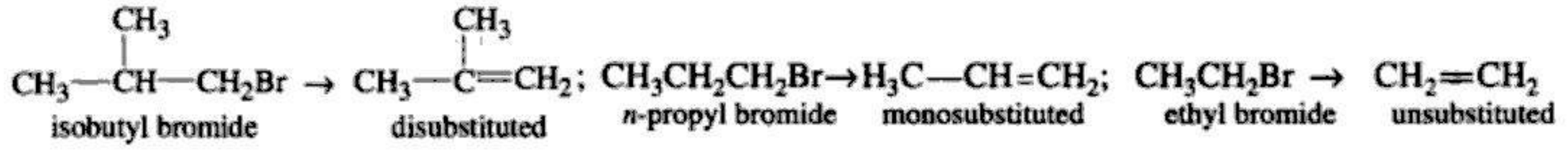
The bromine atoms pull electron in the opposite direction of C—Cl dipoles. Hence, the dipole moment of bromo derivative will be smaller than the other compound.

18.(a) According to Saytzeff's rule, the more substituted alkene is more stable and is thus a preferred product. Thus, the major product is



2,3-dimethyl-2-butene

(b) Reactivity in E2 dehydrohalogenation depends mainly upon the stability of the alkenes being formed.



isobutyl bromide; disubstituted; *n*-propyl bromide; monosubstituted; ethyl bromide; unsubstituted

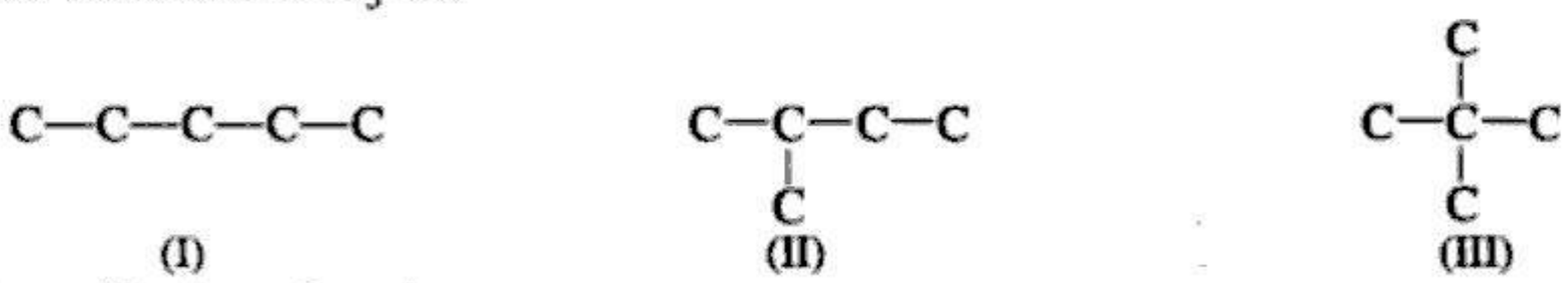
According to Saytzeff's rule, the stability of alkenes increases with increase in the number of substituents on the doubly bonded carbons. Hence, the order of reactivity towards dehydrohalogenation is isobutyl > *n*-propyl > ethyl

(c) A *trans* isomer is usually more stable than a *cis* isomer.

19.(a) The alkene has *E* configuration if the two high-priority substituents (in Cahn-Ingold-prelog sequence rules) are on the opposite side of the double bond. The configuration is *Z* if they are on the same side.

In the given compound, the priority sequence is Br > $CH(CH_3)_2$ > CH_2OH > $CH_2CH_2CH_3$. The two high priority substituents are on the same side of the double bond. Hence, its configuration is *Z*.

(b) The carbon skeletons of C_5 are

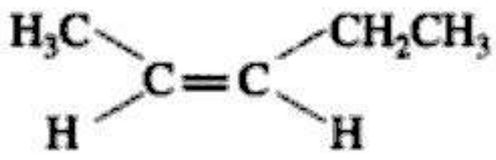


(I) (II) (III)

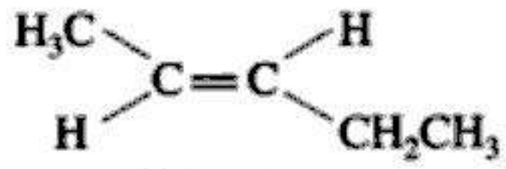
The skeleton (I) gives three isomers



1-pentene



(Z)-2-pentene



(*E*)-2-pentene

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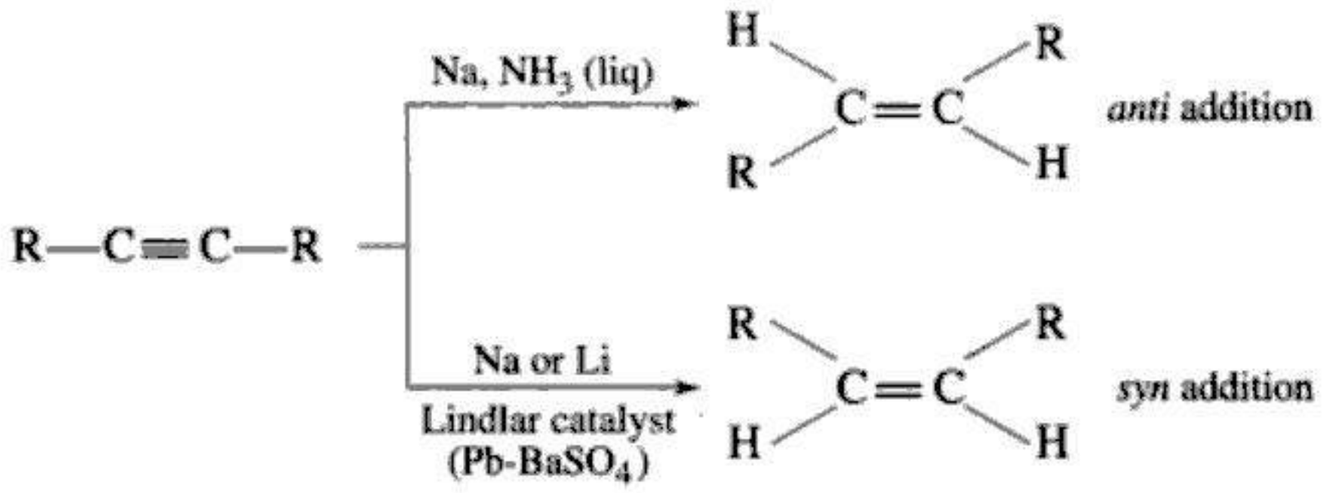
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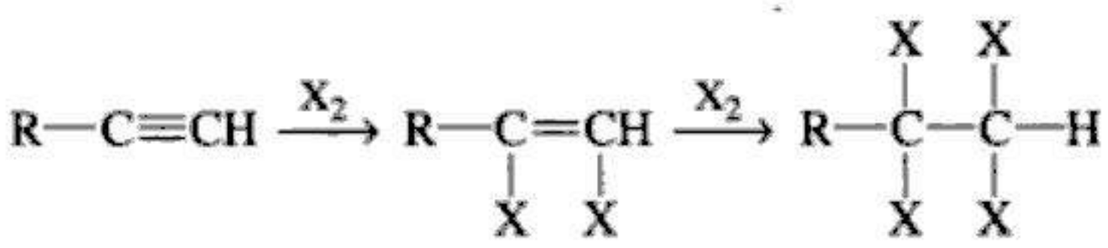
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Further reduction produces an alkane. Catalytic hydrogenation occurs at the surface of catalyst resulting into *cis* addition.

In general, alkyne undergoes catalytic hydrogenation at faster rate than alkene. This is due to the fact that the alkyne forms less constrained transition state with the surface of a catalyst as compared to that formed by an alkene.

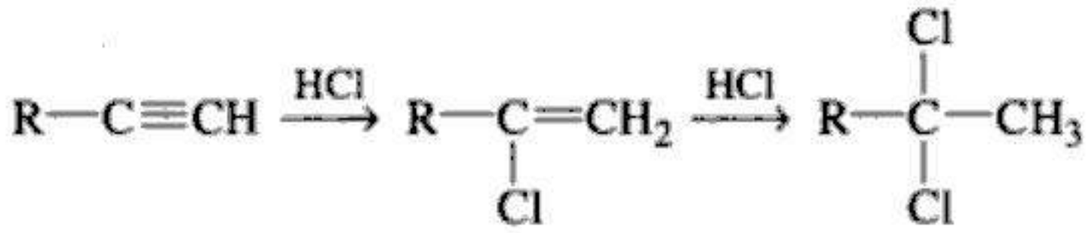
Addition of halogens Chlorine and bromine add on alkyne:



Alkynes are less reactive than alkenes. The mechanism of the reaction involves the initial formation of a cyclic halonium ion which is formed with greater difficulty in case of alkynes resulting in the lower activity of alkynes.

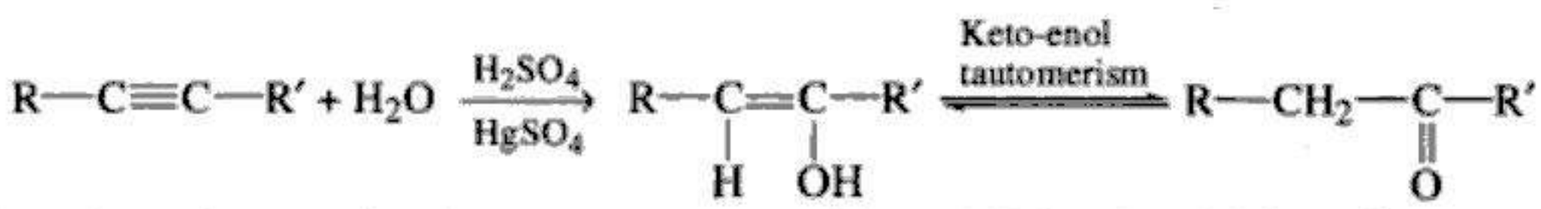
In fact, the cyclic halonium ion formed from alkyne is more strained due to the presence of double bond (shorter bond length). Moreover, its carbon atoms have more s-character. These factors make the halonium ion less stable than that formed from alkene.

Addition of hydrogen halides (HCl, HBr, HI)



The addition takes place in accordance with Markovnikov's rule. Peroxides have the same effect on addition of HBr to acetylenes as they have on alkenes.

Addition of water In the presence of acid and $HgSO_4$, a molecule of water adds to the triple bond. Initially enol is formed which is rapidly converted into an equilibrium mixture containing keto form in excess.



The final product is a mixture of both possible ketone (RCH_2COR' and $RCOCH_2R'$).

Formation of metal acetylides A triply bonded carbon which is sp hybridized has a high electronegativity and hydrogen atom attached to it shows appreciable acidity. For example, acetylene reacts with Na and Li liberating H_2 gas:

$$HC{\equiv}C{-}H + Na \rightarrow \underset{\text{sodium acetylide}}{HC{\equiv}C^{-}:Na^{+}} + \tfrac{1}{2}H_2$$

Compared to H_2O, NH_3 and alkane, the order of acidity of acetylene is as follows.

$$H_2O > HC{\equiv}CH > NH_3 > RH$$

The order of conjugate base will be $OH^- < HC{\equiv}C^- < NH_2^- < R^-$

Acetylene like any other acid undergoes Bronsted acid-base reaction. For example

$$\underset{\text{stronger acid}}{HC{\equiv}CH} + \underset{\substack{\text{stronger}\\\text{base}}}{Li^{+}\,NH_2^{-}} \rightleftharpoons \underset{\substack{\text{weaker}\\\text{acid}}}{NH_3} + \underset{\text{weaker base}}{HC{\equiv}C^{-}\,Li^{+}}$$

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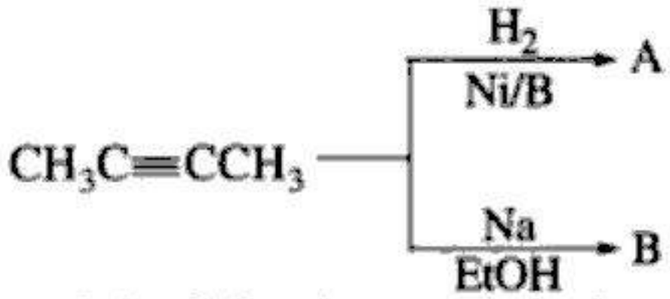


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(i) In the reaction



which one of the following products is correct?

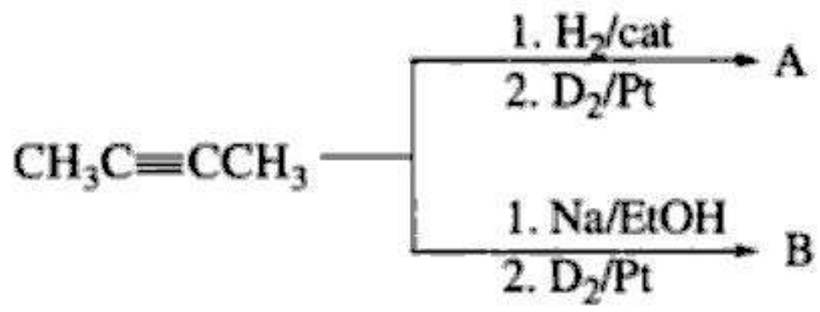
(a) A is (*Z*)-$CH_3CH{=}CHCH_3$ and B is (*E*)-$CH_3CH{=}CHCH_3$

(b) A is (*E*)-$CH_3CH{=}CHCH_3$ and B is (*Z*)-$CH_3CH{=}CHCH_3$

(c) Both A and B are (Z)-$CH_3CH{=}CHCH_3$

(d) Both A and B are (E)-$CH_3CH{=}CHCH_3$

(ii) In the reaction



which one of the following products is correct?

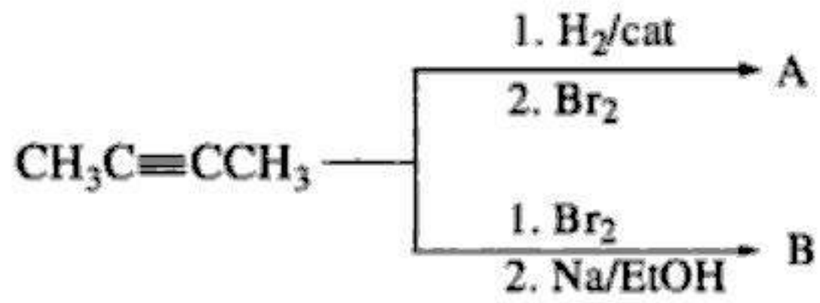
(a) Both A and B are *meso*-2, 3-dideuterobutane

(b) Both A and B are *rac*-2, 3-dideuterobutane

(c) A is *meso*-2, 3-dideuterobutane and B is *rac*-2, 3-dideuterobutane

(d) A is *rac*-2, 3-dideuterobutane and B is *meso*-2, 3-dideuterobutane.

(iii) In the reaction



which one of the following products is correct?

(a) Both A and B are *meso*-2, 3-dibromobutane

(b) Both A and B are *rac*-2, 3-dibromobutane

(c) A is *meso*-2, 3-dibromobutane and B is *rac*-2, 3-dibromobutane

(d) A is *rac*-2, 3-dibromobutane and B is *meso*-2, 3-dibromobutane.

Assertion and Reason Type

Given below are the two statements for each questions. Based on the following key, answer correctly each question.

(a) Both statements are correct and Statement-2 is a correct explanation of Statement-1.

(b) Both statements are correct but Statement-2 is not a correct explanation of Statement-1.

(c) Statement-1 is correct and Statement-2 is incorrect.

(d) Statement-1 is incorrect and Statement-2 is correct.

	Statement-1	Statement-2
1.	Alkynes are less reactive than alkene towards bromination.	The bromination of alkyne follows free radical mechanism while than of alkene follows *syn*-addition of Br_2.
2.	The terminal C—H in alkyne is more acidic as compared to that of alkene.	The more s character in the orbital used by the C bonded to the H, the more acidic is the H.
3.	$CH_3CHBrCH_2Br$ on treatment with with alcoholic KOH gives $CH_3CBr{=}CH_2$ as the major product.	In E2 elimination the more acidic H is removed preferentially.

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Chapter 24

Benzene

Structure of Benzene

According to Kekule, benzene is a resonance hybrid of the following resonating structures.



The resonance energy of benzene is about 150.6 kJ mol^{-1}, i.e. benzene is more stable than cyclohexatriene by 150.6 kJ mol^{-1}. The above structure of benzene accounts for the following characteristics of benzene.

1. Molecular formula of benzene is C_6H_6.
2. Benzene yields only one monosubstitution product.
3. Benzene yields three isomeric disubstitution products.
4. All carbon-carbon bond distance in benzene are equal (139 pm) and are intermediate in length between single (154 pm) and double bonds (134 pm).
5. Benzene undergoes substitution rather than addition reactions.

For example, the addition reaction of alkenes with cold dilute/alkaline $KMnO_4$, Br_2/CCl_4 and HCl are not shown by benzene. However, under drastic conditions benzene is reduced to cyclohexane. Benzene undergoes substitution reactions in which H is replaced by another atom or group of atoms. For examples

(i) $C_6H_6 + HONO_2 \xrightarrow{H_2SO_4} \underset{\text{nitrobenzene}}{C_6H_5—NO_2} + H_2O$

(ii) $C_6H_6 + Cl_2 \xrightarrow{Fe} \underset{\text{chlorobenzene}}{C_6H_5—Cl} + HCl$

(iii) $C_6H_6 + HOSO_3H \xrightarrow{SO_3} \underset{\text{Benzenesulphonic acid}}{C_6H_5—SO_3H} + H_2O$

(iv) $C_6H_6 + RCl \longrightarrow \underset{\text{alkylbenzene}}{C_6H_5—R} + HCl$

(v) $C_6H_6 + ROCl \xrightarrow{AlCl_3} C_6H_5—COCH_3 + HCl$

Reaction (iv) is known as Friedel-Crafts alkylation and reaction (v) is known as Friedel-Crafts acylation.

6. The enthalpies of hydrogenation and combustion of benzene are lower than those expected for cyclohexatriene.

Orbital Representation of Benzene Benzene is a planar molecule where each carbon is sp^2 hybridized. Of the three hybrid orbitals, two are used in σ–bonding with two other carbon atoms and the third is used in σ–bonding with hydrogen atom. In addition to these orbitals, each carbon has one p orbital occupied by one electron. Since this orbital lies perpendicular to the plane of benzene ring, the electron in this orbital is of π–type. The p orbital of each carbon atom can overlap with the adjacent p orbitals of carbon atoms making additional bond of π-type. But this bond is not localized between two carbon atoms but form two continuous doughtnut-shaped electrons cloud one lying above and the other below the plane of cyclic carbon skelton. It is the overlap of the p orbitals in both directions that corresponds to the resonance hybrid of two Kekule structures. The delocalization of π-electrons gives rise to resonance energy and makes the molecule more stable.

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48. The oxidation of 1-nitronaphthalene and α-naphthylamine results, respectively, into
(a) Phthalic acid and 3-nitrophthalicm acid
(b) Phthalic acid and phthalic acid
(c) 3-nitrophthalic acid and phthalic acid
(d) 3-nitrophthalic acid and 3-nitrophthalic acid

49. The oxidation of naphthalene with (i) CrO_3/acetic acid and (ii) O_2/V_2O_5, heat results, respectively, into
(a) Phthalic acid and phthalic acid
(b) Phthalic acid and 1, 4-naphthaquinone
(c) 1,4-Naphthaquinone and 1,4-naphthaquinone
(d) 1,4-naphthaquinone and phthalic acid

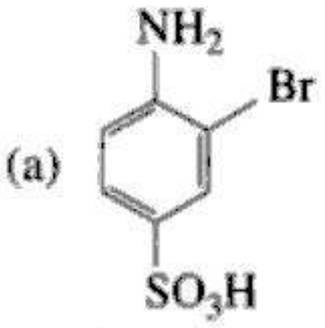
50. The sulphonation of toluene at 100 °C produces
(a) more of *ortho*-product than *para*-product
(b) more of *para*-product than *ortho*-product
(c) 50% each of *ortho*- and *para*-products
(d) 66% of *ortho*- and 33% *para*- product since there are two *ortho*-positions and one *para*-position.

51. The mononitration of Ph—Ph produces
(a) o-$O_2NC_6H_4$Ph as the major product
(b) p-$O_2NC_6H_4$Ph as the major product
(c) m-$O_2NC_6H_4$Ph as the major product
(d) 50% each of o-$O_2NC_6H_4$Ph and p-$O_2NC_6H_4$Ph

52. The relative reactivity of *p*-nitrochlorobenzene (X), chlorobenzene (Y) and 2,4-dinitrochlorobenzene (Z), with electrophilic reagent E^+ is
(a) X > Y > Z (b) X > Z > Y (c) Y > X > Z (d) Y > Z > X

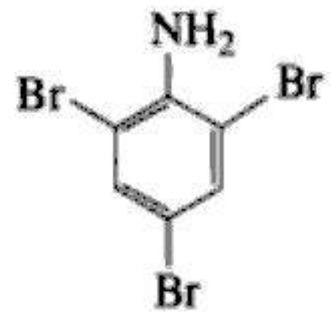
53. The relative reactivity of acetanilide (X), aniline (Y) and acetophenone (Z) with electrophilic reagent E^+ is
(a) X > Y > Z (b) X > Z > Y (c) Y > X > Z (d) Y > Z > X

54. The treatment of p-$H_2NC_6H_4SO_3H$ with bromine in water gives

(a) 

(b) 

(c) 

(d) 

55. The order of relative reactivity of the given halides towards S_N1 reaction is
(a) benzylchloride > *p*-methoxybenzylchloride > *p*-nitrobenzylchloride
(b) *p*-methoxylbenzylchloride > benzylchloride > *p*-nitrobenzylchloride
(c) *p*-methoxybenzylchloride > *p*-nitrobenzylchloride > benzylchloride
(d) benzylchloride > *p*-nitrobenzylchloride > *p*-methoxybenzylchloride

56. The order of relative reactivity of the given halides towards S_N1 reaction is
(a) $PhCH_2Cl > PhCHClCH_3 > PhCCl(CH_3)_2$
(b) $PhCH_2Cl < PhCHClCH_3 < PhCCl(CH_3)_2$
(c) $PhCH_2Cl > PhCCl(CH_3)_2 > PhCHClCH_3$
(d) $PhCCl(CH_3)_2 > PhCH_2Cl > PhCHClCH_3$

57. The order of relative reactivity of the given halides toward S_N2 reaction is
(a) $PhCH_2Cl > PhCHCl(CH_3) > PhCCl(CH_3)_2$
(b) $PhCH_2Cl < PhCHCl(CH_3) < PhCCl(CH_3)_2$
(c) $PhCHCl(CH_3) > PhCH_2Cl > PhCCl(CH_3)_2$
(d) $PhCHCl(CH_3) > PhCCl(CH_3)_2 > PhCH_2Cl$

58. The treatment of $PhCH{=}CHCH_2CH_3$ with (i) HBr and (ii) HBr in the presence of peroxide, respectively, give
(a) $PhCH_2CH(Br)CH_2CH_3$ and $PhCH(Br)CH_2CH_2CH_3$
(b) $PhCH(Br)CH_2CH_2CH_3$ and $PhCH_2CH(Br)CH_2CH_3$
(c) $PhCH_2CH(Br)CH_2CH_3$ and $PhCH_2CH(Br)CH_2CH_3$
(d) $PhCH(Br)CH_2CH_2CH_3$ and $PhCH(Br)CH_2CH_2CH_3$

59. The correct order of reactivity of PhMe(A), $PhNMe_2$(B) and $PhN(Me)_3^+$ (c) towards electrophilic substitution is
(a) B > A > C (b) B > C > A (c) C > A > B (d) C > B > A

60. Silver nitrate is added to each of 7-bromo-1,3,5-cycloheptatriene (A) and 5-bromo-1, 3-cyclopentadiene(B). It is observed that
(a) both A and B give AgBr precipitation
(b) both A and B do not give AgBr precipitation
(c) A gives AgBr precipitation while B does not give AgBr precipitation
(d) A does not give AgBr precipitation while B forms AgBr precipitation.

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4. The Birch reduction involves the reduction of alkynes to alkenes. The reagent used in this reduction is Li or Na in liquid NH_3 and EtOH. An alkali metal in liquid NH_3 is a source of solvated electrons which is responsible for reduction. Even benzene undergoes reduction by this method. Based on this reduction of benzene, answer the following three questions.

(i) The rate-controlled product in Birch reduction of benzene is

(a)  (b)  (c)  (d) 

(ii) Birch reduction of toluene gives

(a) 50% yield of 1-methyl-1, 4-cyclohexadiene free from its isomeric 3-methyl-1, 4-cyclohexadiene.
(b) 50% yield of 3-methyl-1, 4-cyclohexadiene free from its isomeric 1-methyl-1, 4-cyclohexadiene
(c) 50% yield of both 3-methyl-1, 4-cyclohexadiene and 1-methyl-1, 4-cyclohexadiene
(d) 1-methylhexaene as the only product.

(iii) Birch reduction of benzoic acid gives

(a) 1, 4-cyclohexadiene-1-carboxylic acid
(b) a mixture of 1, 4-cyclohexadiene-1-carboxylic acid and 2, 5-cyclohexadiene-1-carboxylic acid.
(c) 2, 5-cyclohexadiene-1-carboxylic acid
(d) 1-cyclohexaene-1-carboxylic acid.

Assertion Reason Type

Given below are the two statements for each question. Based on the following key, answer correctly each question.
(a) Both statements are correct and Statement-2 is a correct explanation of Statement-1.
(b) Both statements are correct but Statement-2 is not a correct explanation of Statement-1.
(c) Statement-1 is correct and Statement-2 is incorrect.
(d) Statement-1 is incorrect and Statement-2 is correct.

	Statement 1	**Statement-2**
1.	The overall rate of an electrophilic reaction, except sulphonation in benzene and deuterated benzene, are identical.	The rate-determining step in electrophilic substitution reaction is the binding of the electrophile to the aromatic ring without cleavage of a C—H or C—D bond.
2.	Iodine solution in benzene is brown in colour.	Brown colour is due to charge-transfer complex between iodine and benzene.
3.	Phenyl cation is more stable than cyclohexyl cation.	Vinyl carbocation is less stable than 2° carbocation.
4.	Azulene is a aromatic molecule.	Azulene satisfies $4n + 2$ rule.
5.	Benzene is a suitable solvent for the Friedel-Crafts alkylation of PhBr.	Benzene is more reactive than bromobenzene in the Friedel-Crafts reaction.
6.	Both cyclopentadienyl anion and cyclohexadienyl anion contain 6 electrons in the ring but only former is aromatic.	There exists continuous cyclic overlap in cyclopentadienyl anion and not in cyclohexadienyl anion.
7.	Cyclopentadiene is much less acidic than 1,3-cyclohexadiene	Removal of H^+ converts cyclopentadiene into aromatic species but not in 1,3-cyclohexadiene
8.	Though [14]-annulene ($C_{14}H_{14}$) contains 14 electrons (= 4 × 3 + 2), yet it is not aromatic	[14]-annulene is not a planar molecule
9.	Unlike in benzene, all bond lengths in naphthalene are not of the same size.	Naphthalene is the resonance hybrid of three structures.
10.	Borazine behaves as an aromatic molecule	Borazine is planar with six delocalized electrons.
11.	Iodine solution in benzne is brown in colour.	Iodine forms brown-coloured π complex with benzene.

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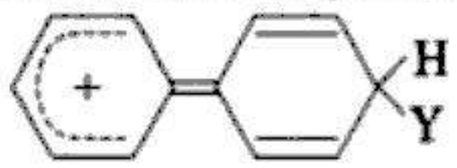


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(d) The positive charge of the intermediate can be dispersed by the second phenyl group when the latter is attached to *ortho* or *para*, but not to *meta*.

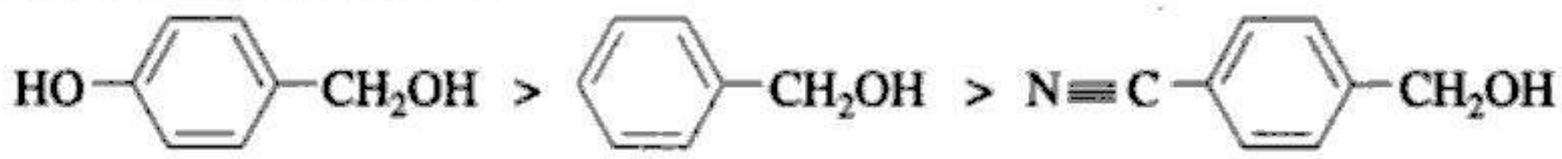


Intermediate

14. (a) The two hydrogens are in the same plane as the ring. This arrangement permits overlap of π cloud with the p orbital of the side carbon.

