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December 2016 | ₹ 35.00

CHEMISTRY Spectrum

TARGET 2017

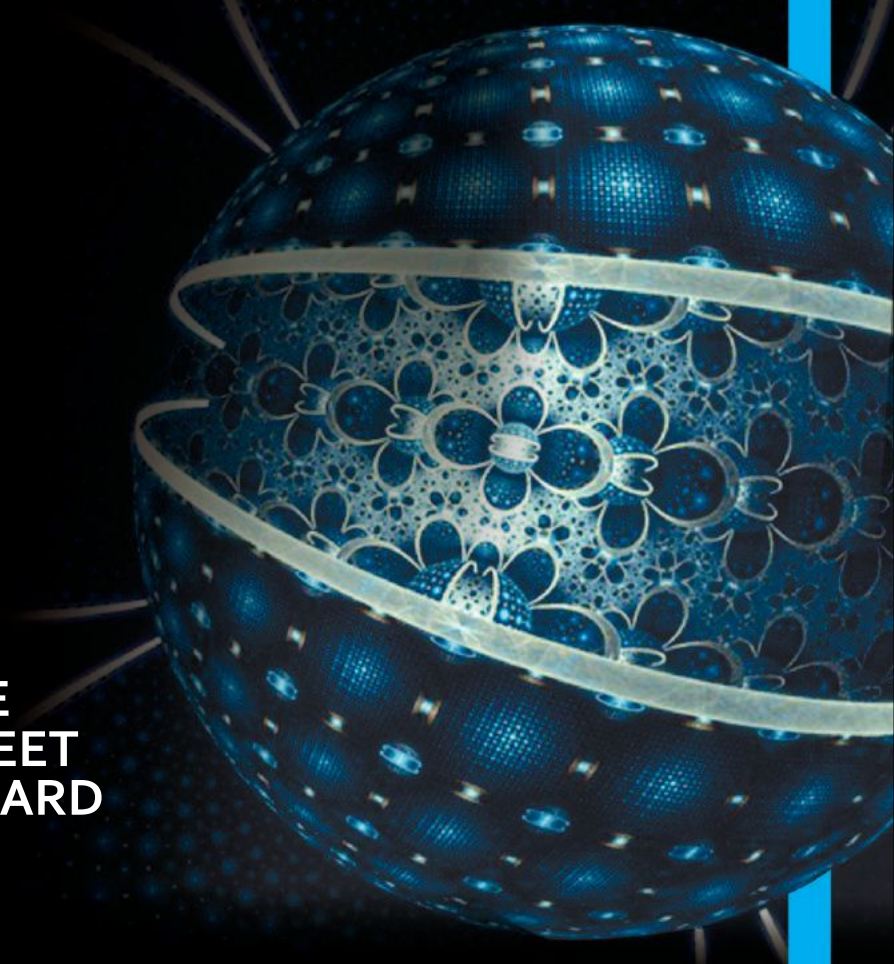
Rapid Concept Revision

Some Basic Concepts of Chemistry
Atomic Structure
Redox Reactions

FROM CLASS 11 SYLLABUS

Solid State
Solutions
Electrochemistry

FROM CLASS 12 SYLLABUS



TEST RIDER FOR JEE
MEDI QUEST FOR NEET
TEST DRIVE FOR BOARD

JUVENILEZ

GOLDEN OLDIES *p-block elements*
RAINBOW *Nucleophilic Substitution*
FUN ARCADE

MEGA ISSUE 1
More Pages
More Features
More Practice...

15 SAMPLE QUESTION PAPERS

CBSE CLASS XI & XII
EXAMINATION 2017

Fast Track Revision at the Start of the Book Three Stages; I,II & III of Sample Papers
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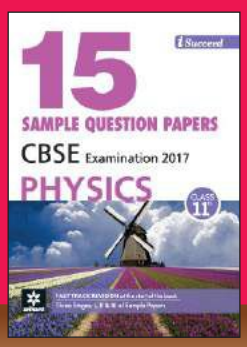

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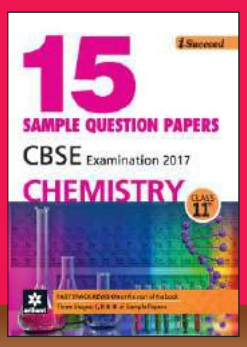

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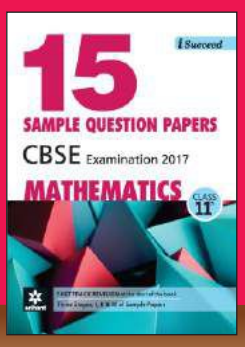

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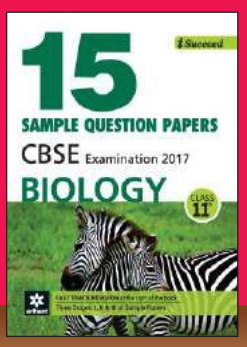

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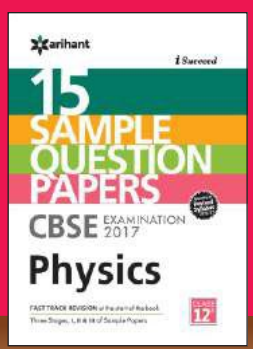

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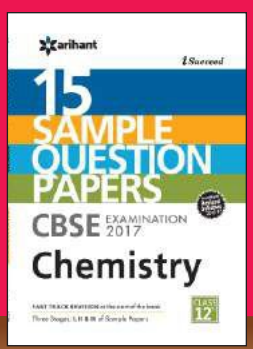

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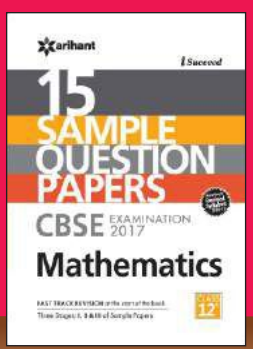

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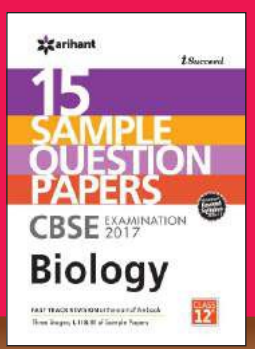

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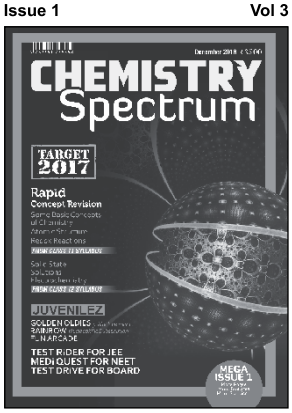


Dear Aspirants,

For many of you the month of December is very precious as it is the first month to gear up your studies. For an aspirant it is very difficult to maintain a proper balance between emotions, performance, attitude, work pressure and time availability during this month.This balancing requires cool, calm and focused approach. So, in my opinion one must follow "no aggression – only devotion" policy during this month.

Change or Updations are the prime requirements to live in a system with dynamically changing environment. We as Spectrum family also follow the same and always try to incorporate something new for you. With this ideology in this first Mega issue of this season with ***more pages, more practice*** *and* ***more features*** we are introducing two new columns from this issue, i.e.

Rapid Concept Revision and
Test Drive

Both of these columns are targeted to fine tune your preparations in synchrony with Target 2017. Hope, these columns will prove their worth with a difference and you will like the change. Remember

"Minds are like parachutes; they only function when open"
Thomas R. Dewar

So, open up yourself, be positive and work hard to succeed. The spectrum team will be anxiously waiting for your feedbacks and comments.

Good luck

Contents

@ CLASS XI SYLLABUS

Rapid CONCEPT REVISION

TARGET 2017

SOME BASIC CONCEPTS OF CHEMISTRY

MATTER, ITS PROPERTIES AND MEASUREMENTS

- Matter is anything that has mass and occupies space.
- Matter exist in three different forms such as solid, liquid and gas according to the competition between intermolecular interactions and thermal energy.
- The two other states of matter are also known. These are named as **Plasma** and **Bose-Einstein condensate** but exist only in extreme conditions of temperature and pressure.
- Properties of matter can be classified as physical and chemical properties which are quantitative in nature.
- To measure a quantitative property, various systems of measurement have been introduced, that vary according to their region.
- International system of unit (SI system) was introduced to standardise measurements which contains 7 basic units and 2 derived units.
- The following prefixes are also useful in representing a measurement.

Multiple	Prefix	Symbol	Multiple	Prefix	Symbol
10	deca	da	10^{-1}	deci	d
10^{2}	hecto	h	10^{-2}	centi	c
10^{3}	kilo	k	10^{-3}	milli	m
10^{6}	mega	M	10^{-6}	micro	μ
10^{9}	giga	G	10^{-9}	nano	n
10^{12}	tera	T	10^{-12}	pico	p
10^{15}	peta	P	10^{-15}	femto	f
10^{18}	exa	E	10^{-18}	atto	a
10^{21}	zetta	Z	10^{-21}	zepto	z
10^{24}	yotta	Y	10^{-24}	yocto	y

Precision and Accuracy

- A measurement is said to be precise when the values of different measurements are close to each other.
- A measurement is said to be accurate when the average values of different measurements are closed to the true value.
- Uncertainty in measurement is expressed in terms of **significant figures**.
- Significant figure is defined as the total number of digits in a quantity whose values are uncertain.

Rules in Significant Figures

- During addition or subtraction, the final result should not contain more significant figures to the right of decimal point than either of the original numbers.

  e.g. $\underset{2\ SF}{0.13} + \underset{2\ SF}{1.5} + \underset{5\ SF}{20.911} = 22.541 = \underset{1\ SF}{22.5}$

- During multiplication or division, the final result should not contain more significant figures than the quantity containing least significant figures.

  e.g. $\dfrac{4.28 \times 0.146 \times 3.00}{0.0418} = 44.84784 = \underset{3\ SF}{44.8}$

- Some important unit conversions in chemistry are given in the following table.

	Physical quantity	Units
1.	Mass	$1u = 1.66 \times 10^{-27}$ kg $= 931.48$ MeV 1 ton $= 10^3$ kg $= 10^6$ g $= 10^9$ mg 1 metric ton $= 10^6$ kg; 1 pound $= 0.454$ kg
2.	Volume	$1\ m^3 = 10^3$ L $= 10^6$ mL $= 10^6\ cm^3$ $1\ L = 1\ dm^3 = 10^3$ mL $= 10^{-3}\ m^3$
3.	Temperature	$K = 273 + {}^\circ C$; ${}^\circ C = 5/9\ ({}^\circ F - 32)$
4.	Pressure	$1\ atm \approx 1.013 \times 10^5 Pa (N/m^2)$ ≈ 1.013 bar ≈ 760 torr ≈ 760 mm of Hg ≈ 76 cm Hg
5.	Energy	$1\ eV = 1.602 \times 10^{-19}$ J; MeV $= 10^6$ eV 1 cal ≈ 4.18 J; 1 J $= 10^7$ erg

Classification of Matter

At macroscopic level matter can be classified into the following types :

- **Mixtures** contains two or more substances mixed in any composition with variable properties. Mixtures are further classified into two categories, homogeneous and heterogeneous mixtures.
- **The homogeneous mixtures** have same composition throughout (e.g. sugar solution) while **heterogeneous mixtures** do not have the same composition throughout (e.g. ores, colloidal solution).
- **Pure substances** have fixed composition with non-variable properties. Pure substances are further classified into elements and compounds.
- **Elements** contains only one type of atom or molecule (e.g. H_2, N_2) while **compound** contains two or more different atoms but in fixed ratio, (e.g. H_2O, CH_4).

Best Practice SHOTS

1. Which of the following statement is incorrect?
(a) Matter is anything that has mass and occupies space
(b) Weight (w) is the force experienced by an object on earth and is equal to its mass m multiplied by acceleration due to gravity (g), i.e. $w = mg$
(c) Energy and matter is neither created nor destroyed, but it can change its form and the total quantity of them in the universe is constant
(d) Matter cannot be converted into energy and *vice-versa*

2. The solid like conducting state of gases with free electrons is called
(a) sol state *(b)* gel state
(c) plasma state *(d)* All of these

3. Match the following quantities (Column I) with their SI base units (Column II).

Column I		Column II	
A.	Density	p.	$JA^{-1}\ s^{-1}$
B.	Pressure	q.	As
C.	Electric charge	r.	$kg\ m^{-1}s^{-2}$
D.	Electric potential	s.	Candela
E.	Amount of substance	t.	$kg\ m^{-3}$
F.	Luminous intensity	u.	mole

Codes

	A	B	C	D	E	F
(a)	t	r	q	p	u	s
(b)	u	s	t	t	r	q
(c)	p	q	r	s	t	u
(d)	u	t	s	t	p	q

4. Select the incorrect relation(s) and choose the correct option.
I. 200 lb $= 90.7$ kg
II. 2 km $= 345$ miles
III. 0.8 carat $= 0.1$ kg
IV. $-20^\circ C = 253.15\ K = -4^\circ F$
(a) I and II *(b)* III and IV
(c) I and IV *(d)* II and III

5. Match the following numbers (Column I) with the number of significant figures (Column II).

Column I		Column II	
A.	π	p.	Infinite
B.	Sum of $7.65 + 2.72 \times 10^{-2}$	q.	Five
C.	Product of $(7.6 \times 10^7) \times (3.8 \times 10^{-4})$	r.	Four
D.	1.456×10^1	s.	Three
E.	34000	t.	Two

Codes

	A	B	C	D	E
(a)	s	q	q	r	t
(b)	p	q	q	r	t
(c)	p	s	r	r	t
(d)	s	s	r	q	q

6. Which of the following is not an element?
(a) Graphite *(b)* Silica
(c) Diamond *(d)* Plasma sulphur

7. Which of the following is homogeneous mixture?
(a) Dust *(b)* Bronze
(c) Pencil led *(d)* Antena rod

8. A measured temperature on Fahrenheit scale is 200°F. The reading on celsius scale will be
(a) 40° C *(b)* 93.3° C
(c) 94° C *(d)* 30° C

LAWS OF CHEMICAL COMBINATIONS, DALTON'S ATOMIC THEORY AND DIFFERENT MASSES

Laws of Chemical Combinations

Chemical reactions involving matter are governed by the following laws.

- **Law of conservation of mass** (Antoine Lavoisier) During a chemical reaction, total mass of reactants before a reaction is equal to total mass of products after a reaction.
- **Law of definite proportions** (Joseph Proust) A given compound always contains exactly the same proportion of elements by weight.
- **Law of multiple proportions** (John Dalton) When two elements combine to form more than one compound, the masses of one element that combine with a fixed mass of other elements bear a simple ratio.
- **Gay-Lussac's law of gaseous volumes** In a chemical reaction involving gases, the volumes of the reactants and those of gaseous products bear a simple ratio.
- **Law of reciprocal or equivalent proportions** (Richter) When two elements combine with fixed weight of third element then it is either the same or simple multiple ratio of weight of two elements which combine directly with each other.
- **Avogadro's law** At constant temperature and pressure, equal volumes of all gases is proportional to the equal number of molecules. The volume of one mole of a gas at STP is 22.4 L and it contains Avogadro's number of molecules ($N_A = 6.023 \times 10^{23}$).

Exceptions Related to Laws

- Law of conservation of mass is not applicable to nuclear reactions. In a nuclear reaction, mass is converted into energy. Thus, the law has been modified and known as law of conservation of mass and energy. According to which "the mass and energy are interconvertible but the total sum of the mass and energy during any physical or chemical change remains constant."
- Law of definite proportions is not applicable in case of isotopes as they form different compounds with different properties but have same composition.
- Law of multiple proportions is not applicable to non-stoichiometric compounds like $Fe_{0.95}O$. It also doesn't work well with polymers and oligomers.

Dalton's Atomic Theory

In 1803, Dalton proposed the first atomic theory having the following postulates.

- Matter consists of small indivisible particles called atom, which take part in chemical reaction. However, it is no more considered as indivisible after the discovery of proton, electron and neutron.
- Atoms of same elements have similar properties and that of different elements have different properties.
- Compounds are formed when different atoms combine in a fixed ratio through chemical reaction.
- Chemical reactions involve reorganisation of atoms. These are neither created nor destroyed during a chemical reaction.

Atomic Mass and Gram Atomic Mass

- The mass of one atom of any element is called **atomic mass** and is represented by amu or u (1 amu= 1.66×10^{-27}).
- Atomic mass of one mole of an atom is called **gram atomic mass** and is represented in gram.
- Many atoms exist as different isotopes in different percentages. In such case, average atomic mass is calculated.

$$\text{Average atomic mass} = \frac{X_1A_1 + X_2A_2 + \ldots}{X_1 + X_2 + \ldots}$$

where X_1, X_2, ... are percentage of relative abundance of atomic masses A_1, A_2 ... , respectively.

Molecular and Molar Mass

- The sum of atomic masses of all elements present in a molecule is called **molecular mass**.
- The mass of one mole of a molecule is called **molar mass**.

Equivalent Mass

- It is the number of parts of a substance that combines or displaces either directly or indirectly, 1.008 parts by mass of hydrogen or 8 parts by mass of oxygen or 35.5 parts by mass of chlorine.
- $$\text{Equivalent mass of metal} = \frac{\text{Mass of metal}}{\text{Mass of } X \text{ displaced}} \times Y$$

where, $X = H_2$, O_2 and Cl_2 and $Y = 1.008$, 8 and 35.5, respectively.

FORMULAE RELATED TO EQUIVALENT MASS (E)

- $E_{\text{element}} = \dfrac{\text{Atomic mass of element}}{\text{Valence electrons of element}}$
- $E_{\text{ion}} = \dfrac{\text{Formula mass of ion}}{\text{Charge of ion}}$
- $E_{\text{salt}} = \dfrac{\text{Formula mass of salt}}{\text{Total positive or negative charge on cation / anion}}$
- $E_{\text{acid/base}} = \dfrac{\text{Molecular mass of acid / base}}{\text{Basicity / acidity}}$
- $E_{\text{oxidising/reducing agent}} = \dfrac{\text{Molecular mass of oxidising / reducing agent}}{\text{Change in oxidation number of oxidising / reducing agent}}$
- During metal displacement reaction,

$$\frac{\text{Mass of metal added}}{\text{Mass of metal displaced}} = \frac{E_{\text{metal}}\text{added}}{E_{\text{metal}}\text{displaced}}$$

Best Practice SHOTS

9. In an experiment, 2.4 g of iron oxide on reduction with hydrogen gave 1.68 g of iron. In another experiment, 2.9 g of iron oxide gave 2.09 g of iron on reduction. Which law is illustrated from the above data?

(a) Law of constant proportions
(b) Law of multiple proportions
(c) Law of reciprocal proportions
(d) Law of conservation of mass

10. Assuming that the results given below taken together illustrate the law of reciprocal proportions, calculate the masses of oxygen and hydrogen in 1.25 g of water.

I. 0.46 g of Mg produces 0.77 g of MgO.
II. 0.82 g of Mg liberates 760 mL of hydrogen at STP from an acid·(Weight of 1 mL of H_2 at STP = 0.00009 g).

(a) 0.8 g, 0.1 g *(b)* 1.11 g, 0.14 g
(c) 0.674 g, 0.083 g *(d)* 0.31 g, 0.068 g

11. Carbon dioxide contains 27.27% of carbon, carbon disulphide contains 15.79% of carbon and sulphur dioxide contains 50% of sulphur. This data is an agreement with

(a) law of conservation of mass
(b) law of definite proportions
(c) law of multiple proportions
(d) law of reciprocal proportions

12. If 6.3 g of $NaHCO_3$ are added to 15 g of CH_3COOH solution, the residue is found to weigh 18 g. What is the mass of CO_2 released in the reaction?

(a) 4.5 g *(b)* 3.3 g *(c)* 2.6 g *(d)* 2.8 g

13. The law of definite proportions is not applicable to nitrogen oxide because

(a) atomic weight of nitrogen is not constant
(b) molecular weight of nitrogen is variable
(c) equivalent weight of nitrogen is variable
(d) atomic weight of oxygen is variable

14. Which of the following statements is incorrect regarding Dalton's atomic theory?

(a) This theory could explain the law of chemical combinations except law of gaseous volumes
(b) It explains about the properties of atoms of same or different elements but does not explain why these elements combine to form molecules
(c) It does not explain why atoms of different elements have different masses, sizes, valencies etc.
(d) It could explain the nature of binding forces between the atoms of molecule responsible for the existence of matter in solids, liquids and gases

15. Match the following (Column I) which represents terms to the (Column II) representing their facts.

Column I		Column II	
A.	Average atomic mass	p.	Sum of masses of all atoms in an ionic compound
B.	Gram molecular mass	q.	Relative percentage of occurrence of isotopes
C.	Formula mass	r.	One mole of a substance in grams
D.	Molar mass	s.	One mole of a gas at STP
E.	Molar volume	t.	Sum of masses of all atoms in a compound expressed in grams

Codes

	A	B	C	D	E
(a)	r	p	q	s	t
(b)	q	t	p	r	s
(c)	p	q	s	t	r
(d)	s	r	t	q	p

16. Carbon has three isotopes which are carbon-12, carbon-13 and carbon-14. The percentage abundances are 98.92%, 1.108% and 2×10^{-10}% and atomic masses are 12, 13.00335 and 14.00317 u, respectively. What is the approximate average atomic mass of carbon?

(a) 12.1 u *(b)* 12.0 u
(c) 12.9 u *(d)* 12.5 u

17. Match the items of Column I with Column II.

Column I		Column II	
A.	1.6 µg of CH_4	p.	3.408 ppm
B.	6.0 µ moles of Na_2SO_4 in 250 mL	q.	6.022×10^{16} molecules
C.	Mass of one atom of $A = 3.9854 \times 10^{-23}$ g	r.	Molecular mass = 64 g/mol
D.	16 g gas occupies 5.6 L at STP	s.	2.5092×10^{22} atom/gram

Codes

	A	B	C	D
(a)	q	p	s	r
(b)	s	r	q	p
(c)	r	s	p	q
(d)	p	q	r	s

AMAZING REALITIES

Out of 26 alphabets of English the only alphabet that doesn't appear on the Periodic Table of Elements is J.

MOLE CONCEPT, FORMULAE OF COMPOUNDS AND STOICHIOMETRY

Mole Concept

- One mole is defined as the number of carbon atoms present in 12 g of pure C isotopes.
- It is nearly equal to 6.023×10^{23} which is called **Avogadro's number** and denoted by N_A.
- 1 mole = 6.023×10^{23} atom or molecule or ion.
- Number of moles

$$= \frac{\text{Mass of atom or molecule or ion}}{\text{Molar mass of atom or molecule or ion}}$$

$$= \frac{\text{Volume of gas at STP (in mL)}}{22400}$$

$$= \frac{\text{Number of atoms or molecules or ions}}{6.023\times10^{23}\ (N_A)}$$

Percentage Composition

- The percentage of different elements present in a compound is called its **percentage composition**.
- Mass per cent of an element

$$= \frac{\text{Mass of the element in the compound}\times 100}{\text{Molar mass of the compound}}$$

Empirical and Molecular Formulae

- The simplest whole number ratio of different elements present in a compound is called **empirical formula**.
- The exact number of different atoms present in a molecule is called **molecular formula**.
- Molecular formula = $n\times$ (empirical formula)

where, $n = \frac{\text{Molar mass}}{\text{Empirical formula mass}}$

Chemical Stoichiometry

- It deals with the quantitative study of reactants and products present in a chemical reaction.
- By applying laws of chemical combination, the problems in stoichiometry can be solved.
- When reaction is balanced.

$2NH_3(g)$ +	$\frac{5}{2}O_2(g)$ ⟶	$2NO(g)$ +	$3H_2O(l)$
2 molecules	$\frac{5}{2}$ molecules	2 molecules	3 molecules
2 moles	$\frac{5}{2}$ moles	2 moles	3 moles
34 g	80 g	60 g	54 g
2 vol	$\frac{5}{2}$ vol	2 vol	3 vol
2×22.4 L	$\frac{5}{2}\times22.4$ L	2×22.4 L	3×22.4 L (at STP)

- If the reaction is not balanced, apply the concept that atoms in a chemical reaction are conserved, i.e. POAC.

Principle of Atomic Conservation (POAC)

If reaction is given like,

$$NH_3 + O_2 \longrightarrow NO + H_2O \text{ (unbalanced)}$$

- Moles of N-atom in NH_3 = moles of N-atom in NO or, $1\times$ mole of $NH_3 = 1\times$ mole of NO
- Moles of H-atom in NH_3 = moles of H-atom in H_2O or, $3\times$ moles of $NH_3 = 2\times$ moles of H_2O
- Similarly,

$$2\times \text{moles of } O_2 = 1\times \text{mole of NO} + 1\times \text{mole of } H_2O$$

- We can calculate moles and masses of reactants and products easily by solving the above equation.

Limiting Reagent or Reactant

- During a chemical reaction, the reactant that is consumed first is called limiting reagent as it limits the amount of product formed.
- The limiting reagent is determined depending upon the condition given in the question. But in the balanced chemical reaction, one reagent acts as limiting reagent. The products formed will in accordance with the limiting reagent. Volume of 1 mole of gas at STP will be taken as 22.4 L.

Strategies Related to Stoichiometry

Consider the following steps while solving problems related to stoichiometry.

***Step* 1** Write down the reaction given in the question. If the reaction is not balanced apply principle of atomic conservation (POAC).

***Step* 2** Find out the type of relationship among reactants and products given, i.e.

(i) mole-mole relationship (ii) mass-mass relationship
(iii) mass-volume relationship (iv) volume-volume relationship

***Step* 3**

(i) **In mole-mole relationship**, the reactants and products are given in terms of mole. Apply molar interpretation in the chemical reaction.

(ii) **In mass-mass relationship**, the reactants and products are given in terms of mass. Apply mass interpretation in the chemical reaction. These problems can also be solved by converting them into mole.

(iii) **In mass-volume relationship**, reactant is given in mass and asked to calculate product in volume and *vice-versa*. In this case, apply ideal gas equation, $pV = nRT = \frac{W}{M}RT$ to convert mass into volume.

(iv) **In volume-volume relationship**, both reactants and products are given in volume. Such problems can be solved by applying Avogardro's law and Gay-Lussac's law.

Best Practice SHOTS

18. The vapour density of a mixture consisting of NO_2 and N_2O_4 is 38.3 at 26.7°C. Calculate the number of moles of NO_2 in 100 g of the mixture.
(a) 0.437 *(b)* 0.528 *(c)* 0.612 *(d)* 0.324

19. 1.0 g of magnesium is burnt with 0.56 g of O_2 in a closed vessel. Which reactant is left in excess and how much? (Atomic weight, Mg = 24, O = 16)
(a) Mg, 0.16 g *(b)* O_2, 0.16 g
(c) Mg, 0.44 g *(d)* O_2, 0.28 g

20. In the analysis of 0.5 g sample of feldspar, a mixture of chloride of sodium and potassium is obtained, which weighs 0.1180 g, subsequent treatment of the mixed chlorides with silver nitrate gives 0.2451g of silver chloride. What is the per cent of sodium oxide and potassium oxide, respectively in the sample?
(a) 0.36%, 1.06% *(b)* 3.58%, 10.6%
(c) 10.6%, 3.58% *(d)* 10.6%, 0.36%

21. A solid mixture (5.0 g) consisting of lead nitrate and sodium nitrate was heated below 600°C until the weigh of the residue was constant. If the loss in weigh is 28.0 per cent, find the amount of lead nitrate and sodium nitrate, respectively in the mixture.
(a) 3.3 g, 1.7 g *(b)* 1.7 g, 3.3 g *(c)* 3.8 g, 1.2 g *(d)* 1.2 g, 3.8 g

22. A mixture of $CaCl_2$ and NaCl weighing 4.44 g is treated with sodium carbonate solution to precipitate all the Ca^{2+} ions as calcium carbonate. The calcium carbonate, so obtained is heated strongly to get 0.56 g of CaO. The percentage of NaCl in the mixture (atomic mass of Ca = 40) is
(a) 75 *(b)* 30.6 *(c)* 25 *(d)* 69.4

23. An organic compound contains 49.30% carbon, 6.84% hydrogen and its vapour density is 73. Molecular formula of the compound is
(a) $C_3H_8O_2$ *(b)* $C_3H_{10}O_2$ *(c)* C_6H_9O *(d)* $C_6H_{10}O_4$

24. *A* is a binary compound of a univalent metal. 1.422 g of *A* reacts completely with 0.321 g of sulphur in an evacuated and sealed tube to give 1.743 g of a white crystalline solid *B*, that forms a hydrated double salt, *C* with $Al_2(SO_4)_3$. Identify *A*
(a) NaO_2 *(b)* K_2O *(c)* KO_2 *(d)* Na_2O

25. A solution containing 4.77g of NaCl is added to a solution of 5.77 g of $AgNO_3$. The weight of AgCl precipitated will be
(a) 3.61 g *(b)* 4.87 g *(c)* 5.32 g *(d)* 2.66 g

26. The weight of lime (CaO) that can be prepared by heating 200 kg limestone ($CaCO_3$) which is 95 per cent pure is
(a) 201.2 kg *(b)* 151.7 kg *(c)* 106.4 kg *(d)* 110.8 kg

CONCENTRATION TERMS

The concentration and composition of solution can be expressed by the following terms.

Molarity (M)

- It is the number of moles of solute present in 1 L of a solution.
- $$M = \frac{n_{solute}}{V_{solution}\,(\text{in L})} = \frac{n_{solute}\times 1000}{V_{solution}\,(\text{in mL})} = \frac{W_{solute}\times 1000}{M_{solute}\times V_{solution}\,(\text{in mL})}$$

  where, n, W, M and V are moles, weight, molecular weight and volume respectively.

Note When molecular mass in equation of molarity are replaced by formula mass, it is called **formality** (*F*).

Normality (N)

- It is the number of gram-equivalents of solute present in 1L of a solution.
- $$N = \frac{\text{Gram equivalents of solute}}{V_{solution}\ (\text{in L})} = \frac{W_{solute}}{E_{solute}\times V_{solution}\,(\text{in L})} = \frac{W_{solute}\times 1000}{E_{solute}\times V_{solution}\,(\text{in mL})}$$
$$= \frac{W_{solute}\times 1000}{\left(\frac{M_{solute}}{n}\right)\times V_{solution}\,(\text{in mL})} = n\times M$$
- Normality = n × molarity where, n is the valency factor.
- Moles of solute = $M \times V$ (in L)
  Equivalents of solute = $N \times V$ (in L)

Note **In neutralisation reaction**, when acid and base are mixed, same equivalents of acid and base react with each other to form salt. Hence, $N_AV_A = N_BV_B$.

Mole Fraction (χ)

- It is the ratio of mole of a particular component to the total number of moles present in a solution.
- $$\chi_{solute} = \frac{n_{solute}}{n_{solute}+n_{solvent}};\quad \chi_{solvent} = \frac{n_{solvent}}{n_{solute}+n_{solvent}}$$

Molality (m)

- It is the number of moles of solute dissolved in 1 kg of solvent.
- $$m = \frac{n_{solute}}{W_{solvent}\,(\text{in kg})} = \frac{W_{solute}}{M_{solute}\times W_{solvent}\,(\text{in kg})} = \frac{W_{solute}\times 1000}{M_{solute}\times W_{solvent}\,(\text{in g})}$$

Note Molarity (M) and normality (N) of a solution change with temperature as they depend on volume. However, molality (m) is independent of temperature as it depends only on mass of solvent.

Concentration in Terms of Percentage (%)

- Percentage by weight $(W/W) = \frac{W_{solute}}{W_{solution}} \times 100$
- Percentage by volume $(W/V) = \frac{W_{solute}}{V_{solution}} \times 100$
- Parts per million (ppm) $= \frac{W_{solute}}{W_{solution}} \times 10^6$
- Percentage yield $= \frac{\text{Experimental yield}}{\text{Calculated (theoretical) yield}} \times 100$

Interconversion of Concentration Terms

- Molarity (M) and mole fraction (χ) are related as :
$$M = \frac{\chi_{solute} \times 1000 \times \rho}{(\chi_{solute} \times M_{solute}) + (\chi_{solvent} \times M_{solvent})}$$
- Molality (m) and mole fraction are related as :
$$m = \frac{\chi_{solute} \times 1000}{(1-\chi_{solute}) M_{solvent}}$$
- Molarity (M) and molality (m) are related as :
$$\frac{1}{m} = \frac{\rho}{M} - \frac{M_{solute}}{1000}$$
- Weight percentage and molarity (M) are related as :
$$M = \frac{\frac{W_{solute}}{W_{solution}} \times 1000 \times \rho_{solution}}{M_{solute}}$$
- Relation between normality (N) and molarity (M).
$$\frac{\text{Normality}}{\text{Molarity}} = \frac{\text{Molecular weight}}{\text{Equivalent weight}} = \text{Acidity}$$

Best Practice SHOTS

27. Calculate the molarity of 10 mL sample of human urine having 5 mg of urea on analysis.
(Molar mass of urea = 60 g/mol)
(a) 0.008 M *(b)* 0.005 M
(c) 0.003 M *(d)* 0.08 M

28. Upon mixing 45.0 mL of 0.25M lead nitrate solution with 25.0 mL of 0.1 M chromic sulphate solution, precipitation of lead sulphate takes place. Calculate the molar concentrations of reactant species left unreacted in the final solution
(a) 0.054 M *(b)* 0.071 M
(c) 0.075 M *(d)* 0.0375 M

29. 2.5 L of 0.5N HCl and 7.5 L of 0.05 N $FeCl_3$ was added to 25 L of 0.1 N NaOH. Weight of Fe_2O_3 obtained is xg and normality of NaOH left in resultant solution is y N. The values of x and y are, respectively
(a) 10,0.025 *(b)* 20,0.05
(c) 40,0.05 *(d)* 30,0.15

30. What would be the molality of a solution obtained by mixing equal volumes of 30% by weight H_2SO_4 (d = 1.218 g/mL) and 70% by weight H_2SO_4 (d = 1.610 g/mL), if the resulting solution has density 1.425 g/mL?
(a) 4.2 m *(b)* 1.5 m *(c)* 7.61 m *(d)* 11.22 m

31. When ammonia was passed through 30 mL of 1 N H_2SO_4 solution, acid normality decreased to 0.2 N. What volume of ammonia gas at STP is used?
(a) 408.2 mL *(b)* 537.6 mL
(c) 224.7 mL *(d)* 167.4 mL

32. In what ratio should you mix 0.2 M of $NaNO_3$ and 0.1M of $Ca(NO_3)_2$ solution so that in resulting solution, the concentration of negative ions is 50% greater than the concentration of positive ions?
(a) 1 : 1 *(b)* 2 : 1 *(c)* 1 : 2 *(d)* 3 : 2

33. 100 mL of 0.1 M HCl, 100 mL of 0.2 M H_2SO_4 and 100 mL of 0.1 M H_3PO_4 are mixed together.
I. The final concentration of the solution is… *A*… N.
II. If the solution is made of 1 L by adding water, then the final concentration of the solution is … *B*… N.
A and *B* are, respectively.
(a) 0.23 and 0.06 *(b)* 0.26 and 0.08
(c) 0.36 and 0.02 *(d)* 0.26 and 0.03

34. 100 g solution of urea in water contain 40 g of urea (molar mass = 60 g/mol). What is the molality of urea solution?
(a) 9.09 m *(b)* 10.10 m *(c)* 11.11 m *(d)* 12.12 m

35. Fill in the blanks.
I. Aqueous urea solution is 20% by mass of solution and … *A*…% by mass of solvent.
II. If the mole fraction of solute is 0.167, then the molality of aqueous solution is … *B*… m.
III. 18 M H_2SO_4 aqueous solution (density of solution = 1.8 gL^{-1}) is … *C*… molal.
IV. The molarity of K^+ in aqueous solution that contains 17.4 ppm of K_2SO_4 (174 g/mol) is … *D*… M.
Choose the correct codes
Codes

	A	*B*	*C*	*D*
(a)	30	10·10	400	1×10^{-4}
(b)	25	11.11	500	2×10^{-4}
(c)	20	1.11	300	3×10^{-4}
(d)	15	1.01	200	4×10^{-4}

36. Match the following species undergoing chemical change in (Column I) with the *n*-factor in (Column II).

n-factor, $n = \dfrac{\text{Molecular weight}}{\text{Equivalent weight}}$

	Column I		Column II
A.	As_2O_3 is oxidised in basic medium	p.	$n = 8$
B.	Br_2 undergoes disproportionation in basic medium	q.	$n = \frac{3}{7}$
C.	H_2O_2 undergoes disproportionation in acidic medium	r.	$n = 1$
D.	1 mole of $K_2Cr_2O_7$ reacts with 14 moles of HCl	s.	$n = \frac{10}{6}$
E.	Salt $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$	t.	$n = 28$

Codes

	A	B	C	D	E
(a)	p	q	r	s	t
(b)	q	t	q	p	r
(c)	r	p	q	t	s
(d)	t	s	r	q	p

Answers

1. (d)	**2.** (c)	**3.** (a)	**4.** (d)	**5.** (c)
6. (b)	**7.** (b)	**8.** (b)	**9.** (a)	**10.** (b)
11. (d)	**12.** (b)	**13.** (c)	**14.** (d)	**15.** (b)
16. (b)	**17.** (a)	**18.** (a)	**19.** (a)	**20.** (b)
21. (a)	**22.** (a)	**23.** (d)	**24.** (c)	**25.** (b)
26. (c)	**27.** (b)	**28.** (a)	**29.** (a)	**30.** (d)
31. (b)	**32.** (c)	**33.** (b)	**34.** (c)	**35.** (c)
36. (d)				

MASTER STROKES

1. The molecular formula of a commercial resin used for exchanging ions in water softening is $C_8H_7SO_3Na$ (molecular weight = 206). What would be the maximum up take of Ca^{2+} ions by the resin when expressed in mole per gram resin? [JEE Main 2015]

(a) $\frac{1}{103}$ *(b)* $\frac{1}{206}$ *(c)* $\frac{2}{309}$ *(d)* $\frac{1}{412}$

2. Aluminium and sulphuric acid react according to the reaction :

$$2Al(s) + 3H_2SO_4(aq) \longrightarrow Al_2(SO_4)_3(aq) + 3H_2(g)$$

If 0.5 mole Al are added to H_2SO_4 solution containing 0.2 mole H_2SO_4 how many moles of H_2 are produced?

(a) 0.2 *(b)* 0.6 *(c)* 0.4 *(d)* 0.7

3. 1.0 L of mixture of CO and CO_2 is taken. This mixture is passed through a tube containing red hot charcoal. The volume now becomes 1.6 L, the volumes are measured under the same conditions. Find the composition of mixture by volume.

(a) 55% CO, 45% CO_2 *(b)* 50% CO, 50% CO_2
(c) 60% CO, 40% CO_2 *(d)* 40% CO, 60% CO_2

4. A plant virus is found to consist of uniform cylindrical particles of 150Å in diameter and 5000Å 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

(a) 70.92×10^6g *(b)* 1.2×10^6g
(c) 8.8×10^6 g *(d)* 7.5×10^6g

5. Which of the following statements illustrate the law of multiple proportion?

(a) 3.47 g of $BaCl_2$ reacts with 2.36 g of Na_2SO_4 to give 3.88 g $BaSO_4$ and 1.95 g NaCl

(b) Hydrogen sulphide contains 5.89% hydrogen, water contains 11.1% hydrogen and sulphur dioxide contains 50% oxygen

(c) An element forms two oxides XO and XO_2 containing 50% and 60% oxygen, respectively. The ratio of masses of oxygen which combines with 1g of element is 2 : 3

(d) 20 mL ammonia gives 10 volumes of N_2 and 30 volumes of H_2 at constant temperature and pressure

6. Match the activity of HNO_3 in (Column I) with the equivalent weight of HNO_3 in (Column II).

	Column I		Column II
A.	As an acid	p.	63 g
B.	Conc. HNO_3 as an oxidising agent (OA)	q.	21 g
C.	Dil. HNO_3(OA)	r.	10.5 g
D.	Cold dil. HNO_3	s.	7.875 g
E.	Very dil. HNO_3(OA)		

Codes

	A	B	C	D	E
(a)	q	r	s	t	p
(b)	s	r	q	r	p
(c)	p	p	q	r	s
(d)	r	q	r	p	s

7. A compound H_2X with molar weight of 80 g is dissolved in a solvent having density of 0.4 g mL^{-1}. Assuming no change in volume upon dissolution, the molality of 3.2 molar solution is [JEE Advanced 2014]

(a) 6 *(b)* 2 *(c)* 8 *(d)* 10

8. The mole fraction of a solute in a solution is 0.1. At 298 K, molarity of this solution is same as its molality. Density of this solution at 298 K is 2 g cm^{-3}. The ratio of the molecular weights of the solute and solvent is

(a) 6 *(b)* 9
(c) 5 *(d)* 7

9. Excess of carbon dioxide is passed through 50 mL of 0.5 M calcium hydroxide solution. After the completion of the reaction, the solution was evaporated to dryness. The solid calcium carbonate was completely neutralised with 0.1 N hydrochloric acid. The volume of hydrochloric acid required is (Atomic mass of calcium = 40)

(a) 200 cm^3 *(b)* 500 cm^3 *(c)* 400 cm^3 *(d)* 300 cm^3

10. Match the following properties of one of the components of a mixture in (Column I) that is used by separation method in (Column II).

Column I	Column II
A. Insolubility of a solid in solvent	p. Magnetic separation
B. Solid component vaporises	q. Solvent extraction
C. Liquid component vaporises	r. Distillation
D. Magnetic property	s. Sublimation
E. Preferential solubility in a particular solvent	t. Filtration

Codes

	A	B	C	D	E
(a)	p	q	r	s	t
(b)	t	s	r	p	q
(c)	t	s	q	r	q
(d)	r	p	q	s	t

11. Sodium bicarbonate on heating decomposes to form sodium carbonate, CO_2 and water. If 0.2 mole of sodium bicarbonate is completely decomposed, how many mole of sodium carbonate is formed?

(a) 0.1 *(b)* 0.2
(c) 0.05 *(d)* 0.025

12. 50 mL of 0.2 M HCl, 50 mL of 0.2 N H_2SO_4 and 200 mL of 0.2 M $Ba(OH)_2$ are mixed together and the volume is made to 1 L by adding H_2O. What is the final concentration of the solution and the nature of the final solution?