(b) Resonance stabilisation of the anion, with dispersal of negative charge, increases the acidity.

(c) The reactivity is largely determined by the stability of the carbocations being formed. The electron releasing group stabilises the carbocation. The group  is most strongly electron releasing group, followed by  and then  (in fact, the latter is electron withdrawal group). Hence, the correct order is

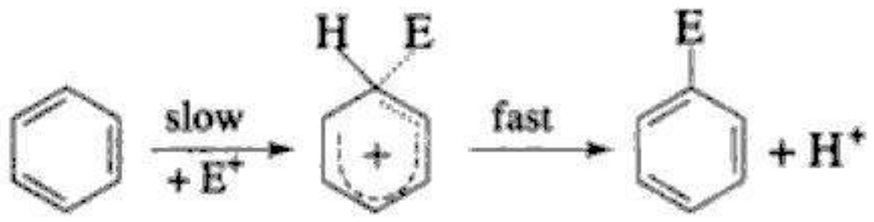


(d) The reactivity is largely determined by the stability of the carbocation being formed.

15. (a) The formation of intermediate arenium cation is slow while the elimination of H^+ from this cation is fast. The former involves the removal of aromaticity while the latter restores aromaticity.

(b) The C—D bonds are stronger than C—H bonds. In fact, the bond with the heavier isotope is slightly stronger than that with the lighter isotope.

(c) In electrophilic substitution reactions, the rate-determining step is the formation of arenium cation.



In this step, E^+ bonds to the aromatic ring without cleavage of a C—H bond. The latter is broken in the second step, which is fast as it restores the stable aromatic system. Since C—H or C—D bond is not broken in the rate-determining step, the overall rates of reaction are identical.

16. (b) In sulphonation reaction, both steps involving the formation of arenium cation and its conversion to the substituted benzene determine the overall rate of reaction. In the second step, the loss of D^+ from the deuterated σ complex is a little slower than the loss of H^+ from the ordinary σ complex.

(d) The product contains both $PhCH_2CH_2CH_3$ and $PhCH(CH_3)_2$.

17. (a) ICl is more electrophilic than I_2 because it is polarised as $^{\delta+}I—Cl^{\delta-}$.

(b) In $—NH_2COCH_3$, the C of the $^{\delta+}C{=}O^{\delta-}$ has a positive charge and this diminishes the ability of $—\ddot{N}—$ to donate a pair of electrons to the arenonium ion.

(d) In acidic medium, $PhN(CH_3)_2$ exists as $PhNH(CH_3)_2$ which is a *meta* director.

18. (a) At low temperature, kinetic control prevails for formation of the rate-determining transition state while at higher temperature, the thermodynamically more stable product (*p*-toluenesulphonic acid) predominates.

(b) Benzene is more reactive than bromobenzene in the Friedel-Crafts reaction and thus benzene is alkylated in preference to bromobenzene. Nitrobenzene is a suitable solvent as it is not alkylated due to the presence of nitro-group which has a deactivating effect.

(c) In attack at the *o*, *p*-positions the unreacted ring can stabilise the +charge on the attached C of the σ complex by electron-releasing delocalisation that results in delocalising the +charge to both rings.

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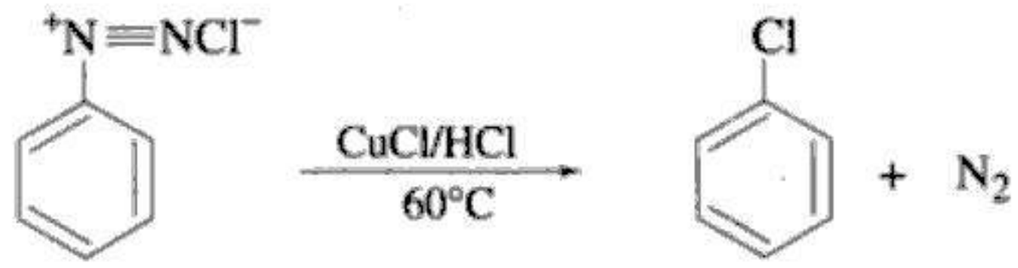
$$R{-}C{\equiv}N + H_2O \xrightarrow[\text{or } H_2O_2 - NaOH]{\text{conc. HCl}} RCONH_2; \qquad R{-}C{\equiv}N + H_2O \xrightarrow[\text{or alkali}]{\text{Mineral acid}} RCOOH + NH_3$$

$$R{-}C{\equiv}N + 4H \xrightarrow[\text{or } H_2/Ni \text{ or } LiAlH_4]{Na/C_2H_5OH} RCH_2NH_2$$

Alkyl Halides

Methods of preparation

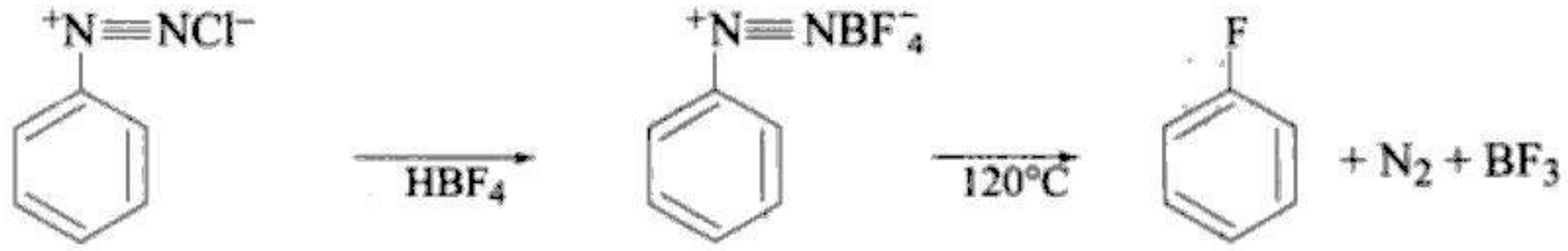
These can be prepared by Friedel-Crafts halogenation. Iodination cannot be carried out by this method as the reaction is endothermic. Aryl halides can also be prepared by Sandmeyer reaction. In this reaction, benzenediazonium chloride is treated with cuprous chloride or cuprous bromide dissolved in the corresponding acid.



Iodobenzene is obtained by warming diazonium salt solution with aq. KI solution.

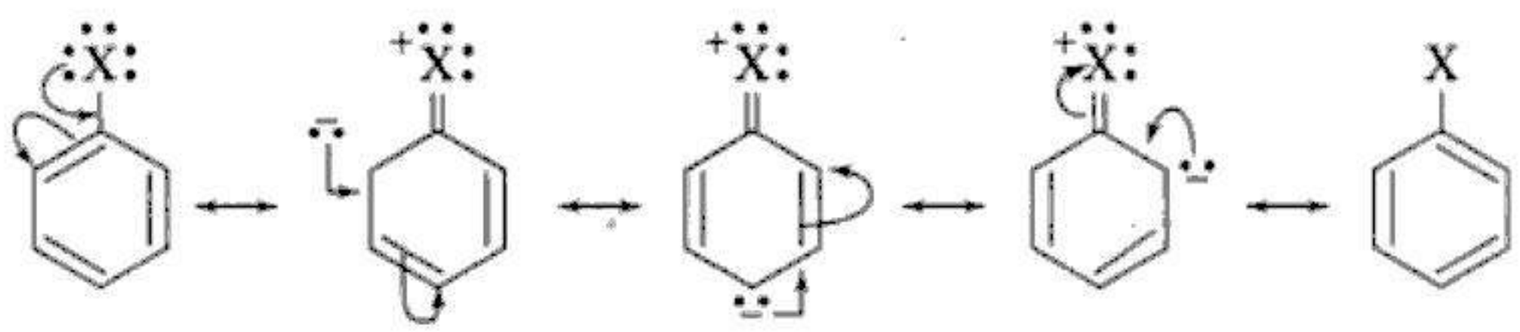


Fluorination is carried out by warming diazonium salt solution with HBF_4. This reaction is known as Schiemann reaction.



Chemical Reactions

In general, aryl halides are less reactive than alkyl halides towards nucleophilic substitution reactions. This is due to the resonance effect in which lone pair of electron on halogen atom is delocalized to benzene ring imparting a partial double bond character to C—X bond.



In alkyl halide, the C—X bond involves sp^3(C) whereas in aryl halide, sp^2(C) is involved. Since the sp^2(C) is more electronegative than the sp^3(C), the C—X bond in aryl halide is shorter than in alkyl halides. This makes C—X bond more strong in aryl halides.

Under normal conditions, halobenzenes are inert to nucleophiles. However, chlorobenzene can be made to react if the experimental conditions are drastic, i.e. high temperature and high pressure.

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(i) The percentages of optical purity of partially racemized bromo and alcohol, respectively, are
(a) 85.7, 60 (b) 60, 85.7 (c) 75, 25 (d) 25, 75

(ii) The percentages of inversion and racemization of the conversion, respectively, are
(a) 30, 70 (b) 70, 30 (c) 33, 67 (d) 67, 33

(iii) The percentage of frontside and backside attack in the conversion, respectively, are
(a) 65, 35 (b) 67, 33 (c) 15, 85 (d) 83, 16

Assertion and Reason Type

Given below are questions, each containing two statements. Answer each question correctly using the following key.
(a) Both statements are correct and Statement-2 is correct explanation of Statement-1.
(b) Both statements are correct and Statement-2 is not correct exsplanation of Statement-1.
(c) Statement-1 is correct and Statement-2 is incorrect.
(d) Statement-1 is incorrect and Statement-2 is correct.

	Statement–1	Statement–2
1.	Aryl halides undergo nucleophilic substitution with ease.	The carbon-halogen bond in aryl halides has partical double bond character.
2.	Benzonitrile is prepared by the reaction of chlorobenzene with potassium cyanide.	CN^- is a strong nucleophile.
3.	The rate of solvolyses of an alkyl halide following S_N1 mechanism increases in the presence of $AgNO_3$.	The precipitation of AgX helps increasing the rate of reaction.
4.	The more acidic the nucleophlic solvent, the faster the rate of S_N1 solvolysis.	The greater the acidity of the H, the more effective is the hydrogen bonding which leads to acceleration of dissociation of alkyl halide.
5.	The rate of solvolysis $(CH_3)_3CBr$ decreases with increase in polarity of the solvent.	The formation of $(CH_3)_3C^+$ increase with increase in polarity of solvent.
6.	In E1cb mechanism, the rate of overall elimination reaction in RX is independent of the nature of X.	X is eliminated in the fast step from a carboc--ation.
7.	The order of nucleophilic displacement of X follows the order RI > RBr > RCl >>RF.	The weaker the Brönsted basicity of X^-, the better leaving group is X^- and the more reactive is RX.
8.	The C—Cl bond of vinyl chloride is shorter and stronger than the C—Cl bond of alkyl chloride.	The vinyl chloride involves reonance $CH_2{=}CH_2{-}Cl \leftrightarrow + \overset{+}{C}H_2{-}CH{=}\overset{+}{C}l$.
9.	Vinyl chloride does not undergo S_N1 and S_N2 substitution reactions.	Vinyl cation is unstable species.
10.	Strong base leads to less elimination than substitution in alkyl halide.	Strong base helps extracting H^+ from the β-position.
11.	The E2 elimination in alkyl halide is stereospecific.	The transition state in E2 elimination in alkyl halide involves *cis*-coplanar conformation.
12.	*tert*-Butyl fluoride is solvolyzed only in very acidic conditions.	H- Bonding of F with a strong acid helps departuring F.
13.	*tert*-Butyl chloride is solvolyzed much slower than 2-chloro-1,1,1-trifluoro-2-methylpropane (A).	Carbocation formed in A is destabilized due to electron-withdrawing F_3C group.
14.	$(CD_3C^+$ is not stable as $(CH_3)_3C^+$.	CD_3 is as good an electron-donator as CH_3.

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$$\underset{\text{isopropyl alcohol}}{CH_3CHOH(CH_3)} \xrightarrow{K_2Cr_2O_7} \underset{\text{acetone}}{CH_3C(=O)CH_3}$$

3° alcohol is not oxidizable as it does not contain α-hydrogen.

The Jones reagent (a chromic acid in aqueous acetone solution) is a mild oxidizing agent. It oxidizes –OH without affecting or rearranging the double bond (if present). For example,

$$CH_3CH{=}CHCH(OH)CH_3 \xrightarrow{\text{Jones reagent}} CH_3CH{=}CHCOCH_3$$

MnO_2, a milder oxidizing agent, oxidizes allylic and benzylic — OH group without affecting double bond, if present. For examples

$$CH_3CH_2CH{=}CHCH_2OH \xrightarrow{MnO_2} CH_3CH_2CH{=}CHCHO.$$

$$PhCH_2OH \xrightarrow{MnO_2} PhCHO$$

$$PhCH(OH)CH_2CH_2OH \xrightarrow{MnO_2} PhCOCH_2CH_2OH$$

Characterization of Alcohols

1. Oxidation Method

$$1^\circ \text{ alcohol} \xrightarrow{[O]} \text{aldehyde} \xrightarrow{[O]} \text{carboxylic acid}$$

$$2^\circ \text{ alcohol} \xrightarrow{[O]} \text{ketone}$$

$$3^\circ \text{ alcohol} \xrightarrow{[O]} \text{no reaction}$$

However, drastic oxidation will convert ketone (formed from 2° alcohol) and 3° alcohol into carboxylic acid containing fewer carbon atoms.

When the vapours of alcohols are passed over hot metallic Cu at 570 K, limited oxidation takes place.

$$1^\circ \text{ alcohol}: \quad CH_3CH_2OH \xrightarrow{[O]} CH_3CHO + H_2O$$

$$2^\circ \text{ alcohol}: \quad CH_3\underset{\underset{OH}{|}}{C}HCH_3 \xrightarrow{[O]} CH_3COCH_3 + H_2O$$

$$3^\circ \text{ alcohol}: \quad (CH_3)_3COH \xrightarrow{[O]} CH_3\underset{\underset{CH_3}{|}}{C}{=}CH_2 + H_2O$$

2. Victor-Meyer Method The alcohols are treated with P_4 and I_2 to form an alkyliodide. This on treatment with $AgNO_2$ yields nitroalkanes. On treating the latter with aqueous $NaNO_2$ acidified with HCl and then alkaline with NaOH produces different colouration.

1° alcohol

$$CH_3CH_2OH \xrightarrow{P+I_2} CH_3CH_2I \xrightarrow{AgNO_2} CH_3CH_2NO_2 \xrightarrow{HNO_2} CH_3{-}\underset{\underset{NOH}{\|}}{C}{-}NO_2$$

nitrolic acid
(Blood red colour)

2° alcohol

$$(CH_3)_2CHOH \xrightarrow{P+I_2} (CH_3)_2CHI \xrightarrow{AgNO_2} (CH_3)_2CHNO_2 \xrightarrow{HNO_2} (CH_3)_2\underset{\underset{NO}{|}}{C}NO_2$$

pseudo nitrol
(Blue colour)

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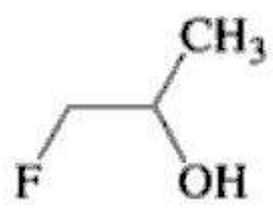
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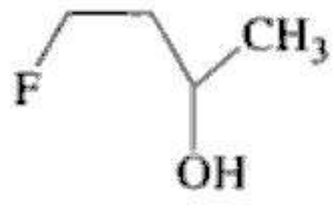
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23. The dehydration of 1-butanol gives
(a) 1-butene as the main product
(b) 2-butene as the main product
(c) equal amounts of 1-butene and 2-butene
(d) 2-methylpropene

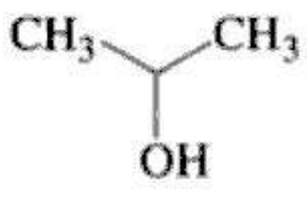
24. The order of reactivity of the following alcohols



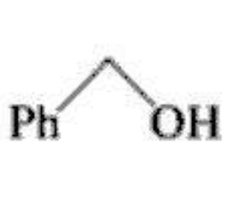
I



II



III



IV

towards concentrated HCl is
(a) I > II > III > IV (b) I > III > II > IV (c) IV > III > II > I (d) IV > III > I > II (1997)

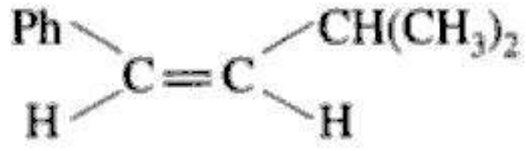
25. 3, 3-Dimethyl-2-butanol, on reacting with concentrated HCl, gives
(a) 3,3-dimethyl-2-chlorobutane
(b) 2,3-dimethyl-2-chlorobutane
(c) a mixture of 3,3-dimethyl-2-chlorobutane and 2,3-dimethyl-2-chlorobutane.
(d) 3,3-dimethyl-1-chlorobutane

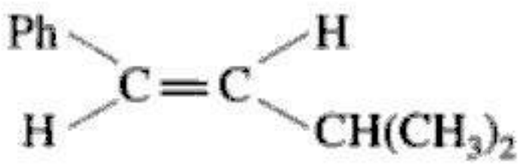
26. The reaction of neopentyl alcohol with concentrated HCl gives
(a) neopentyl chloride
(b) 2-chloro-2-methylbutane
(c) 2-methyl-2-butene
(d) a mixture of neopentyl chloride and 2-methyl-2 butene.

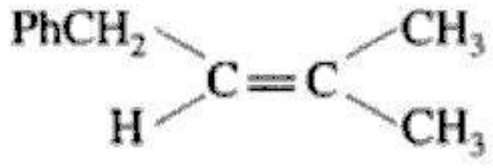
27. The reaction of neopentyl alcohol with $SOCl_2$ gives
(a) neopentyl chloride
(b) 2-chloro-2-methylbutane
(c) 2-methyl-2-butene
(d) a mixture of neopentyl chloride and 2-methyl-2-butene

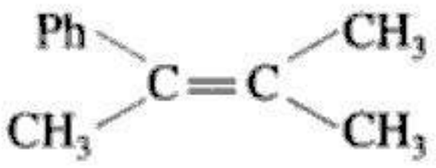
28. The reaction of 3-buten-2-ol with aqueous HBr gives
(a) 3-bromo-1-butene only
(b) 1-bromo-2-butene only
(c) a mixture of 3-bromo-1-butene and 1-bromo-2-butene
(d) 4-bromo-1-butene.

29. The major product in the reaction of $PhCH_2CH(OH)CH(CH_3)_2$ with concentrated H_2SO_4 is

(a) 

(b) 

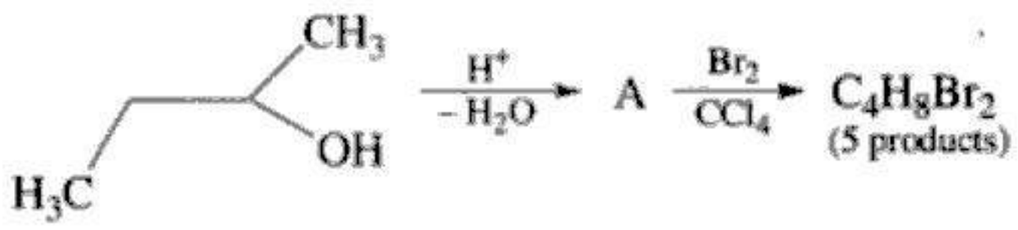
(c) 

(d) 

30. HBr reacts fastest with
(a) $C_6H_5CH_2OH$ (b) p-$O_2NC_6H_4CH_2OH$ (c) p-$CH_3OC_6H_4CH_2OH$ (d) p-$ClC_6H_4CH_2OH$

31. HBr reacts slowest with
(a) $C_6H_5CH_2OH$ (b) p-$O_2NC_6H_4CH_2OH$ (c) p-$CH_3OC_6H_4CH_2OH$ (d) p-$ClC_6H_4CH_2OH$

32. In the reaction



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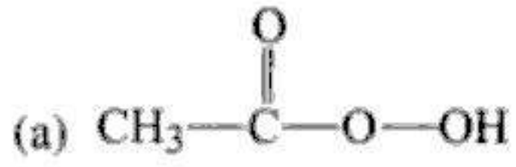
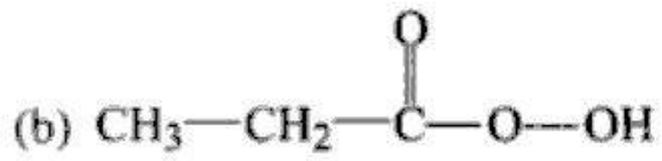
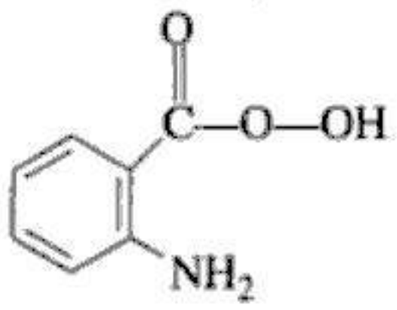
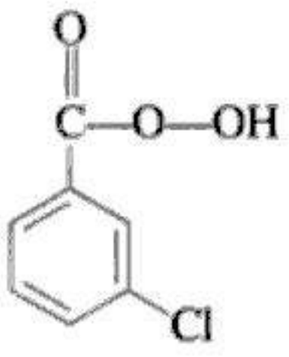
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(ii) The reactions I and II, respectively, follow
(a) first-order and first-order rate laws
(b) first-order and second-order rate laws
(c) second-order and first-order rate laws
(d) second-order and second-order rate laws

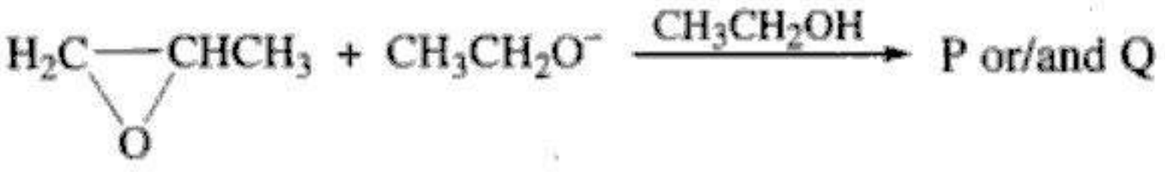
(iii) In both the reactions, the reactants react to give an intermediate, respectively, via
(a) reversible and irreversible steps
(b) reversible and reversible steps
(c) irreversible and reversible steps
(d) irreversible and irreversible steps

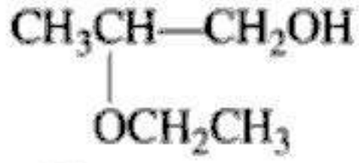
3. Oxiranes are synthesized by treating an alkene with an organic peroxy acid. This process is known as epoxidation. The highly strained three-membered ring in epoxide makes it much more reactive towards nucleophilic substitution than other ethers.

(i) The most commonly used peroxy acid is

(a) 
(b) 
(c) 
(d) 

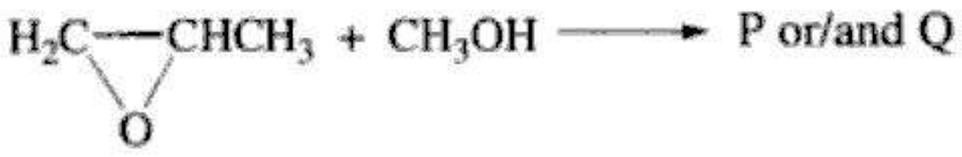
(ii) The base-catalyzed ring opening of the epoxide is represented as follows.

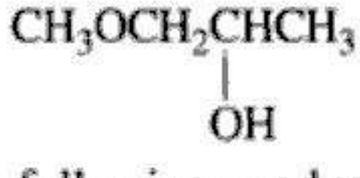
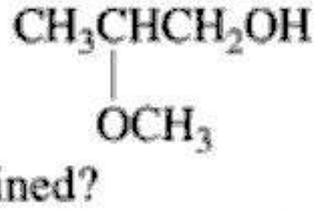


where P is  and Q is 

Which of the following product(s) is/are obtained?
(a) P only
(b) Q only
(c) Equal mixture of P and Q
(d) Unequal mixture of P and Q

(iii) The acid-catalyzed ring opening of the expoxide is represented as follows.

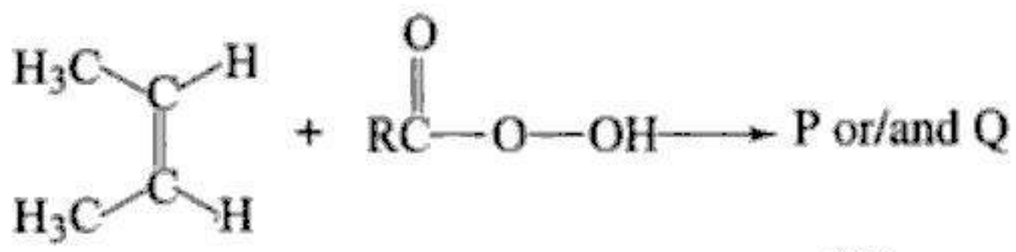


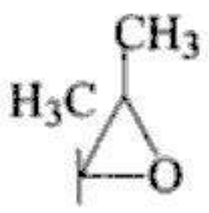
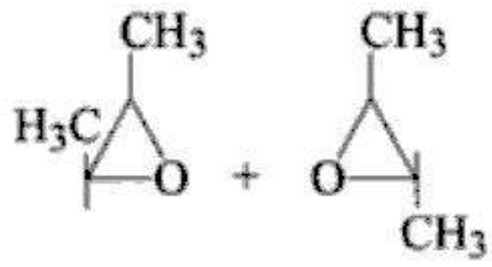
where P is  and Q is 

Which of the following product(s) is/are obtained?
(a) P only
(b) Q only
(c) Equal mixture of P and Q
(d) Unequal mixture of P and Q

4. Oxiranes are synthesized by treating an alkene with an organic peroxy acid. This process is known as epoxidation. The highly strained three-membered ring in epoxide makes it much more reactive towards nucleophilic substitution than other ethers.

(i) In the reaction



where P is  (*cis*-2,3-dimethyoxirane) and Q is  The product(s) obtained

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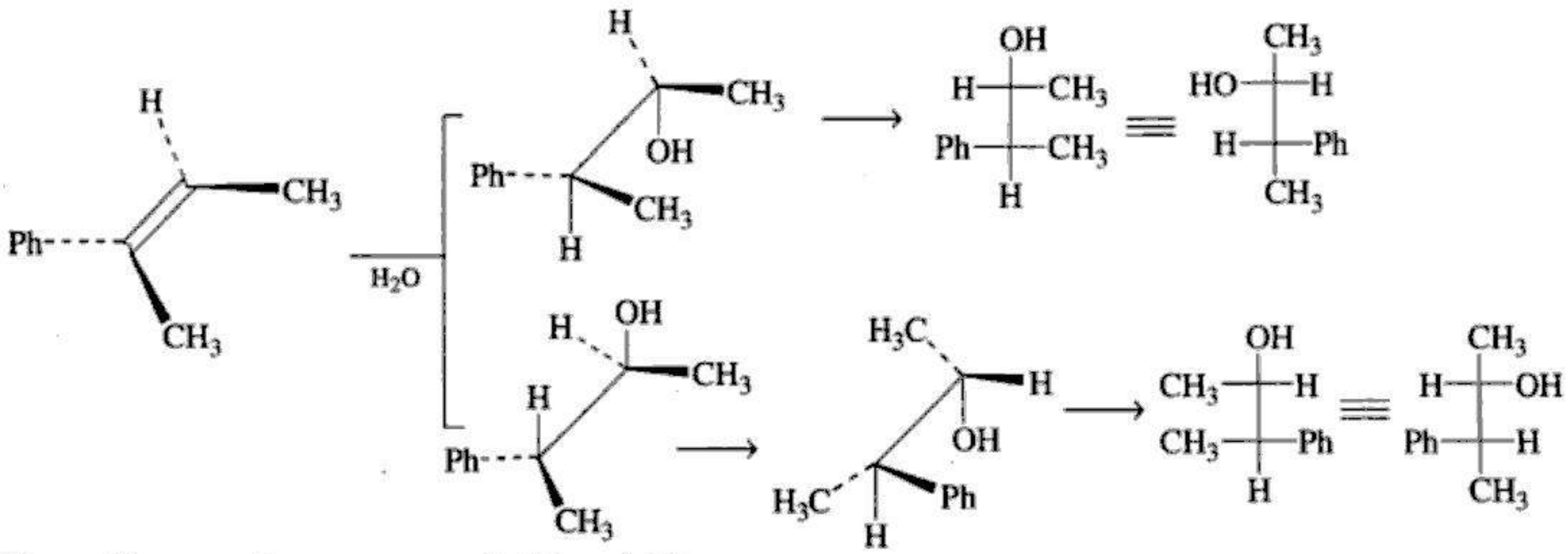
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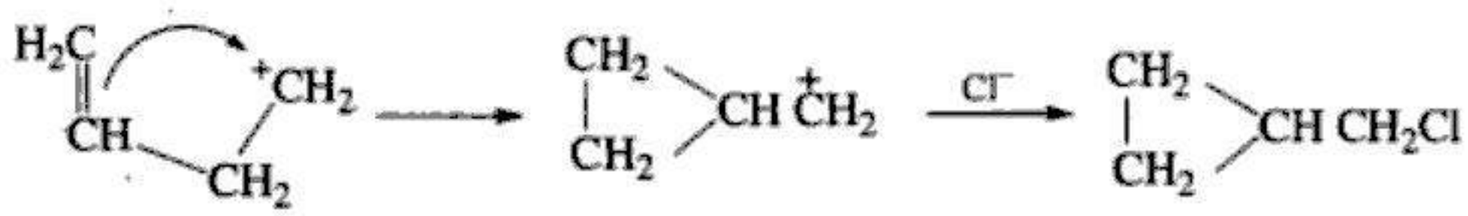
25. 

26. *Trans*-alkene produces compounds (b) and (d).

27. Let R ≡ $-CH_2CH=CH_2$. The reaction proceeds as follows.

$$RCH_2OH \xrightarrow{H^+} RCH_2-\overset{+}{O}H_2 \longrightarrow R\overset{+}{C}H_2$$

$$R\overset{+}{C}H_2 \xrightarrow{Cl^-} RCH_2Cl$$

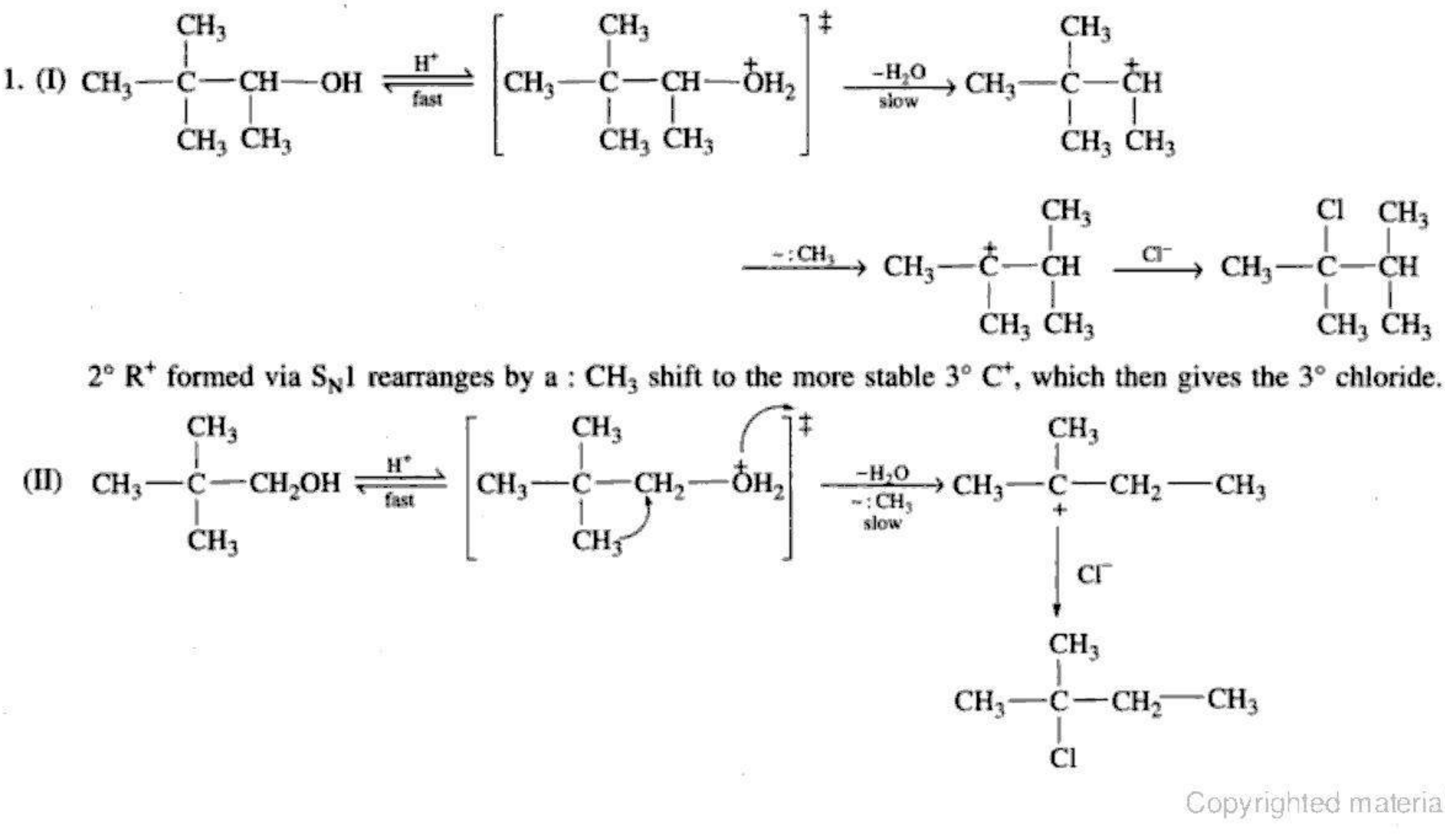


$$H_2C=CHCH_2\overset{+}{C}H_2 \xrightarrow{-H} H_2\overset{+}{C}CH=CHCH_3 \xrightarrow{Cl^-} ClH_2CCH=CHCH_3$$

$$H_2C=CHCH_2\overset{+}{C}H_2 \xrightarrow{-H} H_2C=CH\overset{+}{C}HCH_3 \longrightarrow H_2C=CHCH(Cl)CH_3$$

28. The compounds CH_3CH_2OH and $CH_3CH(OH)CH_3$ show positive iodoform test.

Linked Comprehension Type

1. 

2° R^+ formed via S_N1 rearranges by a : CH_3 shift to the more stable 3° C^+, which then gives the 3° chloride.

(II)

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Aldol Condensation and Cannizzaro Reaction

29. The Cannizzaro reaction is not given by
(a) trimethylactaldehyde (b) benzaldehyde
(c) acetaldehyde (d) formaldehyde (1983)

30. *m*-Chlorobenzaldehyde on reaction with concentrated KOH at room temperature gives
(a) potassium *m*-chlorobenzoate and *m*-hydroxybenzaldehyde
(b) *m*-hydroxybenzaldehyde and *m*-chlorobenzyl alcohol
(c) *m*-chlorobenzyl alcohol and *m*-hydroxybenzyl alcohol
(d) potassium *m*-chlorobenzoate and *m*-chlorobenzyl alcohol (1992)

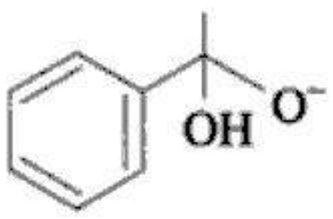
31. Which of the following compounds undergoes the Cannizzaro reaction?
(a) Acetaldehyde (b) Benzaldehyde (c) Acetone (d) Propanal

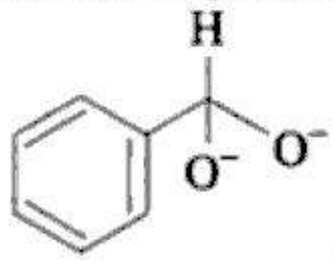
32. In the Cannizzaro reaction given below,

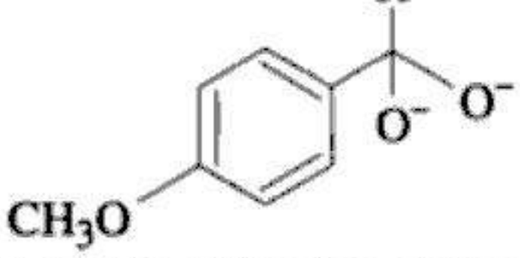
$$2Ph{-}CHO \xrightarrow{{}^{-}OH} Ph{-}CH_2OH + PhCO_2^-$$

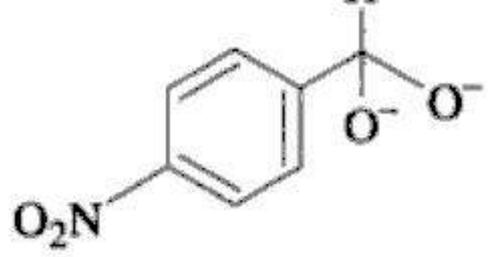
the slowest step is
(a) the attack of ^-OH at the carbonyl group,
(b) the transfer of hydride to the carbonyl group,
(c) the abstraction of proton from the carboxylic acid,
(d) the deprotonation of $Ph{-}CH_2OH$ (1996)

33. In a Cannizaro reaction, the intermediate that will be the best hydride donor is

(a) 

(b) 

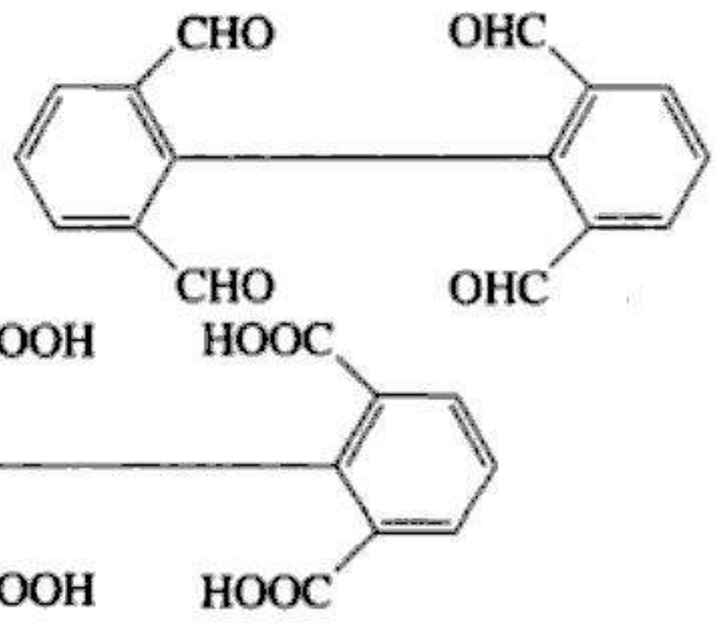
(c) 

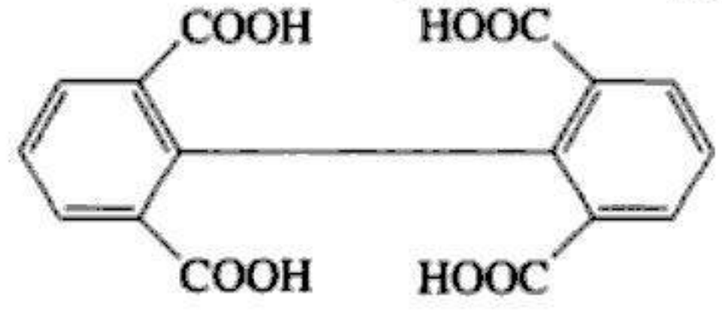
(d) 

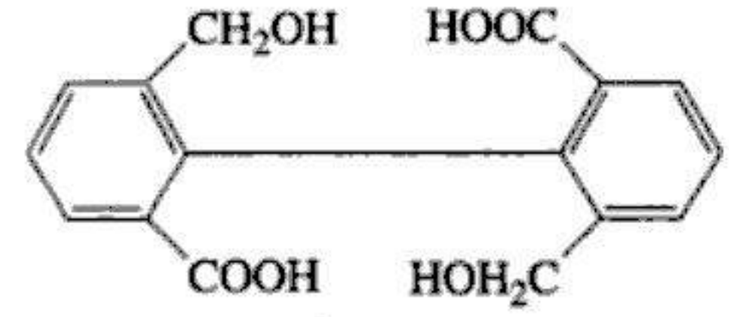
(1997)

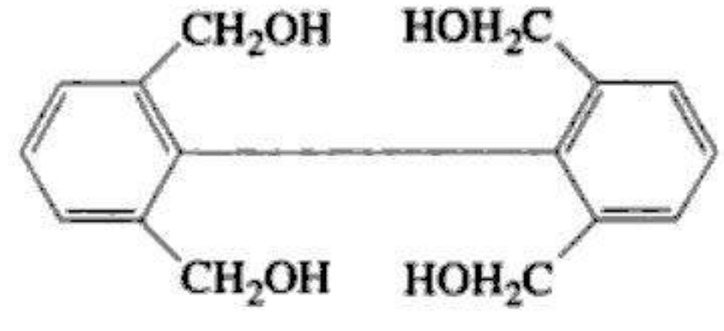
34. Which of the following compounds does not undergo aldol condensation?
(a) $C_6H_5CH_2CHO$ (b) C_6H_5CHO (c) CH_3COCH_3 (d) CH_3CH_2CHO

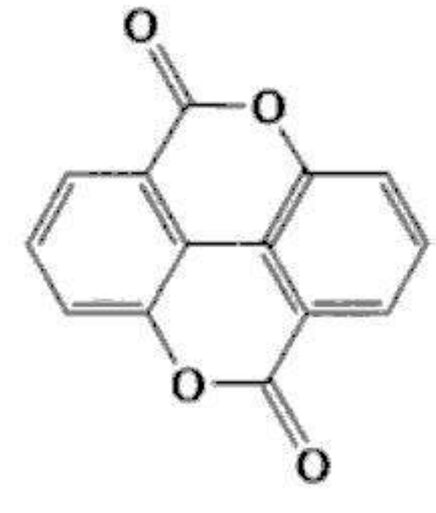
35. A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives
(a) benzyl alcohol and sodium formate (b) sodium bezoate and methyl alcohol
(c) sodium benzoate and sodium formate (d) benzyl alcohol and methyl alcohol (2001)

36. In the reaction 
$\xrightarrow[\text{(ii) } H^+/H_2O]{\text{(i) NaOH/100°C}}$ A the product A is

(a) 

(b) 

(c) 

(d) 

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Assertion and Reason Type

Given below are a few questions containing two statements. Based on the following key, answer correctly each question.

(a) Both statements are correct and Statement-2 is correct explanation of Statement-1.
(b) Both statements are correct and Statement-2 is not correct explanation of Statement-1.
(c) Statements -1 is correct and Statement-2 is incorrect.
(d) Statements-1 is incorrect and Statement-2 is correct.

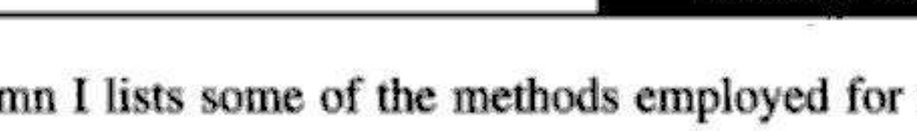
	Statement-1	Statement-2	
1.	Acetic acid does not undergo haloform reaction	Acetic acid has no alpha hydrogen.	(1998)
2.	Aliphatic carbonyl compounds are more reactive than the corresponding aryl compounds towards nuclephilic addition reaction.	The electron-donating resonance effect of benzene makes aryl compounds less reactive.	
3.	Aldol equilibrium generally favours condensation product in the case of mono substituted acetaldehyde (RCH_2CHO). The equilibrium favours starting material for disubstituted acetaldehyde (R_2CHCHO) and for most ketones.	Steric factors seems to be responsible for this behaviour.	
4.	An oxime $>C=\ddot{N}-\ddot{O}H$ is a stronger acid than $NH_2\ddot{O}H$.	The conjugate base of oxime is stablilized due to delocalization of negative charge by extended π-bonding.	
5.	Hydrazone of aldehydes are not prepared in highly acidic medium.	Nucleophicity of hydrazine is enchanced in highly acidic conditions.	
6.	*o*-Hydroxybenzaldehyde is liquid at room temperature while *p*-hydroxy-benzaldehyde is a high melting solid.	*o*-Hydroxybenzaldehy involves inter-molecular hydrogen bonding while *p*-hydroxybenzaldehyde involves intra-molecular hydrogen bonding.	
7.	CH_3COCH_2Cl shows enhanced reactivity towards S_N2 reaction as compared to $CH_3CH_2CH_2Cl$.	The transition state in CH_3COCH_2Cl is stabilized due to extended conjugation by CO group.	

Matrix Match Type

1. Column I lists some of the methods employed for reduction and the reagents used in these methods are given in Column II. Match correctly the items in Column I and II.

Column I	Column II
(a) Wolff-Kishner reduction	(p) Pd/C (S or quinoline)
(b) Clemmensen reduction	(q) $HSCH_2CH_2SH$; Ni
(c) Rosenmund reduction	(r) H_2NNH_2 and strong base
(d) Raney Ni desulphurization	(s) Zn/Hg and HCl

2. Column I lists some of the reduction reactions and Column II lists the reducing agents. Match each entry in Column I with correct choice given in Column II.

Column I	Column II
(a) $CH_3CH(CH_3)COCl \rightarrow CH_3CH(CH_3)CHO$	(p) Lithium aluminium hydride
(b) $CH_3CH(CH_3)COCl \rightarrow CH_3CH(CH_3)CH_2OH$	(q) BH_3/THF followed by H_2O_2, OH^-
(c) 	(r) Lithium tri-*t*-butoxyaluminium hydride
(d) $CH_3CH{=}CHCH_2CHO \rightarrow CH_3CH{=}CHCH_2CH_3$	(s) H_2NNH_2 and strong base

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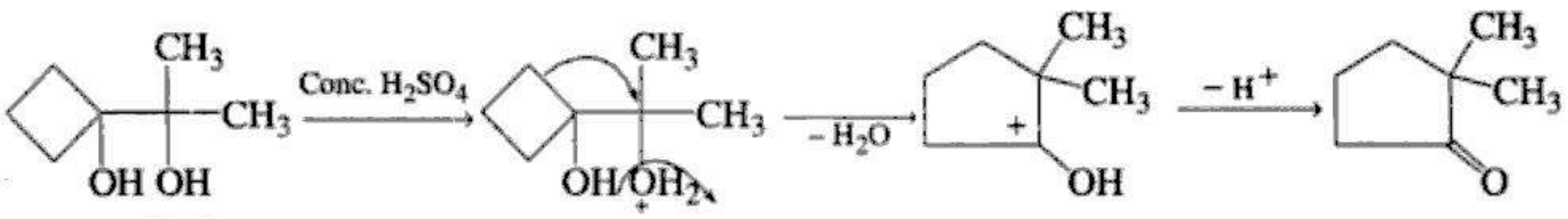
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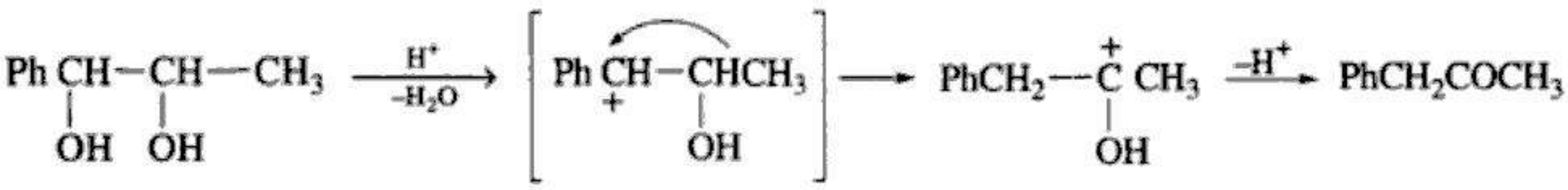


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42. same as Q.41.

43.



First step is the formation of more stable carbocation. In second step, H is migrated rather than CH_3.

44. Grignard reagent reacts both with acetaldehyde and acetone.

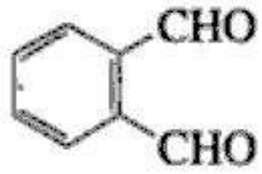
45. A compound containing CH_3CO— or $CH_3CH(OH)$— shows iodoform test. $CH_3CH_2CH_2COCH_3$ (2-pentanone) shows this test.

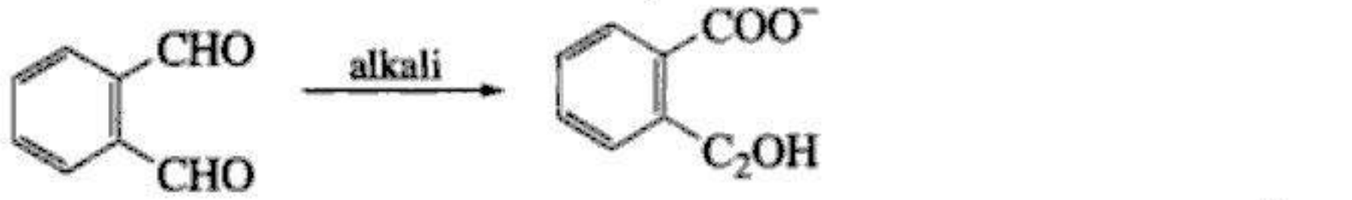
46. Diethyl ketone ($C_2H_5COC_2H_5$) will not show iodoform test.

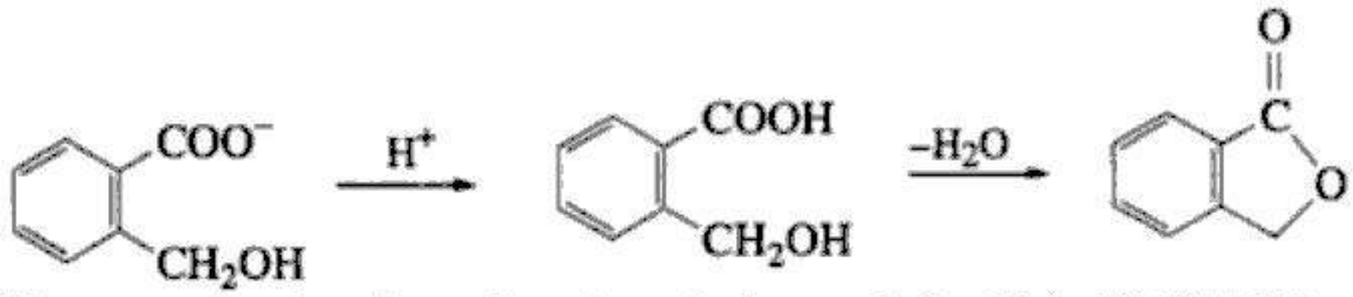
47. $C_2H_5COC_2H_5$ does not show iodoform test.

48. The reaction is called a Perkin condensation.

49. Carboxylic acid whose molecule has a hydroxyl group on a γ or δ carbon undergoes an intramolecular esterification to give cyclic esters known as γ- or δ-lactone. This reaction is acid catalysed.

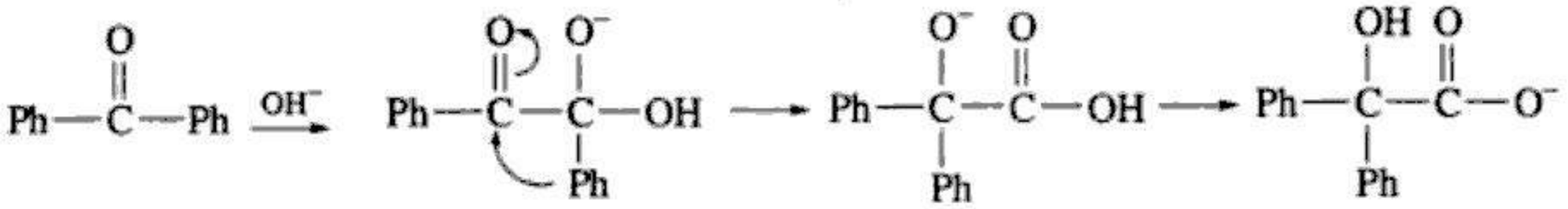
Of the given compounds,  will satisfy the above requirement after it has undergone intramolecular Cannizzaro reaction in the presence of alkali.





50. First reaction involves decarboxylation and the **E** is $PhCO^*CH_3$. The second reaction is iodoform reaction giving $PhCOO^-\ Na^+$ (**F**) and $^*CHI_3$ (**G**).

51. This is benzilic acid rearrangement.



Multiple Correct Choice Type

1. Aldol condensation is shown by an aldehyde or ketone with α-hydrogen atom. Propanal (CH_3CH_2CHO) and 2-methylpropanal ($CH_3CH(CH_3)CHO$) will show this condensation.

2. Acetophenone ($C_6H_5COCH_3$) contains CH_3CO— group. This will show iodoform test. Also 2-hydroxypropane ($CH_3CHOHCH_3$) which contains CH_3CHOH— group will show iodoform test.

3. Ethyl chloride and benzaldehyde will react with ethanolic KCN.

4. Aldehydes and ketones containing α-hydrogen atom show aldol condensation. Thus, the compounds CH_3CHO and CH_3COCH_3 show these condensation.

5. The aryl group in aromatic aldehyde retards the addition reaction across the CO group.

6. Friedel-Crafts alkylation and Reimer-Tiemann reaction involves the formation of C—C bond.

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Chapter 28

Carboxylic Acids

Methods of Preparation

1. Oxidation of primary alcohols $R—CH_2OH \xrightarrow{KMnO_4} R—COOH$

2. Oxidation of alkylbenzenes $C_6H_5—R \xrightarrow[\text{or } K_2Cr_2O_7]{KMnO_4} C_6H_5—COOH$

3. Carbonation of Grignard reagent $RMgX + O{=}C{=}O \rightarrow RCOO^-MgX^+ \xrightarrow{H^+} R—COOH + Mg^{2+} + X^-$

RMgX may be prepared from RX by adding Mg.

4. Hydrolysis of nitriles $R—C{\equiv}N + 2H_2O \xrightarrow[\text{or base}]{\text{acid}} R—COOH + NH_3$

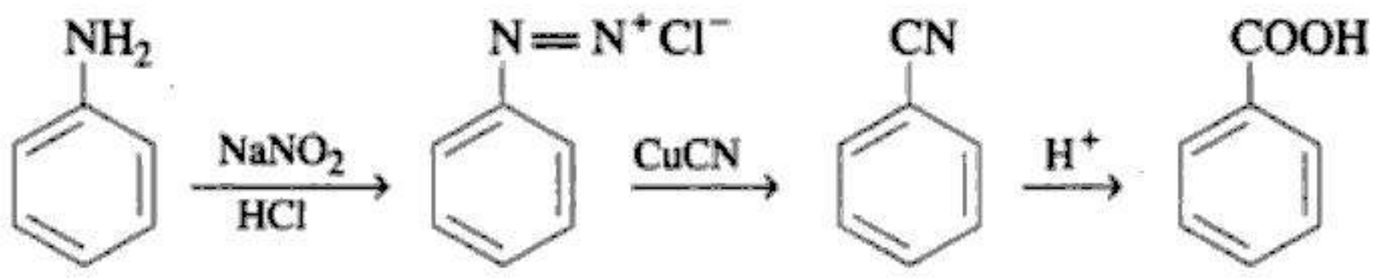
Nitriles may be prepared by adding NaCN to the corresponding halides. For example,

$$CH_3CH_2CH_2Br + CN^- \rightarrow CH_3CH_2CH_2CN \xrightarrow[H^+]{H_2O} CH_3CH_2CH_2COOH$$

The above substitution of X with CN is applicable only when the halide is a primary halide. Tertiary halides yield alkene and for secondary halide, the yield of substitution product is poor.