(a) 0.06 N basic
(b) 0.02 N, acidic
(c) 0.04 N, neutral
(d) None of the above

Answers

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

ATOMIC STRUCTURE

SUBATOMIC PARTICLES, ATOMIC MODELS AND DEVELOPMENT LEADING TO BOHR'S MODEL

Subatomic Particles

- Dalton's atomic theory was unable to explain various properties of matter and also does not explain internal structure of an atom.
- This lead to the discovery of subatomic particles. Some of the important subatomic particles are given in the table below.

Name and symbol	Absolute charge (C)	Relative charge	Mass (g)	Mass (MeV/C^2)	Discoverer
Electron (e)	-1.602×10^{-19}	−1	9.1×10^{-28}	0.511	J.J. Thomson
Proton (p)	$+1.602\times10^{-19}$	+1	1.6726×10^{-24}	938.5	Rutherford
Neutron (n)	0	0	1.6749×10^{-24}	940	Chadwick
Positron (β^+/e^+) (anti-electron)	$+1.602\times10^{-19}$	+1	9.1×10^{-28}	0.511	D. Anderson
Anti-proton ($\bar{p}$)	-1.602×10^{-19}	−1	1.6726×10^{-24}	938.5	Emilio and Owen

Rutherford's Experiment

Rutherford passed energetic α-particles through a very thin gold foil and concluded the following:

- Most of the α-particles passed undeflected, concluding that most of the spaces in an atom are empty.
- The rest of the α-particles were deflected by small angles and only a very few α-particles retraced the path. This concluded that the positive charge and whole mass of atom is concentrated at a small place called **nucleus** (radius of atom and nucleus are 10^{-10} m and 10^{-15} m, respectively).
- Electrons move in circular path called **orbit**. Electrons and nucleus are held together by electrostatic forces of attraction.

Subparticles of Electron, Proton and Neutron

- Although electron, proton and neutron were considered as fundamental particles of atom but now proton and neutron are known to be composed even smaller particles called quarks. The quarks are of six types : up, down, top, bottom, strange and charm.
- Protons are composed of two up quarks and one down quark while neutrons consist one up quark and two down quarks.
- Electrons are truely elementary particles with no internal structures.
- Electron is a type of lepton, i.e. an elementary half integer spin particle that does not undergo strong interaction.
- There are six types of lepton out of which electron has the least mass.

Charge by Mass Ratio (*e*/*m*)

- It is the ratio of charge to the mass of charged particles like electron, proton, etc.
- *e*/*m* ratio for electron was first measured by JJ Thomson.
- Charge of electron was calculated by R. A Millikan by considering the downward movement of a charged oil drop under the influence of electric field. This process is known as Millikan's oil drop method.
- For electron $(e/m) = \dfrac{1.602 \times 10^{-19}\text{C}}{9.1 \times 10^{-28}\text{g}}$
$= 1.76 \times 10^{8}\ \text{Cg}^{-1}$
- For proton $(e/m) = 9.58 \times 10^{4}\ \text{Cg}^{-1}$

Drawbacks of Rutherford's Model

- It fails to explain the stability of atom.
- It fails to explain how the electrons are configured around the nucleus and energy of electron.
- It could not explain atomic spectra of H-atom and discontinuous spectrum.

Terms Related to Atom

Atomic number (Z)	Equal to the number of protons (or electrons) in a neutral atom.
Mass number (A)	Number of protons (p) + number of neutrons (n); ($A = p + N$)
Isotopes	Atoms of same element having different mass number, e.g. $_6C^{12}$, $_6C^{14}$.
Isobars	Atoms of different elements having same mass number, e.g. $_6C^{14}$, $_7N^{14}$.
Isotones	Atoms of different elements having same number of neutrons, e.g. $_{19}K^{39}$, $_{20}Ca^{40}$, $_{16}S^{36}$.
Isoelectronic	Species having same number of electrons, e.g. K^+, Ca^{2+}, Ar, Cl^-
Isodiaphers	Different atoms having same neutron to proton difference (neutron excess) e.g. $_{92}U^{238}$, $_{90}Th^{234}$, both have ($n - Z$) equal to 54.
Isosteres	Species having same number of atoms and electrons are isosteres, e.g. N_2 and CO.

Developments Leading to the Bohr's Atomic Model

Dual Nature of Electromagnetic Radiation (EMR)

EMR possesses both wave as well as particle nature.

Wave Nature

- Electromagnetic radiations are transverse waves propagate in vacuum with the speed of light ($c \approx 3 \times 10^8\ \text{ms}^{-1}$).
- The different types of EMR differ from each other by wavelength or frequency ($\nu = c / \lambda$).
- When these radiations are arranged in the order of their wavelength or frequency, they constitute **electromagnetic spectrum**.

Characteristics of Various Electromagnetic Radiations

Name	Wavelength (Å)	Frequency (Hz)	Generation source
Radiowave	$3 \times 10^{14} - 3 \times 10^{7}$	$1 \times 10^{5} - 1 \times 10^{9}$	Alternating current of high frequency.
Microwave	$3 \times 10^{7} - 6 \times 10^{6}$	$1 \times 10^{9} - 5 \times 10^{11}$	Klystron tube
Infrared (IR) waves	$6 \times 10^{6} - 7600$	$5 \times 10^{11} - 3.95 \times 10^{14}$	Incandescent objects
Visible	7600 – 3800	$3.95 \times 10^{14} - 7.9 \times 10^{14}$	Electric bulb, Sun rays
Ultraviolet (UV) wave	3800 – 150	$7.9 \times 10^{14} - 2 \times 10^{16}$	Sun rays, mercury vapour
X-rays	150 – 0.1	$2 \times 10^{16} - 3 \times 10^{19}$	Cathode rays striking metal plate
γ-rays	0.1 – 0.01	$3 \times 10^{19} - 3 \times 10^{20}$	Radioactive decay
Cosmic rays	0.01 – zero	3×10^{20} – infinity	Outer space

Particle Nature

- Wave nature of electromagnetic radiations is unable to explain properties of electromagnetic radiations like black body radiation, photoelectric effect, etc.
- It can be explained by particle nature of electromagnetic radiations.
- Radiations by a black body which is an ideal body that emits and absorbs radiations of all frequencies can be explained by Planck's quantum theory.

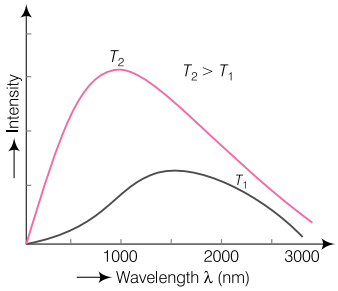
Planck's Quantum Theory

- Atoms emit or absorb energy in discrete quantity called **quanta**.
- Energy associated with a quanta is given by,

$$E = h\nu = \frac{hc}{\lambda} \qquad [\because \nu = \frac{c}{\lambda}]$$

where, h = Planck's constant $(6.626 \times 10^{-34}$ Js)

ν = Frequency of emitted radiation.



- Energy is always emitted in integral multiples of $h\nu$ (i.e. $h\nu$, $2h\nu$, $3h\nu$, ...) or energy is quantised.
- When a black body is heated, the frequency of emitted radiation increases as temperature increases.

Photoelectric Effect

- The phenomenon of photoelectric effect was explained by Albert Einstein using Planck's quantum theory.
- When a beam of light strikes a metal surface, it ejects electrons and the phenomenon is called photoelectric effect.
- When a light of frequency (ν) more than threshold frequency (ν_0), strikes a metal surface, $h\nu_0$ (also called **work function**, w_0) amount of energy is used in removing the electron from metal surface.
- The rest of energy ($h\nu - h\nu_0$) is used in moving the electron with velocity v.

$$\frac{1}{2} m_e v^2 = h\nu - h\nu_0 = h(\nu - \nu_0)$$

Spectrum

- The arrangement of radiations in the order of their wavelength or frequency is called spectrum.
- When radiations are emitted due to the supply of energy, the spectrum is said to be **emission spectrum**.
- When a continuous spectrum passed through a matter, it absorbs radiation of a particular wavelength or frequency and becomes excited. This missing wavelength leaves a dark space in continuous spectrum. This type of spectrum is called **absorption spectrum**.

A spectrum can be further classified into two categories.

(i) Continuous or Band Spectrum

A spectrum in which there is no sharp boundary between two different radiations, e.g. the spectrum produced due to dispersion of white light.

(ii) Discontinuous or Line Spectrum

A spectrum in which radiations of particular wavelength are separated from each other through sharp boundaries. It produced only radiation of some particular wavelengths.

Applications of Line Spectrum

- Discontinuous or line spectra are produced by gaseous atoms in excited state, e.g. hydrogen spectra. Each atom has a unique line spectrum. This concept is used in identifying unknown atoms in chemical reactions by spectroscopic method.
- Emission spectra revealed that each element produced a unique set of spectral line. This observation indicates that the energy levels must be unique for atoms of each element. Therefore, a line spectrum is sometimes referred to as an "**atomic fingerprint**."

Best Practice SHOTS

1. When alpha particles are sent through a thin metal foil, most of them go straight through the foil, because
(a) electrons are much heavier than alpha particles
(b) alpha particles are positively charged
(c) most part of the atom is empty space
(d) alpha particles move with high velocity

2. The stability of nucleus depends on the ratio n/p (number of neutrons to number of protons). Which of the following statements regarding nuclear stability is incorrect?
(a) If $n/p = 1$, nucleus is found to be very stable
(b) With increase in atomic number, number of neutrons goes on increasing in comparison to the number of protons
(c) Upto atomic number 40, $n/p = 1$
(d) When the ratio of n/p is more than 1.5, nucleus becomes stable and radioactive (i.e. at. no. > 83)

3. An element X has the following isotopic composition, ^{200}X : 90%, ^{199}X : 8%, ^{202}X : 2.0%.
The weighted average atomic mass of the naturally occurring element X is closest to
(a) 200 u *(b)* 201 u *(c)* 199 u *(d)* 202 u

4. Many elements have non-integral atomic masses, because
(a) they have isotopes
(b) their isotopes have non-integral masses
(c) their isotopes have same masses
(d) the constituents, neutrons, protons and electrons, combine to give fractional masses

5. The increasing order (lowest first) 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

6. Which of the following statements are correct regarding the properties of cathode rays?

I. When cathode rays are focused on a thin metal foil, it gets heated upto incandescence.
II. These consist of material particles and travels in straight lines.
III. These do not get deflected in presence of electric and magnetic field.
IV. Charge to mass ratio (e/m) of the particles in the cathode is dependent on the nature of the gas taken in the discharge tube and the nature of the cathode.

Choose the appropriate option.

(a) I and II *(b)* III and IV
(c) I and III *(d)* II and IV

7. Match the following items (Column I) with items of (Column II) Rutherford's scattering equation.

Column I	Column II
A. Distance of closest approach	p. $N = K_2/[\sin^4(\theta/2)]$
B. Kinetic energy of α-particles	q. $N = K_3 (Ze)^2$
C. Scattering angle 'θ'	r. $N = K_1/[(1/2)mv^2]^2$
D. Nuclear charge	s. $r_0 = \frac{1}{4\pi\varepsilon_0}\cdot\frac{2Ze^2}{E_K}$

Codes

	A	B	C	D
(a)	p	q	r	s
(b)	s	r	p	q
(c)	s	r	q	p
(d)	p	q	s	r

8. Particle nature of electromagnetic radiation is not observed in which of the following phenomenon?

(a) Black body radiation and photoelectric effect
(b) Interference and diffraction
(c) Variation of heat capacity of solids as a function of temperature
(d) Line spectra of atoms

9. Determine the percentage of F in a mixture sample F and Cl atoms, when removal of an electron from each atom of the sample absorbs energy equal to 284 kJ, while addition of an electron to each atom of the mixture releases energy of 68.8 kJ.

(Given, $EA_F = 5.53\times 10^{-22}$kJ, $EA_{Cl} = 5.78\times 10^{-22}$ kJ, $IE_F = 27.91\times 10^{-22}$ kJ and $IE_{Cl} = 20.77\times 10^{-22}$ kJ)

(a) 62.19% *(b)* 37.81%
(c) 20.77% *(d)* 27.91%

10. Which of the following statements are incorrect?

I. Canal rays are simply charged gaseous ions.
II. Charge to mass ratio of these particles is found to depend on the gas from which these originate.
III. Some of the positively charged particles carry a multiple of fundamental unit of electrical charge.
IV. Behaviour of canal rays in the electrical or magnetic field is opposite to that observed for cathode rays or electron. Choose the correct option.

(a) I and II
(b) I, II and III
(c) I, II, III and IV
(d) None of these

11. Consider the following facts regarding α, β and γ-rays.

I. α-rays consist of high energy particles carrying two units of positive charge and four units of atomic mass.
II. β-rays are negatively charged particles similar to electrons.
III. γ-rays are high energy radiation like X-rays, neutral in nature and do not consist of particles.
IV. Penetrating power : α-rays > β-rays > γ-rays.

Choose the correct statements.

(a) I and II
(b) I, II and III
(c) I, II, III and IV
(d) None of the above

12. In Millikan's experiment, static electric charge on the oil drops has been obtained by shining X-rays. If the static electric charge on the oil drop is -1.282×10^{-18}C, then the number of electrons present in it is

(a) 7 *(b)* 6
(c) 8 *(d)* 10

13. Which of the following statements would you consider as the observation made by Rutherford in α-particle scattering experiment?

I. Whenever α-particles struck the fluorescent screen, a tiny flash of light was produced at that point.
II. Most of the α-particles ($\sim$ 99%) passed through the gold foil undeflected.
III. A small fraction of α-particles were deflected by small angles.
IV. Very few α-particles bounced back, that is they were deflected by nearly 180°.

Choose the correct option.

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

BOHR'S MODEL, DUAL NATURE OF MATTER AND HEISENBERG'S UNCERTAINTY PRINCIPLE

Bohr's Atomic Model

Bohr proposed the following postulates to remove the drawbacks in Rutherford's atomic model.

- Electrons move around the nucleus in circular paths called **orbits**, each having a particular amount of energy. The energy of orbit increases as the distance of orbit from nucleus increases.
- An electron does not radiate energy as long as it revolves in a particular orbit. It makes a transition from one orbit to another, when it emits or absorbs energy.
- The angular momentum associated with an orbit is integral multiple of $h / 2\pi$.

$$mvr = \frac{nh}{2\pi}$$

- During the revolution in an orbit, the necessary centripetal force is provided by the electrostatic force of attraction between electron and nucleus.

Bohr's Formulae

Properties	Formulae	Numerical value
Radius Bohr's orbit(r)	$r_n = \frac{n^2h^2}{4\pi^2 mKZe^2}$	$r_n = 0.529\left(\frac{n^2}{Z}\right)$ Å
Energy of orbits (a) Kinetic energy (KE)	$KE = \frac{2\pi^2 mK^2Z^2e^4}{n^2h^2}$	$KE = 13.6\left(\frac{Z^2}{n^2}\right)$ eV atom^{-1} $= +21.8\times10^{-19}\left(\frac{Z^2}{n^2}\right)$ J atom^{-1}
(b) Potential energy (PE)	$PE = \frac{-4\pi^2 mK^2Z^2e^4}{n^2h^2}$	$PE = -27.2\left(\frac{Z^2}{n^2}\right)$ eV atom^{-1}
(c) Total energy (E_n = KE + PE)	$E_n = \frac{-2\pi^2 mK^2Z^2e^4}{n^2h^2}$	$E_n = -13.6\left(\frac{Z^2}{n^2}\right)$ eV atom^{-1} $= -21.8\times10^{-19}\left(\frac{Z^2}{n^2}\right)$ J atom
(d) Velocity of electron (v)	$v_n = \frac{2\pi K Ze^2}{nh}$	$v_n = 2.188\times10^6\left(\frac{Z}{n}\right)$ m s^{-1}
(e) Time period of revolution of electron (T)	$T_n = \frac{n^3h^3}{4\pi^2 mK^2Z^2e^4}$ $\left(T_n = \frac{2\pi r_n}{v_n}\right)$	$T_n = 1.5\times10^{-16}\left(\frac{n^3}{Z^2}\right)$ s
(f) Orbital frequency $\left(\nu = \frac{1}{T_n}\right)$	$\nu = \frac{1}{T_n} = \frac{4\pi^2 mK^2Z^2e^4}{n^3h^3}$	$\nu = \frac{1}{T_n} = 6.66\times10^{15}\left(\frac{Z^2}{n^3}\right)$ s^{-1}

- Energy of different orbits of H-atom (in eV)

1	2	3	4	∞
–13.6	–3.4	–1.51	– 0.85	∞

→ Increasing order

Line Spectrum of Hydrogen

- When H_2 gas is subjected to electric discharge, the H_2 molecules dissociate and become excited.
- The excited atoms radiate EMR of definite frequency in UV, visible and IR region of electromagnetic spectrum.
- Balmer was the first who observed line spectrum of hydrogen in visible region.
- According to Rydberg,

$$\text{wave number } (\bar{\nu}) = \frac{1}{\lambda} = R_H Z^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right],\ n_1 < n_2$$

where, R_H = Rydberg's constant = 109677 cm^{-1}

Z = atomic number

n_1 and n_2 = lower and higher orbit, respectively.

Line Spectrum of Hydrogen

Series of lines	n_1	n_2	Spectral region	Wavelength range
Lyman series	$n_1 = 1$	$n_2 = 2, 3, 4, \ldots \infty$	UV light < 4000 Å	$1/R_H$ –4/3 R_H
Balmer series	$n_1 = 2$	$n_2 = 3, 4, 5, \ldots \infty$	Visible 4000-7000 Å	$4/R_H$ – 36/5 R_H
Paschen series	$n_1 = 3$	$n_2 = 4, 5, 6, \ldots \infty$	Near infrared > 7000 Å	$9/R_H$ – 144/7 R_H
Brackett series	$n_1 = 4$	$n_2 = 5, 6, 7, \ldots \infty$	Infrared > 7000 Å	$16/R_H$ – 400/9 R_H
Pfund series	$n_1 = 5$	$n_2 = 6, 7, 8, \ldots, \infty$	Far infrared > 7000 Å	$25/R_H$ – 900/11 R_H
Humphrey series	$n_1 = 6$	$n_2 = 7, 8, 9, \ldots \infty$	Far infrared > 7000 Å	$36/R_H$ – 1764/13 R_H

- Maximum number of spectral lines that can be obtained from n_1th orbit to n_2th orbit is $\frac{(n_2 - n_1 + 1)(n_2 - n_1)}{2}$.

STRATEGIES RELATED TO RYDBERG'S EQUATION

The following types of problems are asked related to Rydberg's equation.

Type 1 To find wavelength related to different series of hydrogen spectrum.

Step 1 Find the value of n_1 and n_2.

Step 2 Apply Rydberg's equation.

Type 2 To find energy emitted/absorbed during a transition from n_1 to n_2.

Step 1 Apply Rydberg's equation and find λ.

Step 2 Find the value of energy $(E) = h\nu = \frac{hc}{\lambda}$.

Type 3 To find ionisation energy.

$$IE = E_{\infty} - E_{ground} = 0 - (-13.6\text{ eV}) = 13.6\text{ eV atom}^{-1}$$

Limitations of Bohr's Model

- It is only applicable to atoms or ions having single electron.
- It unable to explain **Zeeman** and **Stark effect**. (Splitting of spectral lines in the presence of static magnetic field and an external electric field, respectively).
- It unable to explain shape of atom in three dimensional space.
- It unable to explain dual nature of electron.

Dual Nature of Matter

- **de-Broglie** suggested that like electromagnetic radiation, matter also possesses dual nature.
- Therefore, like photon, electron has also both momentum and wavelength.
- The above fact can be explained by Planck's quantum theory and Einstein's equation $(E = mc^2)$.
- The wavelength and momentum associated with matter is given by $\lambda = \frac{h}{mc} = \frac{h}{p} = \frac{h}{\sqrt{2mE}}$ (de-Broglie equation).
- When a charged particle (q) is accelerated by a potential V, the kinetic energy and wavelength of charged particle is $KE = \frac{1}{2}mv^2 = qV$ or $p = \sqrt{2qV_m}$ or $\lambda = \frac{h}{\sqrt{2qV_m}}$

Heisenberg's Uncertainty Principle

It stated that the exact position and velocity (momentum) of subatomic particles cannot be determined simultaneously.

$$\Delta p \times \Delta x \geq \frac{h}{4\pi};\ \Delta v \times \Delta x \geq \frac{h}{4\pi m} \text{ or } \Delta E \times \Delta t \geq \frac{h}{4\pi}$$

Best Practice SHOTS

14. A stream of electron from a heated filament was passed between two charged plates kept at a potential difference of Vesu. If e and m are charge and mass of an electron, respectively then the value of h/λ (where, λ is wavelength associated with electron wave) is given by [JEE Main 2016]

(a) 2 meV (b) $\sqrt{\text{meV}}$
(c) $\sqrt{2\text{meV}}$ (d) meV

15. A photon of frequency, ν causes photoelectric emission from a surface with threshold frequency ν_0. The de-Broglie wavelength (λ) of photoelectron emitted is given by

(a) $\lambda = \frac{h}{2m\Delta n}$ (b) $\lambda = \frac{h}{\Delta n}$
(c) $\lambda = \left[\frac{1}{\nu_0} - \frac{1}{\nu}\right]$ (d) $\lambda = \sqrt{\frac{h}{2m\Delta v}}$

16. Which of the following is the energy of a possible excited state of hydrogen? [JEE Main 2015]

(a) + 13.6 eV (b) – 6.8 eV
(c) – 3.4 eV (d) + 8.8 eV

17. In Sommerfeld's modification of Bohr's theory, the trajectory of an electron in a hydrogen atom is

(a) a perfect ellipse
(b) a closed ellipse like curve, narrower at the perihelion position and flatter at the apehelion postion.
(c) a closed loop on spherical surface
(d) a rosette

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

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

19. In the Balmer series of atomic spectra of hydrogen, there is a line corresponding to wavelength 4344 Å. Calculate the number of higher orbits from which the electron drops to generate other line $(R \times c = 3.289 \times 10^{15})$,

(a) 3 (b) 4 (c) 5 (d) 6

20. Positronium consists of an electron and a positron (same mass, opposite charge) orbiting around their common centre of mass. The spectrum is, therefore expected to be hydrogen like, the difference arising from the mass difference. Calculate the wave number of third line of Balmer series of positronium.

(a) 7620.6 (b) 10288
(c) 11522 (d) 54868

21. Which of the following statements is correct for a H-like species?

(a) The energy gap between the consecutive energy orbits decreases as the value of 'n' increases

(b) The longest wavelength in any spectral series corresponds to α-line in that series

(c) Each spectral series is bounded by minimum and maximum wavelength and the range follows a continuous distribution as given by Bohr's theory

(d) KE of the electron decreases, whereas the PE increases as the value of 'n' increases

22. The minimum atomic number which results in a transition from $n = 2$ to $n = 1$ energy level in the emission of X-rays with wavelength 3×10^{-8} m is

(a) 3 *(b)* 2
(c) 4 *(d)* 6

23. The kinetic energy of an electron in the second Bohr's orbit of a hydrogen atom is [a_0 is Bohr radius]

(a) $\frac{h^2}{4\pi^2 m a_0^2}$ *(b)* $\frac{h^2}{16\pi^2 m a_0^2}$

(c) $\frac{h^2}{32\pi^2 m a_0^2}$ *(d)* $\frac{h^2}{6\pi^2 m a_0^2}$

24. A body of mass x kg is moving with a velocity of 100 ms^{-1}. Its de-Broglie wavelength is 6.62×10^{-35} m. The value of x is ($h = 6.62 \times 10^{-34}$ Js)

(a) 0.25 kg *(b)* 0.15 kg *(c)* 0.2 kg *(d)* 0.1 kg

25. If the uncertainties in the measurement of position and momentum of an electron are equal calculate the uncertainty in measuring the velocity.

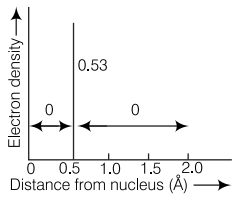
(a) 7.98×10^{12} m/s *(b)* 1.16×10^{10} m/s
(c) 1.46×10^{-33} m/s *(d)* 6.95×10^{-7} m/s

QUANTUM MECHANICAL MODEL, QUANTUM NUMBER AND ELECTRONIC CONFIGURATION

Quantum Mechanical Model of an Atom

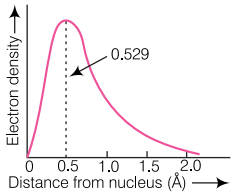
This is the most successful model of atom that describes the structure and configuration of atom in three dimensional space.

- It is based on dual nature of matter and Heisenberg's uncertainty principle.
- Erwin Schrodinger modified Bohr's theory, who considered the position and momentum of electron at a time.
- For H-atom, he considered that an electron in ground state always stays at a distance of 0.529 Å from the nucleus.



(a) Graphical distribution of electron density (Bohr's)

- According to Schrodinger, the electron can exist at any distance from the nucleus, but maximum probability is when the distance is 0.529 Å from the nucleus.



(b) The graphical representation of probability distribution of electron cloud (Schrodinger)

During our approach to wave mechanical model of atom, we will be coming across three key words about the atom which can be defined according to the probability concept as :

1. **Orbit** It is a two dimensional imaginary space around the nucleus where probability of finding electrons is maximum. It can contain 2 to 32 electrons of variable energy, but same family.
2. **Subshell** Aggregation or group of orbitals of exactly similar energy which make an orbit. Subshells are named as *s*, *p*, *d* and *f*.
3. **Orbital** A three dimensional real space around nucleus where probability of finding a particular electron is maximum. An orbital can accommodate maximum of two electrons with exactly equal energy.

- He achieved this by considering wave motion of electron in three dimensional space satisfying the following equation.

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$

where, ψ = wave function, h = Planck's constant

E = total energy of electron (KE + PE)

V = potential energy of electron

- Different wave functions ψ_1, ψ_2, ψ_3... satisfy the above equation having either positive or negative probability of finding electron.
- ψ^2 is used in place of ψ to represent the probability of finding electron in a small space as probability can never be negative.

Quantum Numbers

There are four quantum numbers, i.e. probability factors which properly describes the exact position of an electron.

Principal Quantum Number (n)

- It describes the principle shell (orbit) in which an electron revolves around the nucleus.
- It represents distance of electron from nucleus and represented by 'n'.
- The energy of orbit increases as the value of n increases.

$$K \text{ shell} < L \text{ shell} < M \text{ shell} < N \text{ shell}$$

- Maximum number of electrons that can be found in an orbit is $2n^2$.

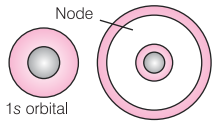
Radial and Angular Nodes for Different Orbitals

For *s*-orbital, number of nodes = $(n-1)$, i.e. 1*s* orbital contain no node, 2*s* orbital contains one node, 3*s* orbital contains 2 nodes and so on. Infact nodes are of two types,

(i) Radial nodes (ii) Angular nodes

A **radial node** is the spherical region around nucleus where probability of finding an electron is zero as shown in the figure of 2*s* orbital.

Similarly, if such a distribution is seen at an angle from the nucleus, the node is called **angular node**.



Spherical s-orbitals symmetrically disposed about the nucleus

For an orbital, number of nodes are calculated as

Number of radial nodes = $n - l - 1$

Number of angular nodes = l, Total nodes = $n - 1$

For example, in 3*p* orbitals

Angular node = 1, Radial number = $3 - 1 - 1 = 1$

So, total nodes = 2 (one radial, one angular)

Azimuthal Quantum Number (l)

- It describes the name of subshell (s, p, d, f) and their shape. Its value range from 0 to $(n-1)$.

n	l	Name of orbital	Shape of orbital	Dependence of probability of finding electron
1	0	s	Spherical	Only on distance from nucleus and uniform in all direction.
2	1	p	Dumb-bell	Both distance and any one direction (x, y or z).
3	2	d	Double dumb-bell	Both distance and any two directions (xy, yz, zx, z^2, or x^2-y^2)
4	3	f	Complicated	

- Relation between angular momentum and l is given by

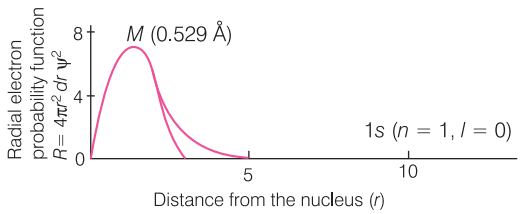
$$mvr = \frac{h}{2\pi}\sqrt{l(l+1)}$$

Magnetic Quantum Number (m)

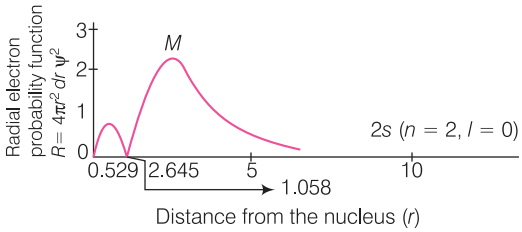
- It describes the splitting of spectral lines under the influence of magnetic field (Zeeman effect).
- For $n = 1$, $l = 0$ and $m = 0$, there exist one spherical *s*-orbital.
- For $n = 2$, $l = 1$ and $m = -1, 0, +1$, there exists 3 degenerate *p*-orbitals, i.e. (p_x, p_y, p_z)
- For $n = 3$, $l = 2$ and $m = -2, -1, 0, +1, +2$, there exists five degenerate *d*-orbitals, i.e. $(d_{xy}, d_{yz}, d_{xz}, d_{x^2-y^2}, d_{z^2})$

Plots of Radial Probability Function, $R(r)$ versus Distance (r) from the Nucleus

- Radial probability function (R) is defined as the probability of finding electron at a distance 'r' from the nucleus.
- Probability of finding electron at origin (nucleus) is zero.
- The distance for maximum probability of finding electron increases as 'n' increases, e.g. $1s < 2s < 3s$.
- Total number of peaks appearing in the curves for s, p and d-orbitals are equal to n, $(n-1)$ and $(n-2)$, respectively, where 'n' is principal quantum number.
- For 1*s* electron, $R = 0$ at $r = 0$ and ∞ and R = maximum at $r = 0.529$ Å.

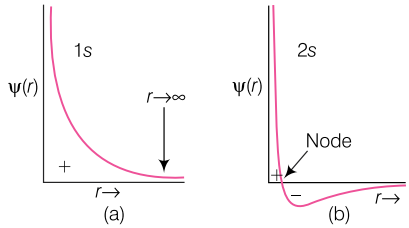


- For 2*s* electron, the value of R is zero at $r = 0$. The distance (i.e. 1.058 Å) at which the probability of finding electron is zero is called **node** or **nodal plane** or **nodal surface**.



Orbital Wave Function *vs r*

- The curves between orbital wave function and r are similar as discussed above with the difference that here negative values of wave function is also visible because ψ can be negative or positive but ψ^2 can only be positive.



- When $n = 4$, $l = 3$ and $m = -3, -2, -1, 0, +1, +2, +3$, there exists seven degenerate orbitals.
- Total number of m, for a particular $n = n^2$.
- Total number of m, for a particular $l = (2l + 1)$.
- Each degenerate orbital can hold maximum of two electrons.

Spin Quantum Number(s)

- When electrons in a particular orbit rotate around nucleus, they also rotate (spin) around their own axis, either in clockwise $\left(+\frac{1}{2}\right)$ or in anti-clockwise $\left(-\frac{1}{2}\right)$.
- Spin angular momentum $= \frac{h}{2\pi}\sqrt{s(s+1)}$
- In diamagnetic species, the magnetic moment (μ) of two opposite spin electron cancel making net magnetic moment equal to zero.
- In paramagnetic species, all unpaired electrons have same spin and the net magnetic moment equals to $\mu = \sqrt{n(n+2)}$ BM where, n = number of unpaired electrons.

Pauli's Exclusion Principle

- No two electrons in an atom can have the same set of four quantum numbers.
- For two electrons in the same orbital, the n, l and m values are same but the value of s is different, i.e. $+\frac{1}{2}$ or $-\frac{1}{2}$, respectively.

Rules for Filling up of Electrons in Orbitals

Aufbau Principle

- Electrons are placed one by one in orbitals in the increasing order of energy level which can be calculated by $(n + l)$ rule.
- Lower the value of $(n + l)$, lower is the energy of the orbital.
- If $(n + l)$ value are same for two orbitals then the orbital with lower 'n' value has lower energy and filled first.
- The order in which electrons are filled in the orbital according to this rule is
  $1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d < 7p$

Hund's Rule

While filling up of electrons in orbitals, pairing of electrons does not take place until each and every degenerate orbital occupies a single electron.

Extra Stability of Completely Filled and Half-Filled Orbitals

In Cr and Cu, one electron jumps from lower energetic $4s$ orbital to higher energetic $3d$ to obtain half-filled and fully-filled configuration, respectively.

Electronic configuration of such elements are given below.

- Cr-24 - [Ar] $3d^5, 4s^1$
- Nb-41 - [Kr] $4d^4, 5s^1$
- Ru-44 - [Kr] $4d^7, 5s^1$
- Pd-46 - [Kr] $4d^{10}, 5s^0$
- La-57 - [Xe] $4f^0, 5d^1, 6s^2$
- Au-79 - [Xe] $4f^{14}, 5d^{10}, 6s^1$
- Cu-29 - [Ar] $3d^{10}, 4s^1$
- Mo-42 - [Kr] $4d^5, 5s^1$
- Rh-45 - [Kr] $4d^8, 5s^1$
- Ag-47 - [Kr] $4d^{10}, 5s^1$
- Pt-78 - [Xe] $4f^{14}, 5d^9, 6s^1$

Best Practice SHOTS

26. Which of the following statements are true about the wave function?

I. When an electron is present in an energy state, the wave functions corresponds to that energy state and contain all information about the electron.

II. It is a mathematical function whose value depends upon the coordinates of the electron in the atom and does not carry any physical meaning.

III. Wave functions of hydrogen or hydrogen like species with one electron are called atomic orbitals.

IV. Wave function pertaining to one-electron species are called one-electron system.

The correct set of statements are

(a) I, II and III
(b) III and IV
(c) I and II
(d) All of the above

27. The total number of orbitals associated with the principal quantum number 5 is [JEE Main 2016]

(a) 5 *(b)* 20
(c) 25 *(d)* 1

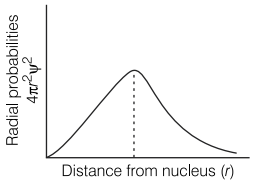
28. Match the following quantum number (Column I) with the information provided (Column II).

Column I (Quantum number)	Column II (Information provided)
A. Principal quantum number	p. Orientation of the orbital
B. Azimuthal quantum number	q. Energy and size of the orbital
C. Magnetic quantum number	r. Spin of electron
D. Spin quantum number	s. Shape of the orbital

Codes

	A	B	C	D		A	B	C	D
(a)	q	s	p	r	*(b)*	r	s	q	p
(c)	p	q	r	s	*(d)*	s	r	q	p

29. Radial probability density in the occupied orbital of a hydrogen atom in the ground state (1*s*) is given below



Select the correct alternate(s).

(a) Radial probability is minimum when $(r = a_0)$

(b) Radial probability is maximum when $\left(r = \frac{1}{a_0}\right)$

(c) Radial probability almost falls to zero when, $r > 1$ Å

(d) Radial probability is independent of *r*

30. Consider the following statements.

I. For an atom having a single electron, the principal quantum number (*n*) is only a parameter to determine the energy of the orbital.

II. In case of multielectron atoms, the energy of an electron depends not only on its principal quantum number but also on its azimuthal quantum numbers, $(n + 1)$ rule is followed.

III. The energies of the orbitals in the same subshell decrease with an increase in the atomic number, i.e. $E_{25(H)} > E_{25(Li)} > E_{25(Na)} > E_{25(K)}$.

IV. Z_{eff} experienced by the orbital decreases with an increase in the azimuthal quantum number and thus order of energies of various sub-shell within an energy level is $s < p < d < f$....

The correct set of statements is

(a) I, II and III

(b) III and IV

(c) II, III and IV

(d) All of the above

31. The quantum numbers of electrons are given below.

Case	*n*	*l*	m_l	m_s
I.	4	2	− 2	$-\frac{1}{2}$
II.	4	1	0	$+\frac{1}{2}$
III.	3	2	− 2	$-\frac{1}{2}$
IV.	4	1	+ 1	$+\frac{1}{2}$

The correct order of increasing energies are

(a) IV > III = II > I *(b)* III < IV = II < I

(c) IV < III < II < I *(d)* IV < II < III < I

32. Suppose that Pauli exclusion principle states that an orbital can accommodate three electrons, what are the respective atomic numbers of the second members of alkali metal family and the first member of halogen family?

(a) 16, 14 *(b)* 11, 9 *(c)* 16, 9 *(d)* 34, 17

33. Which of the following should be correct according to Hund's rule?

(a) $_6C = 1s^2\ 2s^2$ 2*p*: ↿⇂ | | |

(b) $_8O = 1s^2\ 2s^2$ 2*p*: ↿⇂ | ↿⇂ | |

(c) $_7N = 1s^2\ 2s^2$ 2*p*: ↿⇂ | ↿ | |

(d) $_9F = 1s^2\ 2s^2$ 2*p*: ↿⇂ | ↿⇂ | ↿

34. If the nitrogen atom had electronic configuration $1s^7$, it would have energy lower than that of the normal ground state configuration $1s^2 2s^2 2p^3$, because the electrons would be closer to the nucleus yet $1s^7$ is not observed, because it violates

(a) Heisenberg uncertainty principle

(b) Hund's rule

(c) Pauli exclusion principle

(d) Bohr postulate of stationary orbits

35. For a *d*-electron, the orbital angular momentum is

(a) $\sqrt{6}\left(\frac{h}{2\pi}\right)$ *(b)* $\sqrt{2}\left(\frac{h}{2\pi}\right)$

(c) $\left(\frac{h}{2\pi}\right)$ *(d)* $2\left(\frac{h}{2\pi}\right)$

36. The quantum numbers of the last electron of an element are given below. Predict the atomic number and name of the element from the following quantum numbers. $n = 3, l = 2, m = 0, s = -\frac{1}{2}$

(a) V *(b)* Sc

(c) Cu *(d)* Ni

RAPID CONCEPT REVISION

37. Which of the following statements is incorrect?
(a) Angular quantum number signifies the shape or the orbital
(b) Energies of stationary states in hydrogen like atoms is inversely proportional to the square of the principal quantum number
(c) Total number of nodes for 3*s* orbital is three
(d) The radius of the first orbit of He^+ is half than that of the first orbit of hydrogen atom.

38. The set of quantum numbers $n = 4$, $l = 0$, $m = 0$ and $s = +\frac{1}{2}$ corresponds to the most loosely bound, ground state electron of which one of the following atoms.
(a) Na *(b)* Cl *(c)* Cr *(d)* Rb

Answers

1. (c)	**2.** (c)	**3.** (a)	**4.** (a)	**5.** (d)
6. (a)	**7.** (b)	**8.** (b)	**9.** (b)	**10.** (d)
11. (b)	**12.** (c)	**13.** (d)	**14.** (c)	**15.** (d)
16. (c)	**17.** (b)	**18.** (a)	**19.** (c)	**20.** (c)
21. (c)	**22.** (b)	**23.** (c)	**24.** (d)	**25.** (a)
26. (d)	**27.** (c)	**28.** (a)	**29.** (c)	**30.** (d)
31. (b)	**32.** (a)	**33.** (d)	**34.** (c)	**35.** (a)
36. (a)	**37.** (c)	**38.** (c)		

MASTER STROKES

1. Which of the following statements is true regarding absorption and emission spectra?
(a) Emission spectrum is observed, when white light is passed through the substance and the transmitted radiation are analysed by the spectroscope
(b) Absorption spectra is always discontinuous whereas emission spectra may be continuous or may be discontinuous
(c) Absorption spectrum gives bright line (coloured) on dark background whereas emission spectrum gives dark lines on bright background
(d) Radiations from emitting source are analysed by the spectroscope in absorption spectrum.

2. Which electronic level would allow the hydrogen atom to absorb a photon but not to emit a photon?
(a) 3*s* *(b)* 2*p*
(c) 2*s* *(d)* 1*s*

3. The ratio of de-Broglie wavelength of a deuterium atom to that of an α-particle, when the velocity of former is five times greater than that of the later, is
(a) 4 *(b)* 0.4 *(c)* 2 *(d)* 0.2

4. The wave number of the spectral line in the emission spectrum of H-atom will be equal to $\frac{8}{9}$ times the Rydberg's constant if the electron jumps from
(a) $n = 3$ to $n = 1$ *(b)* $n = 10$ to $n = 1$
(c) $n = 9$ to $n = 1$ *(d)* $n = 2$ to $n = 1$

5. In an atom, the total number of electrons having quantum number $n = 4, |m_l| = 1$ and $m_s = -\frac{1}{2}$ is
(a) 4 *(b)* 5 *(c)* 6 *(d)* 7

6. A compound of vanadium has a magnetic moment of 1.73 BM. The electronic configuration of vanadium is
(a) [Ar] $3d^3\ 4s^0$
(b) [Ar] $3d^1\ 4s^2$
(c) [Ar] $3d^2\ 4s^1$
(d) [Ar] $3d^1\ 4s^0$

7. According to Bohr's theory, E_n = total energy; K_n = kinetic energy V_n = potential energy; r_n = radius of *n*th orbit. Match the following

Column I	Column II
A. V_n / K_n = ?	p. 0
B. $r_n \propto E_n^x, x$ = ?	q. –1
C. Angular momentum in lowest orbital	r. –2
D. $\frac{1}{r_n} \propto Z^y, y$ = ?	s. + 1

Codes

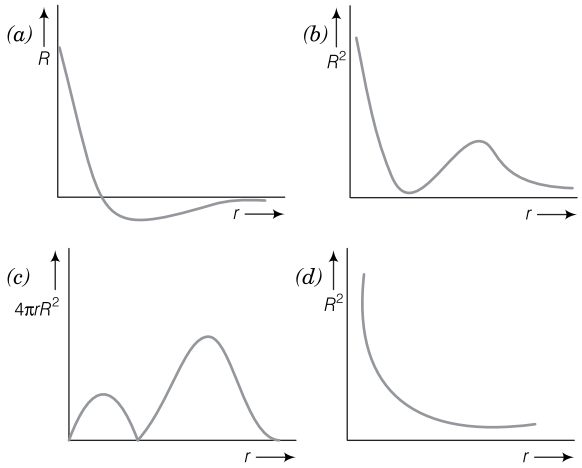
	A	B	C	D
(a)	p	q	r	s
(b)	r	p	q	s
(c)	s	r	q	p
(d)	q	s	p	r

8. The atomic masses of He and Ne are 4 and 20 amu, respectively. The value of de-Broglie wavelength of He gas at –73 °C is '*M*' times that of the de-Broglie wavelength of Ne at 727°C. *M* is
(a) 3 *(b)* 6
(c) 5 *(d)* 7

AMAZING REALITIES

If you expose a glass of water to space, it will boil rather than freeze however the water vapor would almost immediately crystallize into ice.

9. Variations of radial wave function R against distance r is given for $2s$ orbital. Select the incorrect one.



10. In Heisenberg's uncertainty experiment, which of the statements is incorrect?

(a) Use of high intensity light increases accuracy in the measurement of distance of electron from nucleus

(b) Use of high frequency light increases accuracy in the measurement of distance of electron from the nucleus

(c) Use of long wavelength light increases accuracy in the measurement of speed of electron.

(d) If an experiment is designed to measure the distance of electron from nucleus, the speed measured in same experiment would be highly imprecise.

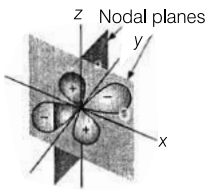
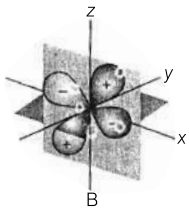
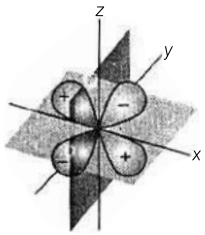
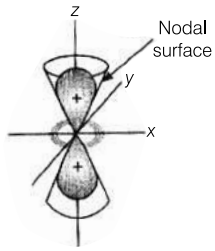
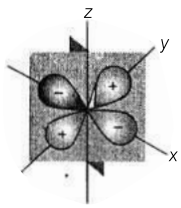
11. The normalised wave function of $1s$-orbital is $\psi = \sqrt{N}e^{-Zr/a_0}$ and the radial distribution function $= 4\pi^2\psi^2$ where, $N = \frac{1}{\pi}\left(\frac{Z}{a_0}\right)^3$.

Most probable distance at which the $1s$ electron of H-like atom with atomic number Z is to be found, is

(a) a_0 *(b)* $\frac{a_0}{Z}$

(c) $\frac{Z}{a_0}$ *(d)* $\frac{a_0^2}{Z}$

12. Match the (Column I) with (Column II) and choose the correct option from the codes given below.

Column I (Boundary surface diagram)		Column II (d-orbital)
A.		p. d_{z^2}
B.		q. $d_{x^2-y^2}$
C.		r. d_{yz}
D.		s. d_{xz}
E.		t. d_{xy}

Codes

	A	B	C	D	E
(a)	s	t	q	p	r
(b)	t	r	s	p	q
(c)	r	s	t	q	p
(d)	t	s	p	q	r

Answers

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

REDOX REACTIONS

OXIDATION-REDUCTION, OXIDATION NUMBER AND TYPES OF REDOX REACTIONS

In a **redox reaction**, both oxidation and reduction occurs simultaneously.

Oxidation and reduction can be defined in many ways as:

	Oxidation	Reduction
I	Addition of oxygen or electronegative element	Removal of oxygen or electronegative element
II	Removal of hydrogen or electropositive element	Addition of hydrogen or electropositive element
III	Loss of electron(s)	Gain of electron(s)

Oxidising and Reducing Agent

- **Oxidising agent** or **oxidant** helps in oxidation of other species by accepting electrons lost during oxidation and itself gets reduced.
- **Reducing agent** or **reductant** helps in reduction by donating electrons to the species undergoing reduction and itself gets oxidised.

REMEMBER

- Molecules consisting of highly electronegative element like oxygen (O), halogen (*X*) etc., are good oxidising agents.
- The molecules in which atom shows high oxidation state like $K\mathbf{Cl}O_3$, $\mathbf{Fe}Cl_3$, $K\mathbf{Mn}O_4$, $H\mathbf{N}O_3$ etc., can get reduced easily.
- Metal oxides, e.g. CaO, MgO, SO_3 etc., are good oxidising agents.
- All the metals are good reducing agents, e.g. Na, Al, etc.
- The compounds having elements in their lower oxidation state like $PtCl_2$ can get oxidised easily.
- Elements having intermediate oxidation state act as both oxidising as well as reducing agents,
  e.g. SO_2, Fe^{2+}, MnO_2, IO^- etc.

Oxidation Number (ON)

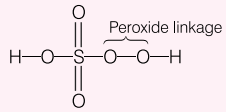
- Oxidation number of an element in a particular compound is equal to the number of electrons lost, gained or shared by that element.
- It is positive when electrons are lost and negative when electrons are gained.

Rules for Assigning Oxidation Number

- Oxidation number of an atom in free state is always 0. e.g. oxidation number of H in H_2, O in O_2, Cl in Cl_2, Na, K, Fe, etc., is zero.
- Oxidation number of hydrogen in a compound is always +1, except in case of metal hydrides (NaH, CaH_2 etc.), where it is –1.
- Oxidation number of oxygen in a compound is always –2 except in peroxides (H_2O_2, Na_2O_2, etc.) where it is –1, superoxides (KO_2, etc.) $-\frac{1}{2}$ and OF_2, +2.
- Oxidation number of fluorine in a compound is always –1.
- Oxidation number of alkali metals and alkaline earth metals in a compound are always +1 and +2, respectively.
- Oxidation number of metals are always positive, except in some metallic hydrides like CuH (–1) and metal carbonyls such as $[Rh(CO)_4]^-$.
- The algebraic sum of oxidation number of all atoms in a neutral compound is always zero and in an ion, it is equal to the total charge on the ion.

Exceptional Cases of Evaluation of Oxidation Numbers

- In H_2SO_5 (Caro's acid), one peroxide linkage is present.
  thus, the oxidation number of S is obtained as
  $\underset{\text{(for H)}}{2\times(+1)} + \underset{\text{(for S)}}{x} + \underset{\text{(for O)}}{3\times(-2)} + \underset{\text{(for O—O)}}{2\times(-1)}$
  $2 + x - 6 - 2 = 0,\ x = +6$



- Similarly, in $H_2S_2O_8$, the oxidation number of S is +6 and CrO_5 (two peroxide linkages), the oxidation number of Cr is +6.
- In $CaOCl_2$ (bleaching powder) or Ca(OCl)Cl, the two Cl atoms are in different oxidation states. The oxidation state of Cl^- is –1 and that present in OCl^- is +1.
- Similarly, in Fe_3O_4, two Fe atoms are in + 3 oxidation state and one Fe atom is in + 2 oxidation state.

Types of Redox Reactions

Intermolecular redox reaction	Intramolecular redox reaction	Disproportionation reaction
Two different molecules/ compounds are oxidised and reduced. e.g. $Fe^{2+} + MnO_4^- \longrightarrow Fe^{3+} + Mn^{2+}$	Different elements of same compounds is oxidised as well as reduced. e.g. $(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$	(Auto-redox) A single atom in a molecule/compound is oxidised as well as reduced. e.g. $3ClO^- \rightarrow 2Cl^- + ClO_3^-$

Best Practice SHOTS

1. Arrange the following in the increasing oxidation number of Mn, N and *X*, respectively.
(a) $MnCl_2$, MnO_2, $KMnO_4$
(b) N_2O, NH_3, N_3H, NO, N_2O_5
(c) HXO, HXO_3, HXO_2,HXO_4

Hint (a) $MnCl_2 < MnO_2 < KMnO_4$
(b) $NH_3 < N_3H < N_2O < NO < N_2O_5$
(c) $HXO < HXO_2 < HXO_3 < HXO_4$

2. Find out the oxidation number of Cr in CrO_2Cl_2, $Na_2Cr_3O_{10}$ and $Cr_2(SO_4)_3$, respectively.

Hint + 6, + 6 and +3.

3. Find out the oxidation number of elements underlined in each case.
(a) $\underline{Fe}SO_4(NH_4)_2SO_4 \cdot 6H_2O$.
(b) $Na_2\underline{S}_4O_6$
(c) $Na_2[\underline{Fe}(CN)_5NO]$

Hint (a) $x - 2 + 0 + 0 = 0, x = 2$
(b) $2 \times (1) + 4x + 6 \times (-2) = 0, x = \frac{5}{2}$
(c) $2 + x + 5(-1) + 1 = 0, x = 2$

4. Which compound amongst the following has the highest oxidation number for Mn.
$KMnO_4$, K_2MnO_4, MnO_2 and Mn_2O_3?

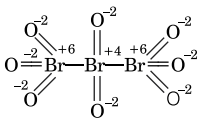
Hint $KMnO_4 \longrightarrow Mn = +7$.

5. Write down the name of the following redox reactions.
(a) $H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$
(b) $Fe + N_2H_4 \longrightarrow NH_3 + Fe(OH)_2$
(c) $2KClO_3 \longrightarrow 2KCl + 3O_2$

Hint (a) Disproportionation reaction
(b) Intermolecular redox reaction
(c) Intramolecular redox reaction

6. What is the oxidation number of Br in Br_3O_8?

Hint



7. Indicate which of the substance/ion in the following reactions is an oxidising agent and which is a reducing agent?
(i) $2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$
(ii) $2Mg + SO_2 \longrightarrow 2MgO + S$
(iii) $2I^- + H_2O_2 \longrightarrow 2OH^- + I_2$

Hint

	Oxidising agent	Reducing agent
(i)	$FeCl_3$	$SnCl_2$
(ii)	SO_2	Mg
(iii)	H_2O_2	I^-

8. Find out the oxidation number of sulphur in the following compounds :
HSO_3^-, $S_2O_8^{2-}$, $S_2O_4^{2-}$, H_2S and H_2SO_4.

Hint The oxidation number of sulphur in HSO_3^-, $S_2O_8^{2-}$, $S_2O_4^{2-}$, H_2S and H_2SO_4 are +4, + 7, +3, –2 and +6, respectively.

9. Write the following equations in ionic form,
(a) $NaHCO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2$
(b) $K_2Cr_2O_7 + 14HI \longrightarrow 2CrI_3 + 2KI + 3I_2 + 7H_2O$

Hint (a) $Na^+ + HCO_3^- + 2H^+ + SO_4^{2-} \longrightarrow$
$2Na^+ + SO_4^{2-} + H_2O + CO_2$
or $Na^+ + HCO_3^- + 2H^+ \longrightarrow 2Na^+ + H_2O + CO_2$
(b) $2K^+ + Cr_2O_7^{2-} + 14H^+ + 14I^- \longrightarrow$
$2Cr^{3+} + 6I^- + 2K^+ + 2I^- + 3I_2 + 7H_2O$
or $14H^+ + Cr_2O_7^{2-} + 6I^- \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$

10. Why $HgCl_2$ and $SnCl_2$ cannot exist as such if present together in an aqueous solution?

Hint When both $HgCl_2$ and $SnCl_2$ present together, undergoes redox reaction (double displacement occur) and a white precipitate will formed.

$$2HgCl_2 + SnCl_2 \longrightarrow SnCl_4 + \underset{\text{White ppt.}}{Hg_2Cl_2}\downarrow$$

11. Name one compound each in which oxidation number of
(a) oxygen is +2 (b) nitrogen is +1 (c) chlorine is +4

Hint (a) F_2O (b) N_2O (c) ClO_2

12. The process of bleaching is represented as
$Cl_2(g) + 2OH^-(aq) \longrightarrow ClO^-(aq) + Cl^-(aq) + H_2O\ (l)$
Identify and name the species that bleaches the substance due to its oxidising action.

Hint Hypochlorite ion

13. Write the oxidation number of hydrogen when combined with non-metals and active metals, respectively.

Hint +1 and –1

BALANCING OF REDOX REACTIONS

While balancing a redox reaction, both mass and charge must be balanced on both sides of the chemical reaction.

The following different methods are followed while balancing a redox reaction.

Half-Cell Reaction Method

This method is usually followed while balancing redox reaction occurring inside a cell.

Steps Followed while Balancing a Redox Reaction using Half-Cell Reaction Method

***Step* 1** Assign oxidation state to the elements undergoing oxidation and reduction,

e.g. $\overset{0}{I_2} + \overset{+2}{S_2}O_3^{2-} \longrightarrow \overset{-1}{I^-} + \overset{+2.5}{S_4}O_6^{2-}$

Here, I_2 is reduced and $S_2O_3^{2-}$ is oxidised.

***Step* 2** Write down the oxidation half-cell and reduction half-cell separately.

$$I_2 \longrightarrow I^- \quad \text{(Reduction half-cell)}$$

$$S_2O_3^{2-} \longrightarrow S_4O_6^{2-} \quad \text{(Oxidation half-cell)}$$

***Step* 3** Balance charge and mass of each half-cell separately.

$$I_2 + 2e^- \longrightarrow 2I^-$$

$$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^-$$

***Step* 4** Equalise the number of electrons on opposite side of the oxidation and reduction half-cell by multiplying with suitable coefficient so that they would cancel out while adding.

Since, there are same number of electrons on both sides, hence there is no need to multiply by coefficients.

***Step* 5** Add both the oxidation and reduction half-cell equations to get the final balanced equation.

$$I_2 + 2e^- \longrightarrow 2I^-$$

$$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^-$$

$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$

(Final balanced redox reaction)

Oxidation Number Method

This method is based on the change in the oxidation number of oxidant and reductant.

Steps Followed to Balance Redox Reactions in Acidic Medium

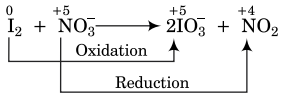
***Step* 1** Assign oxidation number of elements undergoing oxidation and reduction.

$$\overset{0}{I_2} + \overset{+5}{N}O_3^- \longrightarrow \overset{+5}{I}O_3^- + \overset{+4}{N}O_2$$

***Step* 2** Balance only those elements that undergoes a change in oxidation state. Here, I and N-atom undergo a change, in oxidation state.

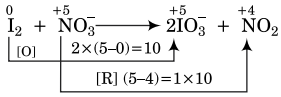
$$I_2 + NO_3^- \longrightarrow 2IO_3^- + NO_2$$

***Step* 3** Connect the elements undergoing oxidation and reduction by a closed bracket. Here, I_2 undergoes oxidation and N-atom of NO_3^- undergoes reduction.



***Step* 4** Indicate the increase in oxidation number for oxidation reaction and decrease in oxidation number for reduction reaction. Multiply them with suitable coefficients to make the increase in oxidation number in oxidation process equal to the decrease in oxidation number in reduction process.

Here, we need to multiply the reduction reaction by 10.



***Step* 5** Write down the new equation after multiplying by coefficients and balance all elements except H and O.

$$I_2 + 10NO_3^- \longrightarrow 2IO_3^- + 10NO_2$$

***Step* 6** In acidic medium, for each excess O-atom, add one H_2O molecule on opposite side and $2H^+$ on same side. There are 4 extra O-atom on reactants side. Hence,

$$I_2 + 10NO_3^- + 8H^+ \longrightarrow 2IO_3^- + 10NO_2 + 4H_2O$$

Now, the reaction is balanced.

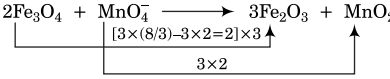
Steps Followed to Balance Redox Reactions in Basic Medium

The first five steps followed while balancing a redox reaction in acidic medium is also followed here. However, while balancing H and O, we follow a different method as described below:

In basic medium, for each excess O-atom, add one H_2O on same side and $2OH^-$ (basic) on opposite side.

If H-atoms are not yet balanced, for one excess H add one OH^- on same side and one H_2O on the opposite side,

e.g. $2Fe_3O_4 + MnO_4^- \longrightarrow 3Fe_2O_3 + MnO_2$ (basic medium)



$$6Fe_3O_4 + 2MnO_4^- \longrightarrow 9Fe_2O_3 + 2MnO_2 \quad \text{(basic medium)}$$

$$H_2O \longrightarrow 2\overline{O}H \quad \text{(1 excess O-atom)}$$

$$6Fe_3O_4 + 2MnO_4^- + H_2O \longrightarrow 9Fe_2O_3 + 2MnO_2 + 2OH^-$$

(final balanced equation)

Best Practice SHOTS

14. Balance the following equation,

(a) $BaCrO_4 + KI + HCl \longrightarrow BaCl_2 + I_2 + KCl + CrCl_3 + H_2O$

(b) $Mn_2O_7 \longrightarrow MnO_2 + O_2$

(c) $As_2S_3 + HNO_3 \longrightarrow H_3AsO_4 + H_2SO_4 + NO$

Hint (a) $2BaCrO_4 + 6KI + 16HCl \longrightarrow 2CrCl_3 + 3I_2 + 6KCl + 2BaCl_2 + 8H_2O$

(b) $2Mn_2O_7 \longrightarrow 4MnO_2 + 3O_2$

(c) $3As_2S_3 + 28HNO_3 + 4H_2O \longrightarrow 6H_3AsO_4 + 9H_2SO_4 + 28NO$

15. Balance the following equation in acidic medium.

(a) $MnO_4^- + Fe^{2+} \longrightarrow Mn^{2+} + Fe^{3+} + H_2O$

(b) $Cu + NO_3^- + 8H^+ \longrightarrow Cu(NO_3)_2 + NO + H_2O$

Hint (a) $MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

(b) $3Cu + 2NO_3^- + 8H^+ \longrightarrow 3Cu^{2+} + 2NO + 4H_2O$

16. Balance the following equation in basic medium.

(a) $MnO_4^- + Fe^{2+} \xrightarrow{\bar{O}H} Mn^{2+} + Fe^{3+}$

(b) $S_2O_4^{2-} + Ag_2O \xrightarrow{\bar{O}H} Ag + SO_3^{2-}$

(c) $H_2 + ReO_4^- \xrightarrow{\bar{O}H} ReO_2 + H_2O$

(d) $ClO_2 + SbO_2^- \xrightarrow{\bar{O}H} ClO_2^- + Sb(OH)_6^-$

Hint (a) $MnO_4^- + 5Fe^{2+} + 4H_2O \longrightarrow Mn^{2+} + 5Fe^{3+} + 8\bar{O}H$

(b) $S_2O_4^{2-} + Ag_2O + 2\bar{O}H \longrightarrow 2Ag + 2SO_3^{2-} + H_2O$

(c) $3H_2 + 2ReO_4^- \longrightarrow 2ReO_2 + 2H_2O + 2\bar{O}H$

(d) $2ClO_2 + SbO_2^- + 2\bar{O}H + 2H_2O \longrightarrow 2ClO_2^- + Sb(OH)_6^-$

17. Balance the following equation by ion electron (half-reaction) method for each of the following equations.

(a) $Cr_2O_7^{2-} + Fe^{2+} \longrightarrow Cr^{3+} + Fe^{3+} + H_2O$

(b) $H_2O_2 + I^- + H^+ \longrightarrow H_2O + I_2$

(c) $Cr_2O_7^{2-} + C_2H_4O + H^+ \longrightarrow Cr^{3+} + C_2H_4O_2 + H_2O$

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

Hint (a) $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

(b) $H_2O_2 + 2H^+ + 2I^- \longrightarrow 2H_2O + I_2$

(c) $Cr_2O_7^{2-} + 8H^+ + 3C_2H_4O \longrightarrow 2Cr^{3+} + 4H_2O + 3C_2H_4O_2$

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

18. Balance the following equations by oxidation number method.

(a) $K_2Cr_2O_7 + FeSO_4 + H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + Fe_2(SO_4)_3 + K_2SO_4 + H_2O$

(b) $Al + KMnO_4 + H_2SO_4 \longrightarrow Al_2(SO_4)_3 + K_2SO_4 + MnSO_4 + H_2O$

Hint (a) $K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + K_2SO_4 + 7H_2O$

(b) $10Al + 6KMnO_4 + 24H_2SO_4 \longrightarrow 5Al_2(SO_4)_3 + 6MnSO_4 + 3K_2SO_4 + 24H_2O$

19. Use the arbitrary coefficient method to balance the following equations.

(a) $Pb(N_3)_2 + Co(MnO_4)_3 \longrightarrow CoO + MnO_2 + Pb_3O_4 + NO$

(b) $K_4[Fe(CN)_6] + KOH + Ce(NO_3)_4 \longrightarrow Fe(OH)_3 + Ce(OH)_3 + K_2CO_3 + KNO_3 + H_2O$

Hint (a) $30Pb(N_3)_2 + 44Co(MnO_4)_3 \longrightarrow 44CoO + 132MnO_2 + 10Pb_3O_4 + 180NO$

(b) $K_4[Fe(CN)_6] + 258KOH + 61Ce(NO_3)_4 \longrightarrow Fe(OH)_3 + 61Ce(OH)_3 + 250KNO_3 + 6K_2CO_3 + 36H_2O$

20. Identify whether the following redox reaction is correctly balanced or not.

$Cu + 2HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO + H_2O$

Hint No, correct balanced reaction is

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

MASTER STROKES

1. Why H_2O_2 acts as a reductant as well as an oxidant?

Hint Oxidation number of O in H_2O_2 is –1. Maximum oxidation state of O is +2 and minimum is –2.

Explanation Hydrogen peroxide has the ability to gain or lose electrons, as its oxygen atoms are in the +1 oxidation state. By gaining electrons they can change upto –2 oxidation state and by losing electrons they can change upto zero oxidation state.

2. Which of the following is/are oxidant and which is/are reductant? Br_2, Fe^{3+}, I^-

Hint $Fe^{3+} + e^- \longrightarrow Fe^{2+}$ [oxidant]

$Br_2 + 2e^- \longrightarrow 2Br^-$ [oxidant]

$2I^- \longrightarrow I_2 + 2e^-$ [reductant]

3. Find out the oxidation number of Cl in Cl_2, HOCl, Cl_2O, ClO_2, $KClO_3$ and Cl_2O_7.

Hint The oxidation number of Cl in Cl_2, HOCl, Cl_2O, ClO_2, $KClO_3$ and Cl_2O_7 are 0, +1, +1, +4, +5 and +7, respectively.

4. Find out the oxidation number of underlined atom.
$\underline{K}IO_3$, $[\underline{Fe}(CN)_6]^{4-}$, $\underline{P}H_4^+$, $Ba\underline{Xe}O_6$, $\underline{N}O_3^-$

Hint $\underline{K}IO_3 = +5$, $[\underline{Fe}(CN)_6]^{4-} = +2$, $\underline{P}H_4^+ = -3$,
$Ba\underline{Xe}O_6 = +8$, $\underline{N}O_3^- = +5$

5. Sulphur dioxide (SO_2) under atmospheric condition changes into SO_x^{2-}. If the oxidation number of S in SO_x^{2-} is + 6. What is the value of x in SO_x^{2-}?

Hint The value of $x = 4$

$\Rightarrow \quad +6 - 2x = -2$

$\Rightarrow \quad +6 + 2 = 2x \Rightarrow x = 4$

6. In alkaline medium, ClO_2 oxidises H_2O_2 to O_2 and reduced itself to Cl^-, then how many moles of H_2O_2 will oxidise by one mole of ClO_2.

Hint $2ClO_2 + 5H_2O_2 + 2OH^- \longrightarrow 2Cl^- + 5O_2 + 6H_2O$

$ClO_2 = 2.5H_2O_2$

7. Calculate the number of moles of MnO_4^- required to oxidise one mole of ferrous oxalate completely in acidic medium.

Hint $2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \longrightarrow 2Mn^{2+} + 10CO_2$

Number of moles of MnO_4^- required to oxidise one mole of oxalate $= \frac{2}{5} = 0.4$.

8. Balance the following chemical equation,

$$H_2O_2 + O_3 \longrightarrow H_2O + O_2$$

Indicating the changes in oxidation number of oxygen, find the equivalent weight of H_2O_2 for this reaction.

Hint $H_2\overset{-1}{O}_2 + \overset{0}{O}_3 \longrightarrow H_2\overset{-2}{O} + 2\overset{0}{O}_2$

Equivalent mass of $H_2O_2 = \frac{34}{2} = 17$

9. Write one equation each for decomposition reactions where energy is supplied in the form of heat, light or electricity.

Hint Heat, $CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g)$

Light, $2AgCl(s) \xrightarrow{h\nu} 2Ag(s) + Cl_2(g)$

Electricity, $2H_2O(l) \xrightarrow[\text{Acidulated}]{\text{Electric current}} 2H_2(g) + O_2(g)$

10. Consider the following redox reaction and identify which element is oxidised and reduced both?

$4P + 3KOH + 3H_2O \longrightarrow 3KH_2PO_2 + PH_3$

Hint Phosphorus (P)

11. For the redox reaction,

$MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow Mn^{2+} + CO_2 + H_2O$

Determine the correct stoichiometric coefficients of MnO_4^-, $C_2O_4^{2-}$ and H^+.

Hint 2, 5 and 16, respectively.

12. Identify whether the following reaction is redox or not.

$2K[Ag(CN)_2] + Zn \longrightarrow 2Ag + K_2[Zn(CN)_4]$

Hint No

13. What products are expected from the disproportionation reaction of hypochlorous acid?

Hint $HClO_3$ and Cl_2O

14. What are the oxidation states of iodine in HIO_4, H_3IO_5 and H_5IO_6, respectively?

Hint +7, + 7, + 7

TARGET JEE 2017

TEST RIDER

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JEE MAIN PREP UP

HALF TEST 2 (XII SYLLABUS) FULLY SOLVED

Mock Questions from Class XIIth Syllabus with Complete Solutions

INSTRUCTIONS

- This test consists of 30 questions and each question is allotted 4 marks for correct response.
- Candidates will be awarded marks as stated above for correct response of each question. 1/4 marks will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
- There is only one correct response for each question. Filling up more than one response in any question will be treated as wrong response and marks for wrong response will be deducted according as per instructions.

1. The compound in which cations occupies all tetrahedral voids in a cubic closed packing (ccp) is
(a) CaF_2 *(b)* Na_2O
(c) ZnS *(d)* CsCl

2. Among the following best reducing agent is
(a) H_3PO_2 *(b)* H_3PO_3
(c) H_3PO_4 *(d)* $H_4P_2O_6$

3. Which of the following compounds is expected to be coloured?
(a) Ag_2SO_4 *(b)* CuF_2
(c) MgF_2 *(d)* CuCl

4. When 1,1-dichloropropane and 2,2-dichloropropane are reacted separately with aqueous potassium hydroxide solution, compounds '*A*' and '*B*' are formed. Both '*A*' and '*B*' gave the same product '*C*' on reduction using amalgamated zinc and HCl. Identify '*C*'
(a) propyl alcohol
(b) isopropyl alcohol
(c) propyl chloride
(d) propane

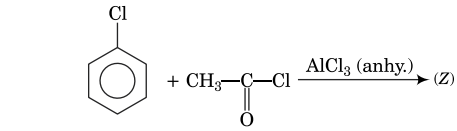
5. Which of the following combination will increases the number of C-atoms with respect to the number of atoms present in aldehyde/ketone?
(a) $H \cdot CHO + RMgX$
(b) $CH_3CHO + RMgX$
(c) $CH_3COCH_3 + RMgX$
(d) All of the above

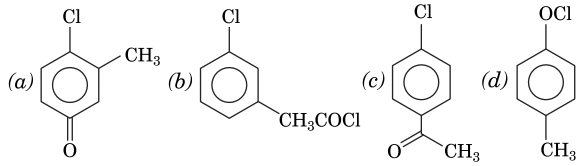
6. In a first order reaction, the concentration of reactant decreases from 400 mol/dm^3 to 100 mol/dm^3 in 2.0 s. The rate constant for the reaction is
(a) 1.38 s^{-1} *(b)* 0.34 s^{-1}
(c) 0.69 s^{-1} *(d)* 0.50 s^{-1}

7. At same temperature 0.008 M solution of an ionic electrolyte A_2B is isotonic with 0.02 M glucose solution. The percentage degree of dissociation of A_2B is
(a) 25% *(b)* 50% *(c)* 75% *(d)* 95%

8. A brown gas *(A)* on cooling changes to a colourless solid *(B)*, *(B)* on heating with NO changes to a blue solid (N_2O_3). *(A)* and *(B)* are respectively
(a) NO_2 and N_2O_4 *(b)* N_2O_4 and NO_2
(c) NO and NO_3 *(d)* N_2O and NO_3

9. In the reaction,





10. Identify the incorrect statement.
(a) Interhalogen compounds are more reactive than its elemental form
(b) When NH_3 react with excess of Cl_2, a compound explosive in nature is formed
(c) Bleaching action of chlorine is due to its oxidising property
(d) Chlorine can reduce ferric ions to ferrous ions

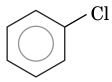
11. $C_2H_5Br \xrightarrow{KCN} (A) \xrightarrow{\text{Reduction}} (B) \xrightarrow{HNO_2}$ Final product(P)

The final product (P) in the above reaction is
(a) C_2H_5OH *(b)* C_3H_7Br
(c) $C_3H_7NO_2$ *(d)* C_3H_7OH

12. 0.3605 g of a metal is deposited on the electrode by passing 1.2 A current for 15 minutes through its salt. The valency of metal if its atomic weight is 96, will be
(a) 2 *(b)* 3
(c) 6 *(d)* 4

13. The reaction,
$Cr_2O_3(s) + 2Al(s) \longrightarrow Al_2O_3(s) + 2Cr(s)$;
$(\Delta G^\circ = (-)\text{ ve})$ is thermodynamically feasible as its free energy value is (–)ve. But the reaction does not takes place at room temperature because
(a) activation energy is required to raise the temperature
(b) the reaction is highly exothermic, difficult to control at room temperature
(c) the reaction is highly endothermic, difficult to control at room temperature
(d) All of the above

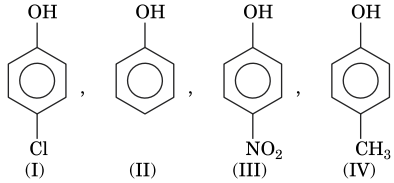
14. Which of the following artificial sweetening agent is unstable at cooking temperature?
(a) Aspartame *(b)* Sucralose
(c) Alitame *(d)* All of these

15. Which one of the following is least reactive towards nucleophilic substitution?
(a) $CH_2{=}CH{-}CH_2Cl$ *(b)* 
(c) $CH_3{-}CH(Cl){-}CH_3$ *(d)* $(CH_3)_3 \cdot C{-}Cl$

16. First five members of 3*d*-transition series can exhibit maximum oxidation states equal to
(a) half the sum of $(n-1)d$ and ns-electrons
(b) sum of $(n-1)d$ and ns-electrons
(c) twice the sum of $(n-1)d$ and ns-electrons
(d) 2 + half the sum of $(n-1)d$ and ns-electrons

17. Which of the following does not exist?
(a) XeF_6 *(b)* XeO_2F_4
(c) XeO_4F_2 *(d)* XeO_2F_2

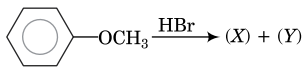
18. Benzophenone and acetophenone can be distinguished by using
(a) iodoform test *(b)* Fehling's test
(c) silver-mirror test *(d)* Benedict's test

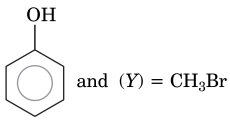
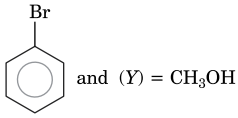
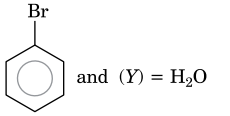
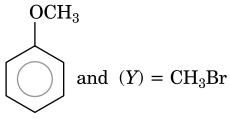
19. Among the given species,


The correct increasing order of acidic strength is
(a) III < I < IV < II
(b) IV < II < I < III
(c) I < II < III < IV
(d) IV < III < II < I

20. Which of the following statement is incorrect for lyophobic sol?
(a) They are irreversible under normal conditions
(b) They are mostly prepared by special methods
(c) They are readily coagulated by addition of electrolytes
(d) They are self stabilised

21. An organic compound $(C_3H_7NO_2)$ on reduction gives a compound *(A)* having molecular formula C_3H_9N. Another compound *(B)* on heating with Br_2 + KOH form the compound *(A)*. Compound *(A)* and *(B)* are respectively.
(a) $C_3H_7NH_2, C_3H_7NO_2$
(b) $C_3H_7{-}NH_2, C_3H_7CONH_2$
(c) $C_2H_5{-}\underset{\displaystyle H}{\underset{|}{N}}{-}CH_3, C_3H_7CONH_2$
(d) $C_2H_5{-}\underset{\displaystyle H}{\underset{|}{N}}{-}CH_3, C_3H_7NO_2$

22. For the reaction,


(X) and (Y) are
(a)  and $(Y) = CH_3Br$
(b)  and $(Y) = CH_3OH$
(c)  and $(Y) = H_2O$
(d)  and $(Y) = CH_3Br$

23. A reddish-brown powder *(A)* on boiling with HCl gives a yellow solution*(B)*, *(B)* on treatment with thiocyanate ions, gives a blood red coloured compound. *(A)* and *(B)* respectively are

(a) $FeCl_2$ and FeO *(b)* Fe_2O_3 and $FeCl_3$
(c) $FeCl_2$ and $FeCl_3$ *(d)* FeO and Fe_2O_3

24. Identify the correct statement.

(a) Lanthanoids can show variety of oxidation states. + 6 and + 7 oxidation states are exhibited frequently by lanthanoids
(b) Among lanthanoid members, except promethium all are radioactive in nature
(c) Actinoids can exhibit oxidation states upto + 6 and + 7
(d) Actinoids show very strong shielding effect

25. Identify the correct statement.

(a) Methanol is a solid at room temperature
(b) All aldehydes and ketones are fairly soluble in organic solvents
(c) Lower members of aldehyde group are insoluble in water
(d) Solubility of aldehydes and ketones increase with the increase in length of alkyl chain

26. An organic compound $C_6H_{12}O_2$ *(A)* on hydrolysis (in presence of dil. H_2SO_4) gives a carboxylic acid *(B)* and alcohol *(C)*, *(B)* on reduction gives propanol. On the basis of given information, *(A)*, *(B)* and *(C)* are respectively.

(a) *(A)* = propyl propanoate, *(B)* = propanoic acid *(C)* = propanol
(b) *(A)* = butyl butanoate, *(B)* = propanoic acid *(C)* = butanol
(c) *(A)* = propyl propanoate, *(B)* = ethanoic acid *(C)* = butanol
(d) *(A)* = ethyl butanoate, *(B)* = ethanoic acid *(C)* = butanoic acid

27. Which of the following species show highest conductivity in aqueous solution?

(a) $K_4[Fe(CN)_6]$ *(b)* $K_3[Fe(CN)_6]$
(c) $[Co(NH_3)_6]\cdot Cl_2$ *(d)* $[Cr(NH_3)_3Cl_3]$

28. The correct statement about $[NiCl_4]^{2-}$ and $[Ni(CO)_4]$ is

(a) Both are tetrahedral and paramagnetic in nature
(b) Both are tetrahedral but $[NiCl_4]^{2-}$ is paramagnetic while $Ni(CO)_4$ is diamagnetic
(c) Both are square planar and diamagnetic
(d) Both are square planar and paramagnetic

29. Which of the following molecule is isostructural with IF_5?

(a) $XeOF_4$ *(b)* XeF_6 *(c)* XeO_3 *(d)* XeF_4

30. Phenoxide ion show more number of resonating structures than carboxylate ion, but carboxylic acid is a stronger acid than phenol, the correct reason is

(a) Phenoxide ion has non-equivalent resonance structures in which negative charge is present at less electronegative atom
(b) The negative charge is localised in carboxylate ion while delocalised in case of phenoxide ion
(c) Due to presence of O^- atom, phenoxide ion is more stable than carboxylate ion
(d) Due to presence of benzene ring in phenoxide ion, it form more stable ion as compared to carboxylate ion

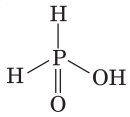
Answers with Explanation

1. ***(b)***

$Na_2O(A_2B)$ ⟶ ccp-type (2 : 1)
- Na^+ ⟶ Present at every tetrahedral void
- O^{2-} ⟶ Present at ccp lattice sites

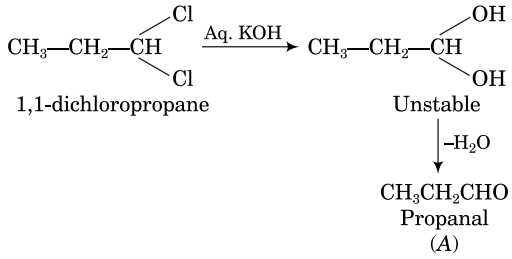
Na_2O have antifluorite structure.

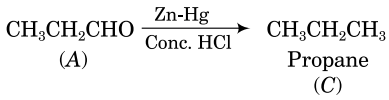
2. ***(a)*** H_3PO_2 is the best reducing agent among the given options as, it contain two replaceable H-atoms directly attached with phosphorus atom.

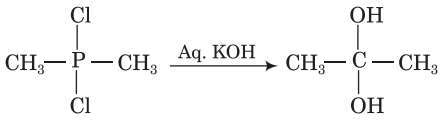


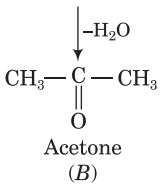
3. ***(b)*** $Cu^{2+}(3d^9)$ undergo *d-d* transition, exhibit colour.

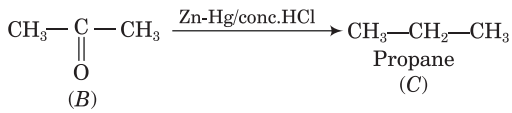
4. ***(d)***









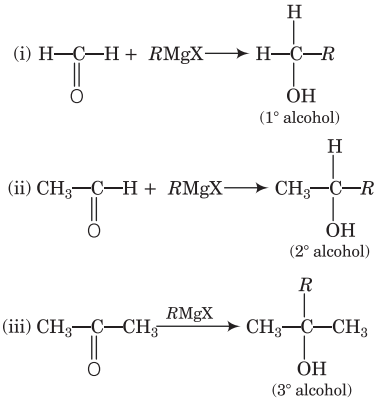


5. ***(d)***

(a) On using HCHO with *R*MgX, one C-atom gets increased and we get a primary alcohol.

(b) On using CH_3CHO with *R*MgX we get secondary alcohol with more number of C-atoms (equal to present in *R*).

(c) On using CH_3COCH_3 with *R*MgX, we get tertiary alcohol with more number of C-atoms (equal to numbers present in *R*) as compared to ketones.



6. ***(c)*** **Key Concept** For a first order reaction,

$$K = \frac{2.303}{t}\log_{10}\frac{a}{a-x}$$

Given, $t = 2$ sec, $a = 400$ and $a - x = 100$

$$\therefore \quad K = \frac{2.303}{2}\log_{10}\frac{400}{100}$$

$$K = 1.15\log_{10} 4$$
$$K = 1.15\,(2\log_{10} 2)$$
$$K = 1.15 \times 2 \times 0.3010$$
$$K = 1.15 \times 0.6020$$
$$K = 0.6923 \approx 0.69\,s^{-1}$$

7. ***(c)*** **Thinking process** *First, calculate the value of van't Hoff factor (i) using formula,*

$$i \times \pi_{A_2B} = \pi_{glucose} \qquad [\because \text{isotonic}]$$

Then, calculate degree of dissociation (α) with the help of following formula.

$$i = (1 - \alpha) + n\alpha$$

For isotonic solutions,

$$i \times \pi_1 = \pi_2$$
$$i \times C_1RT = C_2RT$$

Given, $C_1 = 0.008$ M, $C_2 = 0.02$ M

$$\therefore \quad i \times 0.008 = 0.02$$
$$\therefore \quad i = \frac{0.02}{0.008} = 2.5$$

Also, for dissociation

$$i = 1 - \alpha + n\alpha$$

$n = 3$ for A_2B type ionic electrolyte

$$i = 1 - \alpha + 3\alpha$$
$$2.5 = 1 + 2\alpha$$
$$\therefore \quad \alpha = 0.75$$
or $$\alpha = 75\%$$

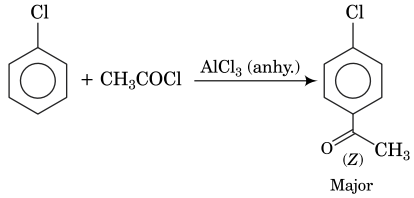
8. ***(a)*** As given gas *(A)* is of brown colour, it is NO_2. On cooling it changes to a colourless solid $N_2O_4(B)$.

N_2O_4 on heating with NO gives blue solid of N_2O_3.

(i) $\underset{\text{Brown}}{2NO_2(g)} \underset{\text{Cooling}}{\rightleftharpoons} \underset{\text{Colourless}}{N_2O_4(s)}$

(ii) $2NO(g) + N_2O_4(s) \xrightarrow{\Delta} \underset{\text{Blue solid}}{2N_2O_3(s)}$

9. ***(c)*** In the given reaction, acetylation of C_6H_5Cl occur at *p*-position as-Cl group is *o-, p*-directing.



10. ***(d)***

(a) Interhalogen compounds are more reactive than its elemental form because of weaker bonds between XX' (X and X' are two different halogens) means have low bond dissociation enthalpy as compared to X_2.

Thus, statement (a) is true.

(b) When NH_3 react with Cl_2 (in excess) produces NCl_3 (nitrogen trichloride), which is explosive in nature therefore, statement (b) is true.

(c) Bleaching action of chlorine is due to its oxidising nature, i.e. $Cl_2 + H_2O \longrightarrow 2HCl + [O]$

Coloured matter + [O] → Colourless matter

Thus, statement (c) is true.