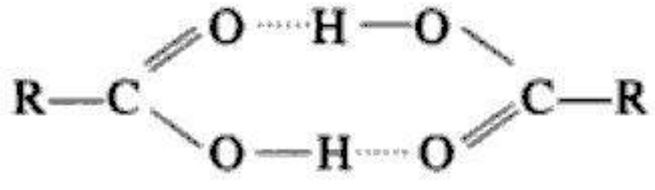
$$\underset{\substack{\text{tert-butyl bromide}}}{CH_3—\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}—Br} + CN^- \rightarrow \underset{\substack{\text{isobutylene}}}{CH_3—\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2} + HCN$$

Aryl halides are unreactive towards substitution. Thus, aromatic nitriles are prepared via diazonium salt. For example,



Physical Properties

The molecules of carboxylic acids are polar and exhibit hydrogen bonding. The boiling point of a carboxylic acid is higher than that of an alcohol of comparable molar mass. This is due to the fact that the carboxylic acids exist as dimer.



Chemical Reactions

1. Acidity Carboxylic acids are weak acids and their carboxylate anions are strong conjugate bases. The aqueous solutions of carboxylate salts are slightly alkaline due to the hydrolysis of carboxylate anion. Compared to other

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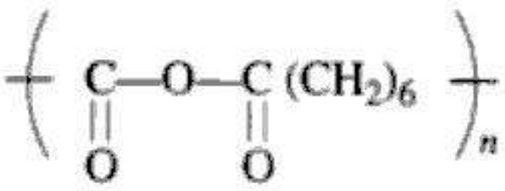
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(v) $HOOC(CH_2)_4COOH \rightarrow$  $+ CO_2$;

Cyclopentanone

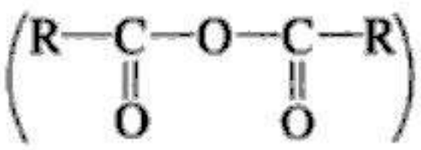
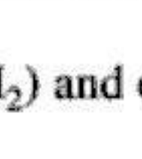
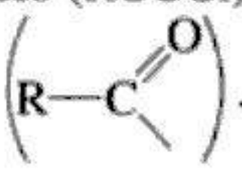
(vi) $HOOC(CH_2)_5COOH \rightarrow$  $+ CO_2$

Cyclohexanone

(vii) $HOOC(CH_2)_6COOH \rightarrow$ 

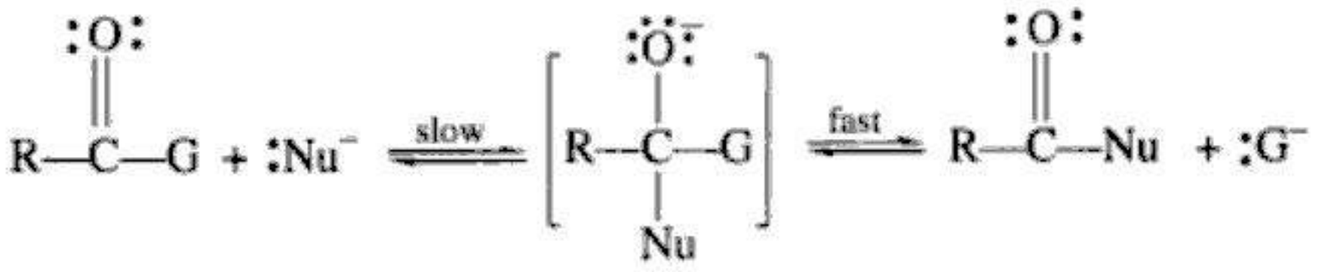
Linear polymeric anhydride

Functional Derivatives of Carboxylic acids

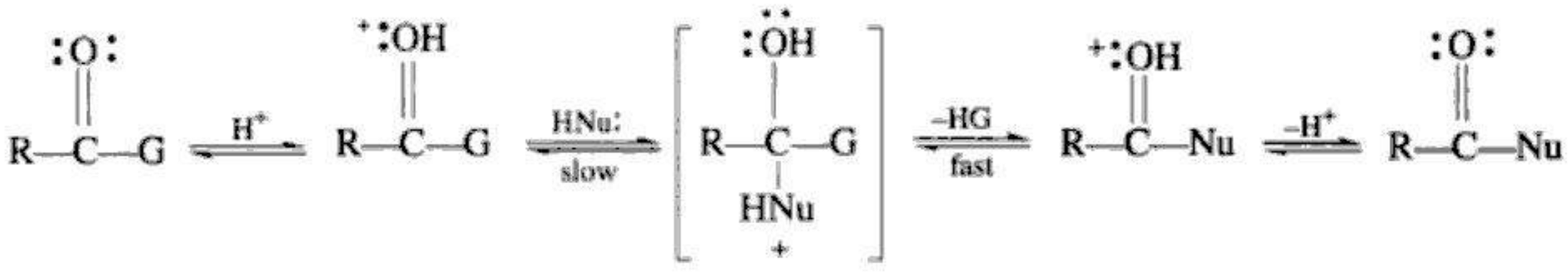
The functional derivatives of carboxylic acids are acid chlorides (RCOCl), anhydride  , amides ($RCONH_2$) and esters  . They all contain acyl group  .

Nucleophilic Substitution Reactions The acyl derivatives undergo nucleophilic substitution reactions. Their mechanisms are as follows.

Basic medium

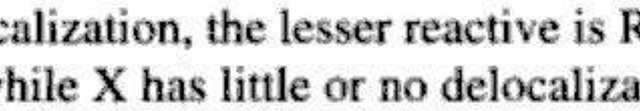


Acidic medium



Reactivity of Acyl Derivatives

The reactivity of RCOG depends on the resonance stabilization of the —CO—G group.



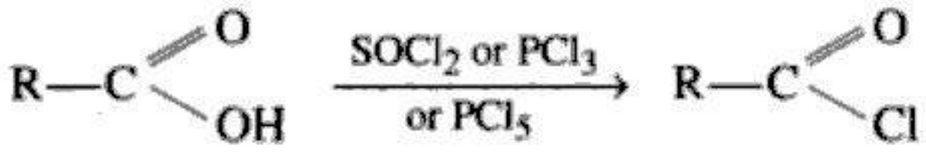
The greater the degree of delocalization, the lesser reactive is RCOG. NH_2 has the greatest degree of delocalization, thus $RCONH_2$ is least reactive, while X has little or no delocalization and thus RCOX is the most reactive.

Thus, the reactivity follows the order: Acid chloride > anhydride > ester > amide

A more reactive derivative may be used to prepare a less reactive derivative by reaction with appropriate nucleophile. Incidently, the reactivity decreases as the base strength of the leaving group increases i.e. $Cl^- < RCOO^- < RO^- < H_2N^-$.

We describe in brief the method of preparation and the main reactions of the above functional derivatives.

Acid Chlorides



($SOCl_2$ is the best as the unwanted products are gases.)

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39. Benzoyl chloride is prepared from benzoic acid by
(a) Cl_2, $h\nu$ (b) SO_2Cl_2 (c) $SOCl_2$ (d) Cl_2, H_2O (2000)

40. Which of the following acids has the smallest dissociation constant?
(a) $CH_3CHFCOOH$ (b) FCH_2CH_2COOH (c) $BrCH_2CH_2COOH$ (d) $CH_3CHBrCOOH$ (2002)

41. Identify the correct order of boiling points of the following compounds:
$\underset{1}{CH_3CH_2CH_2CH_2OH}$, $\underset{2}{CH_3CH_2CH_2CHO}$, $\underset{3}{CH_3CH_2CH_2COOH}$ (2002)
(a) 1 > 2 > 3 (b) 3 > 1 > 2 (c) 1 > 3 > 2 (d) 3 > 2 > 1

42. The reagents used in the reduction reactions
$CH_3COC_6H_4COOH \rightarrow CH_3COC_6H_4CH_2OH$
$CH_3CH{=}CHCH_2COOH \rightarrow CH_3CH{=}CHCH_2CH_2OH$
respectively are
(a) BH_3/THF followed by H_3O^+ and $LiAlH_4$ (b) BH_3/THF and BH_3/THF
(c) $LiAlH_4$ and $LiAlH_4$ (d) $LiAlH_4$ and BH_2/THF

43. The reaction of CH_3CH_2COOH with $2CH_3Li$ yields
(a) CH_3CH_2CHO (b) $CH_3CH_2CH_2CHO$ (c) $CH_3CH_2COCH_3$ (d) $CH_3CH_2C(CH_3)_2$ (OH)

Carboxylic Acid Derivatives

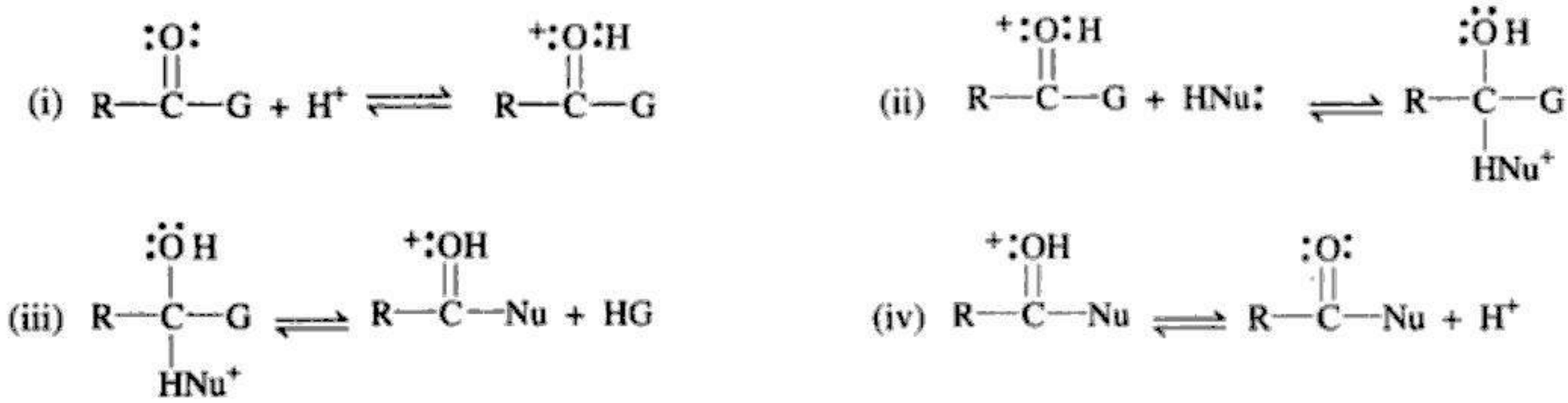
44. Which of the following orders of reactivity of acid derivatives towards a nucleophile is correct?
(a) acid chloride > anhydride > ester (b) acid chloride < anhydride < ester
(c) acid chloride > ester > anhydride (d) anhydride > acid chloride > ester

45. Which of the following orders of reactivity of acid derivatives towards a nucleophile is correct?
(a) anhydride > amide > ester (b) anhydride > ester > amide
(c) amide > anhydride > ester (d) amide > ester > anhydride

46. Which of the following orders regarding the base strength of a leaving group in a reaction of an acid derivative with a nucleophile is correct?
(a) $Cl^- > RCOO^- > RO^-$ (b) $Cl^- > RO^- > RCOO^-$ (c) $RO^- > RCOO^- > Cl^-$ (d) $RO^- > Cl^- > RCOO^-$

47. Which of the following orders regarding the base strength of a leaving group in a reaction of an acid with a nucleophile is correct?
(a) $Cl^- < RO^- < NH_2^-$ (b) $Cl^- > NH_2^- > RO^-$ (c) $RO^- > Cl^- > NH_2^-$ (d) $RO^- > NH_2^- > Cl^-$

48. The mechanism of nucleophilic acyl substitution in the acyl derivative proceeds as follows.



Amongst the above four steps, the slowest step is
(a) Step (i) (b) Step (ii) (c) Step (iii) (d) Step (iv)

49. The correct sequence regarding the activity of the given acid derivative is
(a) $RCOCl > RCON_3 > (RCO)_2O$ (b) $RCOCl > (RCO)_2O > RCON_3$
(c) $RCON_3 > RCOCl > (RCO)_2O$ (d) $RCON_3 > (RCO)_2O > RCOCl$

50. Which of the following statements is correct?
(a) 1° amide liberates N_2 when treated with HNO_2.
(b) 2° amide liberates N_2 when treated with HNO_2.
(c) 3° amide liberates N_2 when treated with HNO_2.
(d) None of 1°, 2° and 3° amides produce N_2 when treated with HNO_2.

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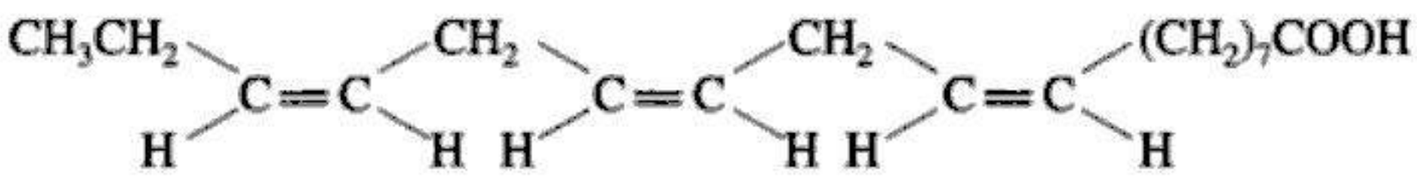
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16. Which of the following statements are correct?
(a) Urea on treatment with NaOH produces ammonium ion and CO_2.
(b) Urea on treating with nitrous acid produces ammonia gas.
(c) With alkaline hypohalites, urea is converted into nitrogen and carbonate.
(d) Reduction of an ester produces two alcohols.

17. Which of the following statements are correct?
(a) Oxalic acid is a weaker acid as compared to malonic acid.
(b) Malonic acid is a stronger acid as compared to succinic acid.
(c) Malonic acid is a stronger acid as compared to acetic acid.
(d) The correct order of acid strength of the following acids is acetic acid > malonic acid > succinic acid

18. Which of the following statements are **not** correct?
(a) The correct order of acid strength of the given acids is
$$H_2SO_4 > CH_3COOH > H_2O > HC{\equiv}CH > C_2H_5OH$$
(b) The presence of bulky substituents in either the alcohol group or the acid group slows down both esterification and hydrolysis.
(c) Naturally occurring fatty acids generally contain even number of carbon atoms.
(d) Unsaturated fatty acids have higher melting points than the corresponding saturated acids.

19. Which of the following statements are correct?
(a) The melting point of a *trans* fatty acid is higher than its *cis* isomer.
(b) The IUPAC name of



is *cis*,*cis*,*cis*-3,6,9-octadecatrien-18-oic acid.
(c) Vinegar is a 5% aqueous solution of acetic acid.
(d) The C=O bond in RCOOH is longer than in RCHO.

20. Which of the following statements are correct?
(a) The reactivity of C=O towards nucleophiles in RCOOH is less than that in RCHO.
(b) Soft soaps are K^+ salts of fatty acids.
(c) Hard soaps are Na^+ salts of fatty acids.
(d) Peroxy acids, $R\overset{\overset{O}{\|}}{C}OOH$, are much stronger than $R\overset{\overset{O}{\|}}{C}OH$.

21. Which of the following statements are correct?
(a) *p*-$NO_2C_6H_4COOH$ is more acidic than the *meta* isomer.
(b) *p*-Chlorobenzoic acid is more acidic than its *meta* isomer.
(c) *m*-Toluic acid is more acidic than its *para* isomer.
(d) Me_3CCH_2COOH is less acidic than Me_3SiCH_2COOH.

22. Which of the following statements are correct?
(a) $H_2C{=}CHCH_2COOH$ is more acidic than CH_3CH_2COOH.
(b) The acid $(CH_3)_3CCH_2C(CH_3)_2COOH$ is less acidic than $CH_3(CH_2)_7COOH$.
(c) *Trans*-4-*t*-butylcyclohexanecarboxylic acid is stronger than the *cis*-isomer
(d) The pK_{a1}° of a dicarboxylic acid is usually greater than the pK_a° of the comparable monoalkylcarboxylic acid.

23. Which of the following statements are correct?
(a) Maleic acid is a weaker acid than fumaric acid.
(b) Maleate monoanion is a weaker acid than fumarate monoanion.
(c) Salicyclic acid, *o*-HOC_6H_4COOH, is a stronger acid than *o*-$H_3COC_6H_4COOH$.
(d) A more reactive acid derivative may be used to prepare a less reactive one by reaction with the appropriate nucleophile.

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11. The product obtained on heating a straight-chain dicarboxylic acid depends on the length of the chain. Identify the correct choice in each of the three following questions

(i) The maximum value of n in $HOOC(CH_2)_nCOOH$ which on heating gives a cyclic anhydride is
(a) 1 (b) 2 (c) 3 (d) 4

(ii) The maximum value of n in $HOOC(CH_2)_nCOOH$ which on heating gives a cyclic alkanone is
(a) 2 (b) 3 (c) 4 (d) 5

(iii) The manimum value of n in $HOOC(CH_2)_nCOOH$ which on heating gives a linear polymeric anhydride is
(a) 2 (b) 4 (c) 5 (d) 6

12. Given are the following reactions.

$$CH_3COCH_3 \xrightarrow{700\ ^\circ C} A \xrightarrow{CH_3COOH} B \xrightarrow[\text{distil}]{RCOOH} C$$

Based on these reactions, answer the following three question.

(i) The compound A is
(a) $CH_3CHOHCH_3$ (b) CH_3COCH_3 (c) $H_2C{=}CHCH_3$ (d) $H_2C{=}C{=}O$

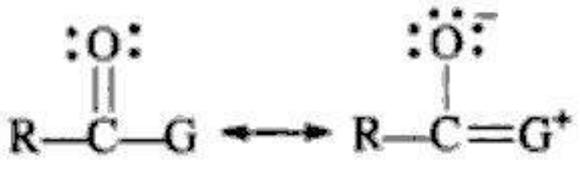
(ii) The compound B is
(a) H_3CCOCH_3 (b) H_3CCHO (c) $(CH_3CO)_2O$ (d) $CH_4 + CO_2$

(iii) The compound C is
(a) $CH_3COOCOCH_3$ (b) RCOOCOR (c) $CH_3COOCOR$ (d) $RCOCH_2OH$

Assertion and Reason Type

Given below are questions, each containing two statements. Answer each question based on the following key.

(a) Both statements are correct and Statement-2 is correct explanation of Statement-1.
(b) Both statements are correct and Statement-2 is not correct explanation of Statement-1.
(c) Statements -1 is correct and Statement-2 is incorrect.
(d) Statements-1 is correct and Statement-2 is correct.

Statement-1	Statement-2
1. Acetate ion is more basic than the methoxide ion.	The acetate ion is resonance stabilized. (1994)
2. p-$NO_2C_6H_4COOH$ is more acidic than the *meta* isomer.	Through resonance p-NO_2 induces positive charge on the ring C beaing the COO– while m-NO_2 induces positive charge on the ring C *ortho* to the C bearing the COO^-.
3. p-$ClC_6H_4COO^-$ is more acid than the *meta* isomer.	Only inductive effect is operating, the effect is stronger acid-strengthening effect from the nearer *meta* position.
4. 3-Butynoic acid is stronger than 3-butenoic acid.	—C ≡ C— is better electron withdrawing group than $\rangle C{=}CH_2 \langle$.
5. pK_{a1}° of dicarboxylic acid $HOOCCH_2CH_2COOH$ is smaller than the pK_a° of $CH_3CH_2CH_2COOH$.	HOOC group has electron withdrawing effect on the second HCOOH group in the dicarboxylic acid making its pK_a° less than the pK_a° value of butanoic acid.
6. It is more efficient to prepare an ester by the route acid → acyl chloride → ester, rather than acid-ester.	The reaction of acid with alcohol is slower.
7. RCOCl can be converted into $(RCO)_2O$ but the reverse of this is not feasible.	A more reactive acyl derivative can be converted into less reactive derivative and not vice versa.
8. The relative reactivity of acyl derivative is governed by resonance stabilization 	The greater the degree of delocalization, the less reactive is acyl derivative RCOG.

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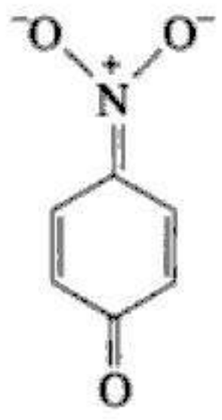


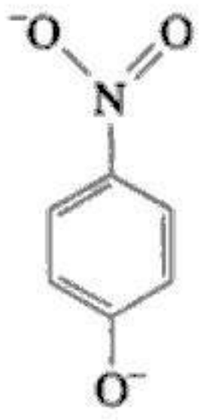
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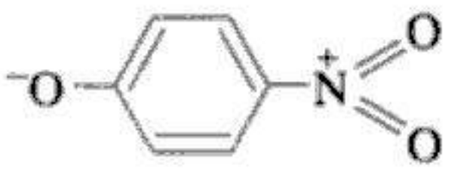


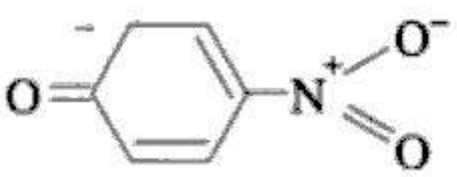
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10. The most unlikely representation of resonance structures of *p*-nitrophenoxide ion is

(a) 

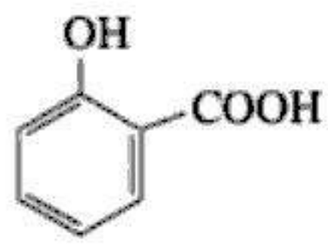
(b) 

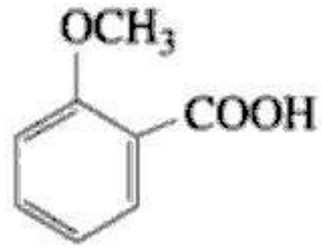
(c) 

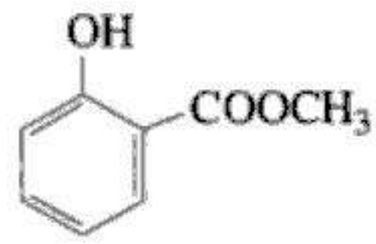
(d) 

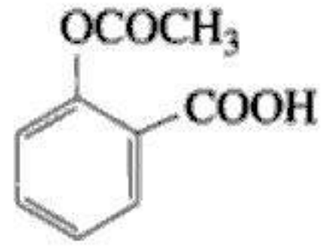
(1999)

11. Which of the following compounds is aspirin?

(a) 

(b) 

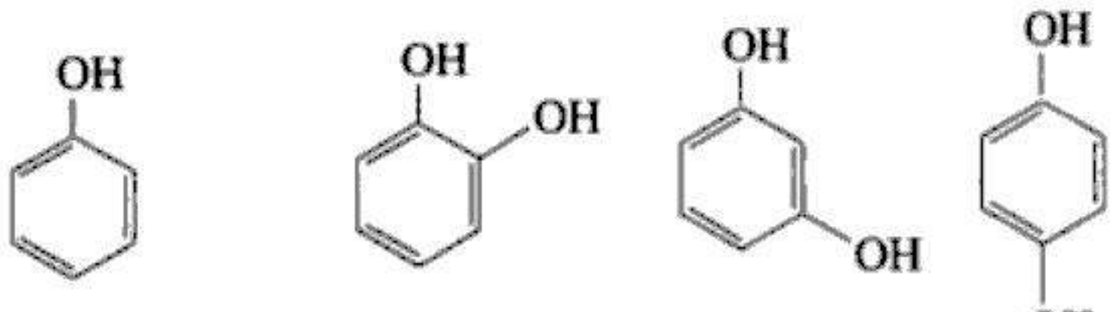
(c) 

(d) 

12. Benzene sulphonic acid and 2,4-dinitrophenol on reaction with sodium bicarbonate respectively liberate

(a) SO_2, NO_2 (b) SO_2, CO_2
(c) CO_2, NO_2 (d) CO_2, CO_2 (2006)

13. The increasing order of the boiling points of the compounds



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

is

(a) A < B < C < D (b) A < B < D < C
(c) D < C < B < A (d) D < A < B < C (2006)

Chemical Reactions

14. When phenol is treated with excess bromine water, it gives

(a) *m*-bromophenol (b) *o*- and *p*-bromophenol
(c) 2,4-dibromophenol (d) 2, 4, 6- tribromophenol (1984)

15. Phenol reacts with bromine in carbon disulphide at low temperature to give

(a) *m*-bromophenol (b) *o*- and *p*-bromophenols
(c) *p*-bromophenol (d) 2, 4, 6-tribromophenol (1988)

16. Salicyclic acid is produced when phenol in alcoholic KOH is treated with

(a) CH_3Cl (b) CH_2Cl_2 (c) $CHCl_3$ (d) CCl_4

17. Phenol gives salicyldehyde on heating with $CHCl_3$ and NaOH. It is known as

(a) Cannizzaro reaction (b) Claisen reaction
(c) Reimer-Tiemann reaction (d) Hell-Volhard-Zelinsky reaction

18. The treatment of phenol with phthalic anhydride in the presence of concentrated sulphuric acid produces

(a) aspirin (b) methyl red (c) methyl orange (d) phenolphthalein

19. In the reaction  + $C_2H_5I \xrightarrow[\text{(anhydrous } C_2H_5OH)]{C_2H_5O^-}$ A, the product A is (2003)

(a) $C_6H_5COC_2H_5$ (b) $C_2H_5OC_2H_5$ (c) $C_6H_5OC_6H_5$ (d) C_6H_5I

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layers are separated with the help of ether. The aqueous phase is hydrolysed with concentrated HCl when the primary amine is regenerated.

The ether layer is distilled and tertiary amine is distilled over. The residue is hydrolysed with concentrated HCl to recover secondary amine.

(b) Hofmann's Method The mixture of amines is treated with diethyloxalate which forms a solid oxamide with primary amine, a liquid oxime ester with secondary amine. The tertiary amine does not react. The resultant mixture is filtered to separate solid which on treating with KOH liberates primary amine. The filtrate is fractionally distilled when tertiary amine distils over. The remaining liquid is treated with KOH and distilled when the secondary amine is distilled over. The reactions occurring are as follows.

$$\begin{matrix}COOC_2H_5\\|\\COOC_2H_5\end{matrix} + 2RNH_2 \longrightarrow \underset{\text{(dialkyloxamide) solid}}{\begin{matrix}CONHR\\|\\CONHR\end{matrix}} + 2C_2H_5OH\ ; \qquad \begin{matrix}COOC_2H_5\\|\\COOC_2H_5\end{matrix} + R_2NH \longrightarrow \underset{\text{(oxamic ester) liquid}}{\begin{matrix}CONR_2\\|\\COOC_2H_5\end{matrix}} + C_2H_5OH$$

Test for Primary Amine (Carbylamine reaction) The treatment of a primary amine with chloroform and alcoholic potash produces carbylamine (isocyanide) which has most offensive smell

$$RNH_2 + CHCl_3 + 3KOH \rightarrow R{-}NC + 3KCl + 3H_2O$$

This reaction is not exhibited by secondary and tertiary amines.

Test for Secondary Amine (Libermann reaction) The secondary amine is converted into nitrosoamine by treating the amine with nitrous acid. The resultant solution is warmed with phenol and concentrated H_2SO_4, a brown or red colour is formed at first. Soon it change to blue and then to green. The colour changes to red on dilution and further changes to greenish-blue or violet on treating with alkali.