(d) Cl_2 is oxidising in nature and will oxidise ferrous ions to ferric ions as follows

$2FeSO_4 + H_2SO_4 + Cl_2 \longrightarrow Fe_2(SO_4)_3 + 2HCl$

11. ***(d)*** $C_2H_5Br \xrightarrow{KCN} \underset{(A)}{C_2H_5CN} \xrightarrow{\text{Reduction}}$

$$C_2H_5-\underset{\underset{NH_2}{|}}{CH_2} \xrightarrow{HNO_2} \underset{(P)}{C_2H_5-CH_2-OH}$$
(B)

i.e. C_3H_7OH (Product)

12. ***(b)*** Amount of electricity passed,

$$Q = it = 1.2 \times 15 \times 60 = 1080\ C$$

Mass of metal deposited by passing 1080 C electricity = 0.3605

Mass of metal deposited by passing 96500 C electricity

$$= \frac{0.3605}{1080} \times 96500 = 32.2\ g$$

∴ Equivalent mass of metal = 32.2 g mol^{-1}

Atomic mass = 96 g mol^{-1}

$$\text{Valency} = \frac{\text{atomic mass}}{\text{equivalent mass}} = \frac{96}{32.2} = 3$$

13. ***(a)*** As reactants are solid, so reaction does not occur at room temperature. They require activation energy, the required activation energy can be achieved only above the room temperature.

14. ***(a)*** Aspartame is a methyl ester of dipeptide formed from aspartic acid and phenylalanine. It is unstable at cooking temperature.

15. ***(b)*** Chlorobenzene is least reactive towards nucleophilic substitution due to presence of double bond character between Cl-atom and C-atom of benzene ring.

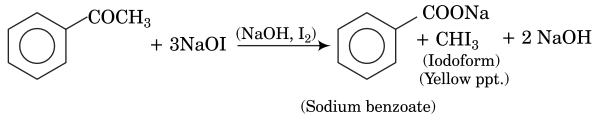
16. ***(b)*** First five members of 3*d*-transition series can exhibit maximum oxidation state equal to the sum of electrons present in $(n-1)d$ and ns, e.g. Mn can exhibit maximum oxidation number = + 7 ($3d^5 4s^2$)

Sc can exhibit maximum oxidation number = + 3 ($3d^1 4s^2$)

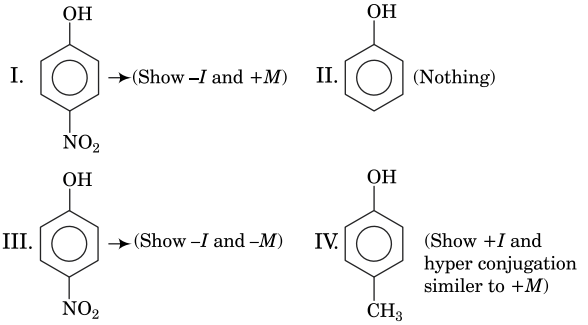
17. ***(c)*** Option (c), i.e. XeO_4F_2 does not exist as 4-oxygen atoms require 8-electrons to make 4-double bonds and two F-atoms require 2-electrons to make two sigma (σ) bonds.

Thus, total 10 electrons are needed to make the XeO_4F_2 molecule which is not possible (as Xe has only 8-electrons in its outer most shell).

18. ***(a)*** Only acetophenone will show (+)ve iodoform test.



19. ***(b)*** Electron withdrawing groups, i.e. groups that show $-I$ and $-M$-effect will increases the acidic strength while, electron releasing groups, i.e. groups that show $+I$ and $+M$-effect will decrease the acidic strength



∴ Correct order is → IV < II < I < III.

20. ***(d)*** Lyophobic sol(s) are

- Irreversible under normal conditions
- Prepared by special methods
- Readily coagulated by addition of electrolytes
- Require stabilising agents, i.e. they are not self stabilised

21. ***(b)*** (i) ∵ On reduction $C_3H_7NO_2$ gives $C_3H_7NH_2$ (molecular formula C_3H_9N)

(ii) On Hofmann bromamide degradation using Br_2 + KOH, we get primary amine with one C-atom less than that of parent amide.

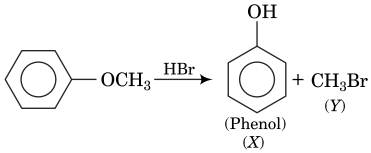
Hence, *(A)* is $C_3H_7NH_2$ (Primary amine)

(B) is $C_3H_7CONH_2$ (Amide)

(I) $C_3H_7NO_2 \xrightarrow{\text{Reduction}} C_3H_7NH_2$

(II) $C_3H_7CONH_2 \xrightarrow{Br_2 + KOH} C_3H_7NH_2$

22. ***(a)***



23. ***(b)*** (i) Fe_2O_3 *(A)* is the reddish brown powder react with HCl to give yellow solution of $FeCl_3$ *(B)*.

$$\underset{\substack{(A)\\(\text{Reddish brown powder})}}{Fe_2O_3} + 6HCl \longrightarrow \underset{(B)\ (\text{Yellow solution})}{FeCl_3} + 3H_2O$$

(ii) $FeCl_3$ on reaction with CNS^- ions gives blood-red colour of $Fe(CNS)_3$.

$$FeCl_3 + 3CNS^- \longrightarrow \underset{(\text{Blood-red})}{Fe(CNS)_3} + 3Cl^-$$

24. ***(c)*** (a) Lanthanoids mainly show + 3 oxidation state alongwith + 2 and + 4 in some cases.
Thus (a) is false.

(b) Except promethium all lanthanoids are non-radioactive.
Thus, (b) is false.

(c) Actinoids can exhibit oxidation state + 6 and + 7.
Thus, (c) is true.

(d) Actinoids show poor shielding effect due to the presence of *d* and *f*-inner electrons.
Thus, (d) is false.

25. ***(b)*** (a) Methanol is a gas at room temperature.

(b) All aldehydes and ketones are fairly soluble in organic solvents.

(c) Lower members of aldehyde are miscible with water.

(d) Solubility of aldehydes and ketones decrease with the increase in length of alkyl chain.

26. ***(a)*** (i) Degree of unsaturation = 1 the compound *(A)* must contain one π-bond or a ring.

(ii) On hydrolysis,
(A) gives a carboxylic acid *(B)* and an alcohol *(C)*.
Therefore, *(A)* is an ester.

(iii) Acid-part on reduction gives propanol, therefore *(B)* contain 3 C-atoms.
Hence, *(A)* = ester

$$CH_3—CH_2—\underset{\underset{O}{\|}}{C}—OCH_2—CH_2—CH_3$$

(Propyl propanoate)

(B) = acid = $CH_3—CH_2—COOH$ (propanoic acid)

(C) = alcohol = $CH_3 \cdot CH_2 \cdot CH_2 \cdot OH$ (Propanol)

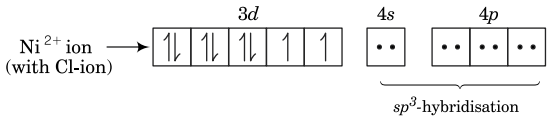
$$\text{(I)}\ CH_3CH_2—\underset{\underset{O}{\|}}{C}—O—\underset{(A)}{CH_2 \cdot CH_2 \cdot CH_3}$$

$$\xrightarrow[\text{Hydrolysis}]{H_2SO_4\ (\text{dil.})} \underset{(B)}{CH_3CH_2COOH} + CH_3CH_2\underset{\underset{OH}{|}}{C}H_2$$

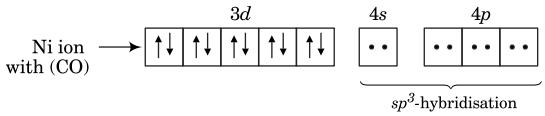
$$\underset{(B)}{CH_2—CH_2—COOH} \xrightarrow{\text{Reduction}} \underset{(C)}{CH_3CH_2CH_2OH}$$

27. ***(a)*** More the ions produced by the species, more is the conducting nature.
As $K_4[Fe(CN)_6]$ will provide $4K^+$ and one $[Fe(CN)_6]^{4-}$ ions. (i.e. total 5-ions)
Therefore, is shows maximum conductivity in solution.
For others, $K_3[Fe(CN)_6]$ = give 4-ions
$[Co(NH_3)_6]Cl_2$ = give 3-ions
$[Cr(NH)_3Cl_3]$ = remains as such

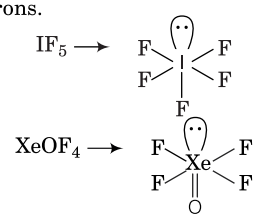
28. ***(b)*** As both are linked with four sigma bonds with 4-ligands and show sp^3-hybridisation thus are tetrahedral by shape. But due to presence of weak ligand (Cl^-) in $[NiCl_4]^{2-}$, Ni will not undergo pairing and two unpaired electrons are present in the geometry.



Whereas CO is a strong field ligand and allows Ni in $[Ni(CO)_4]$ to undergo pairing. It contain completely filled 3*d* orbitals. Therefore, does not show paramagnetism. Hence, diamagnetic in nature.



29. ***(a)*** IF_5 is iso-structural with $XeOF_4$ as central atom of both contain equal number of sigma (σ) bonds and lone pair of electrons.

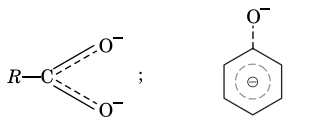


Both have square pyramidal shape.

30. ***(a)*** Phenoxide ion has non-equivalent resonance structures in which the negative charge is at less electronegative carbon atoms.

On the other hand, the negative charge is delocalised over two more electronegative oxygen atom in carboxylate ion.

Thus, carboxylate ion is more stable as compared to phenoxide ion and therefore, phenol is less acidic than carboxylic acid.



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JEE MAIN

(PAPER TWO SCALE UP)

HALF TEST 2

(XII SYLLABUS)

WITH ANSWER KEY

Mock Questions from Class XIIth syllabus to enhance Your Problem Solving Skills

INSTRUCTIONS

- This test consists of 30 questions and each question is allotted 4 marks for correct response.
- Candidates will be awarded marks as stated above for correct response of each question. 1/4 marks will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
- There is only one correct response for each question. Filling up more than one response in any question will be treated as wrong response and marks for wrong response will be deducted according as per instructions.

1. An element crystallises in two forms (x) and (y); (x) form has fcc structure with a = 3.80 Å and (y) has bcc structure with a = 3.0 Å.

The ratio of densities of (x) to that of (y) is

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

2. CN^- and N_2 are isoelectronic but as compared to CN^- ion, N_2 is inert due to

(a) low bond dissociation energy
(b) unsymmetrical electronic distribution of electrons
(c) presence of more electrons in bonding orbitals
(d) absence of polarity

3. Methyl cyanide when treated with methyl magnesium chloride followed by hydrolysis gives

(a) propanal *(b)* propanol
(c) propanone *(d)* ethanol

4. 100 g of ethylene glycol dissolved in 400 g of water at the temperature of – 9.3 °C. The amount of water separates out as ice will be (Molar mass of ethylene glycol = 62 and K_f for water 1.86 K kg mol^{-1}).

(a) 322.5 g *(b)* 77.4 g
(c) 38.7 g *(d)* 200.0 g

5. Which of the following statement about NO_2 and N_2O_4 is correct?

(a) NO_2 is diamagnetic while N_2O_4 is paramagnetic
(b) NO_2 is paramagnetic while N_2O_4 is diamagnetic
(c) Both are diamagnetic
(d) Both are paramagnetic

6. Identify the incorrect statement.

(a) PCl_5 exist but NCl_5 does not
(b) Nitrogen form oxides in all (+ 1 to + 5) oxidation states
(c) All S—O bonds in SO_3^{2-} are not of equal length
(d) None of the above

7. 100 mL of 1 M solution of $CuCl_2$ is electrolysed with the current of 1.0 A for 1 h. The normality of the remaining solution will be

(a) 1 N *(b)* 1.63 N
(c) 2.00 N *(d)* 2.20 N

8. An unknown gas (Z) is used to produce Holme's signal. The gas when burns in air give a pentoxide with white smoke (vortex rings). The gas is highly poisonous and reactive.

The gas (Z) is

(a) PCl_3 *(b)* N_2O
(c) PH_3 *(d)* NCl_3

9. The gas evolved on anode during electrolysis of $K_2SO_4(aq)$ solution using platinum electrodes will be

(a) H_2 *(b)* SO_2
(c) SO_3 *(d)* O_2

10. Which of the following on reaction will give cyclohexane?

(a) Cyclohexene and HBr followed by treatment with KOH (alcoholic)
(b) Cyclohexanol and Mg followed by treatment with CO_2
(c) Bromocyclohexane and Mg in dry ether followed by H_2O
(d) Isopropyl bromide and Na in presence of dry ether

11. Which of the following compound can show tautomerism?
(a) $C_6H_5NO_2$ (b) $(CH_3)_3C \cdot NO_2$
(c) $C_2H_5 \cdot NO_2$ (d) $(C_6H_5)_3C \cdot NO_2$

12. Which of the following statement is correct?
(a) Most common oxidation state for lanthanoids is + 2 and for actinoids is + 2 and + 4
(b) The electronic configuration of actinoids cannot be assigned with accuracy because of small energy difference in 5*f* and 6*d*-energy levels
(c) Basic strength of hydroxides of lanthanoids increases from $La(OH)_3$ to $Lu(OH)_3$
(d) Lu^{3+}, Yb^{3+} and Cu^{4+} are paramagnetic in nature

13. For a reaction,

$$A + B \longrightarrow \text{Products.}$$

Initial concentration ($mol\ L^{-1}$)			Initial rate ($mol\ L^{-1}\ s^{-1}$)
S.No.	$[A]_0$	$[B]_0$	
1.	0.2	0.2	0.1
2.	0.4	0.2	0.2
3.	0.2	0.4	0.1

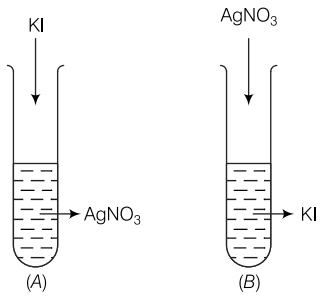
The rate equation for the above reaction is
(a) $r = k[A][B]$
(b) $r = k[A]$
(c) $r = k[B]$
(d) $r = k[A][B]^2$

14. Consider the following statements.
I. White phosphorus is a translucent, white waxy, poisonous and insoluble in water.
II. White phosphorus is a translucent, white waxy, non-poisonous and insoluble in water.
III. White phosphorus is a translucent, white waxy, poisonous and soluble in water.
IV. White phosphorus is a non-translucent, white waxy, poisonous and soluble in water.
Choose the incorrect statement(s) given above.
(a) Only II
(b) Both I and II
(c) II, III and IV
(d) Both III and IV

15. A 6% solution of sucrose (molar mass = 342 g mol^{-1}) is isotonic with 4 per cent solution of an unknown non-volatile substance. At same temperatures, the molecular mass of unknown substance will be
(a) 513 (b) 70 (c) 684 (d) 228

16. Which of the following solution act as disinfectant?
(a) 2 – 3% solution of iodine in alcohol and water
(b) Mixture of chloroxylenol (also known as parachlorometa xylenol) and terpineol
(c) 1% solution of phenol
(d) Both (a) and (b)

17. A sol of AgI is prepared by mixing $AgNO_3$ and KI as follows:



The charge on the colloidal particles of (*A*) and (*B*) are respectively.
(a) positive on both (*A*) and (*B*)
(b) negative on both (*A*) and (*B*)
(c) positive on (*A*) and negative on (*B*)
(d) negative on (*A*) and positive on (*B*)

18. The correct increasing order of basic strength of $C_6H_5NH_2$, $(C_2H_5)_2NH$ and $C_2H_5NH_2$ is
(a) $C_2H_5NH_2 < (C_2H_5)_2NH < C_6H_5NH_2$
(b) $C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$
(c) $C_6H_5NH_2 < C_2H_5NH_2 < (C_2H_5)_2NH$
(d) $(C_2H_5)_2NH < C_2H_5NH_2 < C_6H_5NH_2$

19. A compound (*A*) with molecular formula, $C_4H_{10}O$ is soluble in conc. $H_2SO_4 \cdot$ (*A*) on heating with excess of HI gives a single alkyl halide as product. (*A*) is
(a) C_4H_9OH (b) $C_2H_5—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_3$
(c) $CH_3CH_2OCH_2CH_3$ (d) $CH_3—O—C_3H_7$

20. For a reaction,

$$\underset{\text{[Reactant]}}{X} \longrightarrow \underset{\text{[Product]}}{Y}$$

If, E_a for forward reaction = 20 kJ mol^{-1}
E_a for backward reaction = 10 kJ mol^{-1}
and potential energy of (*X*) = 11 kJ mol^{-1}.
The heat of reaction (ΔH) and value of threshold energy of the reaction will be, respectively
(a) 9 kJ mol^{-1} and 30 kJ mol^{-1}
(b) 9 kJ mol^{-1} and 31 kJ mol^{-1}
(c) 10 kJ mol^{-1} and 30 kJ mol^{-1}
(d) 10 kJ mol^{-1} and 31 kJ mol^{-1}

21. Consider the following observations and identify the compounds *A* and *B*.
(i) Compound *A* is prepared by oxidation of compound *B* using alkaline $KMnO_4$.
(ii) *A* on reduction with $LiAlH_4$ gives *B*.
(iii) *A* and *B* react together in presence of H_2SO_4 to give a fruity smell.
(a) $A = RCH_2OH$, $B = RCHO$
(b) $A = R \cdot COOH$, $B = RCH_2OH$
(c) $A = R \cdot CH_2OH$, $B = R \cdot COOH$
(d) $A = R \cdot CHO$, $B = R \cdot COOH$

22. A complex, $[M(H_2O)_6]Cl_3$ (Z of $M = 24$) show magnetic moment of 3.83 BM then the correct distribution of 3*d*-electrons in the orbitals of M is

(a) $3d^1_{(xy)}, 3d^1_{(yz)}, 3d^1_{(zx)}$

(b) $3d^1_{(xy)}, 3d^1_{(z^2)}, 3d^1_{(x^2-y^2)}$

(c) $3d^1_{(z^2)}, 3d^1_{(xy)}, 3d^1_{(yz)}$

(d) $3d^1_{(x^2-y^2)}, 3d^1_{(xy)}, 3d^1_{(yz)}$

23. Which of the following reaction confirms presence of five —OH groups in glucose?

(a) Glucose + Br_2(aqueous)

(b) Glucose + HNO_3

(c) Glucose + Acetic anhydride

(d) Glucose + NH_2OH

24. Which of the following statement is incorrect when a mixture of NaCl and $K_2Cr_2O_7$ is gently warmed with conc. H_2SO_4?

(a) A deep red vapours is formed

(b) Vapours when passed into NaOH solution gives a yellow solution of Na_2CrO_4

(c) Chlorine gas is evolved

(d) Chromyl chloride is formed

25. For the reaction,

$$2A(g) + 3B(g) + C(g) \longrightarrow \text{Products}$$

Time (in min)	0	100	200
Partial pressure of (*A*) (mm Hg)	800	400	200

At a given temperature, order and rate constant of the said reaction are respectively

(a) zero, 6.93×10^{-3} min

(b) first, 0.693 min

(c) first, 6.93×10^{-3} min

(d) zero, 0.693 min

26. In the following reaction,

$$CH_3CHO + C_2H_5MgCl \xrightarrow{H_2O} (A) \xrightarrow[(443\ K)]{\text{Conc. } H_2SO_4} (B)$$

The major products (*A*) and (*B*) are respectively

(a) $CH_3CH_2CH_2CH_2OH$ and $CH_3CH_2OCH_2CH_3$

(b) $CH_3—\underset{\displaystyle OH}{\underset{|}{C}}H—C_2H_5$ and $CH_3—CH=CH—CH_3$

(c) $CH_3CH_2CH_2CH_2OH$ and $CH_3—OCH_2—CH_2—CH_3$

(d) $CH_3CH_2CH_2CH_2OH$ and $CH_2=CH—CH_2—CH_3$

27. An organic compound (*A*) with molecular formula C_6H_6O, on treatment with NaOH and CO_2 at 400 K under pressure gives (*B*). (*A*) gives a characteristic colour with aqueous $FeCl_3$. (*A*) and (*B*) are respectively

(a) phenol and salicylic acid

(b) hexanol and haxanoic acid

(c) toluene and phenol

(d) phenol and benzyl alcohol

28. Poling is the process used to remove

(a) Al_2O_3 from Al

(b) Cu_2O from Cu

(c) Fe_2O_3 from Fe

(d) ZnO from Zn

29. The correct statement for the use of NaCN is

I. as depressant in froth floating process to separate ZnS and PbS.

II. in leaching of silver and gold during extraction.

III. to remove Zn in extraction of silver and gold.

(a) Only I

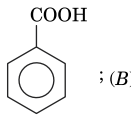
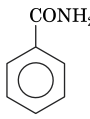
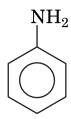
(b) Only III

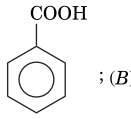
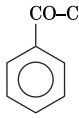
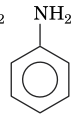
(c) I and II

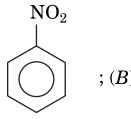
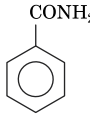
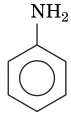
(d) I and III

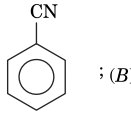
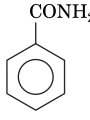
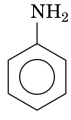
30. An aromatic compound (*A*) on heating with aqueous ammonia gives (*B*). (*B*) on heating with Br_2 and KOH form a compound (*C*) having molecular formula C_6H_7N.

(*A*), (*B*) and (*C*) are, respectively

(a) (*A*) =  ; (*B*) =  ; (*C*) = 

(b) (*A*) =  ; (*B*) =  ; (*C*) = 

(c) (*A*) =  ; (*B*) =  ; (*C*) = 

(d) (*A*) =  ; (*B*) =  ; (*C*) = 

Answers

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

AMAZING REALITIES

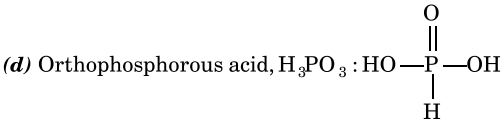
There is about 1/2 lb or 250 g of salt (NaCl) in the average adult human body.

p-BLOCK ELEMENTS

A collection of best asked questions from JEE to revise your concepts

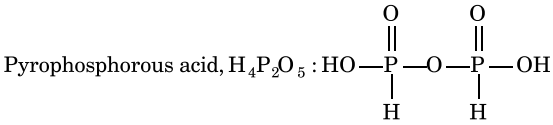
1. The pair in which phosphorus atoms have a formal oxidation state of + 3 is [JEE Main 2016]

(a) pyrophosphorous and hypophosphoric acids
(b) orthophosphorous and hypophosphoric acids
(c) pyrophosphorous and pyrophosphoric acids
(d) orthophosphorous and pyrophosphorous acids

(d) Orthophosphorous acid, H_3PO_3 : 

$\overset{x}{H_3P}O_3 \Rightarrow 3 + x + 3(-2) = 0$

$x = +3$

Pyrophosphorous acid, $H_4P_2O_5$: 

$\overset{x}{H_4P_2}O_5 \Rightarrow 4 + 2x + 5(-2) = 0$

$4 + 2x - 10 = 0$

$x = +3$

2. The increasing order of atomic radii of the following group 13 elements is [JEE Advanced 2016]

(a) Al < Ga < In < Tl *(b)* Ga < Al < In < Tl
(c) Al < In < Ga < Tl *(d)* Al < Ga < Tl < In

(b) **Thinking process** The ionic radii of group 13 elements increases on moving down the group.

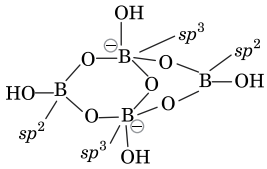
Due to poor shielding of *d*-orbital in Ga, atomic radius of Ga is smaller than that of Al. Thus, the increasing order of atomic radii of group 13 elements is Ga < Al < In < Tl.

3. The crystalline form of borax has [JEE Advanced 2016]

(a) tetranuclear $[B_4O_5(OH)_4]^{2-}$ unit
(b) all boron atoms in the same plane
(c) equal number of sp^2 and sp^3-hybridised boron atoms
(d) one terminal hydroxide per boron atom

(a, c, d) **Key concept** $Na_2B_4O_7 \cdot 10H_2O$ (borax) is actually made of two tetrahedral and two triangular units and written as $Na_2[B_4O_5(OH)_4] \cdot 5H_2O$.

Borax contains the tetrahedral units, i.e. $[B_4O_5(OH)_4]^{2-}$ and its structure can be shown as



Boron atoms are in different planes and each boron has one — OH group. Two sp^2 and two sp^3-hybridised B atoms are present.

4. The nitrogen containing compound produced in the reaction of HNO_3 with P_4O_{10} [JEE Advanced 2016]

(a) can also be prepared by reaction of P_4 and HNO_3
(b) is diamagnetic
(c) contains one N—N bond
(d) reacts with Na metal producing a brown gas

(b, d) **Key concept** P_4O_{10} is a dehydrating agent and converts HNO_3 into N_2O_5.

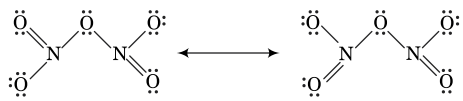
$2HNO_3 \longrightarrow N_2O_5 + H_2O$

$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$

(a) $P_4 + 20HNO_3 \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$

Hence, it produces NO_2. Thus, option (a) is **incorrect**.

(b) N_2O_5 has no unpaired electron and is thus, diamagnetic. Thus (b) is **correct**.

(c) 

There is no N—N bond. Thus, option (c) is **incorrect**.

(d) $N_2O_5 + Na \longrightarrow NaNO_3 + NO_2$

N_2O_5 vapours are of brownish colour.
Thus, option (d) is **correct**.

5. Which one has highest boiling point? [JEE Main 2015]

(a) He *(b)* Ne *(c)* Kr *(d)* Xe

(d) As we move down the group in noble gases, molecular mass increases by which dipole produced for a moment and hence, London forces increases from He to Xe. Therefore, more amount of energy is required to break these forces, thus boiling point also increases from He to Xe.

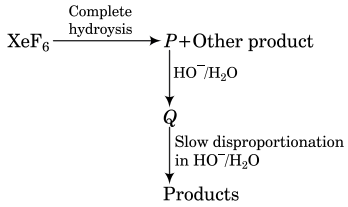
6. Which among the following is the most reactive? [JEE Main 2015]

(a) Cl_2 *(b)* Br_2 *(c)* I_2 *(d)* ICl

(d) Cl_2, Br_2 and I_2 are homonuclear diatomic molecules in which electronegativity of the combining atoms is same, hence, they are more stable and less reactive.
Whereas, I and Cl have different electronegativities and bond between them are polarised and hence, more reactive. Therefore, interhalogen compounds are more reactive than halogens (except fluorine).

Short Trick In this type of question of halogen, only go through the polarity of the molecule. As we know, diatomic molecule does not have polarity but molecules with dissimilar sizes have polarity resulting in more reactivity.

7. Under ambient conditions, the total number of gases released as products in the final step of the reaction scheme shown below is [JEE Advanced 2014]



(a) 0 (b) 1 (c) 2 (d) 3

(c) **Thinking process** This problem can be solved by using concept involved in chemical properties of xenon oxide and xenon fluoride.

XeF_6 on complete hydrolysis produces XeO_3. XeO_3 on reaction with $\bar{O}H$ produces $HXeO_4^-$ which on further treatment with $\bar{O}H$ undergo slow disproportionation reaction and produces XeO_6^{4-} alongwith $Xe(g)$, $H_2O(l)$ and $O_2(g)$ as by-product.

Oxidation half-cell in basic aqueous medium

$$HXeO_4^- + 5\bar{O}H \longrightarrow XeO_6^{4-} + 3H_2O + 2e^-$$

Reduction half-cell in basic aqueous medium

$$HXeO_4^- + 3H_2O + 6e^- \longrightarrow Xe + 7\bar{O}H$$

Balanced overall disproportionation reaction is

$$4HXeO_4^- + 8\bar{O}H \longrightarrow 3XeO_6^{4-} + Xe + 6H_2O$$

Complete sequence of reaction can be shown as

$$XeF_6 + 3H_2O \longrightarrow \underset{(P)}{XeO_3} + 3H_2F_2$$

$$\xrightarrow{\bar{O}H} \underset{(Q)}{HXeO_4^-} \xrightarrow{\bar{O}H + H_2O(\text{disproportionation})}$$

$$XeO_6^{4-}(s) + Xe(g) + H_2O(l) + O_2(g)$$

8. Among the following oxoacids, the correct decreasing order of acidic strength is [JEE Main 2014]

(a) $HOCl > HClO_2 > HClO_3 > HClO_4$
(b) $HClO_4 > HOCl > HClO_2 > HClO_3$
(c) $HClO_4 > HClO_3 > HClO_2 > HOCl$
(d) $HClO_2 > HClO_4 > HClO_3 > HOCl$

(c) **Thinking process** Acidic strength of oxoacids increases with oxidation state of central atom. Find the oxidation state of chlorine in all the oxoacids to decide the decreasing acid strength order among given four oxoacids.

$$HClO_4 = +1 + x + (-2 \times 4) = 0 \therefore x = +7$$
$$HClO_3 = +1 + x + (-2 \times 3) = 0 \therefore x = +5$$
$$HClO_2 = +1 + x + (-2 \times 2) = 0 \therefore x = +3$$
$$HClO = +1 + x + (-2 \times 1) = 0 \therefore x = +1$$

$HClO_4$ is the strongest acid and HClO is the weakest acid. The correct order of acidic strength is

$$HClO_4 > HClO_3 > HClO_2 > HClO.$$

9. The product formed in the reaction of $SOCl_2$ with white phosphorus is [JEE Advanced 2014]

(a) PCl_3 (b) SO_2Cl_2
(c) SCl_2 (d) $POCl_3$

(a) White phosphorus on reaction with thionyl chloride ($SOCl_2$) produces phosphorus trichloride.

$$P_4(s) + 8SOCl_2(l) \longrightarrow 4PCl_3(l) + 4SO_2(g) + 2S_2Cl_2(g)$$

But if sulphuryl chloride (SO_2Cl_2) is used the it produces phosphorus pentachloride.

$$P_4(s) + 10SO_2Cl_2(l) \longrightarrow 4PCl_5(l) + 10SO_2(g)$$

10. The correct statement(s) is/are for orthoboric acid. [JEE Advanced 2014]

(a) It behaves as a weak acid in water due to self ionisation
(b) Acidity of its aqueous solutions increases upon addition of ethylene glycol
(c) It has a three-dimensional structure due to hydrogen bonding
(d) It is a weak electrolyte in water

(b,d) (a) It does not undergo self ionisation in water but accept an electron pair from water, so it behaves as weak monobasic acid.

$$H_3BO_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+$$

Hence, option (a) is **incorrect**.

(b) When treated with 1, 2-dihydroxy or polyhydroxy compounds, they form chelate (ring complex) which effectively remove $[B(OH)_4]^-$ species from solution and thereby produce maximum number of H_3O^+ or H^+ ions, i.e. results in increased acidity.

Hence, option (b) is **correct**.

(c) Boric acid crystallises in a layer structure in which planar triangular BO_3^{3-} ions are bonded together through hydrogen bonds.

Thus, option (c) is **incorrect**.

(d) In water, the pK_a value of H_3BO_3 is 9.25.

$$H_3BO_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+; pK_a = 9.25$$

So, it is a weak electrolyte in water.

Thus, option (d) is **correct**.

11. With respect to graphite and diamond, which of the statement(s) given below is/are correct? [JEE Main 2012]

(a) Graphite is harder than diamond
(b) Graphite has higher electrical conductivity than diamond
(c) Graphite has higher thermal conductivity than diamond
(d) Graphite has higher C—C bond order than diamond

(b, d) Diamond has a three-dimensional network structure, a hard substance whereas graphite is soft due to layered structure.

In graphite, only three valence electrons are involved in bonding and one electron remain free and responsible for electrical conductivity. In diamond, all the four valence electrons are covalently bonded. Diamond is better thermal conductor than graphite. Electrical conductivity is due to availability of free electrons, thermal conduction is due to transfer of thermal vibrational energy from one atom to another atom. A compact and precisely aligned crystals like diamond thus facilitate better movement of heat.

In graphite, C—C bond acquire some double bond character, hence, have higher bond order than in diamond.

12. The reaction of white phosphorus with aqueous NaOH gives phosphine alongwith another phosphorus containing compound. The reaction type, the oxidation states of phosphorus in phosphine and the other product respectively are [JEE Main 2012]

(a) redox reaction, – 3 and – 5
(b) redox reaction, + 3 and + 5
(c) disproportionation reaction, – 3 and + 5
(d) disproportionation reaction, – 3 and + 3

(c) **Key concept** In a disproportionation reaction, an element in one oxidation state is simultaneously, oxidised and reduced.

The reaction of white phosphorus with aqueous alkali is

$$\overset{0}{P_4} + 3NaOH + 3H_2O \longrightarrow \overset{-3}{P}H_3 + 3\,NaH_2\overset{+1}{P}O_2$$

In the above reaction, phosphorus is simultaneously oxidised as well as reduced. Therefore, this is an example of disproportionation reaction. Oxidation number of phosphorus in PH_3 is – 3 and in NaH_2PO_2 is + 1. However, + 1 oxidation number is not given in any option, one might think that NaH_2PO_2 has undergone to further decomposition on heating.

$$2NaH_2PO_2 \xrightarrow{\Delta} Na_2H\overset{+5}{P}O_4 + PH_3$$

13. Which ordering of compounds is according to the decreasing order of the oxidation state of nitrogen? [JEE Main 2012]

(a) HNO_3, NO, NH_4Cl, N_2
(b) HNO_3, NO, N_2, NH_4Cl
(c) HNO_3, NH_4Cl, NO, N_2
(d) NO, HNO_3, NH_4Cl, N_2

(b) Let, oxidation number of N be x
In HNO_3, $+1 + x + 3(-2) = 0 \Rightarrow x = +5$
In NO, $x - 2 = 0 \Rightarrow x = +2$
In N_2, $x = 0$
In NH_4Cl, $x + 4 - 1 = 0 \Rightarrow x = -3$

14. Extra pure N_2 can be obtained by heating [JEE Main 2011]

(a) NH_3 with CuO
(b) NH_4NO_3
(c) $(NH_4)_2Cr_2O_7$
(d) $Ba(N_3)_2$

(d) $\underset{\text{Azide}}{Ba(N_3)_2} \xrightarrow{\text{Heat}} Ba(s) + 3N_2(g)$

Azide salt of barium can be obtained in purest form as well as the decomposition product contain solid Ba as by-product alongwith gaseous nitrogen, hence no additional step for separation is required.

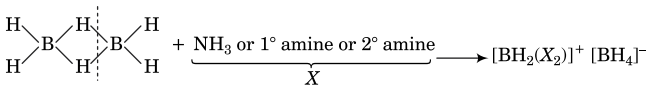
Other reactions are

$$NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$$
$$2NH_3 + 3CuO \xrightarrow{\Delta} 3Cu + 3H_2O + N_2$$
$$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} Cr_2O_3 + 4H_2O + N_2$$

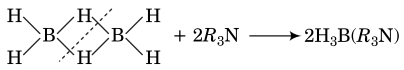
15. In the reaction,
$2X + B_2H_6 \longrightarrow [BH_2(X_2)]^+[BH_4]^-$ the amine(s) X is/are [JEE Main 2009]

(a) NH_3 *(b)* CH_3NH_2
(c) $(CH_3)_2NH$ *(d)* $(CH_3)_3N$

(a, b, c) **Key concept** *Diborane* (B_2H_6) *undergoes unsymmetric cleavage with* NH_3, *primary and secondary amine while tertiary amine brings about symmetrical cleavage of* B_2H_6.



Unsymmetric cleavage

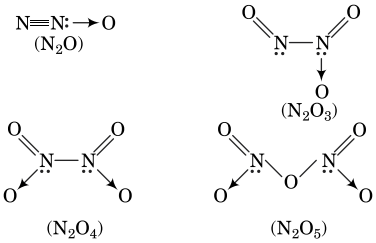


Symmetrical cleavage

16. The nitrogen oxide(s) that contain(s) N—N bond(s) is/are [JEE Main 2009]

(a) N_2O *(b)* N_2O_3 *(c)* N_2O_4 *(d)* N_2O_5

(a, b, c) The structures of the given oxides are



17. The reaction of P_4 with X leads selectively to P_4O_6. The X, is [JEE Main 2009]

(a) dry O_2
(b) a mixture of O_2 and N_2
(c) moist O_2
(d) O_2 in the presence of aqueous NaOH

(b) In limited supply of oxygen, phosphorus is oxidised to its lower oxide P_4O_6 while excess of oxygen gives P_4O_{10}. A mixture of O_2 and N_2 is used for controlled oxidation of phosphorus into P_4O_6.

To be Continued at Page 40

AMPLIFIER

CHEMICAL AND IONIC EQUILIBRIUM

Innovative problems targetted to improve your conceptual learning.

1. *Why gas fizzes out when soda water bottle is opened?*

› The amount of the gas dissolved in soda water bottle is very high due to high pressure. On opening the bottle, the pressure tends to decrease to atmospheric pressure. Thus, the solubility decreases, i.e. the dissolved gas escapes out.

2. *At equilibrium, the mass of each of the reactants and products remains constant. Does it mean that the reaction has stopped?*

› The equilibrium state is dynamic and not static in nature. It means that the reaction does not stop but both the opposing reactions are going on continuously with same speeds. At this state, the number of moles of substances produced per second in the forward direction is equal to the number of moles of substances which disappear per second in the backward direction.

3. *Why the reaction between acetic acid and ethyl alcohol attains a state of equilibrium in an open vessel but decomposition of* $CaCO_3$ *does not?*

› Acetic acid (CH_3COOH) and ethyl alcohol (C_2H_5OH) are liquids and their products, ethyl acetate ($CH_3COOC_2H_5$) and water (H_2O), are also liquids but one of the products of decomposition of calcium carbonate ($CaCO_3$) is gaseous carbon dioxide (CO_2) which escapes out and the reverse reaction cannot occur.

4. *Can the* pH *of a solution ever have a negative value.*

› We use the formula, $pH = -\log[H^+]$ to define the pH of a solution whose H^+ concentration is less than 1 M but more than 10^{-14} M. Hence, pH scale has numbers ranging from 0 to 14. However, in case of highly concentrated solutions having $[H^+] > 1$ M, the value of $\log[H^+]$ becomes greater than zero, making pH negative. Hence, a negative pH simply means, the $[H^+]$ of the solution is greater than 1 M. A solution having negative pH also occurs naturally in some mine areas where the minerals form highly concentrated acidic solution.

5. *For an exothermic reaction, what happens to the equilibrium constant, if temperature is increased?*

› Equilibrium constant $(K) = \frac{K_f}{K_b}$, in an exothermic reaction, with increase of temperature, K_b increases much more than K_f. Hence, K decreases.

6. *Why equilibrium constant is related to standard free energy change and not free energy change?*

› Gibbs free energy change is related to reaction quotient (Q) as $\Delta_r G = \Delta_r G^\circ + RT\ln Q$. When equilibrium is reached, $\Delta_r G = 0$ and $Q = K$. Hence, we have $\Delta_r G^\circ = -RT\ln K$

7. *A reaction,* $A(g) + B(g) \rightleftharpoons 2C(g)$ *is in equilibrium at a certain temperature. Can we increase the amount of products by adding catalyst or increasing pressure.*

› No, because catalyst does not disturb the state of equilibrium and $n_p = n_r = 2$. So, pressure also does not effect the equilibrium.

8. *Why does ice melts slowly at higher altitudes?*

› Melting of ice is endothermic process accompanied by decrease of volume. Hence, on applying Le-Chatelier's principle, the favourable conditions for the melting of ice are high temperature (forward reaction endothermic) and high pressure (forward reaction shows decrease in volume.) At higher altitudes, pressure as well as temperature is low. Hence, in the equilibrium, Ice $\rightleftharpoons$ Water, both the factors favours backward process. Therefore, the melting is slow.

9. *We know that,* $\Delta_r G^\circ = -RT\ln K$. *For the same reaction at the same temperature using* K_p *and* K_c, *the values* $\Delta_r G^\circ$ *are found to be different, why?*

› The numerical value of equilibrium constant depends upon the standard state chosen for expressing concentrations or pressures. In case of pressures, the standard state chosen is 1 bar whereas in case of concentrations, standard state chosen is 1 mol L^{-1}. Hence, $\Delta_r G^\circ$ values are different.

10. *What qualitative information can you obtain from the magnitude of equilibrium constant?*

› (i) Large value of equilibrium constant ($> 10^3$) shows that forward reaction is favoured, i.e. concentration of products is much larger than that of the reactants at equilibrium.

(ii) Intermediate value of $K(10^{-3}$ to $10^3)$ shows that the concentration of the reactants and products are comparable.

(iii) Low value of $K(10^{-3})$ shows that backward reaction is favoured, i.e. concentration of reactants is much larger than that of the products.

AMPLIFIER

11. *Why ammonia termed as a base although it does not contain* $\bar{O}H$ *ions?*

› NH_3 is termed as a base on the basis of Lewis concept because it can donate a lone pair of electrons.

12. *Out of* CH_3COO^- *and* $\bar{O}H$ *which is stronger base and why?*

› $\bar{O}H$ ions can combine with H^+ ions more readily than CH_3COO^- ions can do. Hence, $\bar{O}H$ is a stronger base. Alternatively, the conjugate acid of CH_3COO^- and ^-OH are CH_3COOH and H_2O, respectively . As CH_3COOH is stronger acid than H_2O, the conjugate base of CH_3COOH, *viz*, CH_3COO^- will be a weaker base.

13. *What is the effect of temperature on ionic product of water and why?*

› Ionic product of water (K_w) increases with increase of temperature because, $K_w = [H_3O^+][\bar{O}H]$ and dissociation of H_2O to give H_3O^+ and ^-OH increases with increase of temperature.

14. *Will the* pH *of water be same at* 4°C *and* 25°C*? Explain.*

› No, pH of water is not same at 4°C and 25°C. This is because with increase in temperature, dissociation of H_2O molecules increases. Hence, $[H^+]$ will increase, i.e. pH decreases. Thus, pH at 4°C will be more than at 25°C.

15. *What is the difference between ionic product and solubility product?*

› Both ionic product and solubility product represents the product of the concentrations of the ions in the solution. Ionic product is applicable to all types of solutions, either unsaturated or saturated and varies accordingly. On the other hand, solubility product is applied only to a saturated solution in which there exists a dynamic equilibrium between the undissolved salt and the ions present in the solution.

16. *Explain why* pH *of* 0.1 *molar solution of acetic acid will be higher than that of* 0.1 *molar solution of* HCl*?*

› Acetic acid is a weak electrolyte, it is not completely ionised and hence gives less H^+ ion concentration. HCl is a strong acid, it is completely ionised giving more H^+ ion concentration.
As pH = – log $[H^+]$; less the $[H^+]$, greater will be the pH.

17. *Why solid* NaCl *starts separating out from a saturated solution of* NaCl *if* HCl *gas is passed through it?*

› HCl in the solution provides Cl^- ions. This increases the ionic product of NaCl and so the solid NaCl starts separating out.

18. *Why common salt is added to precipitate out soap from the solution during its manufacture?*

› Soap is sodium salt of higher fatty acid ($RCO\overset{-}{O}\overset{+}{N}a$). On adding common salt, Na^+ ion concentration increases. Hence, the equilibrium, $RCOONa(s) \rightleftharpoons RCOO^- + Na^+$ shifts in the backward direction, i.e. soap will precipitates out.

19. *Why in Group* v *of qualitative analysis, sufficient* NH_4OH *solution should be added before adding* $(NH_4)_2CO_3$ *solution?*

› This is done to convert NH_4HCO_3 usually present in large amounts alongwith $(NH_4)_2CO_3$ to $(NH_4)_2CO_3$.
$NH_4HCO_3 + NH_4OH \longrightarrow (NH_4)_2CO_3 + H_2O$

20. *The ionisation constant of formic acid is* 1.8×10^{-4}*. Around what* pH *will its mixture with sodium formate give buffer solution of highest capacity?*

› Buffer solution of highest capacity is formed when
(i) [salt] = acid, i.e. pH = pK_a for acidic buffer.
(ii) [salt] = [base], i.e. pH = pK_b for basic buffer.
Therefore, pH = pK_a = – log $(1.8 \times 10^{-4}) = 3.74$

Continued from Page 38

18. Aqueous solution of $Na_2S_2O_3$ on reaction with Cl_2 gives [JEE Main 2008]

(a) $Na_2S_4O_6$ *(b)* $NaHSO_4$ *(c)* NaCl *(d)* NaOH

› ***(b)*** **Key concept** Sodium thiosulphate, $Na_2S_2O_3$ gets oxidised by chlorine water.

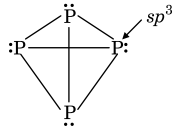
$$Na_2S_2O_3 + 4Cl_2 + 5H_2O \longrightarrow 2NaHSO_4 + 8HCl$$

$FeCl_3$ oxidises $Na_2S_2O_3$ to $Na_2S_4O_6$.

19. The percentage of *p*-character in the orbitals forming P—P bonds in P_4 is [JEE Main 2007]

(a) 25 *(b)* 33 *(c)* 50 *(d)* 75

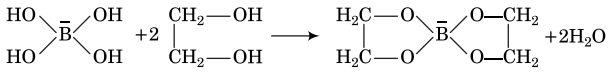
› ***(d)*** In P_4, all phosphorus are sp^3-hybridised and has 75% *p*-character.



20. $B(OH)_3 + NaOH \rightleftharpoons NaBO_2 + Na[B(OH)_4] + H_2O$
How can this reaction is made to proceed in forward direction? [JEE Main 2006]

(a) Addition of *cis*-1, 2-diol
(b) Addition of borax
(c) Addition of *trans*-1, 2-diol
(d) Addition of Na_2HPO_4

› (a) **Key concept** Orthoboric acid is a weak acid, direct neutralisation does not undergo to completion.
Addition of *cis*-1, 2-diol allow the given reaction to go to completion by forming a stable complex with $[B(OH)_4]^-$ as



JEE ADVANCED
DRILL

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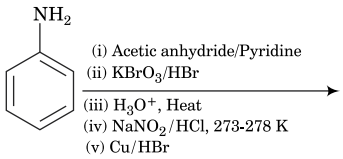
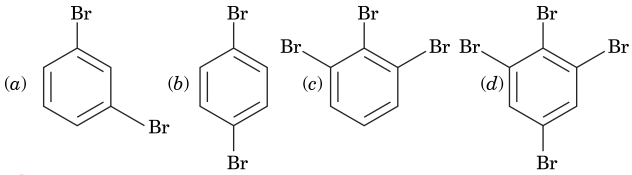
Single Answer Correct Type

1. The product of the following reaction sequence is [JEE Advanced 2016]





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

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

3. The half-life of a first order decomposition of nitramide is 2.1 h at 15°C.

$$NH_2NO_2(aq) \longrightarrow N_2O(g) + H_2O(l)$$

If 6.2 g of nitramide is allowed to decompose then time taken for it to decompose 99% will be

(a) 2.1 h *(b)* 18.61 h *(c)* 13.96 h *(d)* 33 h

4. An industrial method for the preparation of methanol is

(a) catalytic reduction of carbon monoxide in presence of $ZnO—Cr_2O_3$

(b) by reacting methane with steam at 900°C with nickel catalyst

(c) by reduction of formaldehyde with $LiAlH_4$

(d) by reacting formaldehyde with aqueous sodium hydroxide solution

5. For a saturated solution of AgCl at 25°C, specific conductance is $3.41 \times 10^{-6}\ \Omega^{-1}cm^{-1}$ and that of water used for preparing the solution was $1.60 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$. The solubility product of AgCl is $[\Lambda^{\infty}_{eq}(AgCl) = 138.30\ \Omega^{-1}\ cm^{-1}equiv^{-1}]$

(a) 1.31×10^{-5} *(b)* 1.74×10^{-8} *(c)* 1.72×10^{-10} *(d)* 3.24×10^{-4}

One or More than one Option Correct Type

6. Which of the following is the correct statement(s) regarding defects in solids?

(a) Frenkel defect is usually favoured by a very small difference in the sizes of cation and anion

(b) Frenkel defect is a dislocation defect

(c) Trapping of an electron in the lattice leads to the formation of *F*-centre

(d) Schottky defects have no effect on the physical properties of solids

7. Sodium sulphate is soluble in water whereas barium sulphate is sparingly soluble because

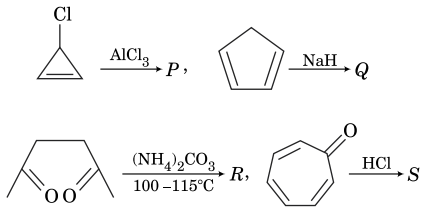
(a) the hydration energy of sodium sulphate is more than its lattice energy

(b) the lattice energy of barium sulphate is more than its hydration energy

(c) the lattice energy has no role to play in solubility

(d) the hydration energy of sodium sulphate is less than its lattice energy

8. Among *P*, *Q*, *R* and *S* the aromatic compound(s) is/are [JEE Advanced 2013]



(a) *P* *(b)* *Q* *(c)* *R* *(d)* *S*

9. The stability of the lyophobic colloidal particles is due to

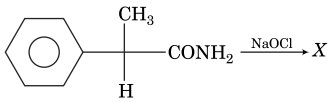
(a) preferential adsorption of solvent on their surface from the solution

(b) preferential adsorption of ions on their surface from the solution

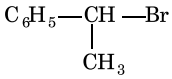
(c) potential difference between the fixed layer and the diffused layer of opposite charges around the colloidal particles

(d) attraction between different particles having opposite charges on their surface

10. Which of the following statements are true about the major product (X) in this reaction?



(a) It is a cyclic amide
(b) It has an asymmetric centre
(c) It is a primary amine
(d) It can also be obtained by treatment of NH_3 with



11. Which of the following statement(s) is/are correct with reference to the ferrous and ferric ions?
(a) Fe^{3+} gives brown colour with potassium ferricyanide
(b) Fe^{2+} gives blue precipitate with potassium ferricyanide
(c) Fe^{3+} gives red colour with potassium thiocyanate
(d) Fe^{2+} gives brown colour with ammonium thiocyanate

12. Three identical adiabatic containers have helium, neon and oxygen gases at the same pressure. The gases are compressed to half of their original volume. Under these conditions
(a) the final temperature of both helium and neon are same
(b) the final pressure of the gas in each container are same
(c) the final temperature of the gas in each container are same
(d) the final pressure of both helium and neon are same

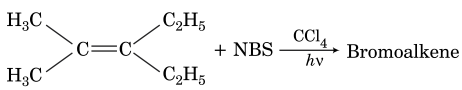
13. Which of the following compound(s) exhibit the dipole moment?
(a) 1, 4-dichlorobenzene
(b) *cis*-1, 2-dichloroethene
(c) *trans*-1, 2-dichloroethene
(d) *trans*-1, 2-dichloro-2-pentene

Integer Type

14. The atomic masses of He and Ne are 4 and 20 amu, respectively. The value of the de-Broglie wavelength of He gas at – 73°C is M times that of the de-Broglie wavelength of Ne at 727°C. M is [JEE Advanced 2013]

15. A total of $n \times 10^{20}$ energy levels are present in 3*s* conduction band of single crystal of sodium weighing 26.8 mg. What is the value of n?

16. Following is free radical allylic bromination reaction



N-bromosuccinimide (NBS)

How many different monobromination product(s) are expected in the above reaction?

17. A compound H_2X with molar weight of 80 g mol^{-1} is dissolved in a solvent having density of 0.4 g mL^{-1}. Assuming no change in volume upon dissolution, the molality of a 3.2 molar solution is [JEE Advanced 2014]

18. How many different chlorides, including stereoisomers by Wurtz coupling reaction with etheral solution of sodium can give 1, 4-dimethyl cyclohexane?

19. A $\frac{M}{10}$ solution of potassium ferrocyanide is 46% dissociated at 18°C. Calculate its osmotic pressure.

20. The volume (in mL) of 0.1 M $AgNO_3$ required for complete precipitation of chloride ions present in 30 mL of 0.01 M solution of $[Cr(H_2O)_5Cl]Cl_2$, as silver chloride is close to

21. One mole of nitrogen gas at 0.8 atm takes 38 s to diffuse through a pin-hole, whereas one mole of an unknown compound XeF_n at 1.6 atm takes 57 s to diffuse through the same hole. Find the value of n.

Comprehension I

Thermal decomposition of gaseous X_2 to gaseous X at 298 K takes place according to the following equation,

$$X_2(g) \rightleftharpoons 2X(g)$$

The standard reaction Gibbs energy, $\Delta_r G^\circ$, of this reaction is positive. At the start of the reaction, there is one mole of X_2 and no X. As the reaction proceeds, the number of moles of X formed is given by β. Thus, $\beta_{equilib.}$ is the number of moles of X formed at equilibrium. The reaction is carried out at a constant total pressure of 2 bar. Consider the gases to behave ideally.
(Given, $R = 0.083$ L bar K^{-1} mol^{-1}) [JEE Advanced 2016]

22. The equilibrium constant K_p for this reaction at 298 K, in terms of $\beta_{equilib.}$ is

(a) $\frac{8\beta^2_{equilib.}}{2-\beta_{equilib.}}$

(b) $\frac{8\beta^2_{equilib.}}{4-\beta^2_{equilib.}}$

(c) $\frac{4\beta^2_{equilib.}}{2-\beta_{equilib.}}$

(d) $\frac{4\beta^2_{equilib.}}{2-\beta^2_{equilib.}}$

23. The incorrect statement among the following for this reaction, is
(a) decrease in the total pressure will result in the formation of more moles of gaseous X
(b) at the start of the reaction, dissociation of gaseous X_2 takes place spontaneously
(c) $\beta_{equilib.} = 0.7$
(d) $K_C < 1$

Comprehension II

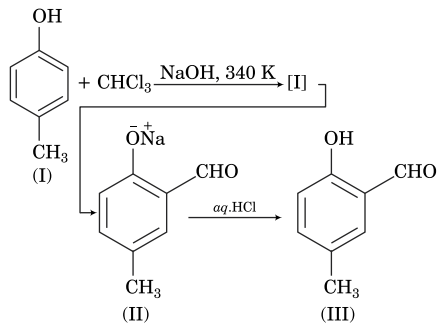
The reactions of Cl_2 gas with cold dilute and hot conc. NaOH in water give sodium salts of two (different) oxoacids of chlorine, P and Q, respectively. The Cl_2 gas reacts with SO_2 gas in the presence of charcoal to give R. R reacts with white phosphorus to give a compound S. On hydrolysis, S gives an oxoacid of phosphorus T.

24. P and Q respectively are the sodium salts of
(a) hypochlorous and chloric acids
(b) hypochlorous and chlorous acids
(c) chloric and perchloric acids
(d) chloric and hypochlorous acids

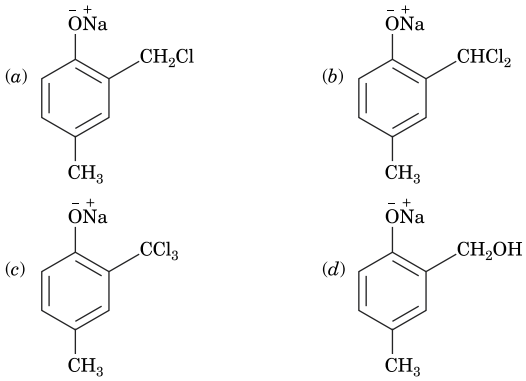
25. R, S and T respectively are
(a) $SOCl_2$, PCl_5 and H_3PO_4
(b) SO_2Cl_2, PCl_3 and H_3PO_4
(c) SO_2Cl_2, PCl_5 and H_3PO_2
(d) SO_2Cl_2, PCl_5 and H_3PO_4

Comprehension III

Riemer-Tiemann reaction introduces an aldehyde group, on to the aromatic ring of phenol, ortho to the hydroxyl group. This reaction involves electrophilic aromatic substitution. This is general method for the synthesis of substituted salicylaldehydes as depicted below.



26. The structure of the intermediate [I] is



27. The electrophile in this reaction is
(a) $:CHCl$ *(b)* $\overset{+}{C}HCl_2$
(c) $:CCl_2$ *(d)* $^{\bullet}CCl_3$

Matrix Match Type

28. The unbalanced chemical reactions given in Column I show missing reagent or condition (?) which are provided in Column II. Match Column I with Column II and select the correct answer using the codes given below the columns. [JEE Advanced 2013]

Column I	Column II
P. $PbO_2 + H_2SO_4 \xrightarrow{?} PbSO_4 + O_2 +$ Other product	1. NO
Q. $Na_2S_2O_3 + H_2O \xrightarrow{?} NaHSO_4$ + Other product	2. I_2
R. $N_2H_4 \xrightarrow{?} N_2$ + Other product	3. Warm
S. $XeF_2 \xrightarrow{?} Xe$ + Other product	4. Cl_2

Codes

	P	Q	R	S		P	Q	R	S
(a)	4	2	3	1	*(b)*	3	2	1	4
(c)	1	4	2	3	*(d)*	3	4	2	1

29. Match the vitamin in Column I with its deficiency disease in Column II.

Column I	Column II
P. Vitamin B_{12}	1. Sterility
Q. Vitamin B_6	2. Haemorrhagic condition
R. Vitamin E	3. Pernicious anaemia
S. Vitamin K	4. Skin disease

Codes

	P	Q	R	S		P	Q	R	S
(a)	1	2	3	4	*(b)*	2	3	4	1
(c)	3	4	2	1	*(d)*	3	4	1	2

30. Match the Column I with Column II and choose the correct option.

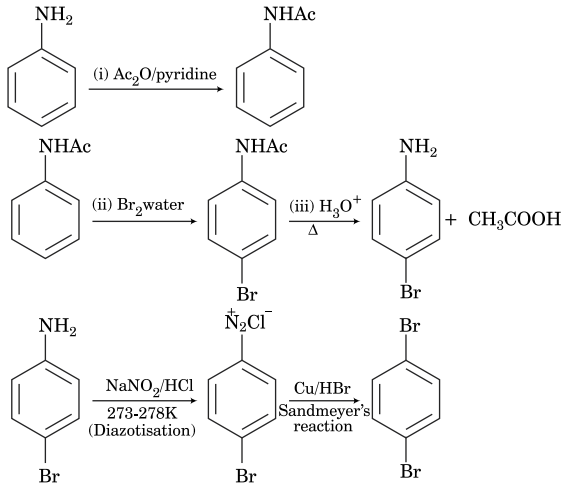
Column I	Column II
P. $[CoF_3(H_2O)_3]$	1. Diamagnetic, low spin complex
Q. $[Cr(C_2O_4)_3]^{3-}$	2. Paramagnetic, outer orbital complex
R. $[AuCl_4]^-$	3. Paramagnetic, inner orbital complex
S. $[Fe(CN)_6]^{3-}$	4. Diamagnetic, high spin complex
	5. Paramagnetic and low spin complex

Codes

	P	Q	R	S
(a)	3	2	1	4
(b)	1, 2	1	2	3, 4
(c)	1	2, 3	1	4
(d)	2	3	1	5

Answers with Explanation

1. ***(b)*** **Key concept** *Ac is CH_3CO-(acetyl), it protects $-NH_2$ group from being oxidised*



2. ***(a)*** Electrolysis of aqueous Na_2SO_4 gives $H_2(g)$ at cathode and $O_2(g)$ at anode.

At cathode $2H_2O + 2e^- \longrightarrow H_2(g) + 2\bar{O}H$

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

3. ***(c)*** For first order reaction,

$$K = \frac{0.693}{t_{1/2}} = \frac{0.693}{2.1} = 0.33\ h^{-1}$$

$$K = \frac{2.303}{t}\log_{10}\frac{a}{a-x}$$

$$t = \frac{2.303}{K}\log_{10}\frac{100}{100-99} = \frac{2.303}{K}\log_{10}(100)$$

$$= \frac{2.303}{0.33} \times 2 = 13.96\ h$$

4. ***(a)*** Methanol is also called wood spirit since, originally it was obtained by destructive distillation of wood. Now-*a*-days, it is prepared commercially by the catalytic hydrogenation of carbon monoxide or water gas. A mixture of carbon monoxide and hydrogen is passed over a catalyst (consisting of oxides of copper, zinc and chromium) at 573-673 K and under 200-300 atm. pressure when methanol is formed

$$CO + 2H_2 \xrightarrow[573-673\ K,\ 200-300\ atm]{CuO-ZnO-Cr_2O_3} \underset{\text{Methanol}}{CH_3OH}$$

The starting materials, i.e. CO and H_2 are obtained either from water gas or by partial oxidation of methane.

5. ***(c)*** For AgCl, molarity = normality

Actual specific conductance = (specific conductance of AgCl – specific conductance of water)

$$= (3.41 - 1.60) \times 10^{-6} = 1.81 \times 10^{-6}\ \Omega^{-1}cm^{-1}$$

For saturated solution of sparingly soluble salt,

$\Lambda_{eq} = \Lambda^{\infty}_{eq}$ and solubility = concentration

$$\Lambda^{\infty}_{eq} = \frac{1000 \times \text{specific conductance}}{\text{solubility}}$$

$$138.3 = \frac{1000 \times 1.81 \times 10^{-6}}{S}$$

$$S(\text{mol L}^{-1}) = \frac{1000 \times 1.81 \times 10^{-6}}{138.3} = 1.31 \times 10^{-5}\ \text{mol L}^{-1}$$

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

$$\therefore \quad K_{sp} = [Ag^+][Cl^-] = S^2$$

$$= (1.31 \times 10^{-5})^2 = 1.72 \times 10^{-10}\ \text{mol}^2\ \text{L}^{-2}$$

6. ***(b, c)*** (a) A small difference in sizes of cation and anion favours Schottky defect while Frenkel defect is favoured by large differences in sizes of cation and anion. Thus, statement (a) is incorrect.

(b) In Frenkel defect the smaller atom or ion gets dislocated from its normal lattice positions and occupies the interstitial space. Thus, statement (b) is correct.

(c) In *F*-centre defect, some anions leave the lattice and the vacant sites hold the electrons trapped in maintaining the overall electroneutrality of solid. Thus, statement (c) is correct.

(d) In Schottky defect, some of the atoms or ions remaining absent from their normal lattice sites without distorting the original unit cell dimension. This lowers the density of solid. Thus, statement (d) is incorrect.

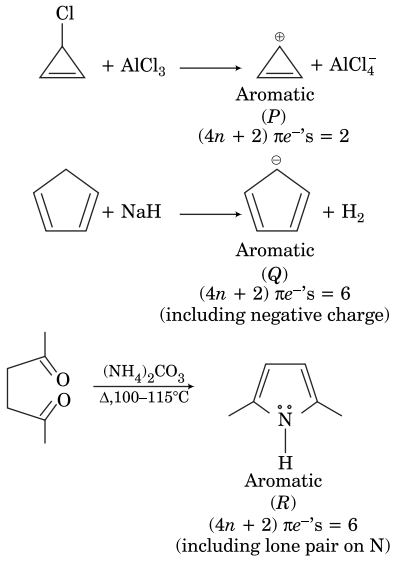
7. ***(a, b)*** (a) For greater solubility, hydration energy must be greater than lattice energy.

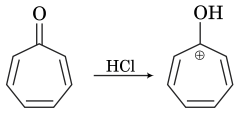
(b) Greater lattice energy decreases dissolution of a salt.

(c) When a salt dissolve, energy is required to break the lattice which comes from hydration process.

(d) As explained in (*a*)

8. ***(a, b, c, d)*** **Key concept** *A specie is said to has an aromatic character if ring is planar, there is complete delocalisation of π-electrons, Huckel rule, i.e. $(4n + 2)\pi$-electrons is followed (n = number of rings).*

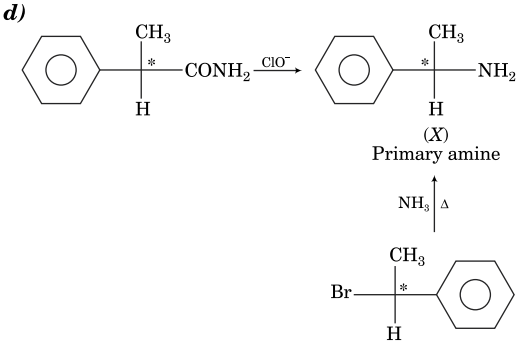




$(4n + 2)\ \pi e^{-}$'s = 6

9. ***(b, c)*** Lyophobic sol, which is otherwise unstable, gets stabilised by preferential adsorption of ions on their surface, thus developing a potential difference between the fixed layer and the diffused layer.

10. ***(b, c, d)***



11. ***(b, c)*** The blue precipitate of Fe^{2+} ion with potassium ferricyanide is due to formation of Turnbull's blue, $KFe[Fe(CN)_6]$

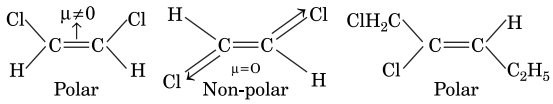
$$Fe^{2+} + K_3[Fe(CN)_6] \longrightarrow \underset{\text{Blue precipitate}}{KFe[Fe(CN)_6]} + 2K^+$$

The red colour of Fe^{3+} ion with potassium thiocyanate is due to formation of $[Fe(SCN)_3]$

$$Fe^{3+} + 3KSCN \longrightarrow \underset{\text{Red colour}}{[Fe(SCN)_3]} + 3K^+$$

12. ***(a, d)*** pV^{γ} = constant and $TV^{\gamma-1}$ = constant. Helium and neon are monoatomic gases ($\gamma = 1.67$), while oxygen is diatomic gas ($\gamma = 1.4$). Therefore, final temperature and pressure of both helium and neon are same.

13. ***(b, d)*** 1, 4-dichlorobenzene is non-polar, individual dipole vectors cancel each other.



14. ***(5)*** **Key concept** $KE = \frac{1}{2}mv^2 = \frac{3}{2}RT$

$$m^2v^2 = 2mKE$$

$$\therefore \quad mv = \sqrt{2mKE}$$

Wavelength, $\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2mKE}} \propto \frac{h}{\sqrt{2mT}}$

where, T = Temperature in kelvin

$$\lambda\ (\text{He at} -73^\circ\text{C} = 200\ \text{K}) \propto \frac{h}{\sqrt{2 \times 4 \times 200}}$$

$$\lambda\ (\text{Ne at } 727^\circ\text{C} = 1000\ \text{K}) \propto \frac{h}{\sqrt{2 \times 20 \times 1000}}$$

$$\frac{\lambda(\text{He})}{\lambda(\text{Ne})} = M = \sqrt{\frac{2 \times 20 \times 1000}{2 \times 4 \times 200}} = 5$$

Thus, $M = 5$

15. ***(7)*** $Na(11) = 1s^2 2s^2 2p^6 3s^1$

Electron in 3*s*-orbital is a conduction band.

Each orbital has one electron, thus one energy level.

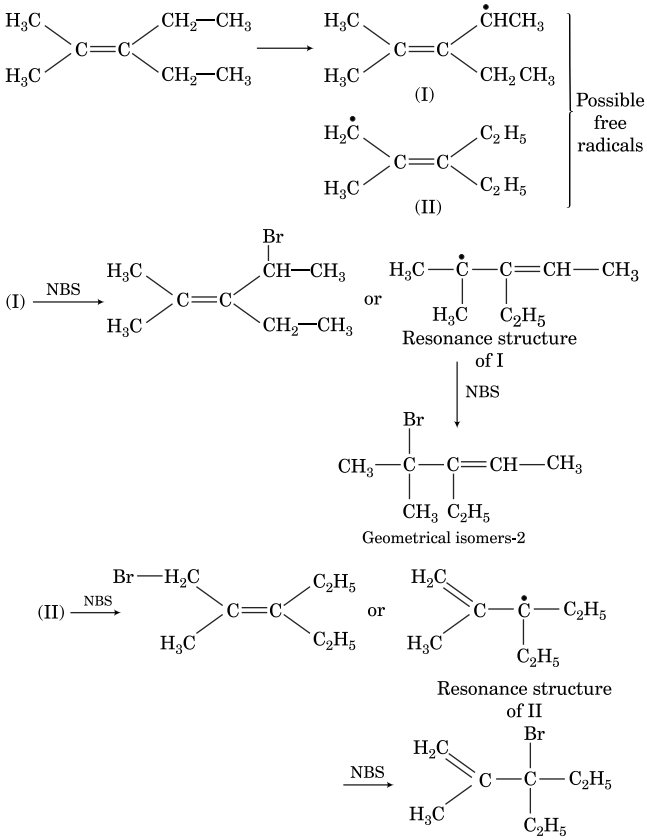
26.8 mg Na = 26.8×10^{-3} g Na-atoms

$$= \frac{26.8 \times 10^{-3}}{23}\ \text{g mol Na}$$

$$= \frac{26.8 \times 10^{-3} \times 6.02 \times 10^{23}}{23}\ \text{Na-atoms}$$

$= 7 \times 10^{20}$ atoms $= 7 \times 10^{20}$ conduction bands

16. ***(6)***



17. ***(8)*** **Thinking process** *This problem can be solved by using concept of conversion of molarity into molality.*

Molarity = 3.2 M

Let, volume of solution = 1000 mL = volume of solvent

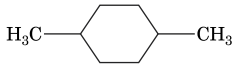
Mass of solvent = $1000 \times 0.4 = 400$ g $\left[\because \text{Density} = \frac{\text{mass}}{\text{volume}}\right]$

Since, molarity of solution is 3.2 molar

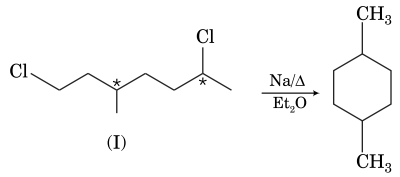
$\therefore\ n_{\text{solute}} = 3.2$ mol

$$\text{Molality}\ (m) = \frac{\text{moles of solute}}{\text{mass of solvent (in kg)}} \quad \frac{3.2}{400/1000} = 8$$

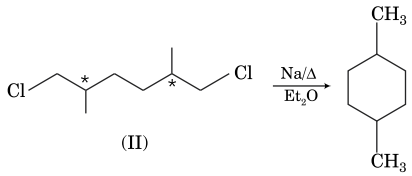
18. ***(7)*** In 1, 4-dimethyl cyclohexane, the following indicated bonds can be formed in the given reaction condition.



Therefore, following dichlorides can be used for this purpose.



I has two chiral carbons, hence it has four stereoisomers.



(II) also has two chiral carbons but there are only three stereoisomers as one of them is meso.

19. ***(7)*** Normal osmotic pressure $= \frac{w_2}{M_2 \times V} \times R \times T$

(when no dissociation has taken place)

$\frac{w_2}{M_2} = 0.1, V = 1\text{ L}, R = 0.0821, T = 18 + 273 = 291\text{ K}$

$\therefore$ Normal osmotic pressure $= \frac{0.1}{1} \times 0.0821 \times 291 = 2.389\text{ atm}$

Potassium ferrocyanide is an electrolyte. It dissociates as

$$\underset{1-\alpha}{K_4[Fe(CN)_6]} \rightleftharpoons \underset{4\alpha}{4K^+} + \underset{\alpha}{[Fe(CN)_6]^{4-}}$$

Total number of particles

$$= 1 - \alpha + 4\alpha + \alpha = 1 + 4\alpha$$

$$\alpha = 0.46$$

So $1 + 4\alpha = 1 + 4 \times 0.46 = 2.84$

Now, $\frac{\text{observed osmotic pressure}}{\text{normal osmotic pressure}} = \frac{2.84}{1}$

Observed osmotic pressure $= 2.84 \times 2.389 \approx 7$ atm

20. ***(6)*** mmol of complex $= 30 \times 0.01 = 0.3$

Also, 1 mole of complex $[Cr(H_2O)_5Cl]Cl_2$ gives only two moles of chloride ion when dissolved in solution.

$$[Cr(H_2O)_5Cl]Cl_2 \longrightarrow [Cr(H_2O)_5Cl]^{2+} + 2Cl^-$$

$\Rightarrow$ mmol of Cl^- ion produced from its 0.3 mmol = 0.6

Hence, 0.6 mmol of Ag^+ would be required for precipitation.

$\Rightarrow$ 0.6 mmol of $Ag^+ = 0.1\text{ M} \times V$ (in mL)

$$V = 6\text{ mL}$$

21. ***(6)*** For the same amount of gas being effused,

$$\frac{r_1}{r_2} = \frac{t_2}{t_1} = \frac{p_1}{p_2}\sqrt{\frac{M_2}{M_1}}$$

$$= \frac{57}{38} = \frac{0.8}{1.6}\sqrt{\frac{M_2}{28}}$$

$$M_2 = 252\text{ g mol}^{-1}$$

Also, one molecule of unknown XeF_n contain only one Xe atom [M(Xe) = 131 g mol^{-1}], formula of the unknown gas can be considered to be XeF_n.

$\Rightarrow$ $131 + 19n = 252$

$n = 6.3$, hence the unknown gas is XeF_6

.

22. ***(b)***

$$X_2(g) \rightleftharpoons 2X(g)$$

At $t = 0$	1	0
At equilibrium	$1 - \frac{x}{2}$	x (where, $x = \beta_{eq}$)

Total moles at equilibrium $= 1 + \frac{x}{2}$

Mole fraction,

$$X_2(g) = \frac{1 - \frac{x}{2}}{1 + \frac{x}{2}};\ X(g) = \left[\frac{x}{1 + \frac{x}{2}}\right] \text{ and } p = 2\text{ bar}$$

Partial pressure,

$$p_{X_2} = \left[\frac{1 - \frac{x}{2}}{1 + \frac{x}{2}}\right] p$$

and $$p_X = \frac{p \cdot x}{1 + \frac{x}{2}}$$

$$\therefore \quad K_p = \frac{(p_X)^2}{p_{X_2}} = \frac{\left[px \,/ \left(1 + \frac{x}{2}\right)\right]^2}{p\frac{\left(1 - \frac{x}{2}\right)}{1 + \frac{x}{2}}}$$

$$= \frac{4px^2}{4 - x^2}$$

$$= \frac{8\beta^2_{\text{equilib.}}}{4 - \beta^2_{\text{equilib.}}}$$

23. ***(c)*** (a) $K_p = \frac{4px^2}{4 - x^2} = px^2 \quad [\because 4 >> x]$

$$\therefore \quad x \propto \sqrt{\frac{1}{p}}$$

If p decreases, x increases. Equilibrium get shifted in the forward direction. Thus, statement (a) is correct.

(b) At the start of the reaction, $Q = 0$ where, Q is the reaction quotient.

$\Delta G = \Delta G^\circ + 2.303RT \log Q$

Since, $\Delta G^\circ < 0$, thus ΔG is –ve

Hence, dissociation takes place spontaneously.

Thus, statement (b) is correct.

(c) If we use $x = 0.7$ and $p = 2$ bar

then, $K_p = \frac{4 \times 2(0.7)^2}{[4 - (0.7)^2]} = 1.11 > 1$

Thus, statement (c) is incorrect.

(d) At equilibrium, $\Delta G = 0$

$\therefore \Delta G^\circ = -2.303RT \log K_p$

Since, ΔG° = +ve

Hence, $K_p < 1$, $K_C = \frac{K_p}{(RT)}$ $(\because \Delta n = 1)$

$\therefore K_C < 1$. Thus, statement (d) is correct.

24. ***(a)*** $Cl_2 + 2NaOH(\text{cold and dil.}) \longrightarrow \underset{(P)}{NaOCl} + NaCl + H_2O$

$NaOCl$ is sodium hypochlorite

$3Cl_2 + 6NaOH(\text{hot and conc.}) \longrightarrow \underset{(Q)}{NaClO_3} + 5NaCl + 3H_2O$

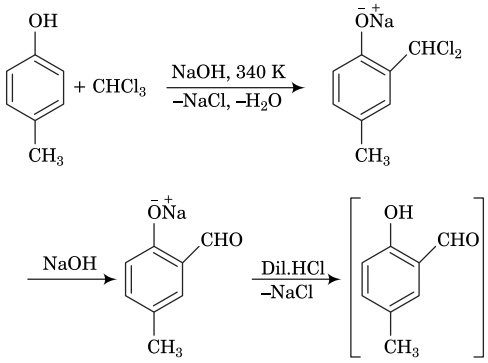
$NaClO_3$ is sodium chlorate.

25. ***(d)*** $Cl_2 + SO_2 \xrightarrow{\text{Charcoal}} \underset{(R)}{SO_2Cl_2}$

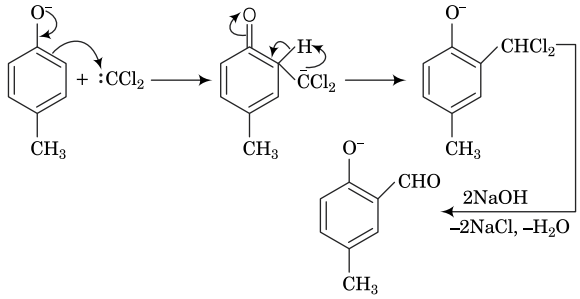
$10SO_2Cl_2 + P_4 \longrightarrow 10SO_2 + \underset{(S)}{4PCl_5}$

$PCl_5 + 4H_2O \longrightarrow 5HCl + \underset{(T)}{H_3PO_4}$

26. ***(b)***



27. ***(c)*** $HO^- + CHCl_3 \rightleftharpoons H_2O + CCl_3^- \longrightarrow \underset{\text{Dichlorocarbene (electrophile)}}{:CCl_2} + Cl^-$



28. ***(d)*** (P) $2PbO_2 + 2H_2SO_4 \xrightarrow{\text{Warm (3)}} 2PbSO_4 + O_2 + 2H_2O$

(Q) $Na_2S_2O_3 + 5H_2O \xrightarrow{4Cl_2(4)} 2NaHSO_4 + 8HCl$

(R) $N_2H_4 \xrightarrow{2I_2\ (2)} N_2 + 4HI$

(S) $XeF_2 \xrightarrow{2NO\ (1)} Xe + 2NOF$

Thus, P → (3), Q → (4), R → (2), S → (1)

29. ***(d)***

Vitamin	Deficiency disease
Vitamin B_{12}	Pernicious anaemia
Vitamin B_6	Skin disease
Vitamin E	Sterility
Vitamin K	Haemorrhogic condition

Thus, P → (3), Q → (4), R → (1), S → (2)

30. ***(d)*** P → (2), Q → (3), R → (1), S → (5)

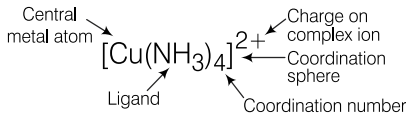
CONCEPT MAP your Revision Tool

COORDINATION COMPOUNDS

The compound which contains complex ions are called **coordination compounds** and the branch of chemistry under which these compounds are studied is called **coordination chemistry**. It retains its identity in solid as well as in solution.

❶ COORDINATION ENTITY

- It is formed by the combination of a simple cation with one or more neutral molecules or one or more simple ions or in some cases positive groups also.
- It exists as a single entity and usually indicated with square bracket.



Ⓐ CENTRAL METAL ATOM OR ION

- The atom/ion to which a fixed number of ions/groups are bound in a definite geometrical arrangement around it.
- It act as a **Lewis acids**.

Ⓑ LIGANDS

- These are molecules, ions or groups which donate electron pairs to the central metal atom through coordinate bond.
- It act as **Lewis bases**.
  - (a) **Unidentate or monodentate ligands** contain only one donor atom.
  - (b) **Polydentate or multidentate ligands** contain two or more donor atoms.
  - (c) **Chelating ligands** contain two or more donor atoms and bind to a single metal ion.
  - (d) **Ambidentate ligands** contain two or more donor atoms but in forming the complexes only one donor atom is attached to the metal ion.

Ⓒ COORDINATION SPHERE

The central atom alongwith ligands are enclosed in a square bracket called coordination sphere.

Ⓓ COORDINATION NUMBER

Total number of ligands attached to central metal atom/ion through coordinate bond.

Ⓔ CHARGE ON THE COMPLEX IONS

It is the algebraic sum of the charges carried by central metal ion and the ligands coordinated to the central metal ion.

❷ EFFECTIVE ATOMIC NUMBER (EAN)

- It is the resultant number of electrons of the metal atom or ion after gaining electrons from the donor atom of the ligand.
- EAN = Z (atomic number of the metal) − number of electrons lost in the ion formation + number of electrons gained from the donor atoms of the ligands.
  e.g. $K_4[Fe(CN)_6]$, EAN = (26 - 2) + (6 × 2) = 36.

❸ WERNER'S THEORY

According to this theory,

- Metal possesses two types of valencies 1° and 2°.
- 1° valencies are ionisable normally satisfied by negative ions.
- 2° valencies are non-ionisable and are satisfied by neutral molecules or negative ions.
- Every metal atom or ion has a fixed number of 2° valencies or coordination number. Thus, the coordination number gives the total number of neutral molecules or negative or positive groups, which may be directly linked to the metal cation in the formation of its complexes.
- Every metal has a tendency to satisfy both its 1° and 2° valencies.

❹ IUPAC NOMENCLATURE OF MONONUCLEAR COORDINATION COMPOUNDS

Coordination compounds are named according to the rules formulated by the IUPAC.

Ⓐ NAMING OF IONS

If the complex compound is ionic, positive ion (cation) whether simple or complex, is named first followed by the negative ion (anion).

Ⓑ NAMING OF LIGANDS

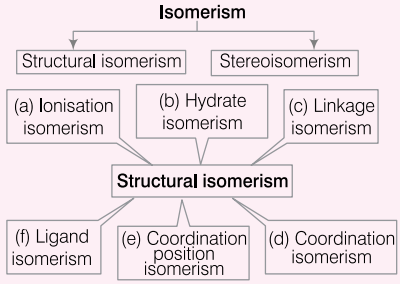
- The number of each kind of ligand is specified using the Greek prefixes di, tri, tetra and penta, etc.
- If the name of ligand itself is complex, i.e. it includes a numerical prefix, e.g. in case of organic molecules such as dipyridyl or ethylenediamine, then terms *bis* (for two), *tris* (for three), *tetrakis* (for four), *pentakis* (for five) etc., are used followed by the name of the ligand placed without brackets.

Ⓒ NAMING OF THE COMPLEX ION

- While naming the complex ion, name the ligands first and then the metal. The names of anionic ligands end with *o*, e.g. (Br^-, bromo), etc. They are usually obtained by changing the anion endings-ide to -*o* and-ate to -ato.
- Neutral ligands are specified by their usual names, except for H_2O, NH_3 and CO, which are called aqua, ammine and carbonyl, respectively.
- If the complex ion is a cation, the name of the central metal ion is given as such followed by its oxidation state indicated by numerals (such as II, III, IV) in the parenthesis at the end of name of the complex without any space between the two.
- If the complex ion is an anion, central atom is made to end with-ate followed by oxidation number in brackets without any space between them.
- For an acid, use a characteristic ending.
  e.g. $H_4[Pt(CN)_6]$ hexacyanoplatinic (II) acid

❺ ISOMERISM

- It is the phenomenon in which compounds having same molecular formula but different arrangement of their constituents atoms.
- Isomers are different compounds with different chemical reactivity and physical properties.



Ⓐ STRUCTURAL ISOMERISM

It is mainly of the following types :

ⓐ IONISATION ISOMERISM

- These isomers yield different ions in solution although they have same composition.
- $[Pt(NH_3)_4Cl_2]Br_2$ and $[Pt(NH_3)_4Br_2]Cl_2$

ⓑ HYDRATE ISOMERISM

- The number of water molecules which may vary, resulting in the formation of hydrate isomers.
- $[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl]Cl_2$,

ⓒ LINKAGE ISOMERISM

- When two or more atoms of a monodentate ligand may function as a donor.
- $[Co(NO_2)(NH_3)_5]^{2+}$, $[CO(ONO)(NH_3)_5]^{2+}$

ⓓ COORDINATION ISOMERISM

- When both cation and anion are complex ions and isomerism is due to interchange of ligands between cation and anion.
- $[Co(NH_3)_6][Cr(CN)_6]$, $[Co(CN)_6][Cr(NH_3)_6]$

ⓔ COORDINATION POSITION ISOMERISM

- It arises due to the difference in the distribution of ligands in two coordination spheres.
- Generally the bridged complex involving different ligands show this isomerism.

ⓕ LIGAND ISOMERISM

- The isomerism arises in those complexes in which the two ligands are isomers themselves.