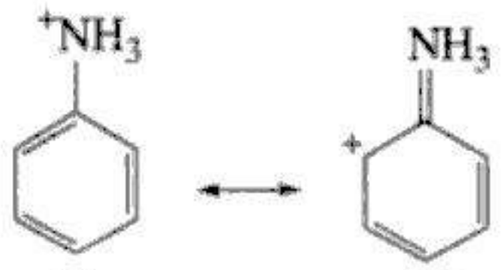
Straight Objective Type

General Characteristics

1. Chlorobenzene can be prepared by reacting aniline with
(a) hydrochloric acid
(b) cuprous chloride
(c) chlorine in the presence of anhydrous aluminium chloride
(d) nitrous acid followed by heating with cuprous chloride (1984)

2. Amongst the following, the most basic compound is
(a) benzylamine (b) aniline (c) acetanilide (d) *p*-nitroaniline (1990)

3. Examine the following two structures for the anilinium ion and chose the correct statement from the ones given below.



(I) (II)

(a) II is not acceptable canonical structure because carbonium ions are less stable than ammonium ions
(b) II is not an acceptable canonical structure because it is nonaromatic
(c) II is not an acceptable canonical structure because nitrogen has 10 valence electrons
(d) II is an acceptable canonical structure (1993)

4. Which of the following statements is **not** correct?
(a) Replacement of halogen by NH_2 in alkyl halide is a nucleophilic substitution reaction
(b) Aryl halides show more reactivity as compared to alkyl halides in the replacements of halogen by the NH_2 group

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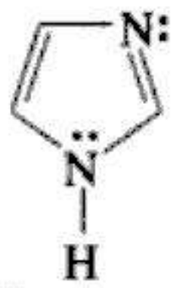
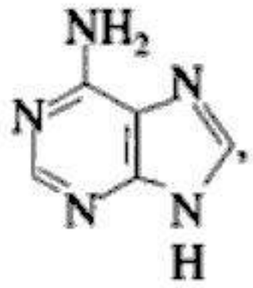
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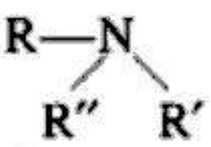


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5. Which of the following statements are **not** correct?
(a) Guanidine $(H_2N)_2C{=}NH$ is expected to be a weak base.
(b) Aniline is more basic than pyridine.
(c) Imidizole,  , has two basic sites.
(d) Purine,  , has five basic sites.

6. Which of the following statements are **not** correct?
(a) Amines have lower boiling points than nonpolar compounds of the same molar mass.
(b) Amines have higher boiling points than alcohols or carboxylic acids of comparable molar mass.
(c) Aliphatic amines are as basic as ammonia but aromatic amines are more basic.
(d) Although nitrogen in  is chiral and also the mirror image of the molecule is not superimposable on the molecule itself, yet the molecule does not show optical activity.

7. Which of the following statements are correct?
(a) Quaternary ammonium salts in which nitrogen holds four different groups show optical activity.
(b) Aliphatic amines can be prepared by ammonolysis of alkyl halides but not aromatic amines.
(c) Ammonolysis of alkyl halides gives highest yield with tertiary halides and is worthless for primary halides.
(d) The more stable the substituted ammonium ion relative to the amine from where it is formed, the more basic is the amine.

8. Which of the following statements are correct?
(a) Aniline is less basic than ammonia because resonance stabilization of aniline is larger than the resonance stabilization of anilinium ion.
(b) Electron-releasing substituent decreases the basicity of aniline.
(c) Electron-withdrawing substituent increases the basicity of aniline.
(d) Base-strengthening substituents are the one that activate an aromatic ring toward electrophilic substitution.

9. Which of the following statements are **not** correct?
(a) Base-weakening substituents are the one that activate an aromatic ring toward electrophilic substitution.
(b) Aliphatic amine forms stable diazonium salt with nitrous acid.
(c) All amino compounds can be distinguished by using the reagents chloroform and potassium hydroxide.
(d) The sulphonamide formed from secondary amine does not form sodium salt and is also insoluble in water.

10. Which of the following statements are correct?
(a) Only one NO_2 group is reduced in *m*-dinitrobenzene if treated with NH_4SH.
(b) $C_6H_5N(CH_3)(C_2H_5)$ can be resolved into enantiomers.
(c) Bromination of aniline produces *ortho*- and *para*-bromoaniline.
(d) Nitration of aniline is carried out by first converting aniline to acetanilide.

11. Which of the following statements are **not** correct?
(a) The order of acid strength in the given compounds is $NH_3 > CH_3CONH_2 > (CH_3CO)_2NH$.
(b) *p*-Aminobenzoic acid is a dipolar ion.
(c) Sulphanilic acid can exist as a dipolar ion.
(d) In Hoffmann elimination, a more substituted alkene is produced.

12. Which of the following statements are correct?
(a) In aqueous solution, R_2NH is a stronger base than RNH_2.
(b) In aqueous solution, R_3N is a stronger base than R_2NH.
(c) In aqueous solution, R_3N is a stronger base then RNH_2.
(d) In gaseous phase, R_3N is a stronger base than R_2NH, which, in turn, is greater than RNH_2.

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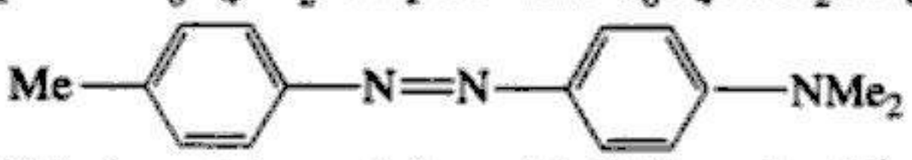
5. Aryl diazonium ions are more stable than alkyl diazonium ions.

Electron-release from the *ortho* and *para* positions of the ring stabilizes the aryl diazonium ion.

6. PhN_2^+ couples with $PhNMe_2$ and not with $PhCH_3$.

PhN_2^+ couples only with the rings activated by strong activating groups.

7. *p*-Me–C_6H_4–N_2^+ couples with $C_6H_4NMe_2$ to give



This is not formed from MeC_6H_5 and p-N_2^+ –C_6H_4 –NMe_2.

MeC_6H_5 is not active enough to couple with *p*-N_2^+–C_6H_4–NMe_2.

8. Sulphanic acid has a very low melting point.

Sulphanic acid exists as dipolar ion *p*-$^-O_3SC_6H_4NH_3^+$.

ANSWERS

Straight Objective Type

1. (d)	**2.** (a)	**3.** (c)	**4.** (b)	**5.** (c)	**6.** (b)	**7.** (a)
8. (d)	**9.** (c)	**10.** (a)	**11.** (a)	**12.** (d)	**13.** (d)	**14.** (d)
15. (b)	**16.** (a)	**17.** (a)	**18.** (c)	**19.** (d)	**20.** (c)	**21.** (a)
22. (b)	**23.** (b)	**24.** (b)	**25.** (c)	**26.** (d)	**27.** (a)	**28.** (b)
29. (a)	**30.** (c)	**31.** (a)	**32.** (c)	**33.** (c)	**34.** (b)	**35.** (c)
36. (c)	**37.** (c)	**38.** (c)	**39.** (a)	**40.** (b)	**41.** (b)	**42.** (a)
43. (a)	**44.** (c)	**45.** (b)	**46.** (a)	**47.** (b)	**48.** (c)	**49.** (b)
50. (b)	**51.** (c)	**52.** (d)	**53.** (c)			

Multiple Correct Choice Type

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

Linked Comprehension Type

1. (i) (c)	(ii) (d)	(iii) (a)
2. (i) (b)	(ii) (c)	(iii) (a)

Assertion and Reason Type

1. (d)	**2.** (d)	**3.** (a)	**4.** (d)	**5.** (a)	**6.** (a)	**7.** (a)
8. (d)						

Hints and Solutions

Straight Objective Type

1. Chlorobenzene can be prepared by reacting aniline with nitrous acid followed by heating with curous chloride.

2. Alkyl amine (benzyl amine, $C_6H_5CH_2NH_2$) is the most basic compound.

4. The choice b is incorrect because aryl halides show less reactivity as compared to alkyl halides in the replacement of halogens by the NH_2 group.

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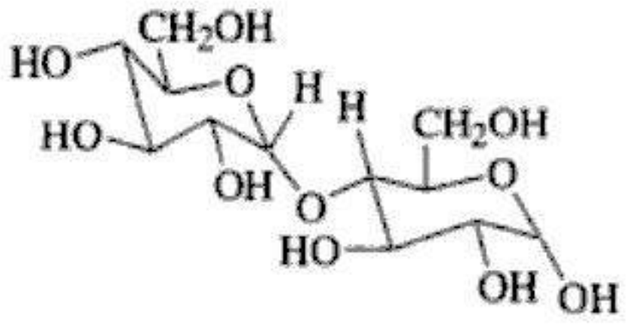


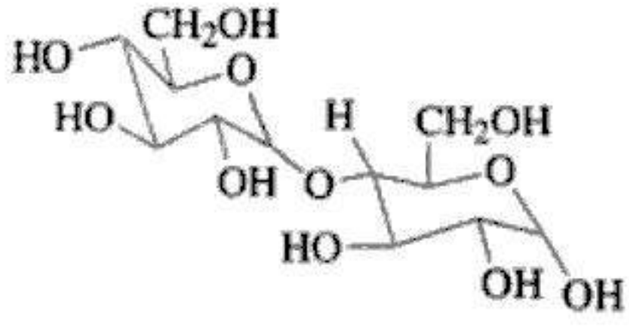
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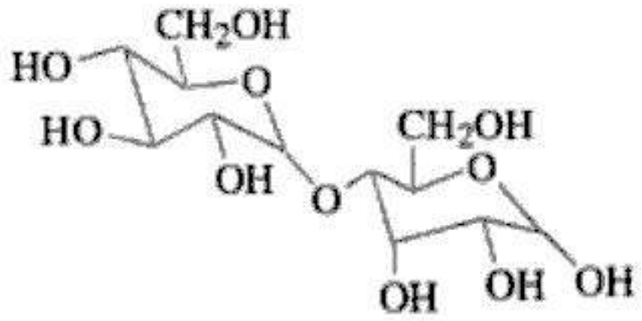


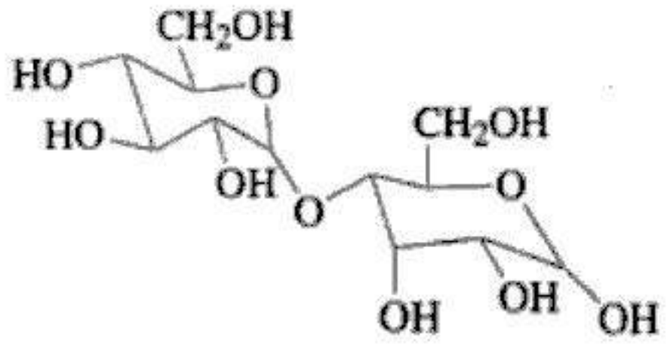
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Which of the following structures also represent maltose?

(a) 

(b) 

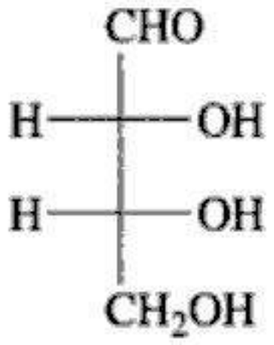
(c) 

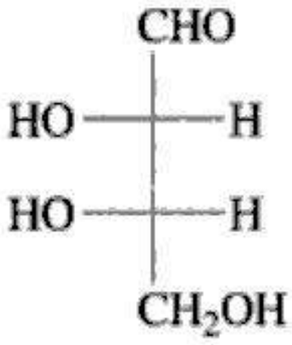
(d) 

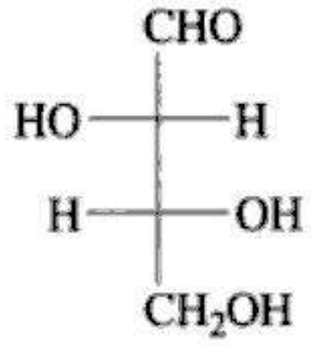
Linked Comprehension Type

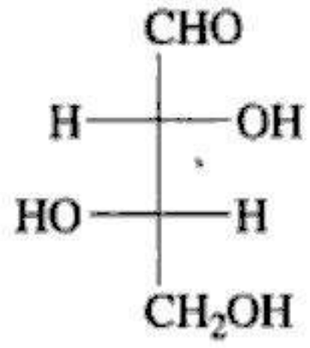
1. Erythrose and threose are aldotetrose. Based on these sugars, answer the following three questions.

(i) Which of the following structures represents D-threose?

(a) 

(b) 

(c) 

(d) 

(ii) The mild oxidation of the compound $OHCCH(OH)CH(OH)CH_2OH$ gives

(a) $HOOCCH(OH)CH(OH)CH_2OH$ (b) $OHCCH(OH)CH(OH)CHO$

(c) $OHCCH(OH)CH(OH)COOH$ (d) $HOOCCH(OH)CH(OH)COOH$

(iii) The mild oxidation of D-erythrose and D-threose, respectively, give

(a) optically active enantiomer and *meso*-isomer (b) optically active enantiomers

(c) *meso*-isomer (d) *meso*-isomer and optically active enantiomer

2. The specific rotations of sucrose, glucose and fructose are as follows

$$[\alpha]_{sugar} = 66.5°; \quad [\alpha]_{glucose} = 52.7°; \quad [\alpha]_{fructose} = -92.4°$$

Based on this information, answer the following three questions

(i) The hydrolysis of sucrose in the presence of dilute acid produces

(a) glucose only

(b) fructose only

(c) a mixture of glucose and fructose

(d) mutarotation where α-sucrose is converted into β-sucrose and vice versa.

(ii) If $[\alpha]_{soln}$ is the specific rotation of the solution, then the fraction of sucrose undergone hydrolysis is given by

(a) $\dfrac{[\alpha]_{soln} - [\alpha]_{sugar}}{[\alpha]_{glucose} + [\alpha]_{fructose}}$ (b) $\dfrac{[\alpha]_{soln} - [\alpha]_{sugar}}{[\alpha]_{glucose} + [\alpha]_{fructose} + [\alpha]_{soln}}$

(c) $\dfrac{[\alpha]_{soln} - [\alpha]_{sugar}}{[\alpha]_{glucose} + [\alpha]_{fructose} - [\alpha]_{soln}}$ (d) $\dfrac{[\alpha]_{soln} - [\alpha]_{sugar}}{[\alpha]_{glucose} + [\alpha]_{fructose} - \{[\alpha]_{soln} + [\alpha]_{sugar}\}}$

(iii) The specific rotation of the solution, when sucrose solution has undergone complete hydrolysis is

(a) – 19.85° (b) – 39.70° (c) – 25.15° (d) – 9.95°

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Multiple Correct Choice Type

1. Which of the following polymers involve(s) cross linkages?
(a) Bakelite (b) Melamine (c) Polythene (d) Vulcanised rubber

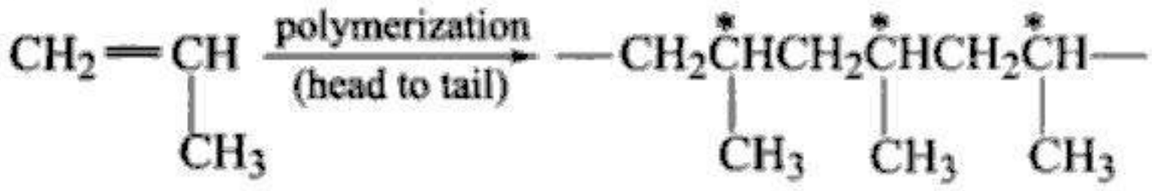
2. Which of the following polymers are examples of thermoplastic polymers?
(a) urea-formaldehyde resin (b) Polystyrene
(c) Nylon-6, 6 (d) Bakelite.

3. Which of the following polymers are examples of synthetic polymers?
(a) Neoprene rubber (b) Cellulose (c) Bunna rubber (d) Glycogen

4. The examples of condensation polymers are
(a) Nylon-6, 6 (b) Teflon (c) Orlon (d) Nylon-6

Linked Comprehension Type

1. Head-to-tail polymerization of propylene produces a polymer in which every other atom is a stereocentre. Many of the physical properties of the polypropylene produced in this way depend on the stereochemistry of these stereocentres.

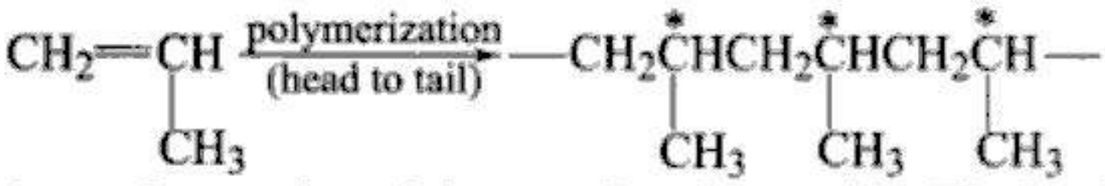


(i) In which of the following polypropylene, the methyl groups are randomly disposed on either side of the stretched carbon chain?
(a) Atactic (b) Syndiotactic (c) Isotactic (d) None of these

(ii) In which of the following polypropylene, all the methyl groups are on the same side of the stretched carbon chain?
(a) Atactic (b) Syndiotactic (c) Isotactic (d) None of these

(iii) In which of the following polypropylene, the methyl group alternate regularly from one side of the stretched carbon chain to the other?
(a) Atactic (b) Syndiotactic (c) Isotactic (d) None of these

2. Head-to-tail polymerisation of propylene produces a polymer in which every other atom is a stereocentre. Many of the physical properties of the polypropylene produced in this way depend on the stereochemistry of these stereocentres.



(i) Which of the following polypropylene is/are produced by using Ziegler–Natta catalysts?
(a) Atactic only (b) Atactic and Syndiotactic
(c) Atactic and Isotactic (d) Syndiotactic and Isotactic

(ii) Which of the following polypropylene is/are noncrystalline?
(a) Atactic only (b) Atactic and Syndiotactic
(c) Atactic and Isotactic (d) Syndiotactic and Isotactic

(iii) Which of the following polypropylene is/are produced at lower pressures and have comparatively high melting point?
(a) Atactic only (b) Atactic and Syndiotactic
(c) Atactic and Isotactic (d) Syndiotactic and Isotactic

Matrix Match Type

1. Match the chemical substances in Column I with type of polymers/type of bond in Column II.

Column I	Column II
(a) Cellulose	(p) natural polymer
(b) nylon-66	(q) synthetic polymer
(c) protein	(r) amide linkage
(d) sucrose	(s) glucoside linkage

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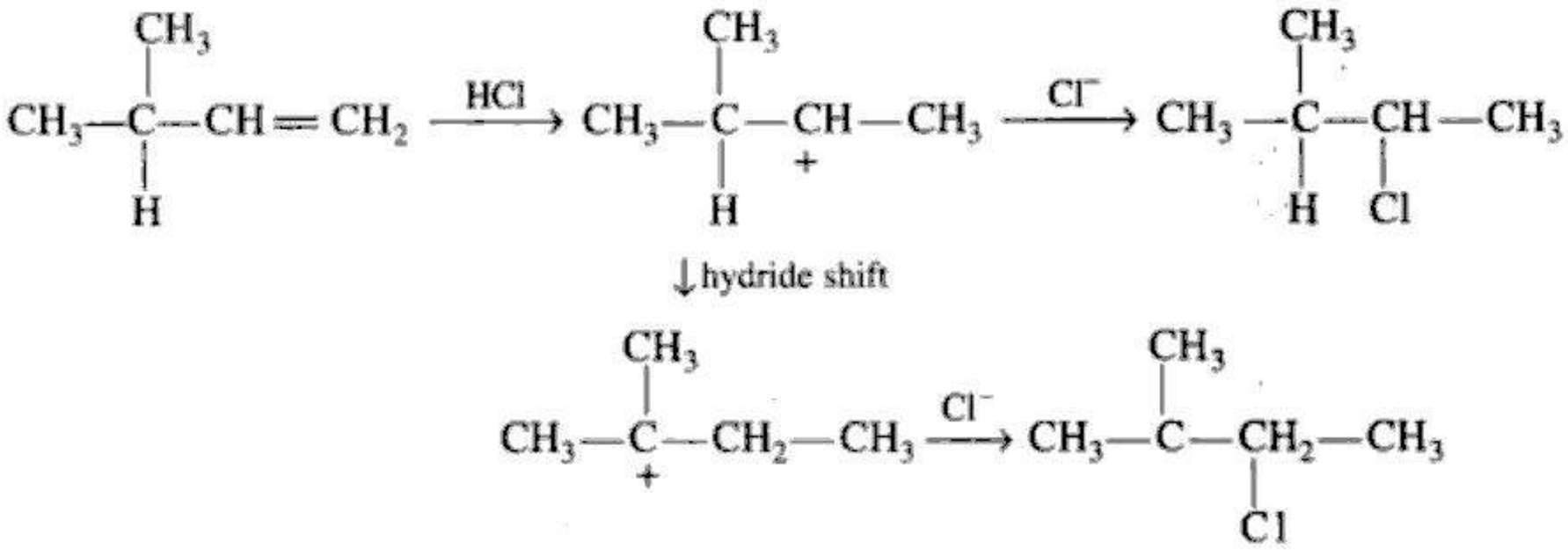
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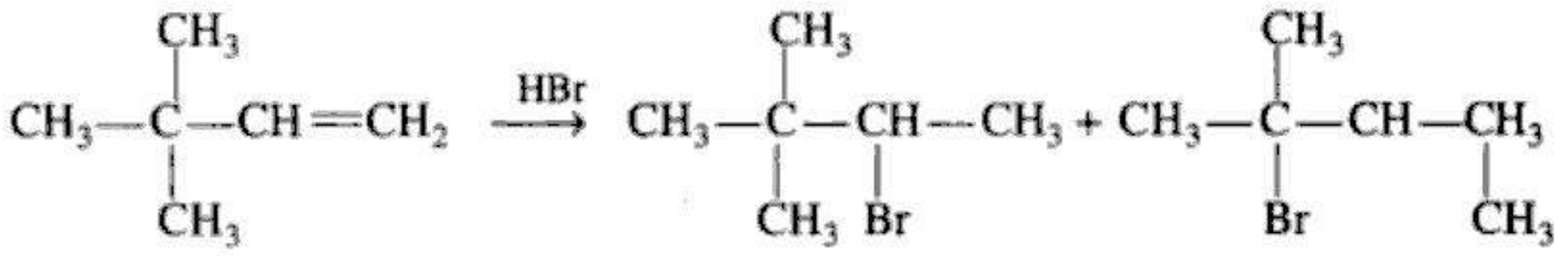


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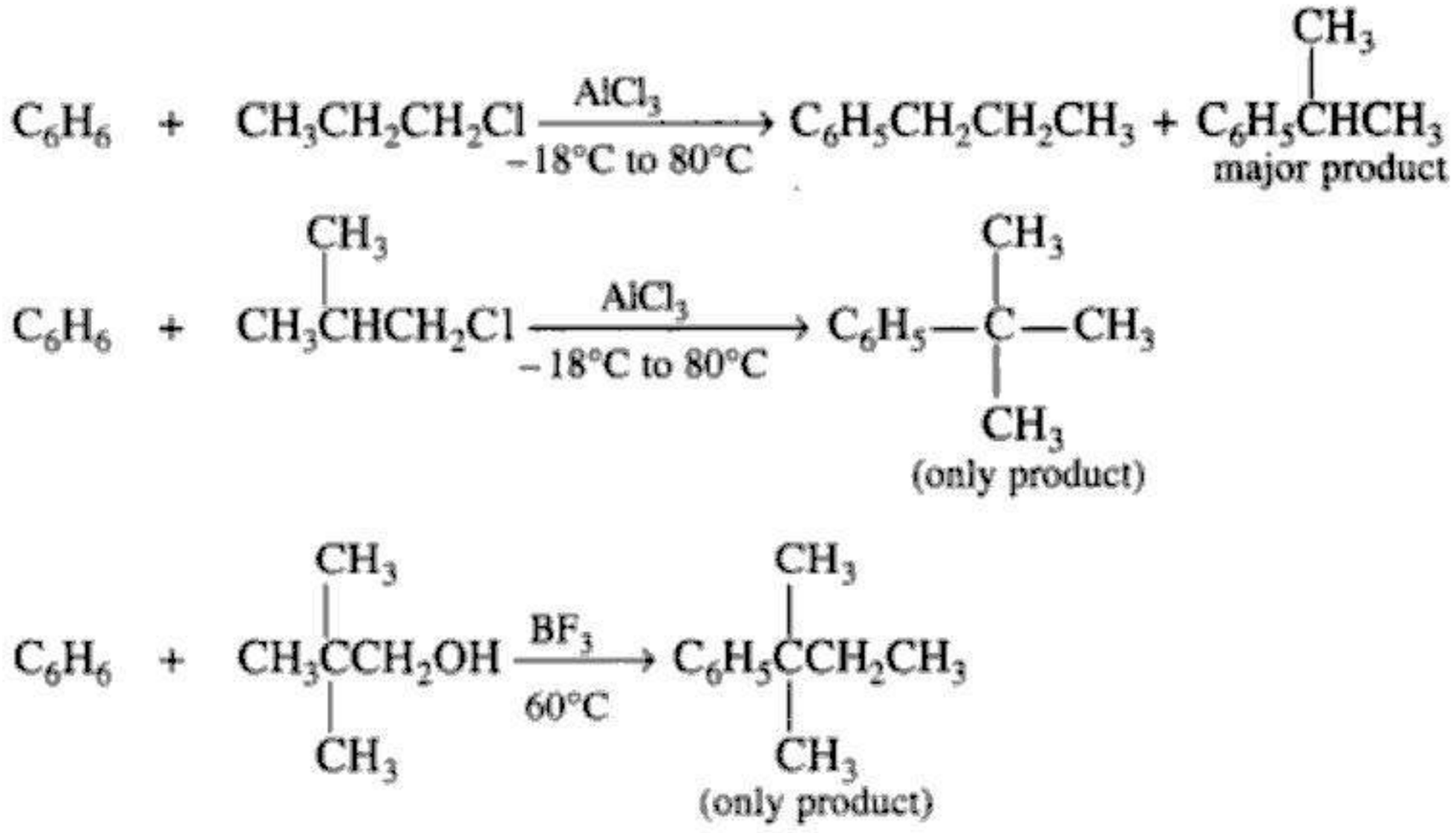


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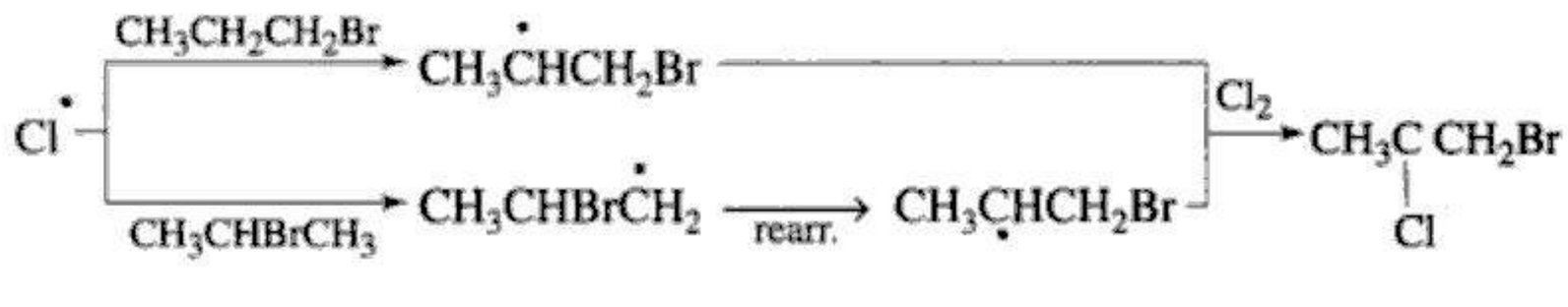


4. Friedel-Crafts Reaction

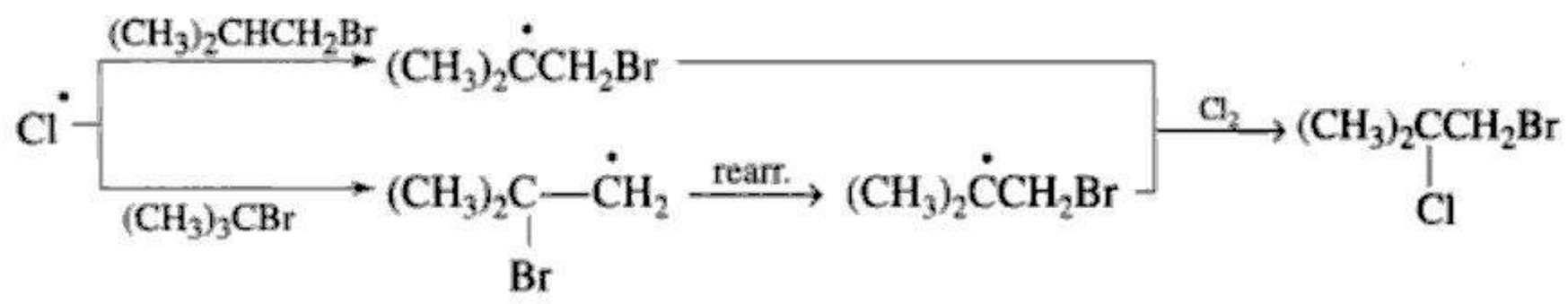


5. Rearrangement, by migration of Br, of initially formed 1° radical into more stable 2° or 3° radical.

Chlorination of either *n*-propyl or isopropyl bromide gives 1-bromo-2-chloropropane.