❻ BONDING IN COORDINATION COMPOUNDS

Ⓐ VALENCE BOND THEORY [VBT]

- The central metal atom provides a number of empty orbitals equal to its coordination number for the formation of coordinate bonds with the ligands.
- The empty orbitals of metal ion hybridise to give equal number of hybrid orbitals of equivalent energy.
- The metal atom or ion can use $(n-1)d$, ns, np and nd orbitals for hybridisation to yield square planar, tetrahedral or octahedral geometry.
- These hybridised orbitals overlap with ligand orbitals. Ligand orbitals donate electron pair to the hybridised orbitals for bonding.
- The overlapping may result in a σ-bond or a coordinate bond.

- $[Co(1,2\text{-diammine propane})_2Cl_2]^+$, $[Co(1,3\text{-diammine propane})_2Cl_2]^+$

Ⓑ STEREOISOMERISM

It arises due to different relative positions of the ligands.

ⓐ GEOMETRICAL ISOMERISM

- It occurs due to different relative arrangements of ligands around central metal atom.
- When two ligands are relatively on same sides, the isomer is called *cis*-isomer and otherwise, *trans*-isomer.
- Complexes having coordination number 1, 2 and 3 do not show geometrical isomerism.

ⓑ OPTICAL ISOMERISM

- It arises when two isomers are structurally the mirror images, non-superimposable on each other and do not possess the plane of symmetry.
- Optical isomerism is common in octahedral complexes involving 2 or 3 symmertical bidentate groups (AA).
- $M(AA)_2X_2$ type, $M(AA)_3$ type $M(AA)B_2X_2$ type $ML_aL_bL_cL_dL_eL_f$ type,
- The optical activity has been observed in tetrahedral complexes in which *bis* chelates with unsymmetrical ligand. These have been found in Be(II), B(III), Zn(II) and Cu(II) complexes.
- Square planar complexes are rarely optically active.

Ⓒ NUMBER OF STEREOISOMERISM

- Geometrical isomerism is possible in square planar complex of types MA_2BC, MA_2B_2, $MABCD$. It is also possible in bridged binuclear planar complexes of the type $M_2A_4X_2$. Octahedral complexes of the types MA_3B_3, MA_4B_2, $M(AA)_2B_2$, $[M(ABCDEF)]$ exhibits geometrical isomerism.
- Geometrical isomerism is not possible in square planar complex of types MA_4 and MA_3B, tetrahedral complex of types MA_4, MA_2B_2 and $MABCD$ and octahedral complex of types MA_6 and MA_5B. In case of octahedral complex of the type MA_3B, the *cis-trans* isomers are also called *fac-mer* isomers. Octahedral complex of the types $[M(AA)_2X_2]$, $[M(AA)_3]$, $[M(AA)B_2X_2]$ generally exhibits optical isomerism $[M(EDTA)]$ and $[M(ABCDEF)]$ also exhibit optical isomerism.

- When complex has unpaired electrons, it behave as paramagnetic and otherwise diamagnetic.
- Under the influence of a strong ligand, the electrons are forced to pair up against the Hund's rule of multiplicity.

ⓐ LIMITATION OF VALENCE BOND THEORY

- It does not explain optical absorption spectra of complexes.
- It does not describe detailed magnetic properties of coordination compounds.
- It does not make exact predictions regarding the tetrahedral and square planar structure of 4 coordinate complex.
- It does not distinguish between weak and strong field ligands.

Ⓑ CRYSTAL FIELD THEORY [CFT]

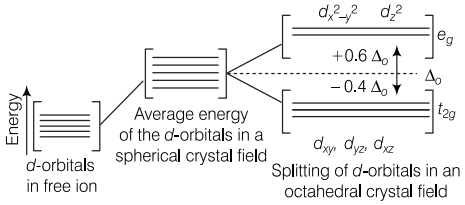
It is an electrostatic approach to describe the splitting of energies associated with metal *d*-orbitals.

ⓐ POSTULATES

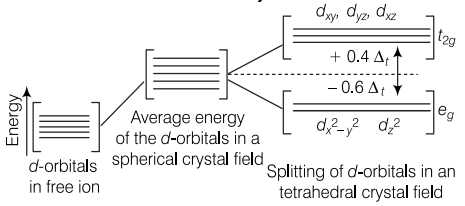
- It consider the anionic ligands as negative point charges and neutral ligand as dipolar. In neutral ligands, the negative end of ligand is oriented towards the metal.
- The interaction between metal ion and ligand is purely electrostatic.
- There is no interaction between metal orbitals and ligand orbitals.
- The five *d*-orbitals in an isolated gaseous atom are of same energy. This degeneracy is maintained till metal ion is surrounded by symmetrical ligands.
- The removal of degeneracy of *d*-orbitals is not affected by ligand field.

ⓑ CRYSTAL FIELD SPLITTING

- In complex, the electrons in *d*-orbitals are repelled by field produced by ligands. This repulsion raises the energy of *d*-orbitals.
- The conversion of degenerate *d*-orbitals into different sets of orbitals having different energies under the influence of field of ligands is called crystal field splitting.



d-orbitals in an octahedral crystal field



d-orbitals in a tetrahedral crystal field

Ⓒ FACTORS AFFECTING CFSE (Δ)

- The ligands with smaller size, large negative charge, with good σ-donor and π-acceptor properties will give large crystal field splitting.

Some ligands in spectrochemical series are given below.

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < N_3^-, F^- <$ Urea, $\overline{O}H <$ oxalate, $O^{2-} < H_2O < NCS^- <$ EDTA < py,

$NH_3 <$ en $\simeq SO_3^{2-} <$ bipy, phen $< NO_2^- < CH_3^- < C_6H_5^- < CN^- <$ CO.

- Δ_t is approximately $\frac{4}{9}$ of Δ_o. The lower value of Δ_t is due to lesser number of ligands in tetrahedral complex.
- Higher is the oxidation state of the metal, more will be crystal field splitting energy.
- The order of CFSE for different transition series is, $3d < 4d < 5d$.
- The value of Δ increases by 30% to 50% for 3*d* to 4*d* series and for 4*d* to 5*d* series.

Ⓓ APPLICATIONS OF CRYSTAL FIELD THEORY

(a) **Electronic arrangement of metal ion in complexes**

If $\Delta_o > P$ (pairing energy), electronic configuration $= t_{2g}^4, e_g^0$.

If $\Delta_0 < P$, elecronic configuration $= t_{2g}^3, e_g^1$.

Pairing energy is the energy which is required to pair up two electrons against electron repulsion in same orbital against Hund's rule.

(b) **Magnetic properties of complexes** Complexes containing unpaired electrons are paramagnetic and if all the electrons are paired then complex will be diamagnetic.

- Magnetic moment $(\mu_B) = \sqrt{n(n+2)}$ BM

  n = number of unpaired electrons
- For diamagnetic complexes, $\mu_B = 0$

(c) **Colour of the Complexes** In complexes, the difference in energies of t_{2g} and e_g lies in visible region and that is why transition metal complexes can absorb specific wavelengths in visible region (400-700 nm) and transmits or reflects the rest of the wavelengths.

Wavelength Associated with Different Colours

Coordination entity	Wavelength of light absorbed (nm)	Colour of light absorbed	Colour of coordinat ion entity
$[CoCl(NH_3)_5]^{2+}$	535	Yellow	Violet
$[Co(NH_3)_5(H_2O)]^{3+}$	500	Blue green	Red
$[Co(NH_3)_6]^{3+}$	475	Blue	Yellow orange
$[Co(CN)_6]^{3-}$	310	Ultraviolet	Pale yellow
$[Cu(H_2O)_4]^{2+}$	600	Red	Blue
$[Ti(H_2O)_6]^{3+}$	498	Blue green	Purple

Ⓔ LIMITATIONS OF CFT

- The calculated position and intensities of spectral bands using CFT do not always coincide with the experimentally determined values.
- A pure electrostatic interaction between central metal ion and ligand fails to explain the relative positions of ligands in spectrochemical series.

❼ STABILITY OF COMPLEXES

- The stability of complexes is proportional to equilibrium constant for association.
- The value of successive stability constants decreases regularly from K_1 to K_n with few exceptions.

$$\beta i = K_1, K_2, K_3 \ldots K_n$$

FACTOR AFFECTING STABILITY OF COMPLEXES

- Higher charge on the central metal ion, i.e. greater ionic potential greater is the stability.
- Greater basic strength of the ligand, greater will be the stability.
- Ring formation (chelation) increases the stability of complexes.

❽ IMPORTANCE OF COORDINATION COMPOUNDS

ⓐ IN QUALITATIVE AND QUANTITATIVE ANALYSIS

- Nickel is detected and estimated as its red dimethyl glyoxime complex which is a chelate compound.
- Mg and Al are estimated as complexes of oxime.

ⓑ IN THE EXTRACTION OF METALS

ⓒ IN MEDICINAL CHEMISTRY

ⓓ IN ESTIMATION OF HARDNESS OF WATER

ⓔ IN ELECTROPLATING OF METALS

ⓕ AS CATALYSTS

@ CLASS XII SYLLABUS

Rapid CONCEPT REVISION

TARGET 2017

SOLID STATE

CLASSIFICATION OF SOLIDS AND CRYSTAL STRUCTURES

- Solid state is the state of matter which is characterised by rigidity, incompressibility and mechanical strength.
- The constituent particles (atoms, molecules or ions) in solid are closely packed, have minimum energy and have very small intermolecular distances.

On the basis of arrangement of constituent particles, solids are classified in the following two types:

Property	Crystalline solids	Amorphous solids
Geometry	Arrangement of constituent particles is regular and long order. Hence, possess definite and regular geometry.	Arrangement of constituent particles is irregular and short order. Hence, do not possess definite geometry.
Melting point	Have sharp melting points.	Do not have sharp melting points.
Nature	Anisotropic (different properties in different directions of the crystal) in nature.	Isotropic (same properties in all directions of solid) in nature.
Cleavage property	On cutting with sharp knife, give regular cut.	On cutting with sharp knife, give irregular cut.
Heat of fusion	Have characteristic heat of fusion.	Do not have characteristic heat of fusion.
Uses	Calcite crystals is used in making optical instrument such as prism	Amorphous silicon is used as photovoltaic material for conversion of sunlight into electricity.
Examples	Crystals of NaCl, CaF_2 etc.	Rubber, glass etc.

Classification of Crystalline Solids

On the basis of nature of bonding, these are classified into the following four types:

Molecular Solids

- These have constituent particles as molecules.
- These molecules may be bonded by either van der Waals' forces (e.g. H_2, Cl_2) or dipole-dipole forces of attraction (e.g. HCl, SO_2) or strong hydrogen bonds (e.g. H_2O, NH_3).

Ionic Solids

- These have constituent particles as cations and anions.
- These ions are bonded together by strong electrostatic force of attraction, e.g. NaCl, KNO_3, etc.

Covalent Solids

- These have constituent particles as non-metal atoms.
- These atoms are linked to adjacent atoms by covalent bond, e.g. diamond, graphite, etc.

Metallic Solids

- These have constituent particles as positively charged metal ions (kernals) and free electrons.
- These constituent particles are bonded each other by metallic bond. e.g. all metals and alloys.

IMPORTANT POINTS

- **Allotropy** is a phenomena in which two or more different forms of an element exist in the same physical state. It is a common phenomena shown by metals, metalloids and non-metals.
- Any material can be made amorphous or glassy either by rapidly cooling its melted form or freezing its vapour.

e.g. $\underset{\text{Quartz}}{SiO_2} \xrightarrow{\text{Melt and rapid cooling}} \underset{\text{Glass}}{SiO_2}$

[SiO_4 unit regularly arranged] [SiO_4 unit randomly arranged]

- Glass of window panes of some very old houses become thick at bottom and thin at the top because particles of glass flow under the effect of gravity just like liquid.

External Features of a Crystal Structure

- **Faces** Crystals are bounded by planar surfaces arranged in definite pattern called faces. They are of two types named as like and unlike faces, with similar and different faces, respectively.
- **Forms** All faces corresponding to a crystal constitute a 'form'. The form may be simple in like faces or combination in unlike faces.
- **Edge and solid angle** The intersection of two faces constituent an edge and when three or more edges intersect they form a solid angle.
- **Interfacial angle** The angle between the normals of the two intersecting faces is called interfacial angle.
- **Zone and zone-axis** The faces of a crystal occur in sets which are called zones. Each zone form a complete belt around a crystal. A line drawn through the center of a crystal in a direction parallel to the edges of a zone is known as zone-axis.

Relationship between Faces, Edges and Interfacial Angles

The faces, edges and interfacial angles are related as,

$$f + c = e + 2$$

where, f = number of faces, e = number of edges

c = number of interfacial angles

Bragg's Law

The arrangement of atoms in a crystal lattice and size of unit cell can be determined with the help of diffraction by X-ray. According to this law, when a beam of monochromatic X-ray strikes two planes of atoms in a crystal at a certain angle θ and reflected, the intensity of the reflected beam is maximum when

$n\lambda = 2d \sin\theta$ (for constructive interference)

$n\lambda = 4d \sin\theta$ (for destructive interference)

where, n = order of diffraction

d = distance between two planes

λ = wavelength of X-rays

θ = angle between X-rays and plane of crystal (angle of diffraction)

Best Practice SHOTS

1. Which of the following conditions favours the existence of a substance in the solid state?

(a) High temperature
(b) Low temperature
(c) High thermal energy
(d) Weak cohesive forces

2. Which of the following is an amorphous solid?

(a) Graphite
(b) Quartz glass (SiO_2)
(c) Chrome alum
(d) Silicon carbide

3. Which of the following is true about the value of refractive index of quartz glass?

(a) Same in all directions
(b) Different in different directions
(c) Cannot be measured
(d) Always zero

4. Which one of the following forms a molecular solid when solidified?

(a) Silicon carbide
(b) Calcium fluoride
(c) Rock salt
(d) Methane

5. A particular solid is very hard and has a high melting point. In solid state, it is a non-conductor and its melt is a conductor of electricity. Classify the solid.

(a) Metallic
(b) Molecular
(c) Network
(d) Ionic

6. An example of a substance possessing giant covalent structure is

(a) solid CO_2
(b) silica
(c) iodine crystal
(d) white phosphorus

7. The second order Bragg diffraction of X-rays with $\lambda = 1.0$ Å from a set of parallel planes in a metal occurs at an angle 60°. The distance between the scattering planes in the crystals is

(a) 0.575 Å *(b)* 1.00 Å
(c) 2.00 Å *(d)* 1.17 Å

8. The sharp melting point of crystalline solids is due to

(a) a regular arrangement of constituent particles observed over a short distance in the crystal lattice
(b) a regular arrangement of constituent particles observed over a long distance in the crystal lattice
(c) same arrangement of constituent particles in different directions
(d) different arrangement of constituent particles in different directions

STRUCTURES OF SOLIDS

Unit Cell

It is the smallest repeating unit of a crystal which is repeated over and again in different directions, regenerating whole of the crystal.

Some important terms related to unit cell are as follows:

Lattice Point

The point at which the atoms may present on the unit cell.

Crystal Lattice or Space Lattice

It is the regular repeating arrangement of particles in three dimensional space.

Crystal Parameters

A unit cell is described by three edges a, b and c and the angles between the edges, α (between b and c), β (between c and a) and γ (between a and b). Thus, a, b, c and α, β and γ are six parameters of a unit cell.

Types of Unit Cell

(i) **Simple or primitive cubic unit cell** The unit cell in which the constituent atoms are present only at the corner.

(ii) **Non-primitive or centred unit cell** The unit cell in which atoms present not only at the corners but also at some other positions of the unit cell.

These cells may be further divided into the following types:

(a) **Face-centred cubic unit cell** (fcc) The unit cell in which atoms are present at corners as well as faces of unit cell.

(b) **Body-centred cubic unit cell** (bcc) The unit cell in which atoms are present on corners as well as body-centre of unit cell.

(c) **End-centred cubic unit cell** (ecc) The unit cell in which atoms are present at corners as well as center of any two opposite faces.

Effective Number of Atoms in a Unit Cell

- Contribution of atoms present at different lattice points are different.
- For cubic unit cell, number of atoms per unit cell, is determined by relation, unit cell constant

$$(Z) = \frac{n_c}{8} + \frac{n_f}{2} + \frac{n_i}{1}$$

where,

n_c = number of atoms at the corners of the cube.
n_f = number of atoms at six faces of the cube.
n_i = number of atoms inside the cube.

Number of Atoms in Different Cubic Unit Cells

Cubic unit cell	n_c	n_f	n_i	Total atoms in unit cells
Simple cubic	8	0	0	1
Body-centred cubic	8	0	1	2
Face-centred cubic	8	6	0	4
End-centred cubic	8	2	0	2

- For hexagonal unit cell, the unit cell constant (Z) is given by

$$Z = \frac{N_c}{6} + \frac{N_e}{3} + \frac{N_f}{2} + \frac{N_i}{1}$$

Crystal System and Bravais Lattices

- There are 7 crystal systems and every crystal system does not have all four types of unit cell.
- There are only 14 types of space lattice corresponding to 7 crystal systems which are known as Bravais lattices.

Seven Crystal Systems

Name of system	Axes	Angles	Bravais lattices
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	Primitive, face-centred body-centred = 3
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	Primitive, body-centred = 2
Rhombohedral or trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	Primitive = 1
Orthorhombic or rhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	Primitive, face-centred, body-centred, end-centred = 4
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°$, $\beta \neq 90°$	Primitive, end-centred = 2
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	Primitive = 1
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°$, $\gamma = 120°$	Primitive = 1
			Total = 14 Bravais lattices

Close Packed Structures

- In solids, the constituent particles are close packed such that these occupy maximum available space and leave minimum vacant space.

- Packing in solids is expressed in terms of **packing fraction** or **packing density**.

$$\text{Packing fraction} = \frac{\text{total volume of sphere}}{\text{volume of the unit cell}} \times 100$$

- The number of spheres surrounding a particular atom is known as **coordination number** (CN).

Packing in solids may be divided into the following categories :

1. One Dimensional Close Packing

Here, the spheres are arranged in a row touching each other.

2. Two Dimensional Close Packing

Here, the spheres are arranged in more than one row by stacking one dimensional closed packed structure.

There are two types of two dimensional close packing :

(i) **Square close packing**

- When one dimensional rows of spheres are placed one over another in a plane such that each sphere is stacked over another, form square close packing structure.
- Coordination number in square close packing = 4

(ii) **Hexagonal close packing**

- One dimensional rows of spheres are placed one over another in a plane such that the spheres of one row lie in the depressions of the spheres of another row.
- Coordination number in hexagonal close packing = 6

3. Three Dimensional Close Packing

The structure obtained by stacking two dimensional layers one above the other is known as three dimensional close packing (e.g. Mg, Zn, Mo, Be, etc.).

There are two types of three dimensional close packing:

(i) **Three dimensional close packing obtained from two dimensional square close packed layers.**

- In this type of arrangement, two dimensional square close packed layers are arranged exactly one over the other. This type of arrangement is known as *AAA* type arrangement.
- The generated cubic lattice is called simple cubic lattice and unit cell is known as simple or primitive unit cell.

(ii) **Three dimensional close packing obtained from two dimensional hexagonal close packed layers**

- When hexagonal close packed layers are stacked one over another, they form three dimensional close packing.
- When second layer is placed over first layer in depressions, it leads to the formation of three dimension close packed structure.

There are two types of arrangements which are possible:

(a) **Hexagonal close packing** When third layer is placed over second layer in such a way that they constitute tetrahedral void, the arrangement is called *ABAB* pattern, e.g. Mg, Zn, Mo and Be.

(b) **Cubic close packing** When the third layer is placed over second layer in such a way that sphere covers octahedral voids, the arrangement is called *ABCABC* pattern, e.g. Fe, Ni, Cu, Ag, Au and Al.

(iii) **Body-centred cubic close packing**

- This arrangement is obtained when the spheres of the first layer are opened up and spheres of second layer are placed at the top of the hollows in the first layer.
- The spheres of the third layer are placed exactly above the spheres of first layer, e.g. Li, Na, K, Rb, Cs, etc.

Formulae for Calculation of Unit Cell Parameters

Unit cell	Number of atoms per unit cell	Atomic radius (r)	Volume unit cell (V)	Volume of all atoms in a unit cell (v)	Packing fraction $\left(\frac{v}{V}\right)$	Coordination number
sc	1	$r = \frac{a}{2}$	a^3	$\pi\frac{a^3}{6}$	$52\%\left(\frac{\pi}{6}\right)$	6
bcc	2	$4r = \frac{a}{\sqrt{3}}$	a^3	$\frac{\sqrt{3}\ \pi a^3}{8}$	$68\%\left(\frac{\sqrt{3}\pi}{8}\right)$	8
fcc	4	$4r = a\sqrt{2}$	a^3	$\frac{\pi a^3}{3\sqrt{2}}$	$74\%\left(\frac{\pi}{3\sqrt{2}}\right)$	12
hcp	6	$2r = a$, $r = \sqrt{\frac{3}{2}} \times \frac{h}{2}$	$3\sqrt{2}\ a^3$	πa^3	$74\%\left(\frac{\pi}{3\sqrt{2}}\right)$	12

In the above table, a = edge length and h = height of hexagonal.

Density of a Crystal

It can be calculated as density (d) of unit cell by the following formulaes,

$$d = \frac{\text{mass of all atoms in a unit cell}}{\text{volume of unit cell } (V)} = \frac{n \times M_0}{N_A} \times \frac{1}{V} = \frac{nM_0}{N_A a^3}\ \text{g cm}^{-3}$$

where, n = number of atoms in a unit cell

a = edge length of unit cell

M_0 = molecular mass of crystal

$N_A = 6.023 \times 10^{23}$ atoms mol^{-1}

(when, M_0 and a are given in g and cm, respectively).

$$d = \frac{nM_0}{N_A a^3} \times 10^{30}\ \text{g cm}^{-3}$$

(when, M_0 and a are given in g and pm, respectively).

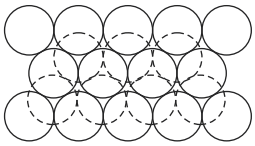
Voids

The empty space between atoms stacked is known as void.
There are following three types of voids:

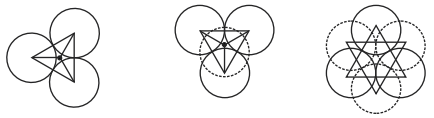
(i) **Trigonal voids** This type of voids exist in two dimensional arrangement.

(ii) **Tetrahedral voids** This type of voids are generated by the stacking of four atoms.

(iii) **Octahedral voids** This type of voids are generated by the stacking of six atoms.



A stack of two layers of close packed spheres and voids



(i) Trigonal void (ii) Tetrahedral void (iii) Octahedral void

Note

- The decreasing order of size of voids are trigonal < tetrahedral < octahedral.
- Number of tetrahedral voids = Number of atoms in ccp × 2 = 2 N
- Number of octahedral voids = Number of atoms in ccp = N

Relation between Radius Ratio and Coordination Number

Radius ratio	Cations occupies	Coordination number	Example
0.155-0.225	Trigonal void	3	B_2O_3
0.225-0.414	Tetrahedral void	4	ZnS
0.414-0.732	Octahedral void	6	NaCl
0.732-1.0	Cubic void	8	CsCl

Note Radius ratio = $\frac{\text{radius of cation}}{\text{radius of anion}}$

Some Ionic Crystals

Type of ionic crystal	Geometry	Coordination number	Number of formula per UCC	Example
NaCl (1 : 1) (Rock salt type)	ccp: Na^+ → Every element of ccp; Cl^- → At every OHV	6 : 6	$4Na^+ + 4Cl^-$ 4NaCl (4)	Halide of Li, Na, K, oxides and sulphides of III A (some exceptions AgF, AgCl, AgBr, NH_4X
CsCl type (1 : 1)	bcc: Cs^+ → At every corner; Cl^- → At body centred or cubic void	8 : 8	$1Cs^+ + 1Cl^-$ 1CsCl (1)	Halides of Cs, TiCl, TiBr, CaS.
ZnS type (1:1) (Zinc blende type sphalerite)	ccp: Zn^{2+} → Every element of ccp; S^{2-} → At 50% of THV at alternate tetrahedral void	4 : 4	$4Zn^{2+} + 4S^{2-}$ 4ZnS (4)	BeS, BeO, CaO, AgI, CuCl, CuBr, CuI
CaF_2 type (1 : 2) (Fluorite type)	ccp: Ca^{2+} → Every element of ccp; F^- → At every THV	$4Ca^{2+}$ $8F^-$ → 8 : 4	$4Ca^{2+} + 8F^-$ $4CaF_2$ (4)	$BaCl_2$, BaF_2 $SrCl_2$, SrF_2, $CaCl_2$, CaF_2.
Na_2O type (2 : 1) (Antifluorite)	ccp: Na^+ → At every THV; O^{2-} → Every element of ccp	$8Na^+$ $4O^{2-}$ → 4 : 8	$8Na^+ + 4O^{2-}$ $4Na_2O$ (4)	Li_2O, Li_2S, Na_2O, Na_2S, K_2O, K_2S.
ZnS type (1 :1) (Wurtzite another geometry of ZnS)	hcp: Zn^{2+} → Every element of hcp; S^{2-} → 50% of THV (or at alternate THV)	4: 4	$6Zn^{2+} + 6S^{2-}$ 6ZnS (6)	Same as sphalerite

Best Practice SHOTS

9. A metal has bcc structure and the edge length of its unit cell is 3.04 Å. The volume of the unit cell in cm^3 will be
(a) 1.6×10^{21} cm^3 (b) 2.81×10^{-23} cm^3
(c) 6.02×10^{-23} cm^3 (d) 6.6×10^{-24} cm^3

10. In A^+B^- ionic compound, radii of A^+ and B^- ions are 180 pm and 187 pm, respectively. The crystal structure of this compound will be
(a) NaCl type (b) CsCl type
(c) ZnS type (d) similar to diamond

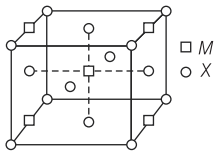
11. In octahedral voids,
(a) a bi-triangular void surrounded by six spheres
(b) a bi-triangular void surrounded by four spheres
(c) a bi-triangular void surrounded by eight spheres
(d) a simple triangular void surrounded by four spheres

12. Experimentally it was found that a metal oxide has formula $M_{0.98}O$. Metal M is present as M^{2+} and M^{3+}. Its oxide fraction of the metal which exists as M^{3+} would be
(a) 4.08% (b) 6.05% (c) 5.08% (d) 7.01%

13. In which of the following structures coordination number for cations and anions in the packed structure will be same?
(a) Cl^- ions form fcc lattice and Na^+ ions occupy all octahedral voids of the unit cell
(b) Ca^{2+} ions form fcc lattice and F^- ions occupy all the eight tetrahedral voids of the unit cell
(c) O^{2-} ions form fcc lattice and Na^+ ions occupy all the eight tetrahedral voids of the unit cell
(d) S^{2-} ions form fcc lattice and Zn^{2+} ions go into alternate tetrahedral voids of the unit cell

14. In the fluorite structure, the coordination number of Ca^{2+} ion is
(a) 4 (b) 6 (c) 8 (d) 3

15. A compound M_pX_q has cubic close packing (ccp) arrangement of X. Its unit cell structure is shown sideways. The empirical formula of the compound, is



(a) MX (b) MX_2
(c) M_2X (d) M_5X_{14}

16. Which of the following statement(s) is incorrect?
(a) The coordination number of each type of ion in CsCl crystal is 8
(b) A metal that crystallises in bcc structure has a coordination number of 12
(c) A unit cell of an ionic crystal shares some of its ions with other unit cells
(d) The length of the unit cell in NaCl is 552 pm
(r_{Na^+} = 95 pm; r_{Cl^-} = 181 pm)

17. How many unit cells are present in a cube shaped ideal crystal of NaCl of mass 1g
[Atomic masses, Na = 23, Cl = 35.5]
(a) 2.57×10^{21} (b) 1.28×10^{21}
(c) 1.71×10^{21} (d) 5.14×10^{21}

18. The Ca^{2+} and F^- are located in CaF_2 crystal, respectively at body-centred cubic lattice points and in
(a) tetrahedral voids
(b) half of tetrahedral voids
(c) octahedral voids
(d) half of octahedral voids

19. In a solid AB having the NaCl structure, A atoms occupy the corners of the cubic unit cell. If all the face-centred atoms along one of the axis are removed, then the resultant stoichiometry of the solid is
(a) AB_2 (b) A_2B (c) A_4B_3 (d) A_3B_4

20. The percentages of void space for simple cubic, body-centred cubic and hexagonal close packed arrangement, respectively are
(a) 48, 32, 26 (b) 48, 26, 32
(c) 26, 48, 32 (d) 32, 48, 26

21. Silver forms ccp lattice and X-ray studies of its crystals show that the edge length of its unit cell is 408.6 pm. Calculate the density of silver (atomic mass = 107.9 u).
(a) 5.10 g cm^{-3} (b) 1.05 g cm^{-3}
(c) 5.79 g cm^{-3} (d) 10.5 g cm^{-3}

22. 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^{-1} (b) 5.96×10^{-3}
(c) 5.96 (d) 5.96×10^{-2}

23. A metal crystallises into two cubic phases, face-centred cubic and body-centered cubic, which have unit cell lengths 3.5 and 3.5 Å , respectively. Calculate the ratio of densities of fcc and bcc.
(a) 2.16 : 1 (b) 6.39 : 1
(c) 1.26 : 1 (d) 0.26 : 1

24. In diamond, the coordination number of carbon is
(a) four and its unit cell has eight carbon atoms
(b) four and its unit cell has six carbon atoms
(c) six and its unit cell has four carbon atoms
(d) four and its unit cell has four carbon atoms

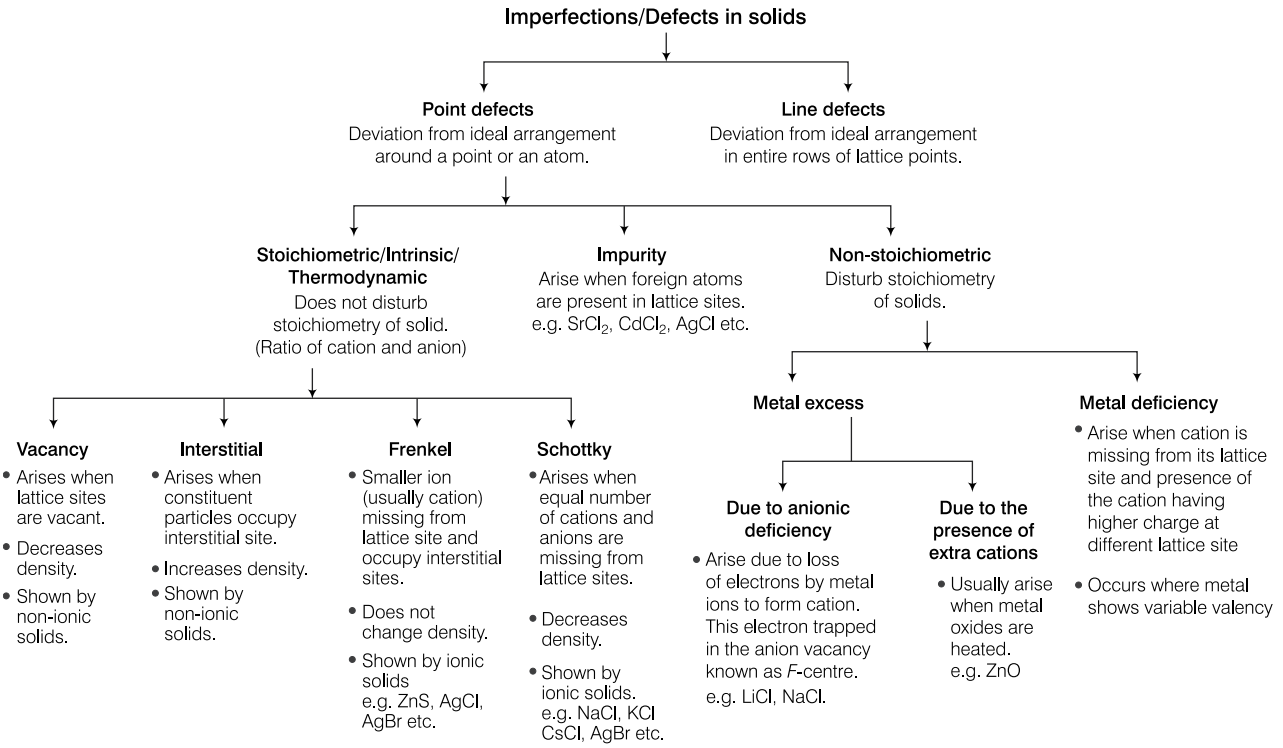
25. Sodium metal crystallises in a body-centred cubic lattice with a unit cell edge of 4.29 Å. The radius of sodium atom is approximately [JEE Main 2015]
(a) 1.86 Å (b) 3.22 Å
(c) 5.72 Å (d) 0.93 Å

26. CsCl crystallises in body-centred cubic lattice. If 'a' is edge length, then which of the following expressions is correct? [JEE Main 2014]
(a) $r_{Cs^+} + r_{Cl^-} = 3a$ (b) $r_{Cs^+} + r_{Cl^-} = \frac{3a}{2}$
(c) $r_{Cs^+} + r_{Cl^-} = \frac{\sqrt{3}}{2}a$ (d) $r_{Cs^+} + r_{Cl^-} = \sqrt{3}a$

CRYSTAL DEFECTS AND PROPERTIES OF SOLIDS

Imperfection or Defects in Solids

Any deviation from perfectly ordered arrangement of constituents of a solid is known as **imperfections** or **defects** in solid.



Properties of Solids

The properties of solids are described below:

Electrical Properties of Solids

Depending upon conduction power, solids are divided into the following types:

(i) **Conductors**

The solids whose conductivity is in the order of $10^7(\Omega m)^{-1}$ are known as conductors. Conductivity is due to the presence of free electrons, e.g. metals.

(ii) **Semiconductors**

The solids whose conductivity ranges from 10^{-6} to 10^4 $(\Omega m)^{-1}$ are known as semiconductors. e.g., semi-metals.

(a) ***n*-type semiconductors**

Group-14 elements when doped with group-15 elements form *n*-type semiconductors.

(b) ***p*-type semiconductors**

Group-14 elements when doped with group-13 elements form *p*-type semiconductors.

(iii) **Insulators**

The solids having conductivity range 10^{-20} to 10^{-10} $(\Omega m)^{-1}$ are known as insulators. e.g. non-metals.

(iv) **Superconductors**

The conductor which allow electricity to pass through them without any resistance. The temperature at which a substance starts behaving as superconductor is called **transition temperature**. e.g. $Ba_2Cu_3O_7$ at 90 K.

AMAZING REALITIES

The first X-ray was an image of a woman's hand with a ring on it. It was of Bertha Rontgen's hand. She believed that seeing her bones was a death omen and her time had arrived.

Types of Magnetic Properties

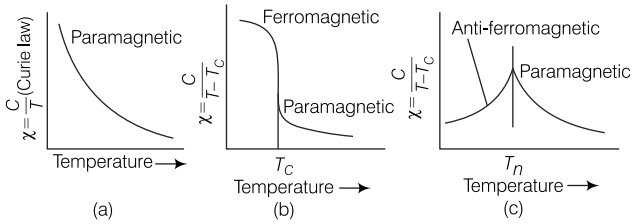
Properties	Description	Alignment of magnetic dipole	Examples	Applications
Diamagnetic	These are feebly repelled by the magnetic fields due to the existence of paired electron.	All electrons are paired. ↑↓ ↑↓ ↑↓	TiO_2, V_2O_5 NaCl, C_6H_6	Insulator
Paramagnetic	Attracted by magnetic field due to the presence of unpaired electrons, acts as a tiny bar magnet.	At least one unpaired electron. ↑ ↓ ↑ ↑	O_2, Cu^{2+}, Fe^{3+}, TiO, Ti_2O_3 VO, VO_2, CuO	Electronic applications
Ferromagnetic	Acts as a permanent magnet even in the absence of magnetic field. Above Curie temperature, no ferromagnetism occurs.	Dipoles are aligned in the same direction. ↑ ↑ ↑ ↑ ↑	Fe, Ni, Co, CrO_2	CrO_2 is used in audio and video tapes.
Anti-ferromagnetic	Net dipole moment becomes zero due to equal and opposite alignment.	↑ ↓ ↑ ↓ ↑ ↓	CoO, Co_3O_4 MnO, MnO_2, M_2O_3, FeO, Fe_2O_3, NiO	
Ferrimagnetic	This arises when there is net dipole moment.	↑ ↓ ↓ ↓ ↑ ↓	Fe_3O_4, Ferrites	

EFFECT OF TEMPERATURE ON MAGNETIC PROPERTY

When a magnetic material is heated, the magnetisation of the material decreases, which is called **Curie's law**. Hence.

$$\chi = \frac{C}{T} \text{ or } \chi = \frac{C}{T - T_C}$$

where, χ = Magnetic susceptibility, T_C = Critical temperature



Graphs showing effect of temperature on magnetic properties

Dielectric Properties of Solids

- These are seen in insulators which show generation of dipoles, when they are placed in an electric field.

The following terms are related to dielectric properties of solids.

(i) **Piezoelectricity** It is produced on applying mechanical stress on polar crystals, e.g. Rochelle's salt.

(ii) **Pyroelectricity** It is produced either by heating or cooling some polar crystals, e.g. cane sugar, lithium sulphate.

(iii) **Ferroelectricity** Piezoelectric crystals with permanent dipoles are said to have ferroelectricity, e.g. $BaTiO_3$, KH_2PO_4, etc.

(iv) **Anti-ferroelectricity** In anti-ferroelectric crystals, the dipoles in alternate polyhedral points up and down in such a way that the crystal does not possess any net dipole moment, e.g. $PbZrO_3$. Used in transistor, telephones and computers to prepare small size capacitor of high capacitance.

Best Practice SHOTS

27. Which of the following statement(s) is/are correct?

I. NaCl and KCl show metal excess defect due to anionic vacancies.

II. *F*-centres are the anionic sites occupied by unpaired electrons.

III. *F*-centres impart yellow colour to the NaCl crystals.

Choose the correct option given below.

(a) II and III *(b)* Only III

(c) I and II *(d)* All of these

28. Which of the following statements is/are correct about metals?

I. Valence band overlaps with conduction band.

II. The gap between valence band and conduction band is negligible.

III. The gap between these bands cannot be determined.

IV. Valence band may remain partially filled.

Choose the correct option given below.

(a) I, II and III *(b)* I, II and IV

(c) II and III *(d)* All of these

29. Which one of the following metal oxides is anti-ferromagnetic in nature?

(a) MnO_2 *(b)* VO_2 *(c)* TiO_2 *(d)* CrO_2

RAPID CONCEPT REVISION

30. When electrons are trapped into the crystal in anion vacancy, the defect is known as
(a) Schottky defect (b) Frenkel defect
(c) Stoichiometric defect (d) *F*-centres

31. Which of the following defects shows decrease in the mass of the crystal lattice?
(a) Frenkel defect (b) Schottky defect
(c) Edge dislocation (d) Constitution of *F*-centres

32. In AgBr crystal, the ion size lies in the order $Ag^+ << Br^-$. The AgBr crystal should have the following characteristics.
(a) defect less (perfect) crystal
(b) Schottky defect
(c) Frenkel defect
(d) Both Schottky and Frenkel defect

33. Which of the following statement(s) is/are correct?
I. Diode is a combination of *n*-types and *p*-types semiconductor.
II. Diode is used as rectifier.
III. *n*-*p*-*n* and *p*-*n*-*p* are the types of rectifier.
IV. *n*-*p*-*n* and *p*-*n*-*p* are used to detect or amplify ratio or audio signals.
Choose the correct option given below
(a) I, II and III (b) Only I
(c) II, III and IV (d) All of these

34. The appearance of colour in solid alkali metal halides is generally due to
(a) *F*-centres (b) Schottky defect
(c) Frenkel defect (d) interstitial positions

35. If NaCl is doped with 10^{-4}mol % of $SrCl_2$, the concentration of cation vacancies will be
($N_A = 6.02 \times 10^{23}$ mol^{-1})
(a) 6.02×10^{15} mol L^{-1} (b) 6.02×10^{16} mol L^{-1}
(c) 6.02×10^{17} mol L^{-1} (d) 6.02×10^{14} mol L^{-1}

36. Which kind of defect is shown by the given crystal?

K^+	Cl^-	K^+	Cl^-	K^+	Cl^-
Cl^-	❑	Cl^-	K^+	❑	K^+
K^+	Cl^-	❑	Cl^-	K^+	Cl^-
Cl^-	K^+	Cl^-	K^+	❑	K^+

(a) Schottky defect
(b) Frenkel defect
(c) Schottky and Frenkel defect
(d) Substitution disorder

37. Some of the polar crystals when heated produces small electrical current. This phenomenon is called
(a) ferroelectricity (b) pyroelectricity
(c) anti-ferroelectricity (d) piezoelectricity

38. Schottky defect in crystals is observed when
(a) density of crystals is increased
(b) an ion leaves its normal site and occupies an interstitial site
(c) equal number of cations and anions are missing from the lattice
(d) unequal number of cations and anions are missing from the lattice

Answers

1. (b)	2. (b)	3. (a)	4. (d)	5. (d)
6. (b)	7. (d)	8. (b)	9. (b)	10. (b)
11. (a)	12. (a)	13. (a)	14. (c)	15. (b)
16. (b)	17. (a)	18. (a)	19. (d)	20. (a)
21. (d)	22. (b)	23. (c)	24. (a)	25. (a)
26. (c)	27. (d)	28. (b)	29. (a)	30. (d)
31. (b)	32. (c)	33. (d)	34. (a)	35. (a)
36. (a)	37. (b)	38. (c)		

MASTER STROKES

1. In a spinel structure, oxide ions are cubical closed packed, whereas 1/8th of tetrahedral voids are occupied by *A* ions and 1/2 of octahedral voids are occupied by *B* ions. The charge present on *A* and *B* ions will be
(a) A^{2+}, B^{3+} (b) A^{3+}, B^{2+}
(c) A^{4+}, B^{2-} (d) A^{-1}, B^{2-}

2. The first order diffraction of X-rays from a certain set of crystal planes occurs at an angle of 11.8° from the planes. If the planes are 0.281 nm apart. What is the wavelength of X-rays?
(a) 0.281 nm (b) 0.2044 nm
(c) 0.1149 nm (d) 0.1180 nm

3. Ferrous oxide has a cubic structure and each edge of the unit cell is 5 Å. Assuming density of the oxide as 4 g cm^{-3}, then the number of Fe^{2+} and O^{2-} ions present in each unit cell will be
(a) two Fe^{2+} and four O^{2-}
(b) three Fe^{2+} and three O^{2-}
(c) four Fe^{2+} and two O^{2-}
(d) four Fe^{2+} and four O^{2-}

4. When a certain crystal was studied by the Bragg's technique using X-rays of wavelength 229 pm, an X-ray reflection was observed at an angle of 23°20′. What is the corresponding interplanar spacing (sin (23°20′) = 0.396).
(a) 375.6 pm (b) 256.5 pm (c) 289.2 pm (d) 315.4 pm

5. The correct option regarding the limiting value of radius ratio r_+ / r_- is
(a) forces of attraction and repulsion are just equal
(b) forces of attraction are smaller than the forces of repulsion
(c) forces of attraction are larger than the forces of repulsion
(d) None of the above

6. In orthorhombic system of crystal lattice, the value of a, b and c are respectively 4.2 Å, 8.6 Å and 8.3 Å. Molecular mass of solute is 155 g mol^{-1} and that of density is 3.3 g/cc, the number of formula units per cell is

(a) 6 *(b)* 4 *(c)* 1 *(d)* 2

7. In fcc lattice of NaCl structure, if the diameter of Na^+ is x and the radius of Cl^- is y, then the edge length of NaCl in the crystal is

(a) $3x + 2y$ *(b)* $\frac{x}{2} + \frac{y}{3}$

(c) $x + 2y$ *(d)* $\frac{1}{2}(x + y)$

8. An element has a body-centred cubic structure with a cell edge of 288 pm. The density (d) of the element is 7.2 g/cm^3. What would be the number of atoms which are present in 208 g of the element?

(a) 7.02×10^{24} atoms

(b) 10.09×10^{25} atoms

(c) 17.04×10^{26} atoms

(d) 24.16×10^{23} atoms

9. Experimentally, the melting point of RbBr is 682°C while that of NaF is 988°C. The principle reason for this difference in melting point is

(a) the bond in RbBr has more covalent character than the bond in NaF

(b) the internuclear distance ($r_c + r_a$) is greater for RbBr than for NaF

(c) the two crystals are not isomorphous

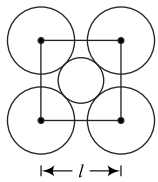
(d) the molar mass of NaF is smaller than that of RbBr

10. Which of the following exists as covalent crystals in the solid state?

(a) Iodine *(b)* Silicon

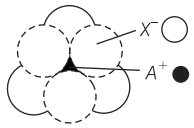
(b) Sulphur *(d)* Phosphorus

11. The packing efficiency of the two-dimensional square unit cell shown below is



(a) 39.27% *(b)* 68.02% *(c)* 74.05% *(d)* 78.54%

12. The arrangement of X^- ions around A^+ ion in solid AX is given in the figure (not drawn to scale). If the radius of X^- is 250 pm, the radius of A^+ is



(a) 104 pm *(b)* 125 pm *(c)* 183 pm *(d)* 57 pm

Answers

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

SOLUTIONS

TYPES OF SOLUTION, SOLUBILITY AND CONCENTRATION TERMS

- Solution is a homogeneous mixture of two or more substances whose composition can be varied within certain limits.
- A **solvent** is that component of the binary solution which is present in large amount by mass than the other component termed as **solute.**
- A solution in which water is the solvent is called an **aqueous solution.**

Different Types of Solutions

Types of solutions	Solute	Solvent	Common examples
Gaseous solutions (Homogeneous mixtures)	Gas	Gas	Mixture of nitrogen and oxygen gases, air.
	Liquid	Gas	Chloroform mixed with nitrogen gas.
	Solid	Gas	Camphor in nitrogen gas, dust of smoke-particles in air.
Liquid solutions	Gas	Liquid	Oxygen dissolved in water, CO_2 dissolved in H_2O.
	Liquid	Liquid	Ethanol dissolved in water.
	Solid	Liquid	Sucrose/salt dissolved in water.
Solid solutions	Gas	Solid	Solution of hydrogen in palladium (phenomenon of adsorption of gases over metals).
	Liquid	Solid	Mercury with sodium (amalgams)
	Solid	Solid	Copper dissolved in gold (alloys)

Solubility

The maximum amount of a solute that can be dissolved in a given amount of solvent (usually 100 g) at a given temperature is called **solubility** at that temperature.

Solubility of Gas in Liquid

All gases are soluble in water and in other liquids upto a greater or lesser extent.

The solubility of a gas depends upon the following factors:

(i) **Nature of the gas** The gases which can be easily liquified are more soluble in common solvents, e.g. CO_2 is more soluble than H_2 and O_2 in water.

(ii) **Nature of the solvent** The gases which are capable of producing ions in aqueous solutions are much more soluble than in other solvent, e.g. gases like NH_3 and HCl are highly soluble in water but not in organic solvents in which they do not ionise.

(iii) **Temperature** As the process of dissolution is an exothermic process, the solubility of gases in general decreases with the increase of temperature.

(iv) **Pressure** According to **Henry's law**, the solubility(S) of a gas in liquid is directly proportional to pressure (p) of gas over the solution at a definite temperature.

Solubility, $S \propto p$ or $S = Kp$.

where, K = proportionality constant which depends upon the nature of gas, solvent and temperature.

Henry's Law for a Mixture of Two or More Non-reacting Gases

When a mixture of two or more non-reacting gases come in contact with solvent, the mole fraction of the gas in the solution is proportional to the partial pressure of the gas

$$p = \frac{1}{K'}\chi = K_H\chi$$

Where, χ = mole fraction of gas
p = partial pressure of gas
K_H = Henry's law constant

Limitations of Henry's Law

Henry's law holds good only during the following conditions.

- The temperature should not be too low.
- The pressure or concentration should not be too high.
- The gas must not chemically react with the solvent.
- The gas must remain in its molecular state, i.e. neither gets dissociate nor associate.

Haemoglobin
A Henry's Law Deviator

Under normal conditions, oxygen gas is sparingly soluble in water. However, when oxygen comes in contact with blood in lungs, its solubility increases many fold due to the presence of high concentration of haemoglobin that associate with oxygen molecule.

$$Hb + 4O_2 \rightleftharpoons Hb(O_2)_4$$

Due to association, Henry's law is not strictly followed in case of solubility of oxygen in blood.

Applications of Henry's Law

- Soft drinks are sealed at high pressure to increase the solubility of CO_2 in soft drinks.
- Rate of respiration increases at high altitude. At high altitude, partial pressure of oxygen is low which results, a lowering in the solubility of oxygen in blood.
- When scuba divers go deep in the sea, solubility of atmospheric gases increases in blood when they come out at land, the dissolved nitrogen gas come out as bubble, feeling painful sensation. To avoid such pain inert He gas is added.

Terms Used for Expressing the Concentration of Solution

- The concentration of a solution is defined as the relative amount of a solute present in a solution.
- The concentration of solution can be calculated as strength in gram per litre (g/L) of solution, percentage by mass, percentage by volume, mole fraction, parts per million (ppm), molarity, molality, formality and normality.

SOME IMPORTANT RELATIONS

- **Dilution law** If normality or molarity and volume of solution are changed from N_1, V_1 to N_2, V_2 then

$$N_1V_1 = N_2V_2 \quad \text{(Normality equation)}$$
$$M_1V_1 = M_2V_2 \quad \text{(Molarity equation)}$$

- Suppose n_1 moles of reactant '1' react with n_2 moles of reactant '2' then

$$\frac{N_1V_1}{n_1} = \frac{N_2V_2}{n_2}$$

- Suppose two solutions of the same solute are mixed then normality of the resulting solution, is

$$N = \frac{N_1V_1 + N_2V_2}{V_1 + V_2}$$

- Volume of water added to get a solution of normality N_2 from V_1 mL of normality N_1 is

$$V_2 - V_1 = \left(\frac{N_1 - N_2}{N_2}\right)V_1$$

Best Practice SHOTS

1. The solubility of N_2 in water at 300 K and 500 torr partial pressure is 0.01 g L^{-1}. The solubility (in g L^{-1}) at 750 torr partial pressure is [JEE Main 2016]
(a) 0.02 *(b)* 0.015 *(c)* 0.0075 *(d)* 0.005

2. The dissolution of ammonium chloride in water is an endothermic reaction. The solubility of this solution
(a) increases on increasing temperature
(b) decreases on decreasing temperature
(c) decreases on increasing temperature
(d) increases on decreasing temperature

3. Aquatic species are more comfortable in cold water rather than in warm because
(a) solubility of gases decreases with increase in temperature
(b) solubility of gases decreases with decrease in temperature
(c) solubility of a gas in liquid is higher
(d) does not change

4. Henry's law constant for the solubility of nitrogen gas in water at 298 K is 1.0×10^{-5} atm. The mole fraction of nitrogen in air is 0.8. The number of moles of nitrogen from air dissolved in 10 mL of water at 298 K and 5 atm pressure is
(a) 4.0×10^{-4} atm *(b)* 4×10^{-5} atm
(c) 5.0×10^{-4} atm *(d)* 4.0×10^{-6} atm

5. What is the molarity of H_2SO_4 solution that has a density 1.84 g/cc at 35°C and contains 98% solute by weight?
(a) 4.18 M *(b)* 1.84 M *(c)* 18.4 M *(d)* 8.14 M

6. Calculate the molality of 1 L solution of 93% H_2SO_4 (*w*/*V*). The density of the solution is 1.84 g mL^{-1}.
(a) 11.05 m *(b)* 14.05 m *(c)* 13.05 m *(d)* 12.05 m

7. 3.65 g of HCl is dissolved in 16.2 g of water. The mole fraction of HCl in the resulting solution is
(a) 0.1 *(b)* 0.4
(c) 0.2 *(d)* 0.3

8. 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) $\frac{2}{3}$ *(b)* $\frac{1}{3} \times \frac{273}{298}$
(c) $\frac{1}{3}$ *(d)* $\frac{1}{2}$

9. The density of a solution prepared by dissolving 120 g of urea in 1000 g of water is 1.15 g/mL. The molarity of the solution is
(a) 0.178 M *(b)* 0.50 M
(c) 1.02 M *(d)* 2.05 M

10. The volume of 10 N and 4 N HCl required to make 1 L of 7 N HCl are
(a) 0.50 L of 10 N HCl and 0.50 L of 4 N HCl
(b) 0.60 L of 10 N HCl and 0.40 L of 4 N HCl
(c) 0.80 L of 10 N HCl and 0.20 L of 4 N HCl
(d) 0.75 L of 10 N HCl and 0.25 L of 4 N HCl

11. To prepare a solution of concentration of 0.03 g/mL of $AgNO_3$, what amount of $AgNO_3$ should be added in 60 mL of solution?
(a) 1.8 g
(b) 0.8 g
(c) 0.18 g
(d) None of the above

VAPOUR PRESSURE OF SOLUTIONS AND AZEOTROPIC MIXTURE

Vapour Pressure

It is defined as the pressure exerted by the vapours over the liquid when it is present in equilibrium state at a given temperature.

Factors Affecting Vapour Pressure

(i) **Purity of the solute** Pure liquid always has a higher vapour pressure than its solution.

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

(iii) **Temperature** The vapour pressure of liquid increases with increases in temperature.

(iv) **Effect of adding solute** If a solute is added to the solution, then some molecules of solute are replaced by the molecules of solvent from the surface and lower its vapour pressure.

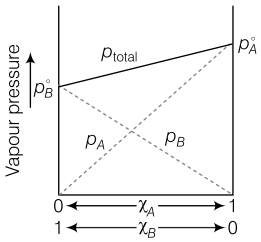
- When the solute is volatile, the vapour pressure of the solution depends upon the escaping tendency of the solute molecules from the surface of the solution.
- When solute is non-volatile then the vapour pressure of the solution decreases due to the decrease in escaping tendency of solvent molecules from the surface.

Raoult's Law

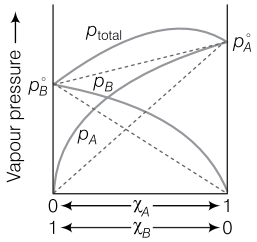
For a solution of two miscible liquids, the vapour pressure of each liquid in solution is less than the respective vapour pressure of the pure liquid and at the equilibrium, partial vapour pressure of the liquid is directly proportional to its mole fraction in solution.

Comparison of Raoult's Law between Ideal and Non-ideal Solutions

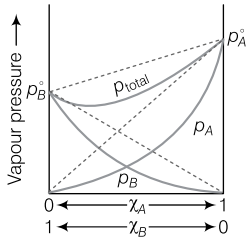
Ideal solutions	Non-ideal solutions	
	Positive deviation from Raoult's law	**Negative deviation from Raoult's law**
Obey Raoult's law for any concentration.	Do not obey Raoult's law	Do not obey Raoult's law
Neither heat is evolved nor heat is absorbed ($\Delta H_{mix} = 0$)	Heat is required ($\Delta H_{mix} > 0$)	Heat is evolved ($\Delta H_{mix} < 0$)
There is no change in volume ($\Delta V_{mix} = 0$).	Volume is increased after dissolution ($\Delta V_{mix} > 0$).	Volume is decreased after dissolution ($\Delta V_{mix} < 0$).
The two mixing parts are identical in shape, size and intermolecular forces (i.e. $A—A$, $A—B$, $B—B$ interaction should be same).	The two mixing parts have different shape, size and intermolecular forces and $A—B$ attractive force is weaker than $A—A$ and $B—B$ attractive forces.	The two mixing parts have different shape, size and intermolecular forces and $A—B$ attractive force is stronger than $A—A$ and $B—B$ attractive forces.
Escaping tendency is same before and after mixing.	Escaping tendency increases after mixing, increasing vapour pressure.	Escaping tendency decreases after mixing, decreasing vapour pressure.
$p_A = p_A^\circ \chi_A$ $p_B = p_B^\circ \chi_B$ $p_T = p_A + p_B$ e.g. chlorobenzene + bromo benzene, benzene + toluene *n*-hexane + *n*-heptane, etc.	$p_A > p_A^\circ \chi_A$ $p_B > p_B^\circ \chi_B$ $p_T > p_A + p_B$ e.g. acetone + ethanol, water + ethanol, acetone + CS_2, acetone + benzene, etc.	$p_A < p_A^\circ \chi_A$ $p_B < p_B^\circ \chi_B$ $p_T < p_A + p_B$ e.g. acetone + aniline, acetone + $CHCl_3$, CH_3OH + CH_3COOH, water + HCl, CH_3COOH + pyridine, etc.



Plot of solution showing Raoult's law



Plot of solution showing positive deviation from Raoult's law



Plot of solution showing negative deviation from Raoult's law

Limitations of Raoult's Law

- It is applicable only for very dilute solutions.
- It is applicable only for the solutions having non-volatile and non-electrolytic solutes which exist as a single molecule.
- It is not applicable for those solutes which associate or dissociate in the particular solution.

Vapour Pressure *vs* Temperature

- Vapour pressure of a liquid increases with temperature because the formation of vapour pressure is an endothermic process.
- If p_1 and p_2 are the vapour pressure of a liquid at temperatures T_1 and T_2, respectively, then according **Clausius-Clapeyron equation.**

$$\log_{10}\left(\frac{p_2}{p_1}\right) = \frac{\Delta H_{vap}}{2.303\,R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Azeotropic Mixture

It is a mixture of two liquids which boils at a constant temperature and distills over without any change in composition.

Azeotropic mixtures are of two types :

(i) Minimum Boiling Azeotropes

- These are the mixtures of two liquids whose boiling point is less than either of the two pure components.
- These are formed by non-ideal solutions showing positive deviations.
- e.g. mixture of ethanol (95.63% *w*/*w*) and water (4.37 % *w*/*w*).

(ii) Maximum Boiling Azeotropes

- These are the mixtures of two liquids whose boiling point is more than either of the two pure component.
- These are formed by non-ideal solutions showing negative deviations.
- e.g. mixture of HCl (20.2% *w*/*w*) and water (79.8% *w*/*w*).

Best Practice SHOTS

12. On mixing 10 mL of acetone with 50 mL of chloroform the total volume of the solution become
(a) < 60 mL (b) > 60 mL
(c) = 60 mL (d) unpredictable

13. CH_2Cl_2 is more volatile than $CHCl_3$. This concluded that at equilibrium vapour phase will be always rich in the component which is
(a) less volatile (b) more volatile
(c) concentrated (d) unsaturated

14. In a mixture of X and Y components show negative deviation when
(a) $\Delta V_{mix} > 0, \Delta S_{mix} > 0$
(b) $\Delta V_{mix} = 0, \Delta V_{mix} > 0$
(c) A—B interaction is stronger than A—A and B—B interaction
(d) A—B interaction is weaker than A—A and B—B interaction

15. A solution of two liquids boils at a temperature more than the boiling point of either of them.
Hence, the binary solution shows
(a) negative deviation from Raoult's law
(b) positive deviation from Raoult's law
(c) no deviation from Raoult's law
(d) positive or negative deviation from Raoult's law depending upon the composition

16. Vapour pressure of CCl_4 at 25°C is 143 mm of Hg and 0.5 g of a non-volatile solute (mol.wt. = 65) is dissolved in 100 mL CCl_4. Find the vapour pressure of the solution. (Density of CCl_4 = 1.58 g cm^{-3}).
(a) 141.93 mm (b) 94.39 mm (c) 199.34 mm (d) 134.44 mm

17. Which of the following solutions at the same temperature will be isotonic?
(a) 3.42 g of cane sugar in 1 L water and 0.18 g of glucose in 1 L water
(b) 3.42 g of cane sugar in 1 L water and 0.18 g of glucose in 0.1 L water
(c) 3.42 g of cane sugar in 1 L water and 0.585 g of NaCl in 1 L water
(d) 3.42 g of cane sugar in 1 L water and 1.17 g of NaCl in 1 L water

18. In which of the following case Raoult's law is not applicable
(a) 1 M NaCl (b) 1 M urea
(c) 1 M sucrose (d) 1 M glucose

19. For a dilute solution, Raoult's law states that
(a) the lowering of vapour pressure is equal to the mole fraction of solute
(b) the relative lowering of vapour pressure is equal to the mole fraction of solute
(c) the relative lowering of vapour pressure is proportional to the amount of solute in solution
(d) the vapour pressure of the solution is equal to the mole fraction of solvent

20. Which of the following behaviour is not true for an ideal binary liquid solution?
(a) Plot of p_A *vs* x_A is linear
(b) Plot of p_B *vs* x_B is linear
(c) Plot of p_{total} *vs* x_A (or x_B) is linear
(d) Plot of p_{toal} *vs* x_A (or x_B) is non-linear

21. An azeotropic solution of two liquids have boiling point lower than either when it
(a) shows a negative deviation from Raoult's law
(b) shows a positive deviation from Raoult's law
(c) shows no deviation from Raoult's law
(d) is saturated

22. Lowering of vapour pressure of an aqueous solution of a non-volatile, non-electrolyte having 1m aqueous solution at 100°C is
(a) 14.12 torr (b) 13.45 torr
(c) 312 torr (d) 352 torr

COLLIGATIVE PROPERTIES

- The properties of a dilute solution which depend only on the number of particles present in the solution is known as colligative properties.
- These properties are proportional to the number of solute particles in the solution.
- The following factors affect the colligative properties in the solutions.
  (i) Fraction of solute and solvent particles.
  (ii) Nature of solvent.
  (iii) Dissociation and association of solute particles.

There are four colligative properties which are discussed below:

(i) Relative Lowering of Vapour Pressure

When a non-volatile solute is added to a solvent, the vapour pressure of solution (p_s) is always less than the vapour pressure of pure solvent (p°) at that temperature.

According to Raoult's law, $\frac{p^\circ - p_s}{p^\circ} = \frac{n}{n+N} = \chi_{solute}$

For very dilute solution, $n << N$

$$\therefore \quad \frac{p^\circ - p_s}{p^\circ} \approx \frac{n}{N} \approx \frac{W_{solute} \times M_{solvent}}{W_{solvent} \times M_{solute}}$$

where, n and N are moles of solute and solvent, respectively.

(ii) Elevation in Boiling Point (Ebullioscopy)

- The vapour pressure of a solution decreases on addition of non-volatile solute. Hence, the solution boils at higher temperature than the boiling point of pure solvent, resulting an elevation in boiling point (ΔT_b).
- The elevation in boiling point is proportional to molality (m) of solution.

$$\Delta T_b = T_b - T_b^\circ = K_b m = \frac{K_b \times W_{\text{solute}} \times 1000}{M_{\text{solute}} \times W_{\text{solvent}}}$$

$$= \frac{MR(T_b^\circ)^2}{\Delta H_{\text{vap}} \times 1000} = \frac{0.002(T^\circ)^2}{I_V}$$

where, M = molar mass of solvent

T_b° = boiling point of pure solvent

T_b = boiling point of solution

R = gas constant

K_b = molal boiling point elevation constant or ebullioscopic constant of the solvent (K kg mol^{-1})

T° = normal boiling point of pure solvent

I_V = latent heat of vaporisation in cal/g of pure solvent

(iii) Depression in Freezing Point (Cryoscopy)

- As the vapour pressure of a solution decreases on addition of a non-volatile solute, the freezing point of solution (T_f) is lower down than the freezing point of pure solvent (T_f°).
- The lowering in freezing point is proportional to molality (m) of solution.

$$\Delta T_f = T_f^\circ - T_f = K_f m$$

$$= \frac{K_f \times W_{\text{solute}} \times 1000}{M_{\text{solute}} \times W_{\text{solvent}}} = \frac{MR(T_f^\circ)^2}{\Delta H_{\text{fusion}} \times 1000} = \frac{0.002(T^\circ)^2}{I_f}$$

where, T_f° = freezing point of solvent

T° = normal freezing of solvent

K_f = molar freezing point depression constant or cryoscopic constant of the solvent (K kg mol^{-1})

I_f = latent heat of fusion

Beckmann Thermometer

Beckmann thermometer was invented by Ernst Beckmann, a German chemist to measure colligative properties like **elevation in boiling point** and **depression in freezing point**.

- It is only able to measure small difference in temperature but not absolute temperature.
- This thermometer was popularly used to measure colligative properties during 20th century and is now replaced by electronic thermometers.

(iv) Osmotic Pressure (π)

- It is the external pressure that must be applied to a solution in order to stop the flow of solvent from dilute to concentrated solution through a semipermeable membrane. For dilute solution,

$$\pi = \frac{n_{\text{solute}} \times RT}{V_{\text{solution}}} = \frac{W_{\text{solute}} \times RT}{M_{\text{solute}} \times V_{\text{solution}}} = \frac{dRT}{M_{\text{solute}}}$$

- For mixture of different gases, $\pi = \pi_1 + \pi_2 + \ldots$
- For isotonic solutions, $\pi_1 = \pi_2$
- Osmotic pressure measurement provided very good method for determination of molecular mass of polymers like proteins etc.

Osmosis and Reverse Osmosis

- **Osmosis** is the spontaneous flow of the solvent molecules through semipermeable membrane from a pure solvent to a solution or from a dilute to a concentrated solution.
- Osmosis plays a vital role in biology such as for normal functioning of the living systems, flow of water to various parts of plants, movement of water from roots to the top of plants.
- **Reverse osmosis** occurs when the applied external pressure is greater than the osmotic pressure and solvent flows in a reverse way, i.e. from higher concentration to the lower concentration.
- Water purification is done with the help of reverse osmosis and pure water is obtained.

Abnormal Colligative Properties (van't Hoff Factor)

- Colligative properties depend upon the total number of particles of solute.
- Any change in the number of particles of solute leads to a change in colligative properties.

(i) **In Case of Dissociation** If 1 molecule of solute A dissociates to yield 'n' ions and α is the degree of dissociation then total number of moles in solution

$$= (1 - \alpha) + n\alpha = 1 + (n - 1)\alpha$$

- van't Hoff factor $(i) = 1 + (n - 1)\alpha > 1$ if $n \geq 2$
- degree of dissociation $(\alpha) = \dfrac{i - 1}{n - 1}$

(ii) **In Case of Association** If n molecules associate to form one giant molecule and α is the degree of association then the total number of moles in solution.

$$= (1 - \alpha) + \frac{\alpha}{n} = 1 + \left(\frac{1}{n} - 1\right)\alpha$$

- van't Hoff factor $(i) = 1 + \left(\dfrac{1}{n} - 1\right)\alpha < 1$, if $n \geq 2$
- Degree of association $(\alpha) = \dfrac{(i - 1)}{\dfrac{1}{n} - 1}$

VAN'T HOFF FACTOR (*i*) AND ITS SIGNIFICANCE

$$i = \frac{\text{Observed value (abnormal) of colligative property}}{\text{Calculated (normal) value of colligative property}} = \frac{\text{Calculated molecular mass } (M_c)}{\text{Observed molecular mass } (M_o)}$$

To achieve accurate molecular mass, the expression for colligative properties have to be modified. Hence,

(i) Relative lowering in vapour pressure, $\frac{p_A^\circ - p_A}{p_A^\circ} = i\chi_B$ (ii) Depression in freezing point, $\Delta T_f = iK_f m$

(iii) Elevation in boiling point, $\Delta T_b = iK_b m$ (iv) Osmotic pressure, $\pi = i\frac{n}{V}RT$

van't Hoff Factor (*i*) for Different Electrolytes

Solute type	Example	Ionisation/association	Number of particles in the solution from 1 mole solute	van't Hoff factor '*i*'
Non-electrolyte	Urea, sucrose, glucose		1	1
Binary electrolyte, *AB* type	NaCl, KCl, CH_3COOH, etc.	$\underset{1-\alpha}{AB} \rightleftharpoons \underset{\alpha}{A^+} + \underset{\alpha}{B^-}$	2	$1 + \alpha$
Tertiary electrolyte, AB_2 type or A_2B type	$CaCl_2$, $BaCl_2$, H_2SO_4, $K_2[PtCl_6]$	$\underset{1-\alpha}{AB_2} \rightleftharpoons \underset{\alpha}{A^{2+}} + \underset{2\alpha}{2B^-}$	3	$1 + 2\alpha$
		$\underset{1-\alpha}{A_2B} \rightleftharpoons \underset{2\alpha}{2A^+} + \underset{\alpha}{B^{2-}}$	3	$1 + 2\alpha$
Quaternary electrolyte AB_3 or A_3B type	$AlCl_3$, $K_3[Fe(CN)_3]$, $FeCl_3$, K_3PO_4	$\underset{1-\alpha}{AB_3} \rightleftharpoons \underset{\alpha}{A^{3+}} + \underset{3\alpha}{3B^-}$	4	$1 + 3\alpha$
		$\underset{1-\alpha}{A_3B} \rightleftharpoons \underset{3\alpha}{3A^+} + \underset{\alpha}{B^{3-}}$	4	$1 + 3\alpha$
Association of solute	Benzoic acid forming dimer in benzene	$\underset{1-\alpha}{nA} \rightleftharpoons \underset{\alpha/2}{(A)_n}$	$\frac{1}{n}$	$\left[1 - \left(1 - \frac{1}{n}\right)\alpha\right]$
General electrolyte AB_{n-1}	One mole of solute giving n ions in the solution	$\underset{1-\alpha}{AB_{n-1}} \rightleftharpoons \underset{\alpha}{A^{+(n-1)}} + \underset{(n-1)\alpha}{(n-1)B^-}$	n	$[1 + (n-1)\alpha]$

Best Practice SHOTS

23. Solutions *A*, *B*, *C* and *D* are respectively 0.1 M glucose, 0.05 M NaCl, 0.05 M $BaCl_2$ and 0.1 M $AlCl_3$. Which one of the following pairs is isotonic?

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

24. A solution of urea (molecular mass 56 g mol^{-1}) boils at 100.18°C at the atmospheric pressure. If K_f and K_b for water are 1.86 and 0.512 K kg mol^{-1}, respectively, the above solution will freeze at

(a) – 6.54°C *(b)* 6.54°C *(c)* 0.654°C *(d)* – 0.654°C

25. Dry air was successively passed through a solution of 5 g solute in 80 g water and then through pure water. The loss in the weight of solution was 2.5 g and that of pure water was 0.04 g. The molecular weight of the solute is

(a) 30.31 *(b)* 80.21 *(c)* 60.51 *(d)* 70.32

26. Which has the maximum osmotic pressure at temperature *T*?

(a) 100 mL of 1 M urea solution
(b) 300 mL of 1 M glucose solution
(c) Mixture of 100 mL of 1 M urea solution and 300 mL of 1 M glucose solution
(d) All of the above are isotonic

27. The molar mass of a solute *X* in g mol^{-1}, if its 1% solution is isotonic with a 5% solution of cane sugar (molar mass = 342 g mol^{-1}) is

(a) 68.4 *(b)* 34.2 *(c)* 136.2 *(d)* 171.2

28. Two aqueous solution contain, 7 g urea (molar mass = 60) and 42 g of substance *X* in 100 g of water, respectively freeze at the same temperature. The molecular weight of *X* is

(a) 460 *(b)* 370 *(c)* 120 *(d)* 360

29. When 20 g of naphthoic acid ($C_{11}H_8O_2$) is dissolved in 50 g of benzene (K_f = 1.72 K kg mol^{-1}), a freezing point depression of 2 K is observed. The van't Hoff factor (*i*) is

(a) 0.5 *(b)* 1 *(c)* 2 *(d)* 3

30. Assuming each salt to be 90% dissociated which of the following will have highest osmotic pressure?

(a) Decinormal $Al_2(SO_4)_3$
(b) Decinormal $BaCl_2$
(c) Decinormal Na_2SO_4
(d) A solution obtained by mixing equal volumes of '*b*' and '*c*' and filtering

RAPID CONCEPT REVISION

31. Different movements of plants such as opening and closing of flowers, etc., are controlled by
(a) osmosis *(b)* dissociation
(c) van't Hoff factor *(d)* colligative property

32. The elevation in boiling point of a solution of 13.44 g of $CuCl_2$ in 1 kg of water will be (molecular weight of $CuCl_2 = 134.4\ g\ mol^{-1}$ and $K_b = 0.52\ K\ molal^{-1}$).
(a) 0.16 *(b)* 0.05 *(c)* 0.1 *(d)* 0.2

33. Osmotic pressure measurement is useful particularly for biomolecules which are generally unstable
(a) at lower temperature *(b)* at higher temperature
(c) at lower pressure *(d)* at higher pressure

34. A solution of 1.25 of '*p*' in 50 g of water lowers freezing point by 0.3°C. Molar mass of '*p*' is 94. K_f (water) = 1.86 K kg mol^{-1}. The degree of association of '*p*' in water is
(a) 80% *(b)* 75% *(c)* 60% *(d)* 65%

35. Dissolution of 1.5 g of a non-volatile solute (molecular weight = 60) in 250 g of a solvent reduces its freezing point by 0.01°C. Find the molal depression constant of the solvent.
(a) 0.01 *(b)* 0.001 *(c)* 0.0001 *(d)* 0.1

36. 1×10^{-3} m solution of $Pt(NH_3)_4Cl_4$ in H_2O shows depression in freezing point by 0.0054°C.
The structure of the compound will be
(given $K_{sp}(H_2O) = 1.860\ km^{-1}$).
(a) $[Pt(NH_3)_3Cl]Cl_3$ *(b)* $[Pt(NH_3)_4]Cl_4$
(c) $[Pt(NH_3)Cl_3]Cl$ *(d)* $[Pt(NH_3)_2Cl_2]Cl_2$

37. A solution has higher osmotic pressure than its standard solution. Which of the following term will be used for this solution?
(a) Isotonic *(b)* Hypertonic *(c)* Dilute *(d)* Hypotonic

38. Molecules of acetic acid dimerise in benzene due to hydrogen bonding. It happens in solvents having
(a) high dielectric constant
(b) low dielectric constant
(c) high concentration
(d) normal colligative property

39. Which of the following physical properties is used to determine the molar mass of a polymer solution?
(a) Relative lowering of vapour pressure
(b) Elevation in boiling point
(c) Depression in freezing point
(d) Osmotic pressure

40. Consider separate solution of 0.500 M $C_2H_5OH(aq)$, 0.100 M $Mg_3(PO_4)_2(aq)$, 0.250 M $KBr(aq)$ and 0.125 M $Na_3PO_4(aq)$ at 25°C. Which statement is true about these solutions, assuming all salts to be strong electrolytes?
(a) They all have the same osmotic pressure
(b) 0.100 M $Mg_3(PO_4)_2(aq)$ has the highest osmotic pressure
(c) 0.125 M $Na_3PO_4(aq)$ has the highest osmotic pressure
(d) 0.500 M $C_2H_5OH(aq)$ has the highest osmotic pressure

Answers

1. (b)	**2.** (a)	**3.** (a)	**4.** (a)	**5.** (c)
6. (b)	**7.** (a)	**8.** (c)	**9.** (d)	**10.** (a)
11. (a)	**12.** (a)	**13.** (b)	**14.** (c)	**15.** (a)
16. (a)	**17.** (b)	**18.** (a)	**19.** (b)	**20.** (d)
21. (b)	**22.** (b)	**23.** (a)	**24.** (d)	**25.** (d)
26. (d)	**27.** (a)	**28.** (d)	**29.** (a)	**30.** (a)
31. (a)	**32.** (a)	**33.** (d)	**34.** (a)	**35.** (d)
36. (d)	**37.** (b)	**38.** (b)	**39.** (a)	**40.** (a)

MASTER STROKES

1. 18 g of glucose ($C_6H_{12}O_6$) is added to 178.2 g water. The vapour pressure of water (in torr) for this aqueous solution is [JEE Main 2016]
(a) 76.0 *(b)* 752.4 *(c)* 759.0 *(d)* 7.6

2. Consider the following statements.
I. For same solution, $\Delta T_b = \Delta T_f$
II. 5 per cent solution of urea will have more osmotic pressure than that of 10% solution of glucose.
III. Elevation of boiling point occurs due to increase in vapour pressure of solution on adding solute.
IV. The depression of freezing point is due to decrease in vapour pressure of solution on adding solute.
Among the above statements.
(a) II and IV are true
(b) I, II and IV are true
(c) II and III are false
(d) Only IV is true

3. An aqueous solution of 6.3 g of oxalic acid dihydrate is made upto 250 mL. The volume of 0.1 NaOH required to completely neutralise 10 mL of this solution is
(a) 40 mL *(b)* 20 mL *(c)* 10 mL *(d)* 4 mL

4. 100 cc of 1.5% solution of urea is found to have an osmotic pressure of 6.0 atm and 100 cc of 3.42% solution of cane sugar is found to have an osmotic pressure of 2.4 atm. If the two solutions are mixed, the osmotic pressure of the resulting solution will be
(a) 8.4 atm *(b)* 4.2 atm *(c)* 16.8 atm *(d)* 2.1 atm

5. Which of the following statement is not correct?
(a) Molarity of a solution in liquid state changes with temperature
(b) ΔH_{mix} and ΔV_{mix} for an ideal solution is zero
(c) The lowering of vapour pressure of a solution causes depression in the freezing point
(d) The extent of dissociation decreases steadily with increasing dilution

6. Which is correct order for the molal elevation constant (K_b) values of the following alcohols?

I. $(CH_3)_3C—OH$

II. $(CH_3)_2CH—CH_2OH$

III. $CH_3CH_2CH_2CH_2OH$

(a) III > II > I *(b)* II > III > I *(c)* I > III > I *(d)* II > I > III

7. When a compound $C_{38}H_{30}$ dissolved in benzene, it partially dissociates as in the following reaction. $C_{38}H_{30} \rightleftharpoons 2C_{19}H_{15}$. If 25.6 g of $C_{38}H_{30}$ is dissolved in 400 g of benzene, the freezing point is lowered by 0.680°C. What percentage of $C_{38}H_{30}$ molecules have dissociated? (K_f = 4.9 K kg mol^{-1})

(a) 5.38% *(b)* 7.01% *(c)* 6.20% *(d)* 3.00%

8. The molar mass of a solute from the osmotic pressure which it produce when a mass m of solute is dissolved in volume V is given by the expression

(a) $M = \left(\frac{m}{V}\right)\frac{RT}{\pi}$ *(b)* $M = \left(\frac{m}{V}\right)\frac{\pi}{RT}$

(c) $M = \left(\frac{m}{V}\right)\pi RT$ *(d)* $M = \left(\frac{m}{V}\right)\frac{\pi R}{T}$

9. χ_1 and χ_2 are the mole fractions of components 1 and 2, respectively in ... A ... phase than by using ...B ... law of partial pressure, $p_1 = y_1 p_{total}$ and $p_1 = y_2 p_{total}$. Identify (A) and (B) in order to complete the above statement.

(a) $A \rightarrow$ liquid; $B \rightarrow$ Dalton

(b) $A \rightarrow$ vapour; $B \rightarrow$ Dalton

(c) $A \rightarrow$ vapour; $B \rightarrow$ Henry

(d) $A \rightarrow$ liquid; $B \rightarrow$ Henry

10. Pure benzene freezes at 5.4°C. A solution of 0.223 g of phenyl acetic acid ($C_6H_5CH_2COOH$) in 4.4 g of benzene (K_f = 5.12 K kgmol^{-1}) freezes at 4.47°C. By this observation, one can conclude that

(a) phenyl acetic acid exists in benzene

(b) phenyl acetic acid undergoes partial ionisation in benzene

(c) phenyl acetic acid undergoes complete ionisation in benzene

(d) phenyl acetic acid dimerises in benzene

11. For a dilute solution containing 2.5 g of a non-volatile, non-electrolyte solute in 100 g of water, the elevation in boiling point at 1 atm pressure is 2°C. Assuming concentration of solute is much lower than the concentration of solvent, the vapour pressure (mm of Hg) of the solution is (K_b = 0.76 K kg mol^{-1}).

(a) 724 *(b)* 740 *(c)* 736 *(d)* 718

12. What happens when an egg is kept in saturated solution of NaCl after removing its hard shell in dilute HCl?

(a) Egg will swell

(b) Egg will shrink

(c) Egg will remain same

(d) Egg will first shrink and then swell

Answers

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

ELECTROCHEMISTRY

ELECTROLYSIS, CONDUCTANCE AND CONDUCTIVITY OF ELECTROLYTIC SOLUTION

Electrochemistry is the branch of science which deals with the relationship between electrical and chemical energy and their interconversion.

Electrolysis

- It is the process of decomposition of an electrolyte (which conduct electricity through ions in solution) on passing electric current through its aqueous solution or in the fused state.
- In electrolysis, electric current is used to bring a non-spontaneous chemical reaction (the reaction for which ΔG = +ve and ΔE = – ve).
- e.g. electrolysis of molten NaCl.

$$NaCl\,(molten) \longrightarrow Na^+ + Cl^-$$

At anode $2\,Cl^- - 2e^- \longrightarrow Cl_2 \uparrow$

At cathode $2\,Na^+ + 2e^- \longrightarrow 2\,Na$

Faraday's Laws of Electrolysis

The laws which are governed during the decomposition of substance at electrodes with passage of electric current are called **Faraday's laws of electrolysis**.

Faraday's First Law

- The weight (w) of any substance deposited or liberated at any electrode is directly proportional to the quantity of electricity (i) passed, $w = Zit$

where, Z = proportionality constant also called electrochemical equivalent (ECE)

- $Z = \frac{\text{equivalent weight of substance}}{96500}$

96500 = Faraday's constant (F)

Faraday's Second Law

- When same quantity of electricity is passed through solutions of different electrolytes connected in series, the weight of substance (say w_1 and w_2) produced at the electrodes is directly proportional to their equivalent weights (E_1 and E_2).

$$\frac{w_1}{w_2} = \frac{E_1}{E_2}$$

- Electrical energy (E) required to produce charge (Q) is

$$E = VQ = Vit$$

where, V = voltage

- For gaseous products, $V_g = \frac{V_E\ it}{96500}$

where, V_g = volume of gas evolved at electrode
V_E = equivalent volume of gas

Preferential Discharge During Electrolysis

During electrolysis, if more than two electrolytes are present in the solution, the ions requiring least energy are discharged in preference to other. The increasing power of deposition of some ions are given below:

For cations

$$K^+ < Na^+ < Ca^{2+} < Mg^{2+} < Al^{3+} < Zn^{2+} < H^+ < Cu^{2+} < Hg^{2+} < Ag^+$$

For anions $SO_4^{2-} < NO_3^- < \overset{\ominus}{O}H < Cl^- < Br^- < I^-$

Applications of Electrolysis

- Non-metals like H_2, O_2, Cl_2 etc., are obtained by electrolysis in pure form. Alkanes are obtained by Kolbe's electrolytic method.
- Metals like Na, Al, Ca, Mg, K are obtained by the electrolysis of fused electrolytes.
- Metals like Au, Ag, Al, Sn etc., are refined by electrolysis. Inferior metals are coated with a superior metal like Ag, Au, Pt by electrolysis.
- Thickness of the coated layer can be calculated as

$$(\text{length} \times \text{breadth} \times \text{height}) \times \rho = \frac{Eit}{96500}$$

Conductance and Conductivity of Electrolytic Solution

- Conductance (C) is the power of an electrolytic solution to conduct electricity.
- It is related to resistance (R) as $C = \frac{1}{R} = \frac{A}{\rho l}$

where,

ρ = specific resistance or resistivity, $\frac{l}{A}$ = cell constant

- Specific resistance is the resistance of a conductor of 1 cm length having a cross-sectional area of $1 cm^2$.
- Units of conductance are ohm^{-1} or mho (Ω^{-1}) or Siemen (in S I).