Chlorination of either isobutyl or *tert*-butyl bromide gives 1-bromo-2-chloro-2-methylpropane.



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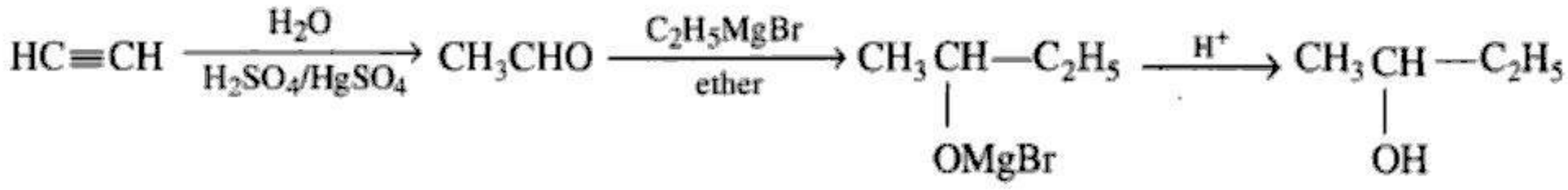


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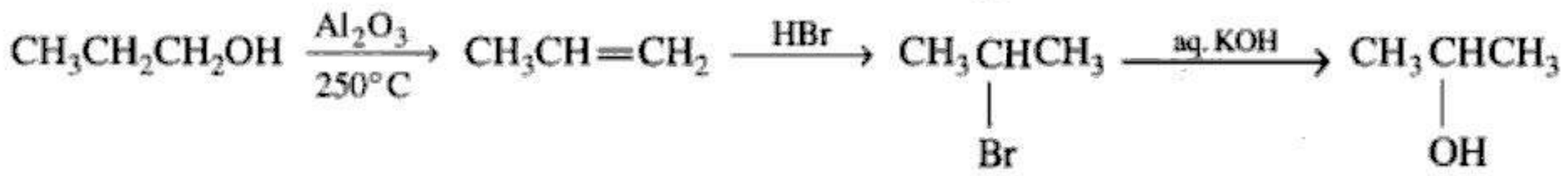


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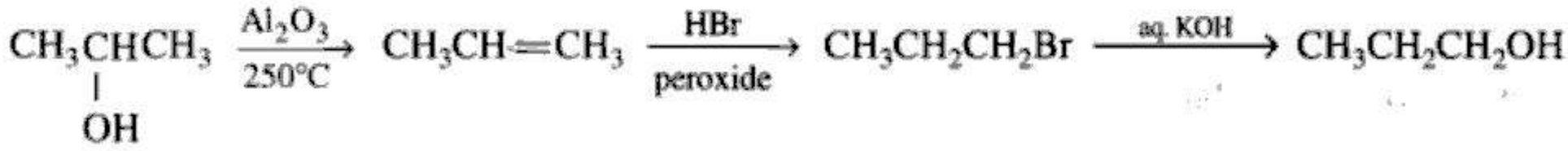
30. Ethyne to 2-butanol



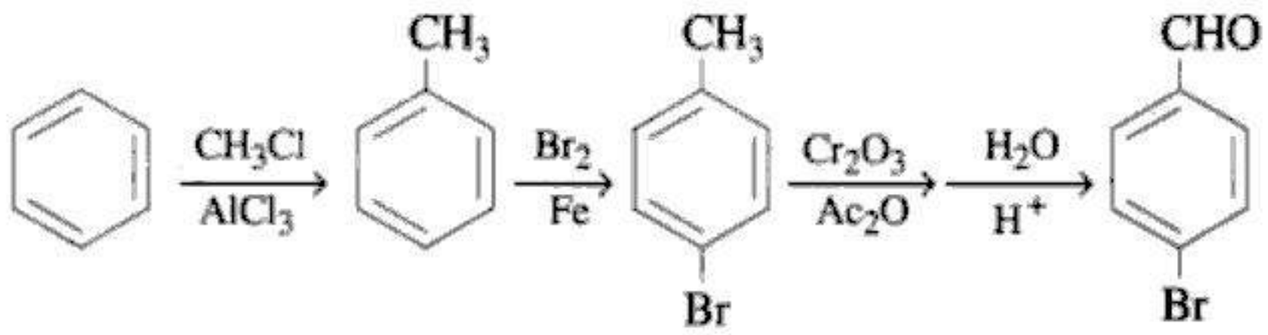
31. 1-Propanol to 2-propanol



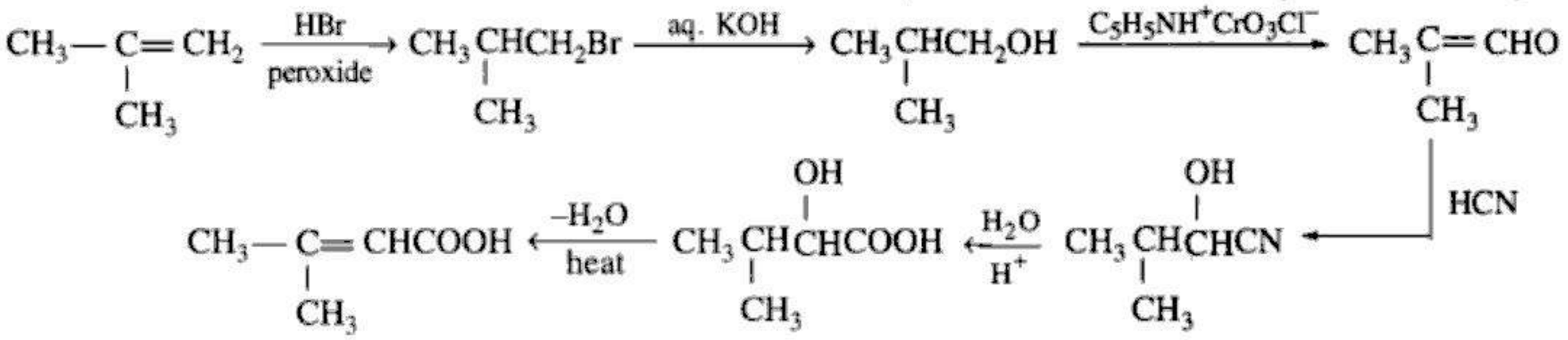
32. 2-Propanol to 1-propanol



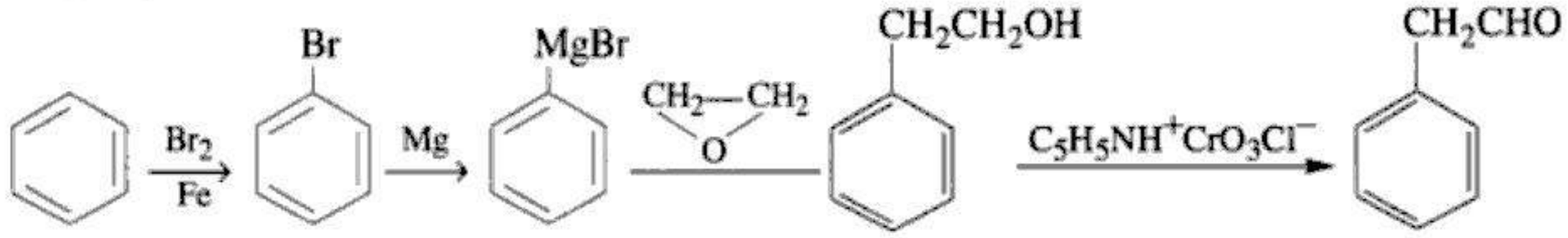
33. Benzene to *p*-bromobenzaldehyde



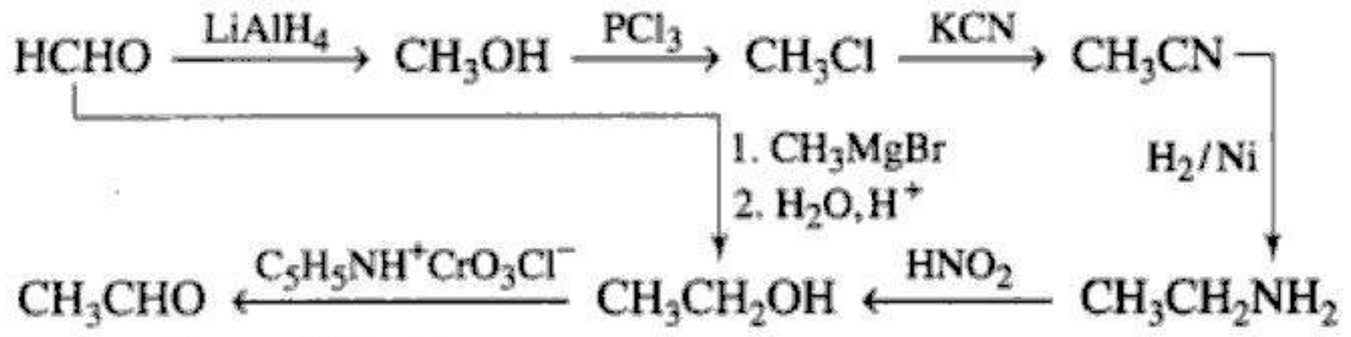
34. 2-Methylpropene to 3-methyl-2-butenoic acid



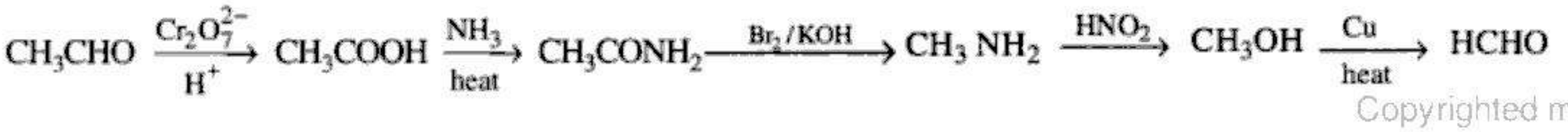
35. Benzene to phenylacetaldehyde



36. Formaldehyde to acetaldehyde



37. Acetaldehyde to formaldehyde



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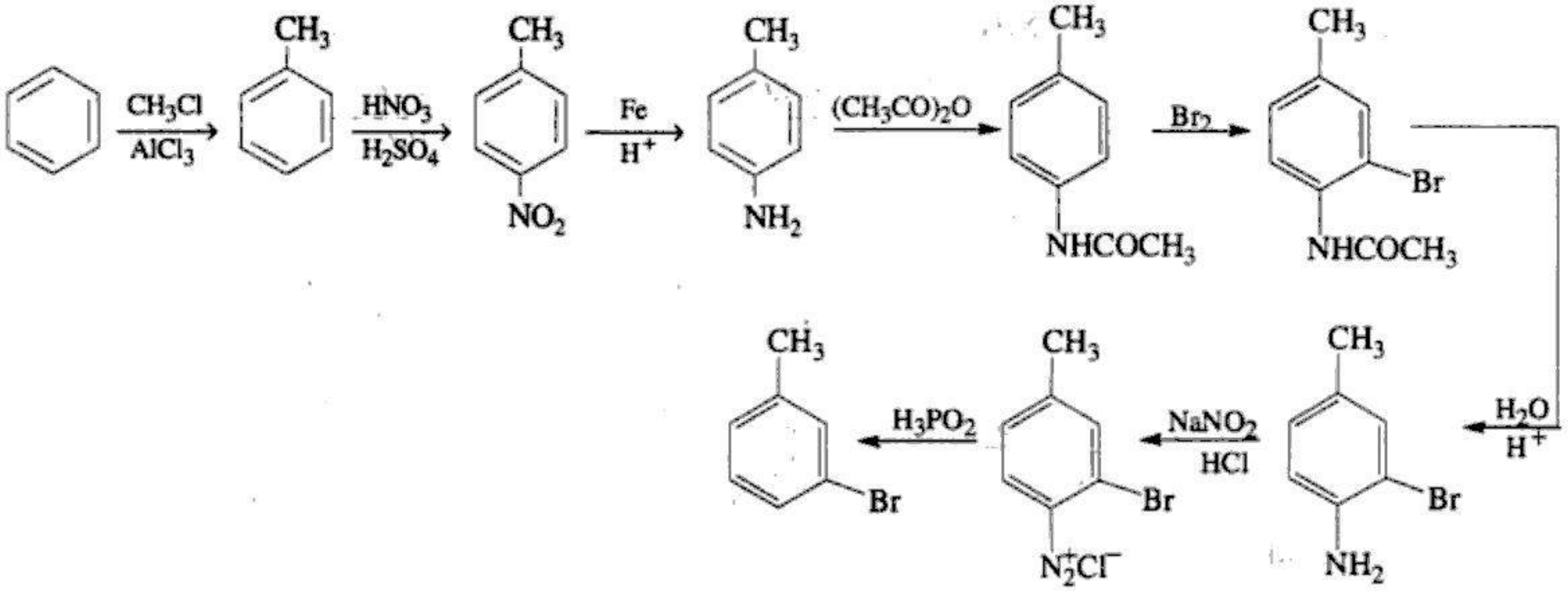


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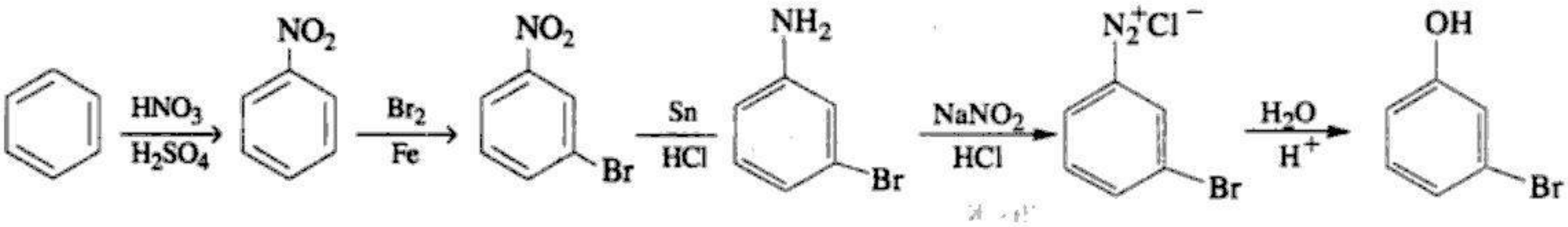


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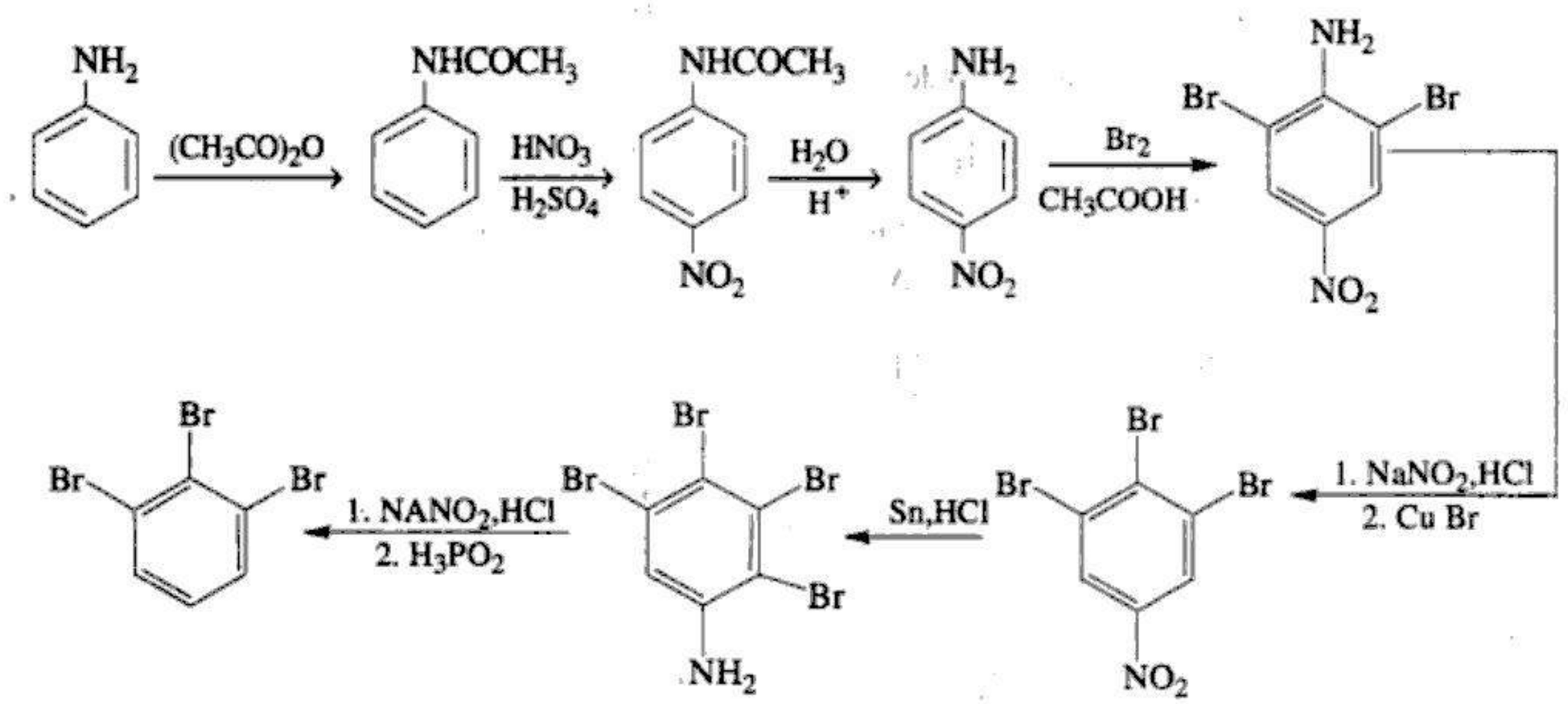
59. Benzene to *m*-bromotoluene



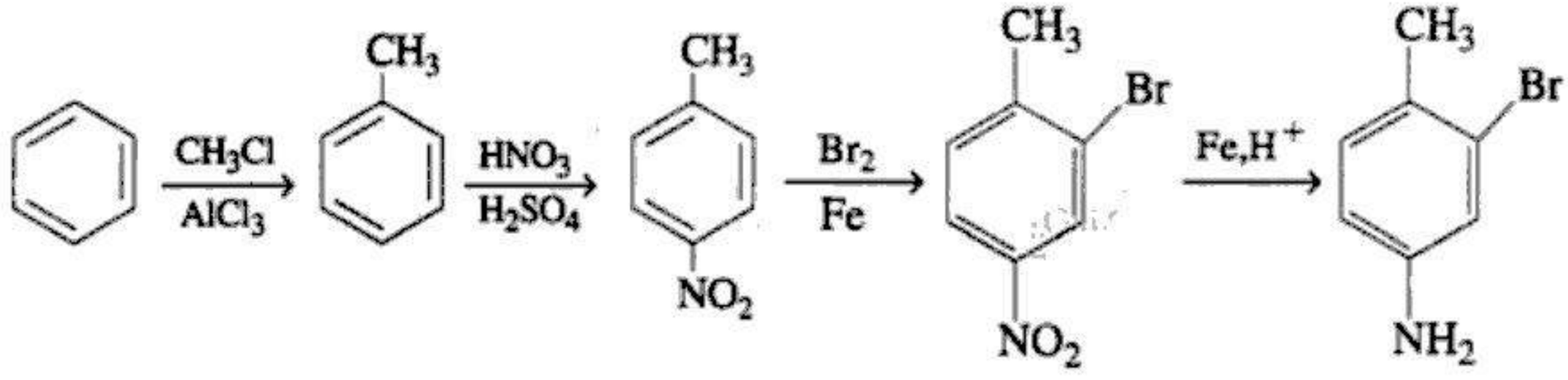
60. Benzene to *m*-bromophenol



61. Aniline to 1, 2, 3-tribromobenzene [1990]



62. Benzene to 4-amino-2-bromotoluene



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Completing the Reactions

1. $HC{\equiv}CH + CH_3CO_2H \xrightarrow{Hg^{2+}} \text{——} \xrightarrow[Hg^{2+}]{CH_3CO_2H} \text{——}$

2. $HC{\equiv}CH + HOCl \rightarrow \text{——} \xrightarrow{HOCl} \text{——}$

3. $CH_3CHO \xrightarrow{NaOH} \text{——} \xrightarrow{heat} \text{——} \xrightarrow{H_2/Ni} \text{——}$

4. $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HOCH_3 \xrightarrow[cold]{HI} \text{——} + \text{——}$

5. $CH_3COCH_3 \underset{HCl}{\rightleftharpoons} \text{——} \underset{CH_3COCH_3}{\rightleftharpoons} \text{——}$

6. $RCOR \xrightarrow[acid]{perbenzoic} \text{——} \xrightarrow{H^+} \text{——} + \text{——}$

7. $Ph{-}\underset{\displaystyle CH_3}{\underset{|}{C}}HCOCH_3 \xrightarrow[acid]{perbenzoic} \text{——}$

8. $C_6H_5CHO + HCHO \xrightarrow{NaOH} \text{——} + \text{——}$

9. $CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}{-}\underset{\displaystyle CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}{-}CH_3 \xrightarrow[distilled]{H^+} \text{——}$

10. $HC(=O)ONa + NaOH \rightarrow \text{——} + \text{——}$

11. $2HC(=O)ONa \xrightarrow{heat} \text{——} + \text{——}$

12. $CH_2{=}C{=}O + CH_3CO_2H \rightarrow \text{——}$

13. $CH_3CHO + (CH_3CO)_2O \rightarrow \text{——}$

14. $CH_2{=}CHCOOH + HBr \xrightarrow[\text{in acetic acid}]{} \text{——}$

15. $CH_2ClCH_2CH_2COOH \xrightarrow[reflux]{NaOH} \text{——}$

16. $\underset{\text{vapour}}{CH_3CHO} + \underset{\text{vapour}}{HCHO} \xrightarrow[silicate]{sodium} \text{——} + \text{——}$

17. $CH_3CH{=}CHCHO \xrightarrow{LiAlH_4} \text{——}$

18. $HCHO + CH_3COCH_3 \xrightarrow{NaOH} \text{——} \xrightarrow{-H_2O} \text{——}$

19. $CH_2{=}CH_2 + (CH_3CO)_2O \xrightarrow{ZnCl_2} \text{——} + \text{——}$

20. $RCHO + CH_2(CO_2C_2H_5)_2 \xrightarrow{pyridine} \text{——} \xrightarrow[2.\ HCl]{1.\ KOH} \xrightarrow{heat} \text{——} + \text{——}$

21. $CH_2{=}CHCH_2Br \xrightarrow{CuCN} \text{——} \xrightarrow{NaOH} [\ \text{——}\ ] \xrightarrow{NaOH} \text{——}$

22. $RCOOH + NH_3 \rightarrow \text{——} \xrightarrow{Al_2O_3} \text{——} + \text{——} \xrightarrow{Al_2O_3} \text{——} + \text{——}$

23. $RCN + R'MgX \longrightarrow \text{——} \xrightarrow{H_2O} \text{——}$

24. $RX + KCN \rightarrow \text{——} + \text{——}$

25. $RI + AgCN \rightarrow \text{——} + \text{——}$

26. $RNH_2 + CHCl_3 + 3KOH \rightarrow \text{——} + \text{——} + \text{——}$

27. $C_6H_5COCH_3 + CH_3MgI \rightarrow \text{——} \xrightarrow{H^+} \text{——} \xrightarrow{heat} \text{——} \xrightarrow{H_2/Ni} \text{——}$

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ANSWERS

1. $H_2C{=}C(H){-}OCCH_3$, $H_3CC(H)(OCCH_3)(OCCH_3)$ (O)

2. $[HC{=}CH(Cl)(OH)]$, $H{-}C(Cl)(Cl){-}CHO$

3. $CH_3CH(OH)CH_2CHO$, $CH_3CH{=}CHCHO$, $CH_3CH_2CH_2CH_2OH$

4. $CH_3CH_2CHOH(CH_3)$, CH_3I

4. In ethers, if one of the alkyl group is methyl, it always produces methyl iodide.

5. $(CH_3)_2C{=}CHCOCH_3$, mesityl oxide ; $(CH_3)_2C{=}CHCOCH{=}C(CH_3)_2$, phorone

6. $RCOOR, RCO_2H, ROH$

7. $Ph{-}CH(CH_3){-}O{-}C(=O){-}CH_3$

8. $C_6H_5CH_2OH$, HCO_2Na

9. $CH_3{-}C(=O){-}C(CH_3)(CH_3){-}CH_3$

10. H_2, Na_2CO_3

11. C_6H_5COONa, H_2

12. $(CH_3CO)_2O$

13. $CH_3CH(OCOCH_3)_2$ ethylidene acetate

14. $BrCH_2CH_2COOH$

15. $CH_2CH_2CH_2C(=O)O$, γ-butyrolactone

16. $CH_2{=}CHCHO$, H_2O

17. $CH_3CH{=}CHCH_2OH$

18. $CH_2CH_2COCH_3(OH)$, $CH_2{=}CHCOCH_3$

19. $CH_2{=}CHCOCH_3$, CH_3COOH

20. $RCH{=}C(CO_2C_2H_5)_2$, $RCH{=}C(COOH)_2$, $RCH{=}CHCOOH$, CO_2

21. $CH_2{=}CHCH_2CN$, $CH_2{=}CHCH_2COOH$, $CH_3CH{=}CHCOOH$

22. RCO_2NH_4, H_2O + $RCONH_2$, H_2O + RCN

23. $R{-}C(R'){=}NMgX$, $RCOR'$

24. $R{-}C{\equiv}N$, KX

25. $R{\equiv}NC$, KI

26. RNC, $3KCl$, $3H_2O$

27. $C_6H_5{-}C(OMgI)(CH_3){-}CH_3$, $C_6H_5{-}C(OH)(CH_3){-}CH_3$, $C_6H_5{-}C(CH_3){=}CH_2$, $C_6H_5{-}C(CH_3)_2{-}CH_3$

28. O_2N, NO_2, NO_2, $CH{=}CH$

29. $R{-}C(=O){-}OC_6H_5$, OH, COR

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Amount of sulphuric acid neutralized by ammonia $= \left(\frac{1}{400} - \frac{1}{800}\right)$ mol $= \frac{1}{800}$ mol

Amount of ammonia evolved $= 2\left(\frac{1}{800} \text{ mol}\right) = \frac{1}{400}$ mol

Mass of nitrogen in the evolved ammonia $= \left(\frac{1}{400} \text{ mol}\right)(14 \text{ g mol}^{-1}) = \frac{7}{200}$ g

Per cent of nitrogen in the given aromatic compound $= \frac{(7/200)\text{ g}}{0.303\text{ g}} \times 100 = 11.6$

Per cent of oxygen in the given aromatic compound = 100 – (69.4 + 5.8 + 11.6) = 13.2

The ratios of atoms present in the given compound are

$$\text{C : H : N : O} :: \frac{69.4}{12} : \frac{5.8}{1} : \frac{11.6}{14} : \frac{13.2}{16} :: 5.8 : 5.8 : 0.83 : 0.83 :: 7 : 7 : 1 : 1$$

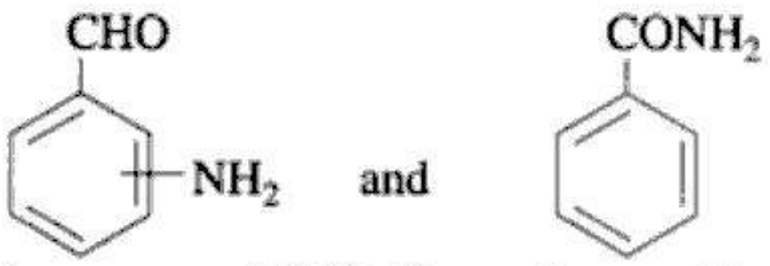
Hence, for the given compound, we have

Empirical formula = C_7H_7NO Empirical molar mass = 121 g mol^{-1}

It is given that 121 g mol^{-1} is also the molar mass. Hence,

Molecular formula = C_7H_7NO

Since, the given compound is aromatic, the two possible structures are



5. An organic compound $C_xH_{2y}O_y$ was burnt with twice the amount of oxygen needed for complete combustion to CO_2 and H_2O. The hot gases, when cooled to 0 °C and 1 atm pressure, measured 2.24 L. The water collected during cooling weighed 0.9 g. The vapour pressure of pure water at 20 °C is 17.5 mmHg and is lowered by 0.104 mmHg when 50 g of the organic compound is dissolved in 1000 g of water. Give the molecular formula of the organic compound. (1983)

Solution The combustion reaction is $C_xH_{2y}O_y + x\,O_2 \rightarrow x\,CO_2 + y\,H_2O$

To start with, the amount of O_2 taken is $2x$. Hence, after the combustion reaction, we will be left with the following amounts.

Amount of oxygen left unreacted = x; Amount of carbon dioxide = x; Amount of water = y

When this mixture is cooled to 0 °C and 1 atm, we will be left with oxygen and carbon dioxide. Hence, the amount $2x$ occupies the given volume of 2.24 L at STP. Hence,

$$\text{Amount } x = \frac{(2.24/2)\text{ L}}{22.4\text{ L mol}^{-1}} = 0.05 \text{ mol}$$

Now, Mass of water collected = 0.9 g Amount of water collected, $y = \frac{0.9\text{ g}}{18\text{ g mol}^{-1}} = 0.05$ mol

Thus, the empirical formula of the compound is $C_{0.05}H_{2\times0.05}O_{0.05}$, i.e. CH_2O. Now, according to Raoult's law

$$-\frac{\Delta p}{p^*} = x_2 \text{ i.e. } \frac{0.104\text{ mmHg}}{17.5\text{ mmHg}} = \frac{(50\text{ g}/M)}{(50\text{ g}/M) + (1000\text{ g}/18\text{ g mol}^{-1})}$$

Solving for M, we get $M = 150.5$ g mol^{-1}

$$\text{Number of repeating units of } CH_2O \text{ in the molecular formula} = \frac{150.5}{12+2+16} \simeq 5$$

Hence, Molecular formula of the compound is $C_5H_{10}O_5$.

6. An alcohol A, when heated with concentrated H_2SO_4 gives an alkene B. When B is bubbled through bromine water and the product obtained is dehydrohalogenated with excess of sodamide, a new compound C is obtained. The compound C gives D when treated with warm dilute H_2SO_4 in presence of $HgSO_4$. D can also be obtained either by oxidizing A with $KMnO_4$ or from acetic acid through its calcium salt. Identify A, B, C and D. (1983)

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20. An organic compound containing C, H and O exists in two isomeric forms A and B. A mass 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 NaOH and $NaHCO_3$ while B is soluble in NaOH. A reacts with concentrated 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 to give compound E of molecular formula, $C_7H_5OBr_3$. Identify A, B, C, D and E with justification and give their structures. (1991)

Solution We have

$$\text{Per cent of carbon in the compound} = \frac{M_C}{M_{CO_2}} \frac{m_{CO_2}}{m_{\text{compound}}} \times 100 = \left(\frac{12}{44}\right)\left(\frac{0.308}{0.108}\right)(100) = 77.78$$

$$\text{Per cent of hydrogen in the compound} = \frac{2M_H}{M_{H_2O}} \frac{m_{H_2O}}{m_{\text{compound}}} \times 100 = \left(\frac{2}{18}\right)\left(\frac{0.072}{0.108}\right)(100) = 7.41$$

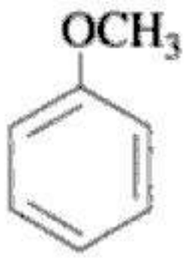
Per cent of oxygen in the compound = 100 – (77.78 + 7.41) = 14.81.

The ratios of atoms in the compound are

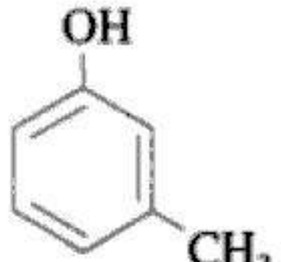
$$C : H : O :: \frac{77.78}{12} : \frac{7.41}{1} : \frac{14.81}{16} :: 6.48 : 7.41 : 0.926 :: 7 : 8 : 1$$

Hence, Empirical formula of the compound is C_7H_8O.

Since the isomer B on reacting with bromine water gives compound E ($C_7H_5OBr_3$), the molecular formula of A and B will be the same as the empirical formula derived above, since both contain the same number of carbon atoms. As E is obtained from B by the substitution of hydrogen with bromine and since there is high carbon content in B, the compounds A and B must be aromatic. Now, since compound A is insoluble in NaOH and $NaHCO_3$ and compound B is soluble in NaOH, it may be concluded that B is a phenolic compound and A is an ether. Hence, the structures of A and B are

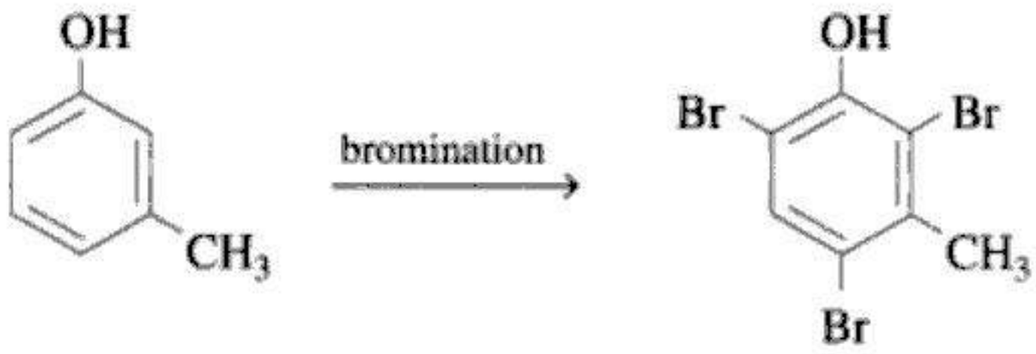


(A)
anisol

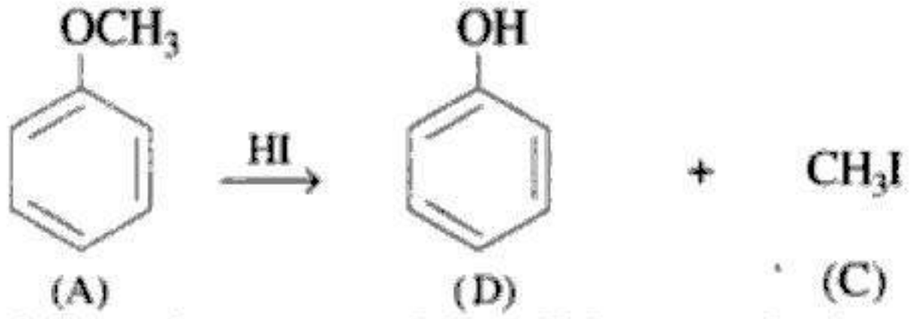


(B)
m-cresol

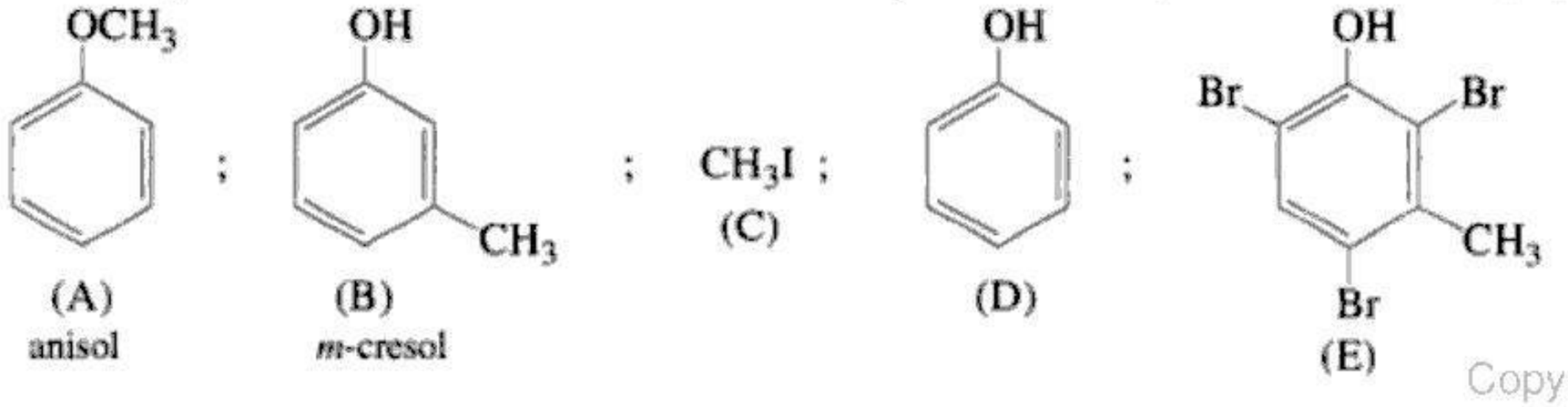
The bromination of B gives



The reaction of compound A with HI is



The compound C can be separated from D by use of ethanolic $AgNO_3$ solution as it is soluble in it whereas D will remain insoluble. The compound D will be soluble in NaOH as it is phenol. Hence, the structures of A, B, C, D and E are



(A) anisol ; (B) *m*-cresol ; CH_3I (C) ; (D) ; (E)

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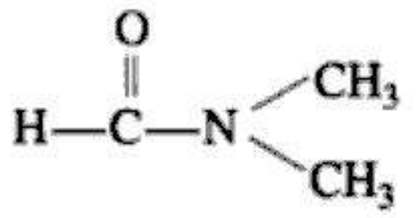


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28. A compound A (C_3H_7NO) on hydrolysis gives an amine B and a carboxylic acid C. Amine B reacts with benzenesulphonyl chloride and gives a product which is insoluble in aqueous sodium hydroxide solution. Acid C on reaction with Tollens reagent gives a silver mirror. Write the structures of A, B and C by writing the chemical equations involved.

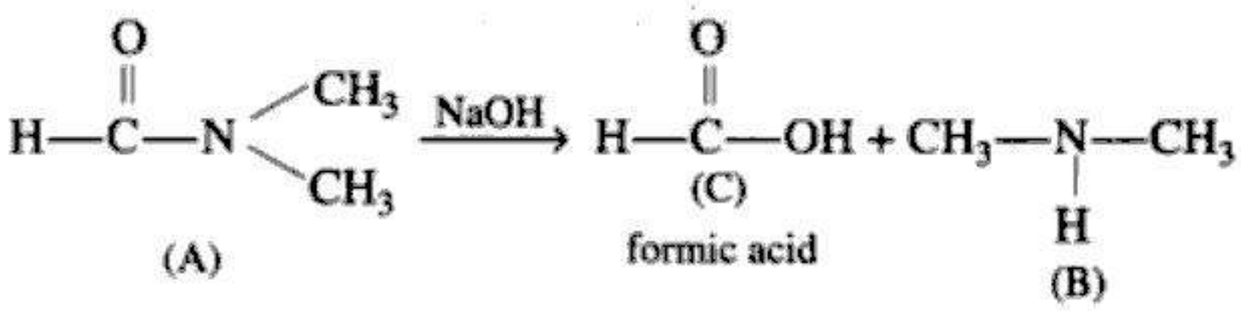
Solution The amine B must be a secondary amine as the product obtained with benzenesulphonyl chloride is insoluble in aqueous sodium hydroxide.

The acid C must be formic acid as it reduces Tollens reagent to give silver mirror.

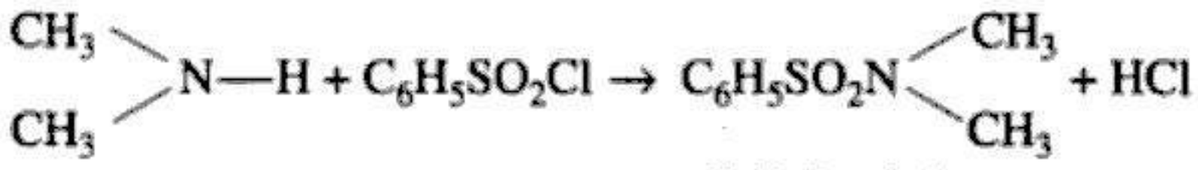
The compound A must be an amide having the structure 

N, *N*-dimethylformamide

The involved chemical reactions are



(A) (C) formic acid (B) dimethyl amine



N, *N*-dimethylbenzene ← sulphonamide

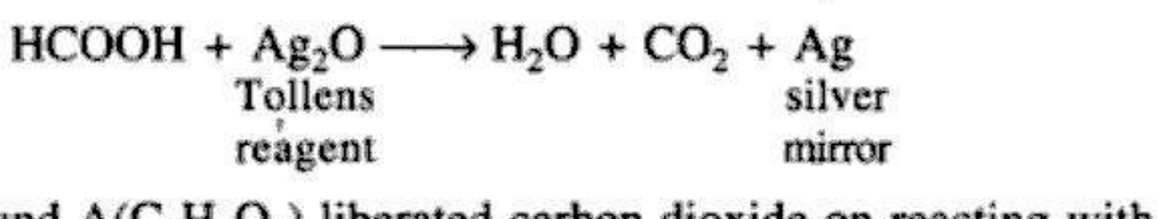
$$HCOOH + \underset{\text{Tollens reagent}}{Ag_2O} \longrightarrow H_2O + CO_2 + \underset{\text{silver mirror}}{Ag}$$

29. Compound A($C_5H_8O_2$) liberated carbon dioxide on reacting with sodium bicarbonate. It exists in two forms neither of which is optically active. It yields compound B ($C_5H_{10}O_2$) on hydrogenation. Compound B can be separated into enantiomorphs. Write the structural formulae for A and B giving reasons.

Solution From the reaction

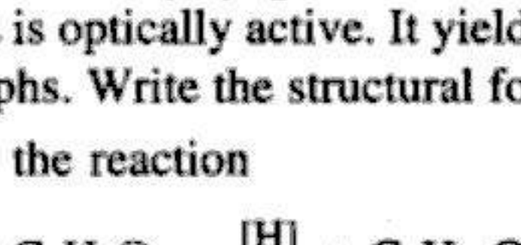
$$\underset{(A)}{C_5H_8O_2} \xrightarrow{[H]} \underset{(B)}{C_5H_{10}O_2}$$

we conclude that the compound A contains a carbon-carbon double bond. The compound A also contains carboxylic group as it liberated CO_2 on reacting with $NaHCO_3$. Since A exists in two forms, we conclude that A contains two methyl groups attached to different carbon atoms of double bond. Hence, the structures of A are



cis-form *trans*-form

Reduction of A generates B containing one asymmetric carbon and thus compound B exists in two enantiomorphs.



30. It required 0.70 g of a hydrocarbon A to react completely with Br_2 (2.0 g). On treatment of A with HBr, it yielded monobromo alkane B. The same compound B was obtained when A was treated with HBr in the presence of peroxide. Write down the structural formulae of A and B and explain the reactions involved.

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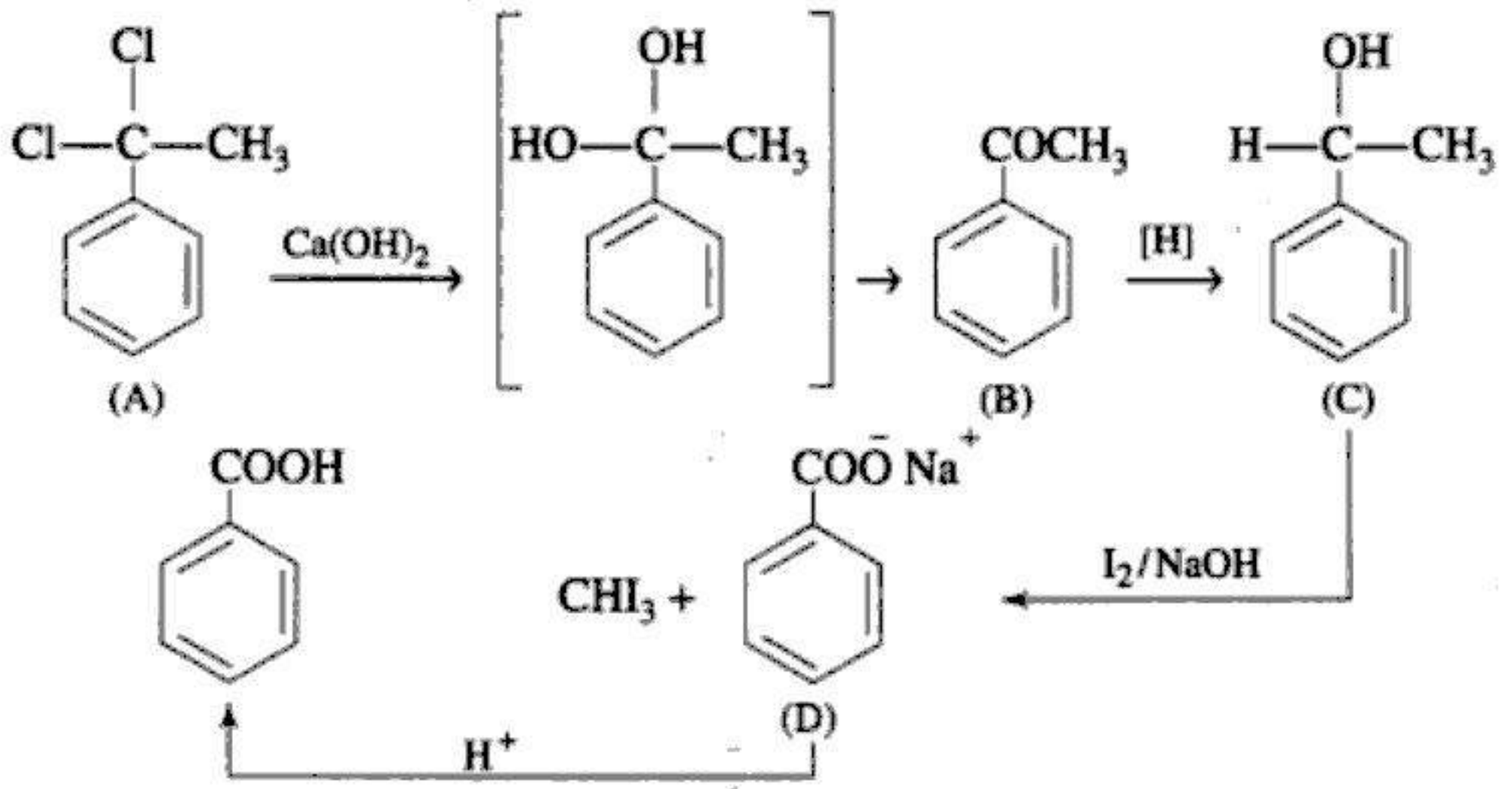
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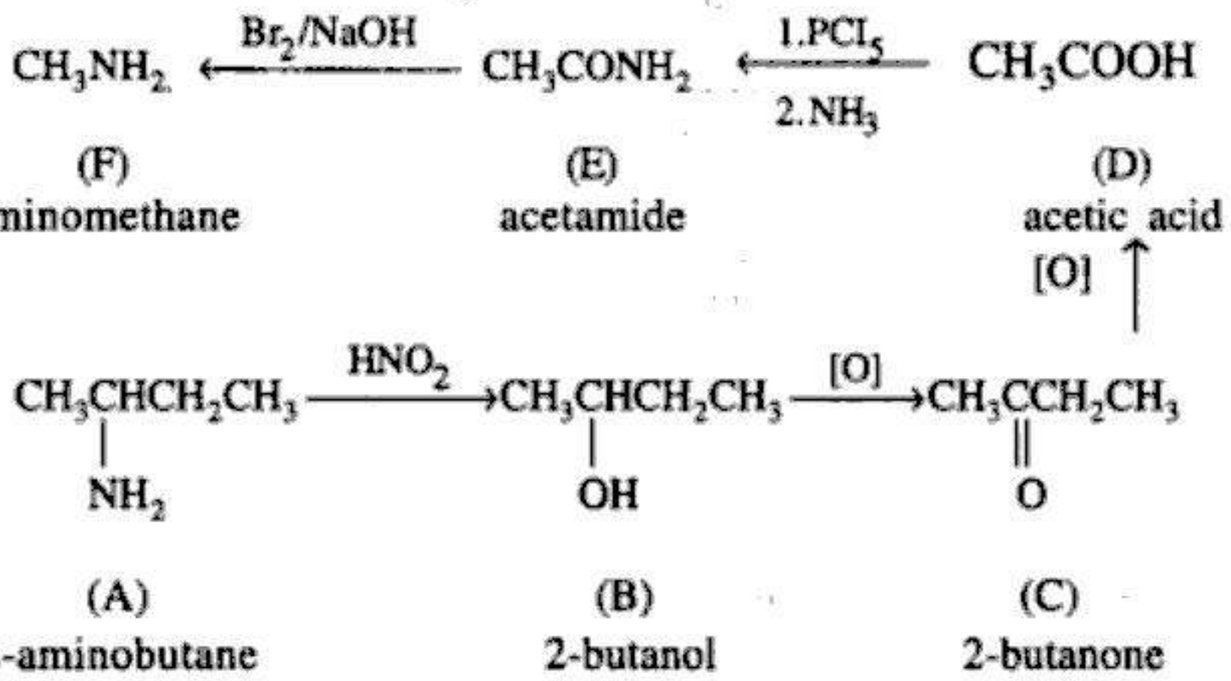


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44. An organic compound A($C_4H_{11}N$) on reacting with HNO_2 gave a compound B($C_4H_{10}O$). Compound B on mild oxidation gave C(C_4H_8O). Compound C on drastic oxidation gave D($C_2H_4O_2$). Compound D on treatment with PCl_5 followed by NH_3 gave E(C_2H_5NO) which on treatment with Br_2/NaOH gave F(CH_5N). Deduce the structures of A, B, C, D, E and F with reasoning. Write down the reactions involved.

Solution The compound A must be an aliphatic amine as it gives B, which is probably a primary alcohol. The compound C which is obtained by mild oxidation of B will be a ketone as the drastic oxidation of C produces a compound (probably carboxylic acid) with fewer carbon atoms. The conversion of D into E is the formation of amide which subsequently undergoes Hofmann degradation to give amine (F). With these reasoning, the given reactions may be formulated as shown in the following.

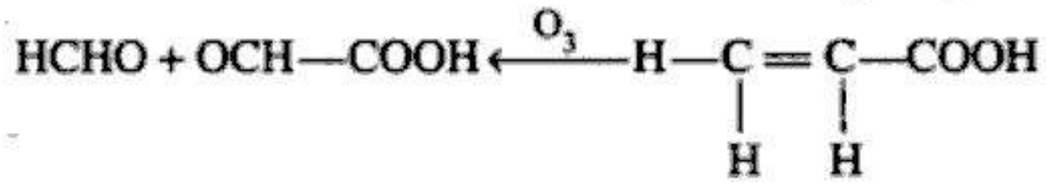


45. An organic compound A(C_4H_9N) on treatment with $NaNO_2$ and dilute HCl formed an alcohol B (C_4H_8O). The alcohol B when treated with I_2/NaOH formed iodoform and an unsaturated acid C($C_3H_4O_2$). The acid C on ozonolysis give formaldehyde and glyoxalic acid. What are the structures of A, B and C? Deduce them giving relevant equations.

Solution The compound A is primary amine as it gives alochol (B) on treating it with $NaNO_2$ and dilute HCl.

The compound B shows positive iodoform test and thus the alcohol will contain $CH_3—\underset{\displaystyle OH}{\overset{\displaystyle |}{\underset{\displaystyle |}{C}}}—$fragment.

The structure of acid C can be obtained from the ozonolysis products as shown in the following equation.



(C)

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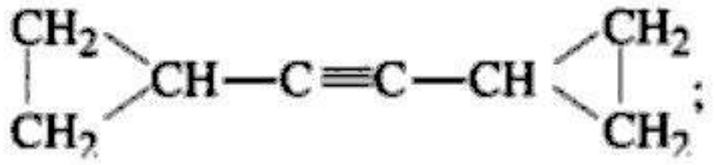
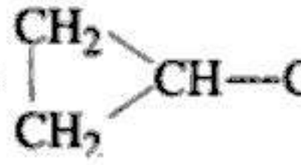
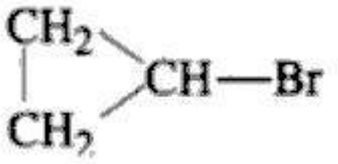


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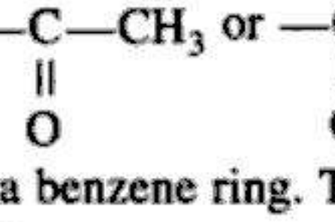


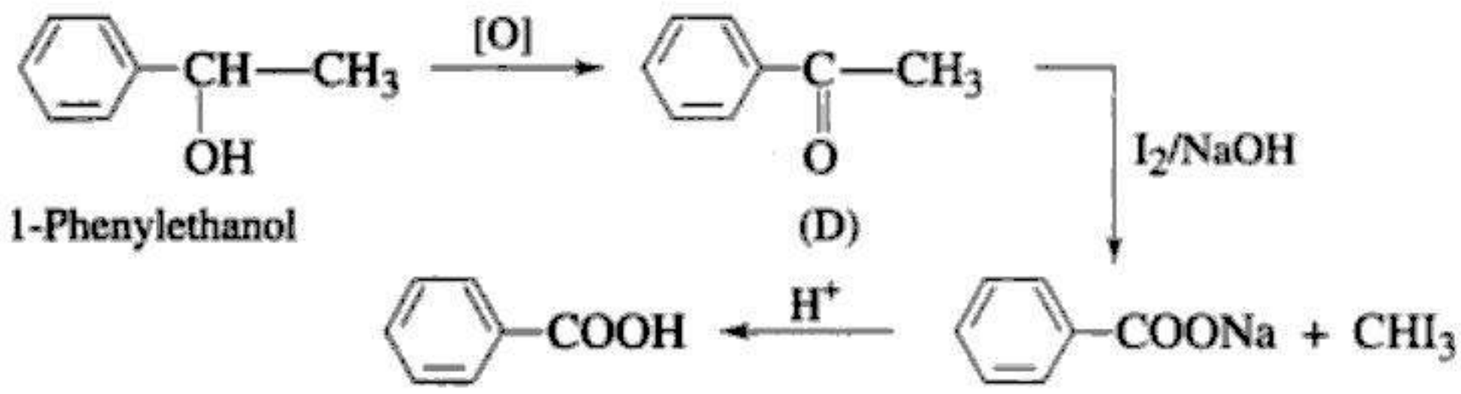
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The species C_3H_5 must be saturated alkyl group. The only possibility is the cyclopropyl group. Hence,

(A) is  ; (B) is  ; (C) is 

60. A compound D($C_8H_{10}O$) upon treatment with alkaline solution of iodine gives a yellow precipitate. The filtrate on acidification gives a white solid E($C_7H_6O_2$). Write the structures of D, E and explain the formation of E. (1996)

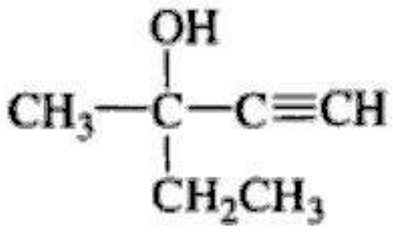
Solution The reaction of $C_8H_{10}O$ with alkaline solution of iodine is an iodoform reaction. This reaction is possible if the compound D has  group. The high carbon content in D indicates that D is an aromatic compound containing a benzene ring. To account for the given formula, the compound D may be $C_6H_5CH(OH)CH_3$. The given reactions are



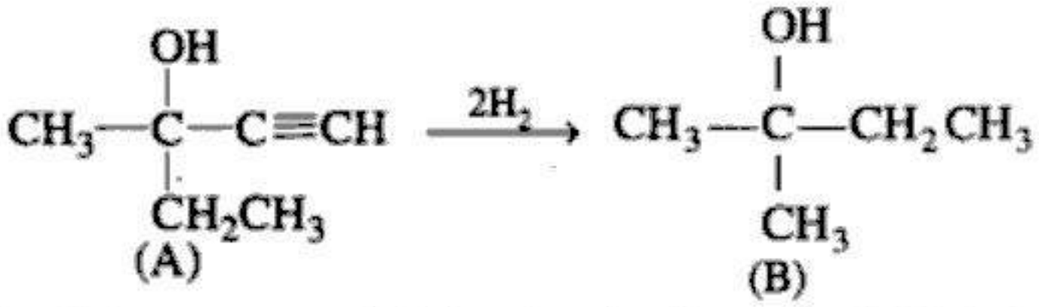
61. An optically active alcohol A($C_6H_{10}O$) absorbs two moles of hydrogen per mole of A upon catalytic hydrogenation and gives a product B. The compound B is resistant to oxidation by CrO_3 and does not show any optical activity. Deduce the structures of A and B. (1996)

Solution The given compound A has the following features.

(i) One alcoholic group as it contains one oxygen atom.
(ii) One asymmetric carbon as it is an optically active compound.
(iii) One triple bond as two moles of hydrogen can be added.
(iv) The carbon atom bearing —OH group does not contain H atom as the compound B is resistant to oxidation.

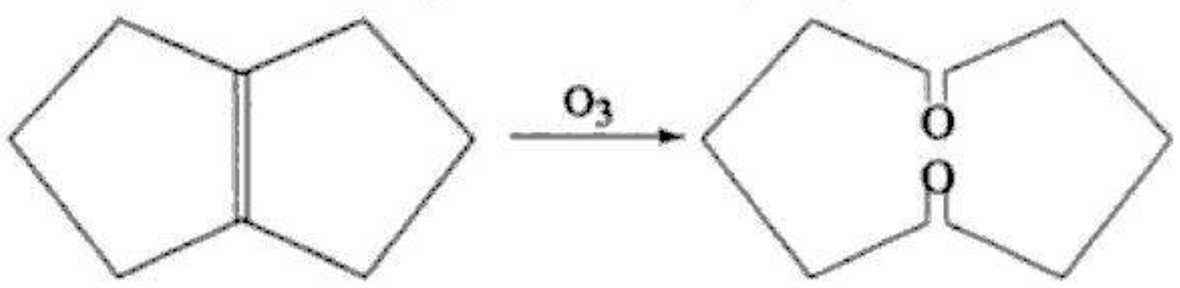
Consistent with the molecular formula, the structure of A may be 

Hence, we have



62. One mole of the compound A (molecular formula C_8H_{12}), incapable of showing stereoisomerism, reacts with only one mole of H_2 on hydrogenation over Pd. A undergoes ozonolysis to give symmetrical diketone B($C_8H_{12}O_2$). What are the structures of A and B? (1997)

Solution Since the compound A on ozonolysis gives only one symmetric diketone B with the same number of carbon atoms and also since A consumes only one mole of hydrogen, the structures of A and B are as follows.



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6. With bromine and caustic potash the straight chain compound C_4H_9ON (A) gives C_3H_9N(B). With caustic soda, it gives $C_4H_7O_2Na$(C) and with phosphorus pentaoxide, C_4H_7N(D). With hydrochloric acid, D gives $C_4H_8O_2$(E) of which C is the sodium salt. B may be converted to an alcohol (F) then to a halide. The Grignard reagent from the latter reacts with carbon dioxide to give E. On oxidation F gives successively C_3H_6O(G) and $C_3H_6O_2$(H). Identify the compounds A to H.

7. 0.4 g of a sample of impure urea on treatment with alkaline sodium hypobromite gave 112.0 cm^3 of nitrogen at STP. Calculate the per cent purity of the sample of urea.

8. An organic compound A($C_3H_6Cl_2$) gives with alkali B(C_3H_6O) or C(C_3H_4). The compound B gives D($C_5H_{12}O$) with ethyl magnesium iodide. The compound D forms an iodide E. The compound C reacts with dilute sulphuric acid containing mercuric sulphate to give F(C_3H_6O) which gives the salt G($C_2H_4O_2$) with bromine in alkali. The Grignard reagent from E reacts with F to give H($C_8H_{18}O$). Identify the compounds A to H giving the reactions involved.

9. An organic compound X contains 68.97% carbon, 14.94% hydrogen, the remaining being nitrogen. It reacts with nitrous acid, producing a substance Y which does not contain nitrogen. Y on oxidation yields an acid Z whose ethyl ester has the vapour density 65. X, Y and Z are optically active. Deduce the structures of X, Y and Z with adequate interpretation.

10. An organic compound A of the formula C_2H_6O on treatment with concentrated H_2SO_4 gives a neutral compound B($C_4H_{10}O$). The latter on treatment with PCl_5 gives a product which on subsequent treatment with KCN yields a compound C(C_3H_5N). The compound C on hydrolysis gives an acid ($C_3H_6O_2$) and on reduction with sodium amalgam gives a base C_3H_9N. What are the compounds A, B and C? Also give the reactions involved.

11. The compound C_8H_9Cl(A) on treatment with KCN followed by hydrolysis gives $C_9H_{10}O_2$(B). Ammonium salt of B on dry distillation yields C which reacts with alkaline solution of bromine to give $C_8H_{11}N$(D). Another compound E($C_8H_{10}O$) is obtained by the action of nitrous acid on D or by the action of aqueous potash on A. E on oxidation gives F($C_8H_6O_4$) which gives the inner anhydride G on heating. Deduce the structures of A to G giving the reactions involved.

12. An organic compound A($C_7H_6O_2$) forms a crystalline derivative with sodium bisulphite. When A is treated with cold sodium hydroxide solution, two substances, the sodium salt of an acid B and C, a primary alcohol, are obtained. B contains 60.9% carbon and 4.35% hydrogen and may also be obtained by oxidation of A. B when distilled with soda lime gives phenol. C contains 67.75% carbon and 6.45% hydrogen and may be obtained by reducing A. Deduce the structures A, B and C giving involved reactions.

13. A substance A shows the following composition : 70.6% carbon, 5.87% hydrogen and 23.5% oxygen. Its vapour density is 68. A when treated with PCl_5 and subsequently with NH_3 gives a substance B. When reacted with Br_2 and KOH, B forms a base C which on diazotization and boiling with water gives *o*-cresol. What are A, B and C?

14. A compound A has the molecular formula $C_{10}H_{12}O_2$ and is soluble in aqueous sodium hydroxide but insoluble in sodium bicarbonate solution. Treatment of compound A with dimethyl sulphate and aqueous sodium hydroxide gives compound B of molecular formula $C_{11}H_{14}O_2$, while treatment of compound A with strong alkali alone gives an isomeric compound A′. Methyl iodide is formed on refluxing compound A with hydriodic acid. Compound B is insoluble in alkali and decolourises potassium permanganate and bromine; treatment with strong alkali converts compound B to an isomer B′. Ozonolysis of A′ gives a compound C of molecular formula $C_8H_8O_3$ and isomeric with vaniline. Ozonolysis of compound B′ gives a compound D of molecular formula $C_9H_{10}O_3$ and which is identical with the product of methylation of vaniline. (4-hydroxy-3-methoxybenzaldehyde). Deduce the structures of compounds A, A′, B, B′, C and D.

15. An aromatic hydrocarbon A containing 91.3% carbon gives on chlorination three isomeric monochloro derivatives X, Y and Z. Percentage of chlorine in each one of these is 28%. On oxidation with potassium permanganate all the three give one monobasic acid. Acid obtained from X gives benzene on distillation with soda lime. Acids obtained from Y and Z on similar treatment give monochlorobenzene. Determine the structural formulae of various compounds. Explain the reactions involved.

16. A compound A of the formula $C_7H_5O_2NCl_2$ is soluble in alkali. The compound on reduction with Fe/HCl followed by treatment with HNO_2 gives a primary alcohol B which contains no nitrogen. B on oxidation gives an acid C, the equivalent mass of which is 191 g mol^{-1}.

Decarboxylation of C furnishes D containing 48.3% chlorine. D forms only one mononitro derivative. Deduce the structures of A to D giving the reactions involved.

17. An aromatic hydrocarbon A has vapour density 46. On oxidation with chromyl chloride (Etard's reaction) it gives compound B which on reaction with concentrated sodium hydroxide yielded an aromatic acid C and an alcohol D. Acid C can be obtained by the oxidation of A with alkaline potassium permanganate. D is obtained when B is reduced with sodium amalgam and an acid. Explain the reactions involved and the structural formulae of A, B, C and D.

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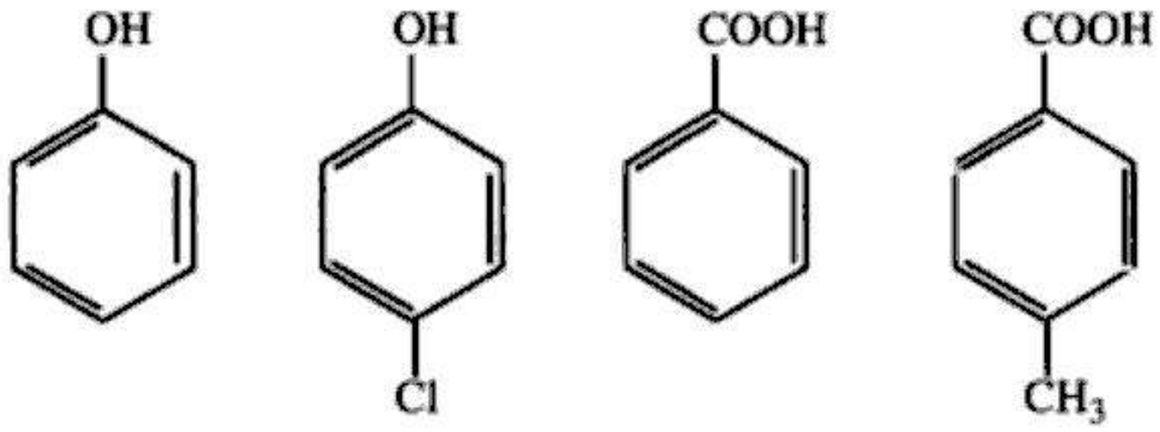


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Solving for n_{N_2}, we get $n_{N_2} = \dfrac{4.0\times10^{-5}\,(10\,\text{mol})}{1-4.0\times10^{-5}} = 4.0\times10^{-4}\ \text{mol}$

Therefore, the **choice (a)** is correct.

2. The correct acidity order of the compounds



(I) (II) (III) (IV)

is

(a) (III) > (IV) > (II) > (I) (b) (IV) > (IIII) > (I) > (II)

(c) (III) > (II) > (I) > (IV) (d) (II) > (III) > (IV) > (I)

SOLUTION

Carboxylic acids are stronger acids than phenols.

Methyl group is an electron-releasing group, it weakens the acidity of carboxylic acid.

Chlorine is electron-attracting group, it strengthens the acidity of phenol. Hence, the correct acidity order of the given compounds is (III) > (IV) > (II) > (I)

Therefore, the **choice (a)** is correct.

3. The reaction of P_4 with X leads selectively to P_4O_6. The X is

(a) Dry O_2 (b) A mixture of O_2 and N_2

(c) Moist O_2 (d) O_2 is the presence of aqueous NaOH

SOLUTION

P_4O_6 is obtained when P_4 is burned in a deficit of oxygen.

Therefore, the **choice (b)** is correct.

4. Among cellulose, poly(vinyl chloride), nylon and natural rubber, the polymer in which the intermolecular force of attraction is weakest is

(a) Nylon (b) Poly(vinyl chloride) (c) Cellulose (d) Natural rubber

SOLUTION

Natural rubber is an elastomer. The irregular geometry of the molecules involves weak van der Waals force of interactions.

Therefore, the **choice (d)** is correct.

5. Given that the abundances of isotopes ^{54}Fe, ^{56}Fe and ^{57}Fe are 5%, 90% and 5%, respectively, the relative atomic mass of Fe is

(a) 55.85 (b) 55.95 (c) 55.75 (d) 56.05

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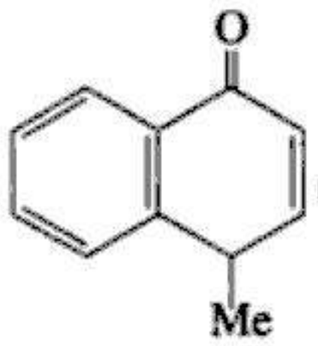


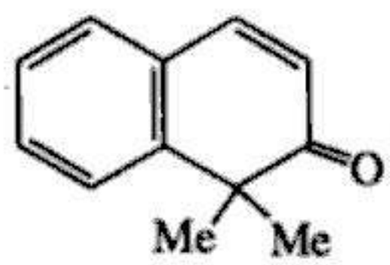
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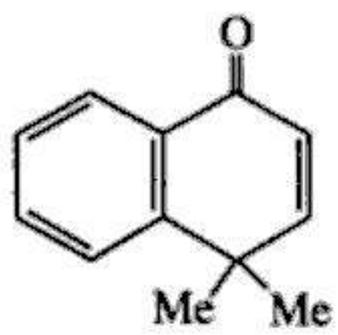
SOLUTION

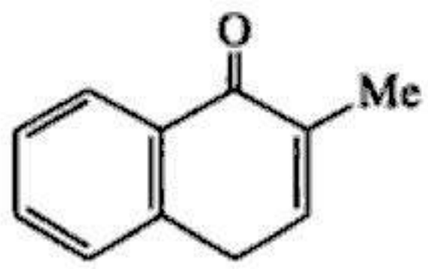
From the reactions shown in Q.13, it follows that the **choice (a)** is correct.

15. The structure of product S is

(a) 

(b) 

(c) 

(d) 

SOLUTION

From the reactions shown in Q.13, it follows that the **choice (b)** is correct.

Paragraph for Question Nos. 16 to 18

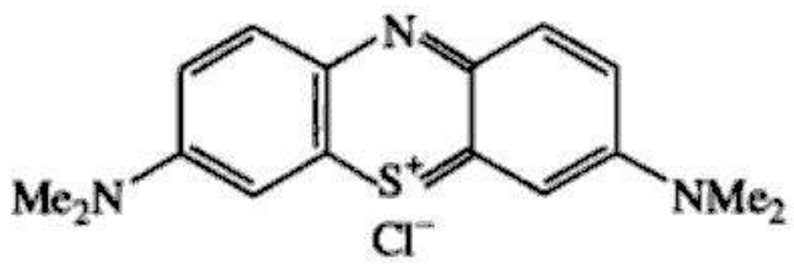
p-Amino-N, N-dimethylaniline is added to a strongly acidic solution of X. The resulting solution is treated with a few drops of aqueous solution of Y to yield blue coloration due to the formation of methylene blue. Treatment of the aqueous solution of Y with the reagent potassium hexacyanoferrate(II) leads to the formation of an intense blue precipitate. The precipitate dissolves on excess addition of the reagent. Similarly, treatment of the solution of Y with the solution of potassium hexacyanoferrate(III) leads to a brown coloration due to the formation of Z.

16. The compound X is

(a) $NaNO_3$ (b) NaCl (c) Na_2SO_4 (d) Na_2S

SOLUTION

The structure of methylene blue is



It follows that X must be Na_2S.

Therefore, the **choice (d)** is correct.

17. The compound Y is

(a) $MgCl_2$ (b) $FeCl_2$ (c) $FeCl_3$ (d) $ZnCl_2$

SOLUTION

The involved reactions are as follows.

$$Fe^{3+} + \underset{\text{excess}}{[Fe(CN)_6]^{4-}} \rightarrow \underset{\text{Blue}}{Fe_4[Fe(CN)_6]_3}$$

$$Fe^{3+} + \underset{\text{Reddish-brown}}{[Fe(CN)_6]^{3-}} \rightarrow Fe[Fe(CN)_6]$$

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$$4Zn + 10HNO_3 \xrightarrow[\text{(dil.)}]{} 4Zn(NO_3)_2 + 5H_2O + N_2O$$

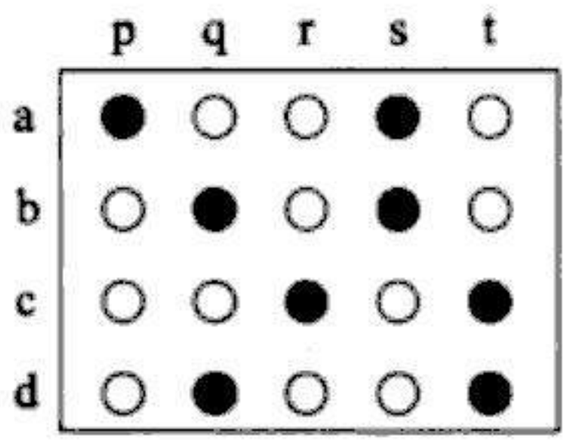
$$Zn + 4HNO_3 \xrightarrow[\text{(conc.)}]{} Zn(NO_3)_2 + 2H_2O + 2NO_2$$

The correct matching are

(a)—(p) and (s)　　(b)—(q) and (s)

(c)—(r) and (t)　　(d)—(q) and (t)

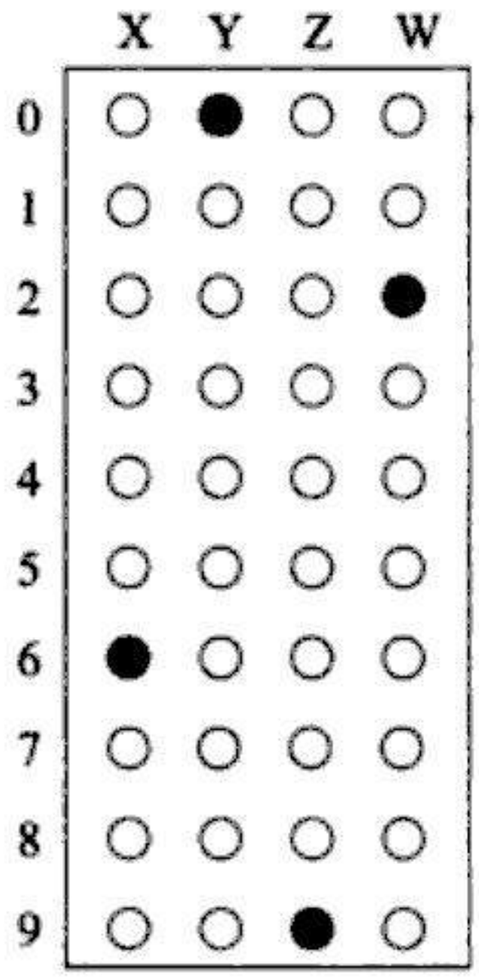
The correct bubbled diagram is



SECTION – IV

INTEGER ANSWER TYPE

This section contains 8 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. The appropriate bubbles below the respective question numbers in ORS have to be darkened. For example, if the correct answers to question numbers X, Y, Z and W (say) are 6, 0, 9 and 2, respectively, then the correct darkening of bubbles will like the following.



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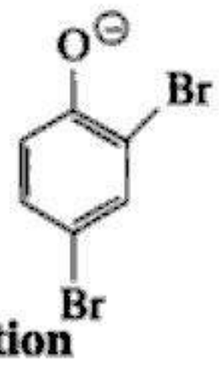
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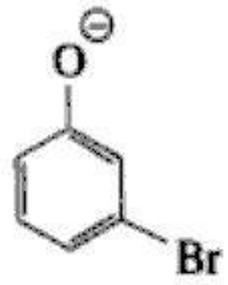


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(a) 

(b) 

(c) 

(d) 

Solution

The intermediates are given by the Choices (a) and (c). The final product is 2,4,6-tribromophenoxide ion. Hence the **Choices (a) and (c)** are correct.

SECTION–III

(Paragraph Type)

This Section contains **2 paragraphs**. Based upon the first paragraph **3 multiple choice questions** and based upon the second paragraph **2 multiple choice questions** have to be answered. Each of these questions has four choices (a), (b), (c) and (d) out of which **ONLY ONE** is correct.

Paragraph for Questions 14 to 16

Copper is the most noble of the first row transition metals and occurs in small deposits in several countries. Ores of copper include chalcanthite ($CuSO_4 \cdot 5H_2O$), atacamite ($Cu_2Cl(OH)_3$), cuprite (Cu_2O), copper glance (Cu_2S) and malachite ($Cu_2(OH)_2CO_3$). However, 80% of the world copper production comes from the ore chalcopyrite ($CuFeS_2$). The extraction of copper from chalcopyrite involves partial roasting, removal of iron and self-reduction.

14. Partial roasting of chalcopyrite produces

(a) Cu_2S and FeO (b) Cu_2O and FeO (c) CuS and Fe_2O_3 (d) Cu_2O and Fe_2O_3

15. Iron is removed from chalcopyrite as

(a) FeO (b) FeS (c) Fe_2O_3 (d) $FeSiO_3$

16. In self-reduction, the reducing species is

(a) S (b) O^{2-} (c) S^{2-} (d) SO_2

Solution

14. Partial roasting of the ore chalcopyrite ($CuFeS_2$) produces Cu_2S and FeO as per equations given below.

(i) $2CuFeS_2 + O_2 \longrightarrow Cu_2S + 2FeS + SO_2\uparrow$ (major)

(ii) $2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$ (minor)

(iii) $2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$ (minor)

Hence, the **Choice (a)** is correct.

15. Iron is removed as $FeSiO_3$.

$$FeO + SiO_2 \longrightarrow FeSiO_3$$

Hence, the **Choice (d)** is correct.

16. The basic reaction are

$$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$$

Here S^{2-} in Cu_2S is changed to $\overset{4+}{S}$ in SO_2. Thus, reducing species is S^{2-} as it undergoes the reaction

$$S^{2-} \longrightarrow \overset{4+}{S} + 6e^-.$$

Hence, the **Choice (c)** is correct.

Paragraph for Question 17 to 18

The concentration of potassium ions inside a biological cell is at least twenty times higher than the outside. The resulting potential difference across the cell is important in several processes such as transmission of nerve impulses and

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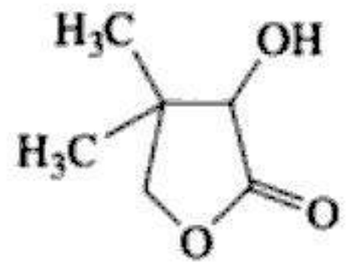
SECTION–III

(Paragraph Type)

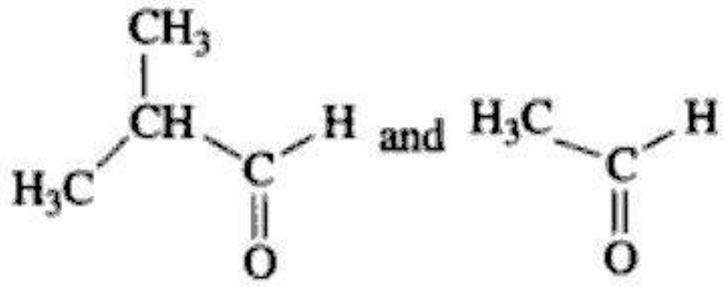
This Section contains **2 paragraphs**. Based upon each of the paragraphs **3 multiple choice questions** have to be answered. Each of these questions has four choices (a), (b), (c) and (d) out of which **ONLY ONE** is correct.

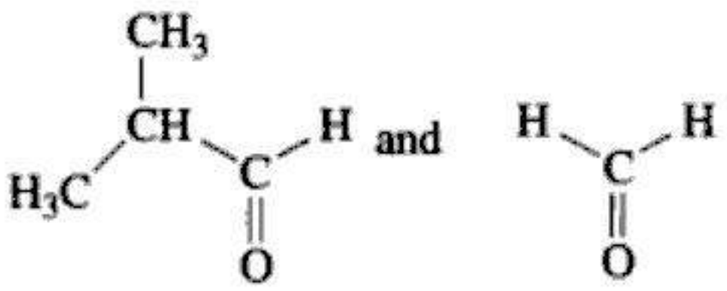
Paragraph for questions 12 to 14

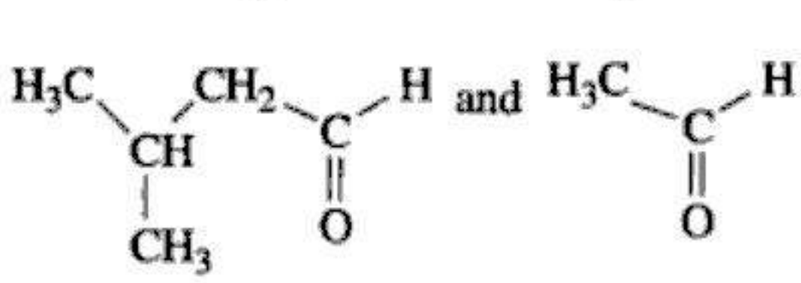
Two aliphatic aldehydes P and Q react in the presence of aqueous K_2CO_3 to give compound R, which upon treatment with HCN provides compound S. On acidification and heating, S gives the product shown below:

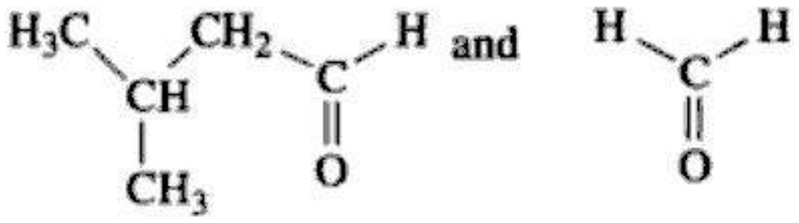


12. The compounds P and Q respectively are

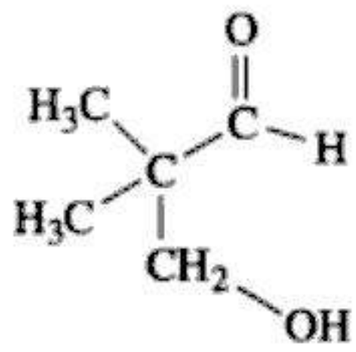
(a)  and

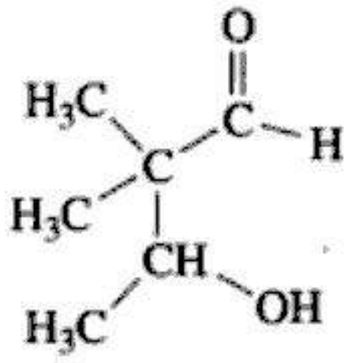
(b)  and

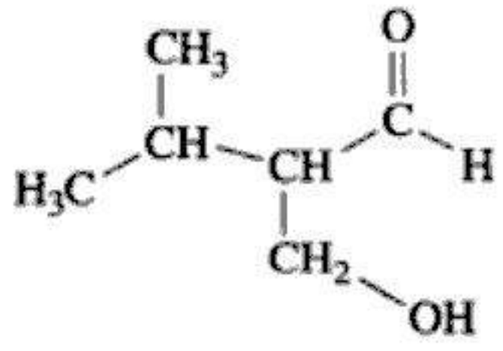
(c)  and

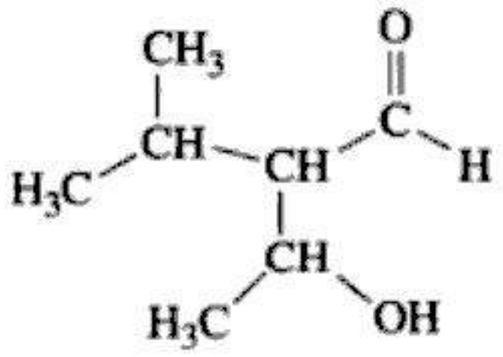
(d)  and

13. The compound R is

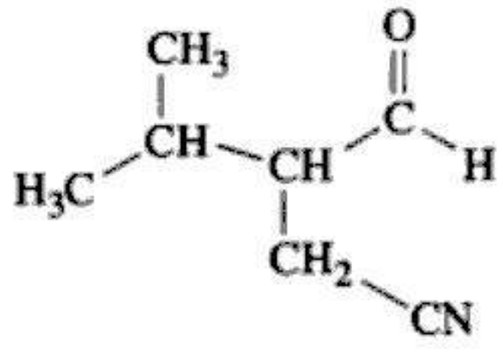
(a) 

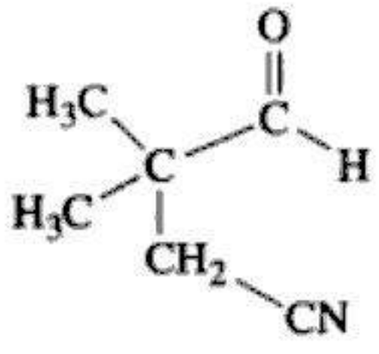
(b) 

(c) 

(d) 

14. The compound S is

(a) 

(b) 

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