Types of Conductivity

There are three types of conductivity as shown in the table below:

Conductivity type	Definition	Formula	Units
Specific conductivity (κ)	It is the reciprocal of specific resistance $\left(\kappa = \frac{1}{\rho}\right)$	$\kappa = \frac{1}{\rho} = \frac{1}{R} \times \frac{l}{A}$ $= C \times \left(\frac{l}{A}\right)$	$\Omega^{-1}\ cm^{-1}$ Sm^{-1}
Molar conductivity (λ_m or μ or Λ_m)	It is the conducting power of a solution containing 1 g mol of an electrolyte	$\mu = \frac{\kappa \times 1000}{M} = \kappa \times V_{mL}$ (V_{mL} = volume of solution containing 1 g mol of an electrolyte)	$\Omega^{-1}cm^2mol^{-1}$ $S\ m^2mol^{-1}$
Equivalent conductivity (λ_{eq} or Λ_{eq})	It is the conducting power of a solution containing 1 g equivalent of an electrolyte	$\Lambda_{eq} = \frac{\kappa \times 1000}{N} = \kappa \times V_{mL}$ (V_{mL} = volume of solution containing 1 g eq of an electrolyte)	$\Omega^{-1}\ cm^2eq^{-1}$ Sm^2eq^{-1}

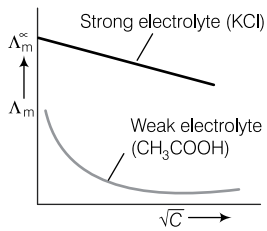
Note Relation between molar and equivalent conductivities
$\Lambda_m = \Lambda_{eq} \times$ valency factor

Variation of Conductivity with Dilution

- At infinite dilution, the conductivity of weak as well as strong electrolytes become almost same and a weak electrolyte behaves as a strong electrolyte.
- The equivalent and molar conductivity of a solution increases with dilution, whereas the specific conductivity decreases with dilution because the number of ions per cm^3 decreases.
- The equivalent and molar conductance increases with dilution because these are the product of specific conductance and volume of solution containing 1 equivalent and 1 mole of electrolyte, respectively.

Debye- Huckel-Onsager Equation

- The variation of molar conductance (Λ_m) for strong electrolyte with concentration (C) is given by **Debye-Huckel -Onsager** equation which is $\Lambda_m = \Lambda_m^\infty - b\sqrt{C}$ where, b = constant, Λ_m^∞ = molar conductance at infinite dilution.



- The value of b for a given solvent and temperature depends upon the nature of electrolyte (charge on cation and anion produced after dissociation).
- It is clear from the graph that for a strong electrolyte, extrapolation of curve at $C = 0$ gives Λ_m^∞ for strong electrolytes. However, such an extrapolation cannot be made for weak electrolytes.
- For weak electrolyte, conductivity increases steeply but Λ_m^∞ cannot be obtained at $C = 0$. Since, at $C = 0$, conductivity of the solution is so low that it cannot be measured accurately.

Estimation of Purification of Water from Conductivity

Conductivity of water is increased due to the presence of ionic impurities. Hence, the purity of water can be measured from its conductivity. Higher the conductivity, lower is the purity of water.

Note The conductance of an electrolytic solution increases with increase in temperature, because the kinetic energy of ions increases resulting to increase in the movement of ions.

Kohlrausch's Law of Independent Migration of Ions

- It states that "the molar conductivity at infinite dilution (Λ_m^∞) of the electrolyte must be equal to the sum of the molar conductivities of the ions produced by the electrolyte at infinite dilution."
- $\Lambda_m^\infty = n^+\Lambda_{cation}^\infty + n^-\Lambda_{anion}^\infty$ where, Λ_{cation}^∞ and Λ_{anion}^∞ are the molar conductivities of cation and anion at infinite dilution, n^+ and n^- are the number of cations and anions, respectively.

Note The multiplication of number of ions with molar conductivity of a particular ion is called **molar ionic conductance** of that particular ion.

Applications of Kohlrausch's Law

- Used for calculating molar conductivities of weak electrolytes at infinite dilution.
- Used for calculating degree of dissociation (α) of weak electrolyte, $\alpha = \frac{\Lambda_m^C}{\Lambda_m^\infty}$

where, Λ_m^C = molar conductance at any concentration

Λ_m^∞ = molar conductance at infinite dilution.

- Used to determine the ionisation constant of a weak electrolyte.
- For calculating the solubility of a sparingly soluble salt $\Lambda_{eq}^\circ = \frac{\kappa \times 1000}{S}$

TRANSPORT NUMBER

- It is defined as the fraction of the current carried by an ion.
- Transport number $= \frac{\text{current carried by an ion}}{\text{total current carried}}$
- Transport number of cation + transport number of anion = 1

Best Practice SHOTS

1. Which of the following solutions has highest equivalent conductance?
(a) 0.01 M KCl (b) 0.05 M KCl
(c) 0.02 MKCl (d) 0.005 M KCl

2. Conductivity of 0.00241 M acetic acid solution is 7.896×10^{-5} S cm^{-1} and Λ_m^∞ for acetic acid is 390.5 S cm^2 mol^{-1}. The value of molar conductivity and dissociation constant are, respectively
(a) 12.2 S cm^2 mol^{-1}, 1.11×10^{-4}
(b) 10.7 S cm^2 mol^{-1}, 2.85×10^{-4}
(c) 22.7 S cm^3 mol^{-1}, 1.85×10^{-5}
(d) 32.76 S cm^{2}mol^{-1}, 1.85×10^{-5}

3. At 25°C, the molar conductances at infinite dilution for the strong electrolytes NaOH, NaCl and $BaCl_2$ are 248×10^{-4}, 126×10^{-4} and 280×10^{-4} Sm^2 mol^{-1}, respectively. The value of $\lambda_m^\circ[Ba(OH)_2]$ in S m^2 mol^{-1} is
(a) 52.4×10^{-4} (b) 524×10^{-4} (c) 262×10^{-4} (d) 402×10^{-4}

4. What current is to be passed for 0.25 s for decomposition of a certain weight of metal which is equal to its electrochemical equivalent?
(a) 4A (b) 100 A (c) 200 A (d) 2 A

5. Electrolytic conduction differs from metallic conduction. In the case of electrolytic conduction
(a) the resistance increases with increasing temperature
(b) the resistance decreases with increasing temperature
(c) the flow of current does not generate heat
(d) the resistance is independent of the length of the conductor

6. How many molecules of chlorine should be deposited from molten sodium chloride in one minute by a current of 300 mA?
(a) 2.616×10^{19} molecules (b) 1.216×10^{12} molecules
(c) 5.616×10^{19} molecules (d) 6.616×10^{12} molecules

7. The sequence of ionic mobility in the aqueous solution is
(a) $K^+ > Na^+ > Rb^+ > Cs^+$ (b) $Cs^+ > Rb^+ > K^+ > Na^+$
(c) $Rb^+ > K^+ > Cs^+ > Na^+$ (d) $Na^+ > K^+ > Rb^+ > Cs^+$

8. For a small increase in temperature, the temperature dependence of molar conductivity is given by
(a) $\mu_t = \mu_{25}[1 - \beta(t - 2b)]$ (b) $\mu_t = \mu_{25}[1 + \beta(t - 2b)]$
(c) $\mu_t = \mu_{25}[1 - \beta(t + 2b)]$ (d) $\mu_t = \mu_{25}[1 + \beta(t + 2b)]$

9. Two Faradays of electricity is passed through a solution of $CuSO_4$. The mass of copper deposited at the cathode is (Atomic mass of Cu = 63.5 u)
(a) 0 g (b) 63.5 g (c) 2 g (d) 127 g

10. The limiting molar conductivity of NH_4OH, i.e. $\Lambda_{m(NH_4OH)}^\circ$ is equal to
(a) $\Lambda_{m(NH_4Cl)}^\circ + \Lambda_{m(NaCl)}^\circ + \Lambda_{m(NaOH)}^\circ$
(b) $\Lambda_{m(NaOH)}^\circ + \Lambda_{m(NH_4OH)}^\circ - \Lambda_{m(NH_4Cl)}^\circ$
(c) $\Lambda_{m(NH_4OH)}^\circ + \Lambda_{m(NH_4Cl)}^\circ - \Lambda_{m(NaCl)}^\circ$
(d) $\Lambda_{m(NH_4Cl)}^\circ + \Lambda_{m(NaOH)}^\circ - \Lambda_{m(NaCl)}^\circ$

11. The conductivity of 0.01 M NaCl solution is 0.00147 $ohm^{-1}cm^{-1}$. What happens to this conductivity, if extra 100 mL of H_2O will be added to the solution?
(a) Increases
(b) Decreases
(c) Remains unchanged
(d) First increases and then decreases

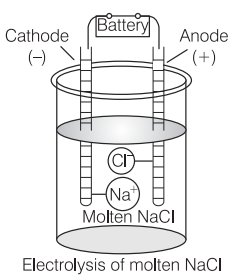
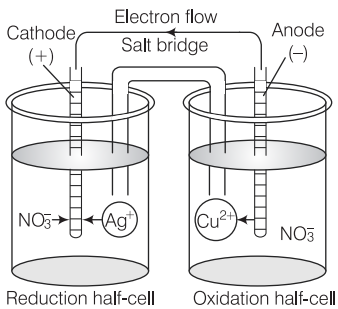
12. The resistance of $\frac{N}{10}$ solution is found to be 2.5×10^3 Ω. The equivalent conductance of the solution is [Cell constant = 1.25 cm^{-1}]
(a) 2.5 $\Omega^{-1}cm^2equiv^{-1}$ *(b)* 5.0 $\Omega^{-1}cm^2equiv^{-1}$
(c) 2.5 $\Omega^{-1}cm^{-2}equiv^{-1}$ *(d)* 5.0 $\Omega^{-1}cm^{-2}equiv^{-1}$

ELECTROCHEMICAL CELLS, ELECTRODE POTENTIAL AND EMF OF A GALVANIC CELL

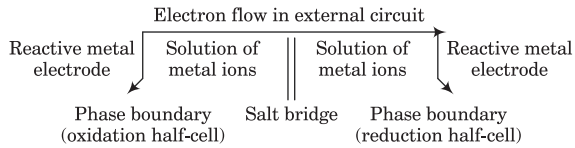
Electrochemical Cells

These are the devices in which interconversion of electrical energy and chemical energy takes place.

Types of Electrochemical Cells

	Electrolytic cell	Galvanic cell (Voltaic cell)
(i)	Electrical energy is converted into chemical energy.	Chemical energy is converted into electrical energy.
(ii)	Non-spontaneous redox reaction occurs.	Spontaneous redox reaction takes place.
(iii)	Anode is positive electrode while cathode is negative electrode.	Anode is negative electrode while cathode is positive electrode.
(iv)	Ions are discharged at both the electrodes.	Ions are discharged only on the cathode.
(v)	If the electrodes are inert, concentration of the electrolyte decreases when the electric current is circulated.	Concentration of the anodic half-cell increases while that of cathodic half-cell decreases when the two electrodes are joined by a wire.
(vi)	Both electrodes are dipped into same electrolytic solution.	Electrode reactions occurs in separate half-cells.
(vii)	No salt bridge is needed.	Salt bridge is an essential requirement.
(viii)	Working of an electrolytic cell can be shown as  Electrolysis of molten NaCl $Na^+ + Cl^- \longrightarrow Na(s) + \frac{1}{2}Cl_2(g)$	Working of a galvanic cell can be shown as  Reduction half-cell Oxidation half-cell $2Ag^+(aq) + Cu(s) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$

Representation of Electrochemical Cell



Electrode Potential (*E*)

It is a measure of the tendency of an electrolyte to gain or lose electrons in the half-cell or it is defined as the potential difference set-up between an electrode and its solution.

Classification of Electrode Potential

	Oxidation potential (E_{oxi})	Reduction potential (E_{red})
(i)	It is the tendency of an electrode to lose electrons or to get oxidised.	It is the tendency of an electrode to gain electrons or to get reduced.
(ii)	$M(s) \rightleftharpoons M^{n+}(aq) + ne^-$	$M^{n+}(aq) + ne^- \rightleftharpoons M(s)$
(iii)	Such an electrode is negatively charged with respect to its salt solution.	Such an electrode is positively charged with respect to its salt solution.

- $E_{oxi} = -E_{red}$
- The electrode potential depends upon nature of metal and its ions, concentration of ions in the solution and temperature.

Standard Electrode Potential (E°)

- It is the potential difference developed between metal electrode and the solution of its ions of unit molarity at 1 atm pressure at 25°C temperature.
- If a reaction is reversed, then the magnitude of standard electrode potential remains same but the sign changes $E^\circ_{oxidation} = -E^\circ_{reduction}$

Different Types of Reference Electrodes

Some important reference electrodes are as follows:

Normal Hydrogen Electrode (NHE)

- Hydrogen electrode is the primary reference electrode.
- It is normally used to know the electrode potential of a half-cell of galvanic cell.

- The reason for such a usage is that it can act as a cathode as well as an anode with respect to other electrode due to the following reactions.

$$H_2(g) \longrightarrow 2H^+ + 2e^-, \quad 2H^+ + 2e^- \longrightarrow H_2(g)$$

- The electrode potential of NHE is taken as zero. It is represented as $Pt|H_2(atm)|H^+(1M)$.

Standard Hydrogen Electrode (SHE)

- A hydrogen electrode in which the pressure of H_2 gas is maintained at 1 atm and concentration of H^+ ions in the solution is 1 M is called **Standard Hydrogen Electrode** (SHE).
- The electrode potential for SHE is taken as 0.00 V at all temperatures.

Electrochemical Series

It is a series of chemical elements arranged in the order of their standard electrode potentials.

Characteristics of Electrochemical Series

- Electrodes with negative Standard Reduction Potential (SRP) when joined with SHE, behave as anode. Electrodes with positive SRP behave as cathode when joined to SHE.
- Elements which are better reducing agents than hydrogen are placed above hydrogen. Elements which are better oxidising agents than hydrogen are placed below hydrogen in electrochemical series.
- Elements which get oxidised easily are good reducing agents (metals) while elements which get reduced easily are good oxidising agents (non-metals).

Applications of Electrochemical Series

- Reactivity of metals decreases from top to bottom in electrochemical series.
- Elements which are placed above hydrogen displace hydrogen from any protic solution, whereas elements below hydrogen are unable to displace.
- Thermal stability of metallic oxides decreases down the series due to decrease in electropositive character.
- Less reactive metals are coated over more reactive metal to prevent corrosion.
- Less electropositive metals are displaced from their ores by adding salt of more electropositive metal.

EMF of a Galvanic Cell

- The galvanic cell is made up of two half-cells which are anode and cathode.
- The potential of the half-cells are always different.
- Due to the difference in electrode potentials, the electric current moves from the electrode at higher potential to the electrode at lower potential.
- The difference in electrode potential of the two half-cells is known as the **electromotive force** (emf) of the cell or **cell potential**.

Measurement of EMF

- The emf of the cell or cell potential can be measured from the values of electrode potentials of the two half-cells constituting the cell.
  (i) E°_{cell} = oxidation potential of anode + reduction potential of cathode.
  $= E^\circ_{oxi} + E^\circ_{red}$
  (ii) E°_{cell} = standard reduction potential of cathode – standard reduction potential of anode $= E^\circ_{cathode} - E^\circ_{anode} = E^\circ_{right} - E^\circ_{left}$
  (iii) E°_{cell} = oxidation potential of anode – oxidation potential of cathode
  $= E^\circ_{oxi(anode)} - E^\circ_{oxi\ (cathode)}$
- For forward spontaneous reaction cell potential value will be positive.
- For backward spontaneous reaction, cell potential value will be negative.

Best Practice SHOTS

13. In the electrolytic cell, flow of electron is from
(a) cathode to anode in the solution
(b) cathode to anode through external supply
(c) cathode to anode through internal supply
(d) anode to cathode through internal supply

14. A gas X, at 1 atm is bubbled through a solution containing a mixture of 1 M Y^- and 1 M Z^- at 25°C. If the reduction potential is in the order, $Z > Y > X$, then
(a) Y will oxidise X but not Z
(b) Y will oxidise Z but not X
(c) Y will oxidise both X and Z
(d) Y will reduce both X and Z

15. Li occupies higher position in the electrochemical series of metals as compared to Cu because
(a) the standard reduction potential of Li^+/Li is lower than that of Cu^{2+}/Cu
(b) the standard reduction potential of Cu^{2+}/Cu is lower than that of Li^+/Li
(c) the standard oxidation potential of Li/Li^+ is lower than that of Cu/Cu^{2+}
(d) Li is smaller in size as compared to Cu

16. What change occurs when a zinc rod is dipped into a blue coloured copper sulphate solution?
(Given, $E^\circ_{Cu^{2+}/Cu} + 0.34\,V$, $E^\circ_{Zn/Zn^{2+}} = +0.76\,V$)
Select the correct option.
(a) Reaction takes place changing blue $CuSO_4$ to colourless $ZnSO_4$
(b) Reaction takes places changing blue $CuSO_4$ to red coloured $ZnSO_4$
(c) Both are correct
(d) None of the above

17. The standard reduction potentials at 298 K for the following half-cells are given

$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$; $E^\circ = -0.726\,V$
$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$; $E^\circ = -0.740\,V$
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$; $E^\circ = 0.000\,V$
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$; $E^\circ = 0.770\,V$

Which is the strongest reducing agent?
(a) $Cr(s)$ *(b)* $Zn(s)$ *(c)* $H_2(s)$ *(d)* $Fe^{2+}(aq)$

RAPID CONCEPT REVISION

18. $Cu^+(aq)$ is unstable in solution and undergoes simultaneous oxidation and reduction, according to the reaction, $2Cu^+(aq) \rightleftharpoons Cu^{2+}(aq) + Cu(s)$

Choose the correct value of E° for the above reaction.
(Given, $E^\circ_{Cu^{2+}/Cu} = 0.34\,V$ and $E^\circ_{Cu^{2+}/Cu^+} = 0.15\,V$)

(a) – 0.34 V (b) + 0.49 V
(c) + 0.34 V (d) – 0.19 V

19. What will occur if a block of copper metal is dropped into a beaker containing a solution of 1 M $ZnSO_4$? [JEE Main 2016]

(a) The copper metal will dissolve and zinc metal will be deposited
(b) The copper metal will dissolve with evolution of oxygen gas
(c) The copper metal will dissolve with evolution of hydrogen gas
(d) No reaction will occur

20. Given below are the half-cell reactions,

$Mn^{2+} + 2e^- \longrightarrow Mn;\ E^\circ = -1.18\ eV$

$2(Mn^{3+} + e^- \longrightarrow Mn^{2+});\ E^\circ = +1.51\ eV$

The E° for $3Mn^{2+} \longrightarrow Mn + 2Mn^{3+}$ will be
(a) – 2.69 V; the reaction will not occur
(b) – 2.69 V; the reaction will occur
(c) – 0.33 V; the reaction will not occur
(d) – 0.33 V; the reaction will occur

21. Saturated solution of KNO_3 is used to make 'salt-bridge' because
(a) velocity of K^+ is greater than that of NO_3^-
(b) velocity of NO_3^- is greater than that of K^+
(c) velocities of both K^+ and NO_3^- are nearly the same
(d) KNO_3 is highly soluble in water

22. In the silver plating of copper, $K[Ag(CN)_2]$ is used instead of $AgNO_3$ because
(a) a thin layer of Ag is formed on Cu
(b) more voltage is required
(c) Ag^+ ions are completely removed from solution
(d) less availability of Ag^+ ions, as Cu cannot displace Ag from $[Ag(CN)_2]^-$ ion

23. E_{cell} is
(a) intensive property (b) extensive property
(c) Both 'a' and 'b' (d) None of these

NERNST EQUATION

- It relates the cell potential of an electrochemical cell with the concentrations of the reactants and products of a chemical reaction at any point of time.
- For the following reaction at equilibrium,

$$pA + qB + \ldots \rightleftharpoons rX + sY + \ldots$$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log \frac{[\text{products}]}{[\text{reactants}]}$$

Applications of the Nernst Equation

(i) **To Calculate the Value of Potential of a Concentration Cell**

- The cell in which both the electrodes are of the same type but the electrolytic solutions have different concentrations are called **concentration cells**.
- As the cell operates, the concentration increases in the dilute half-cell and decreases in concentrated half-cell.
- The generated potential can be calculated with the help of Nernst equation. e.g.

$$Zn\,|\,Zn^{2+}(C_1)\,||\,Zn^{2+}(C_2)\,|\,Zn$$

$$E_{cell} = \frac{0.0591}{2} \log \frac{C_2}{C_1}, \qquad [C_2 > C_1;\ E^\circ_{cell} = 0]$$

(ii) **Determination of Solubility Products**

The concentrations of ions in equilibrium with a sparingly soluble salt are sufficiently low and the Nernst equation can be used to determine the value of K_{sp}.

TRICKS TO SOLVE PROBLEMS RELATED TO CONCENTRATION CELL

Step 1 Write down the concentration cell,
$M|M^{n+}(\text{conc.})||M^{n+}(\text{dil.})|M$

Step 2 If half-reactions are mentioned at cathode and anode, then write the half-cell in which reaction occurs at cathode on RHS in the cell representation,
$M\,|\,M^{n+}$ (anode) $||\,M^{n+}$ (cathode)$|\,M$

Step 3 Write down the Nernst equation, for concentration cell,

$$E_{cell} = E^\circ_{cell} - \frac{2.303RT}{nF} \log \frac{[M^{n+}]_{\text{anode (LHS)}}}{[M^{n+}]_{\text{cathode (RHS)}}}$$

$$E_{cell} = E^\circ_{cell} - \frac{2.303RT}{nF} \log \frac{[M^{n+}]_{\text{conc.}}}{[M^{n+}]_{\text{dil.}}}$$

Step 4 For concentration cell, $E^\circ_{cell} = 0$, put this value in Nernst equation,

$$E_{cell} = -\frac{2.303RT}{nF} \log \frac{[M^{n+}]_{LHS}}{[M^{n+}]_{RHS}}$$

Step 5 Find out the required quantity with the help of Nernst equation.

Step 6 If solubility product (K_{sp}) is asked to find out, then determine the concentrations of M^{n+} and X^{m-}.

Step 7 Determine solubility products as $K_{sp} = (mS)^m(nS)^n$.

(iii) **Potentiometric Titrations**

- Accurate determination of an ion concentration by direct measurement of a cell potential in many situations is impossible due to the presence of other ions and lack of information about activity coefficients.
- It is often possible to determine the ion indirectly by titration with some other ion using the Nernst equation.

(iv) **Measurement of pH**

A hydrogen electrode allows a direct measurement of $[H^+]$ and thus pH is given as $pH = \frac{E_{cell} - E^\circ_{reference}}{0.0591}$

Relationship between Standard Potentials of Half-cells Containing a Metal in Different Oxidation State

- If two half-reactions having potentials E_1° and E_2° are combined to form a third half-reaction having a potential E_3°, then we can write,

$$\Delta G_3^\circ = \Delta G_1^\circ + \Delta G_2^\circ \quad \text{or} \quad -n_3FE_3^\circ = -n_1FE_1^\circ - n_2FE_2^\circ$$

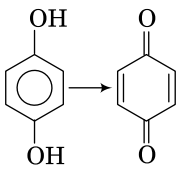
$$\text{or} \quad n_3E_3^\circ = n_1E_1^\circ + n_2E_2^\circ \quad \text{or} \quad E_3^\circ = \frac{n_1E_1^\circ + n_2E_2^\circ}{n_3}$$

Note If $E_{cell} > 0$, $\Delta G < 0$, the reaction is feasible (spontaneous).
If $E_{cell} < 0$, $\Delta G > 0$, the reaction is not feasible (non-spontaneous).

FORMULAE OF THERMODYNAMIC QUANTITIES IN ELECTROCHEMISTRY

- Maximum work done by a cell, $W_{max} = nFE_{cell}$
- Gibbs free energy change of a cell, $\Delta G = -nFE_{cell}$
- Temperature coefficient of emf of a cell reaction, $\left(\frac{dE_{cell}}{dT}\right)_p = \frac{\Delta H}{nFT} + \frac{E_{cell}}{T}$
- Enthalpy change, $\Delta H = -nF\left[E_{cell} - T\left(\frac{dE_{cell}}{dT}\right)_p\right]$
- Entropy change, $\Delta S = nF\left(\frac{dE_{cell}}{dT}\right)_p$
- Relation between ΔG and K_C, $\Delta G = \Delta G^\circ + 2.303RT \log Q$
  At equilibrium, $\Delta G = 0$ and $K_C = Q$ $\quad \therefore \Delta G^\circ = -2.303RT \log K_C$

Various Reference Half-Cell Reactions Showing Nernst Equation

Type	Example	Half-cell reaction	Q	Reversible	Electrode potential (E)(oxidation)
1. Gas ion half-cell	$Pt(H_2)\|H^+(aq)$	$\frac{1}{2}H_2(g) \longrightarrow H^+(aq) + e^-$	$[H^+]$	H^+ ion	$E^\circ - 0.0591 \log[H^+]$
	$Pt(Cl_2)\|Cl^-(aq)$	$Cl^-(aq) \longrightarrow \frac{1}{2}Cl_2(g) + e^-$	$\frac{1}{[Cl^-]}$	Cl^- ion	$E^\circ + 0.0591 \log[Cl^-]$
2. Metal-metal ion half-cell	$Ag\|Ag^+(aq)$	$Ag(s) \longrightarrow Ag^+(aq) + e^-$	$[Ag^+]$	Ag^+ ion	$E^\circ - 0.0591 \log[Ag^+]$
3. Metal- insoluble salt anion half-cell	$Ag, AgCl\|Cl^-(aq)$	$Ag(s) + Cl^-(aq) \longrightarrow AgCl(s) + e^-$	$\frac{1}{[Cl^-]}$	Cl^- ion	$E^\circ + 0.0591 \log[Cl^-]$
4. Calomel electrode	$Hg, Hg_2Cl_2\|Cl^-(aq)$	$2Hg(l) + 2Cl^-(aq) \longrightarrow Hg_2Cl_2(s) + 2e^-$	$\frac{1}{[Cl^-]^2}$	Cl^- ion	$E^\circ + 0.0591 \log[Cl^-]$
5. Metal-metal oxide hydroxide half-cell	$Hg, HgO\|OH^-(aq)$	$Hg(l) + 2OH^-(aq) \longrightarrow HgO(s) + H_2O(l) + 2e^-$	$\frac{1}{[OH^-]^2}$	OH^- ion	$E^\circ + 0.0591 \log[OH^-]$
6. Oxidation-reduction half-cell	$Pt\|Fe^{2+}(aq), Fe^{3+}(aq)$	$Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e^-$	$\frac{[Fe^{3+}]}{[Fe^{2+}]}$	Fe^{2+}, Fe^{3+} ion	$E^\circ - 0.0591 \log \frac{[Fe^{3+}]}{[Fe^{2+}]}$
7. Mercury-mercury sulphate half-cell	$Hg, HgSO_4\|SO_4^{2-}(aq)$	$SO_4^{2-}(aq) + Hg(l) \longrightarrow HgSO_4(s) + 2e^-$	$\frac{1}{[SO_4^{2-}]}$	SO_4^{2-}	$E^\circ + \frac{0.0591}{2} \log[SO_4^{2-}]$
8. Quinhydrone half-cell	$Pt\|$Quinhydrone$\|H^+(aq)$	 $+2H^+ + 2e^-$	$[H^+]^2$	H^+	$E^\circ - 0.0591 \log[H^+]$

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24. The following cell is found to have emf equal to zero Pt, $H_2(x\text{ atm})|0.01\text{ M}H^+||0.1\text{ M}H^+|H_2$ (y atm), Pt. The ratio $\frac{x}{y}$ is

(a) 0.01 (b) 0.1
(c) 10 (d) 0.001

25. If Zn^{2+} / Zn electrode is diluted 100 times, then the change in emf is
(a) increase by 59 mV
(b) decrease by 59 mV
(c) increase by 29.5 mV
(d) decrease by 29.5 mV

26. Which one of the following is always true about the spontaneous cell reaction in a galvanic cell?
(a) $E^\circ_{cell} > 0, \Delta G^\circ > 0, Q > K_C$
(b) $E^\circ_{cell} < 0, \Delta G^\circ < 0, Q < K_C$
(c) $E^\circ_{cell} > 0, \Delta G^\circ < 0, Q < K_C$
(d) $E^\circ_{cell} > 0, \Delta G^\circ < 0, Q > K_C$

27. At 25°C temperature, the cell potential of a given electrochemical cell is 1.92 V.

$Mg(s)|Mg^{2+}(aq)\,x\text{M}||Fe^{2+}(aq)|0.01\text{M Fe}(s)$

$E^\circ_{Mg/Mg^{2+}}(aq) = 2.37\text{ V}, E^\circ_{Fe/Fe^{2+}(aq)} = 0.45\text{ V}$

The value of x will be
(a) $x = 0.01$ M
(b) $x < 0.01$ M
(c) $x > 0.01$ M
(d) x cannot be predicted

28. EMF of hydrogen electrode in terms of pH is (at 1 atm pressure)
(a) $E_{H_2} = \frac{RT}{F}\text{pH}$
(b) $E_{H_2} = \frac{RT}{F} \times \frac{1}{\text{pH}}$
(c) $E_{H_2} = \frac{2.303RT}{F}\text{pH}$
(d) $E_{H_2} = -0.0591\text{ pH}$

29. Zn gives H_2 gas with H_2SO_4 and HCl but not with HNO_3 because
(a) Zn acts as oxidising agent when reacts with HNO_3
(b) HNO_3 is weaker acid than H_2SO_4 and HCl
(c) In electrochemical series, Zn is above hydrogen
(d) NO_3^- is reduced in preference to hydronium ion

30. The emf (E) of a cell is related to its variation in temperature $\left(\frac{\partial E}{\partial T}\right)_p$ and ΔH as

(a) $E = \frac{\Delta H}{nF} + T\left(\frac{\partial E}{\partial T}\right)_p$ (b) $E = \frac{\Delta H}{nF} - T\left(\frac{\partial E}{\partial T}\right)_p$
(c) $E = -\frac{\Delta H}{nF} + T\left(\frac{\partial E}{\partial T}\right)_p$ (d) $E = -\frac{\Delta H}{nF} - T\left(\frac{\partial E}{\partial T}\right)_p$

31. For the reduction of silver ions with copper metal, the standard cell potential is 0.46 V at 25°C. The value of standard Gibbs energy (ΔG°) will be
(a) – 98 J (b) – 89 kJ (c) – 44.5 J (d) 44.5 kJ

32. For the cell reaction,
$Cu^{2+}(C_1, aq) + Zn(s) \longrightarrow Zn^{2+}(C_2, aq) + Cu(s)$ of an electrochemical cell, the change in free energy, ΔG, at a given temperature is a function of
(a) $\ln C_1$ (b) $\ln \frac{C_2}{C_1}$ (c) $\ln C_2$ (d) $\ln(C_1 + C_2)$

33. In an experiment, 0.04 F was passed through 400 mL of 1 M solution of NaCl. What would be the pH of the solution after the electrolysis?
(a) 8 (b) 10 (c) 13 (d) 6

34. The potential of the cell for the reaction,

$$M(s) + 2H^+(1\text{ M}) \longrightarrow \underset{(1\text{ atm})}{H_2(g)} + \underset{(0.1\text{M})}{M^{2+}}$$

is 1.50 V. The standard reduction potential for $M^{2+}/M(s)$ couple is
(a) 0.147 V (b) 1.47 V
(c) – 1.47 V (d) None of these

35. The half-cell reactions for rusting of iron are

$2H^+ + \frac{1}{2}O_2 + 2e^- \longrightarrow H_2O;\ E^\circ = +1.23\text{ V}$

$Fe^{2+} + 2e^- \longrightarrow Fe(s);\ E^\circ_{cell} = -0.44\text{ V}$

ΔG° (in kJ) for the reaction is
(a) – 76 (b) – 322
(c) – 122 (d) – 176

36. The temperature coefficient of a galvanic cell is $+5.0 \times 10^{-5}$ mV/K. During the discharge of the cell, the cell temperature,
(a) increases
(b) decreases
(c) does not change
(d) first increases and then decreases

AMAZING REALITIES

A person suffering from any form of mental illness can be cured with the help of lithium as it is known to be used for the purpose of changing one's thinking.

BATTERY AND CORROSION

Cell or Battery

A cell or a battery (arrangement of one or more cells connected in series) is basically a galvanic cell where the chemical energy of redox reaction is converted into electrical energy. The various voltaic cell are as follows:

Primary Voltaic Cell (The Dry Cell)

It is the cell in which the cell reaction occurs only once and the cell becomes dead after use over a period of time. Examples of dry cells are

(i) **Leclanche cell** The electrode reaction for Leclanche cell is

At anode $Zn(s) \longrightarrow Zn^{2+} + 2e^-$

At cathode

$$MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3$$

Ammonia formed in reaction at cathode combines with Zn^{2+} to form the complex like, $[Zn(NH_3)_4]^{2+}$. The cell has a potential of nearly 1.5 V.

(ii) **Mercury cell** It shows the following electrode reactions

At anode

$Zn(Hg) + 2OH^- \longrightarrow ZnO(s) + H_2O + 2e^-$

At cathode

$HgO(s) + H_2O + 2e^- \longrightarrow Hg(l) + 2OH^-$

The overall reaction is

$$Zn(Hg) + HgO(s) \longrightarrow ZnO(s) + Hg(l)$$

Secondary Voltaic Cell

It is the cell in which original reactants are regenerated by passing current from external source (recharged).

Examples of secondary voltaic cell are

(i) **Lead accumulator** (Lead storage battery)

- It is the most important secondary voltaic cell, commonly used in automobiles and invertors.
- A 38 per cent solution of H_2SO_4 is used as electrolyte.
- The reaction taking place during discharging (when cell is in use) is

$$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$$

- Reverse reaction occurs when cell is charged, E_{cell} is 2.041 V.

(ii) **Nickel cadmium battery**

- Ni-Cd battery has longer life but more expensive.
- The overall reaction during discharge is

$$Cd(s) + 2Ni(OH)_3(s) \longrightarrow CdO(s) + 2Ni(OH)_2(s) + H_2O(l)$$

- The reverse reaction occurs when cell is charged.

Batteries Used in Smart Phones and Digital Watches

- Lithium-ion batteries are used in most of the smart phones of companies like; Micromax, Blackberry, Sony, Motorola, etc.
- Lithium polymer batteries are used in few latest handsets of Micromax, Apple, Sony, Blackberry, etc.
- Silver oxide technology is used now-a-days (earlier mercury technology is used but is highly toxic) for high quality batteries of watches because these are most efficient when squeezing the last bit of electricity into a confined space for storage.

Fuel Cells

- It is the galvanic cells which use energy of combustion of fuels like H_2, CH_4, CH_3OH, etc., as the source to produce electrical energy.
- One of the most successful fuel cell uses the energy of reaction of H_2 and O_2 in gaseous state to form water.

  The electrode reactions for the cell are:

  At anode $2H_2(g) + 4OH^-(aq) \longrightarrow 4H_2O(l) + 4e^-$

  At cathode $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$

  The overall reaction is, $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$
- This type of cell runs continuously as long as the fuels are supplied and produce electricity upto 70 per cent efficiency.

Note The advantage of fuel cells over batteries is that these are pollution free and highly efficient.

Some Other Fuel Cells

1. **Phosphoric acid fuel cell** Liquid H_3PO_4 is used as an electrolyte. This is the first fuel cell to be commercialised.

   Anode reaction $2H_2 \longrightarrow 4H^+ + 4e^-$

   Cathode reaction $O_2(g) + 4H^+ + 4e^- \longrightarrow 2H_2O$
2. **Alkaline fuel cell** It is one of the most efficient fuel cell.

   Anode reaction $2H_2 + 4OH^- \longrightarrow 4H_2O + 4e^-$

   Cathode reaction $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$
3. **Molten carbonate fuel cell** This can operate at extreme high temperature of 600°C and above. It is generally used for industrial purpose.

   Anode reaction $H_2 + CO_3^{2-} \rightleftharpoons H_2O + CO_2 + 2e^-$

   Cathode reaction $CO_2 + \frac{1}{2}O_2 + 2e^- \rightleftharpoons CO_3^{2-}$
4. **Direct methanol fuel cell** Methanol is used as fuel

   Anode reaction

   $$CH_3OH + H_2O \rightleftharpoons 6H^+ + 6e^- + CO_2$$

   Cathode reaction $\frac{3}{2}O_2 + 6H^+ + 6e^- \rightleftharpoons 3H_2O$

RAPID CONCEPT REVISION

Corrosion

- It is the oxidative deterioration of metal surface with the action of its environment to form unwanted corrosion products like oxides, sulphides, carbonates, sulphates.
- It usually affects metallic substances and typically produce oxide(s) or salt(s) of metal.
- Examples are conversion of iron to rust $[Fe_2O_3 \cdot xH_2O]$, tarnishing of silver (due to the formation of Ag_2O), development of green coating on copper and bronze.

Corrosion of Iron or Rusting Involves the Following Reactions

Oxidation half-cell

$$2Fe(s) \longrightarrow 2Fe^{2+} + 4e^-; \; E^\circ_{(Fe^{2+}/Fe)} = -0.44\,V$$

Reduction half-cell

$$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l); \; E^\circ_{(H^+/O_2/H_2O)} = 1.23\,V$$

Overall reaction

$$2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2+}(aq) + 2H_2O(l); \; E^\circ_{cell} = 1.67\,V$$

Ferrous ions, Fe^{2+} undergo oxidation with O_2 to form rust $[Fe_2O_3 \cdot xH_2O]$.

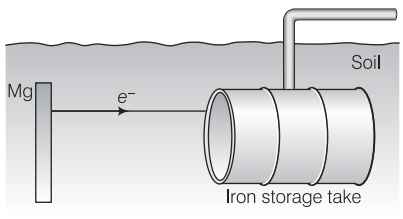
$$2Fe^{2+} + 2H_2O + \frac{1}{2}O_2 \longrightarrow Fe_2O_3 + 4H^+$$

$$\xrightarrow{H_2O} \underset{\substack{\text{(Rust)}\\ \text{Hydrated}\\ \text{ferric oxide}}}{Fe_2O_3 \cdot xH_2O}$$

Prevention of Rusting

(i) **Galvanisation**
In this method, a thin film of Zn is coated over iron, where Zn form a protective oxide layer. Even, if the zinc coating breaks down and iron is exposed to air, Zn reduces Fe^{2+} back to Fe(s), as reduction potential of Fe is more than that of Zn.

(ii) **Cathodic protection**
In this method, the equipment made of Fe is attached to a more easily oxidisable metal like Mg. Here, Mg acts as a sacrificial anode, as it reacts in preference to iron. The Mg rod should be replaced periodically.



$Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^-$ (Oxidation)
$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$ (Reduction)

Best Practice SHOTS

37. The rusting of iron is catalysed by
(a) Fe (b) O_2
(c) H^+ (d) Zn

38. The efficiency of a fuel cell is given by
(a) $\frac{\Delta H}{\Delta G}$ (b) $\frac{\Delta G}{\Delta S}$
(c) $\frac{\Delta G}{\Delta H}$ (d) $\frac{\Delta S}{\Delta G}$

39. In which of the following, reactants are not contained with the cell but are continuously supplied from the external source.
(a) Lithium battery
(b) Fuel cell
(c) Dry cell
(d) Lead-storage battery

40. The rate of corrosion is more in the environment which is
(a) dry (b) humid
(c) salty (d) normal

41. Rusting of iron or corrosion of active metal is initiated by
(a) cathodic reaction when oxygen gas which is dissolved in H_2O is reduced to OH^-
(b) acid rain oxidises metal to metal ion
(c) Both (a) and (b)
(d) None of the above

42. In the following batteries, alkaline electrolytes are used
I. Mercury
II. Nickel-cadmium
III. Modified Leclanche cell
Cell potential is found to be independent of $[OH^-]$ in
(a) I, II, III (b) Both I and II
(c) Both II and III (d) Only III

Answers

1. (d)	2. (d)	3. (b)	4. (a)	5. (b)
6. (c)	7. (b)	8. (b)	9. (b)	10. (d)
11. (b)	12. (b)	13. (b)	14. (a)	15. (a)
16. (a)	17. (b)	18. (c)	19. (d)	20. (a)
21. (c)	22. (d)	23. (a)	24. (a)	25. (b)
26. (c)	27. (a)	28. (d)	29. (d)	30. (c)
31. (b)	32. (b)	33. (c)	34. (c)	35. (b)
36. (b)	37. (c)	38. (c)	39. (b)	40. (b)
41. (c)	42. (a)			

MASTER STROKES

1. A dilute aqueous solution of Na_2SO_4 is electrolysed using platinum electrodes. The products at the anode and cathode are, respectively
(a) O_2, H_2 *(b)* SO_2, Na
(c) O_2, Na *(d)* $S_2O_8^{2-}, H_2$

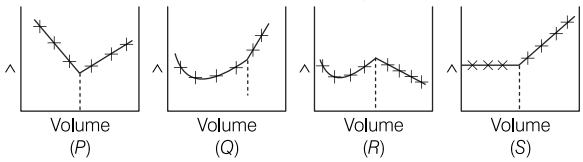
2. What will be the emf of the given cell?

$$Pt|H_2(p_1)|H^+(aq)||H_2(p_2)|Pt$$

(a) $\frac{RT}{F}\ln\frac{p_1}{p_2}$ *(b)* $\frac{RT}{2F}\ln\frac{p_1}{p_2}$
(c) $\frac{RT}{F}\ln\frac{p_2}{p_1}$ *(d)* None of these

3. The equivalent conductance at infinite dilution of HCl and NaCl are 426.15 and 126.15 mho $cm^2 g\ eq^{-1}$, respectively. It can be said that the mobility of
(a) H^+ ions is much more than that of Cl^- ions
(b) Cl^- ions is much more than that of H^+ ions
(c) H^+ ions is much more than that of Na^+ ions
(d) Na^+ ions is much more than that of H^+ ions

4. $AgNO_3$ (aqueous) was added to an aqueous KCl solution gradually and the conductivity of the solution was measured. The plot of conductance (Λ) *versus* the volume of $AgNO_3$ is



(a) *P* *(b)* *Q* *(c)* *R* *(d)* *S*

5. The $E^\circ_{M^{3+}/M^{2+}}$ values for Cr, Mn, Fe and Co are -0.41, $+1.57$, $+0.77$ and $+1.97$ V, respectively. For which one of these metals, the change in oxidation state from $+2$ to $+3$ is easiest?
(a) Cr *(b)* Mn *(c)* Fe *(d)* Co

6. Which of the following statement is correct?
(a) More reactive metals are readily corroded
(b) Corrosion takes place rapidly at bends, scratches and cuts in the metal
(c) Presence of impurities in metals enhances the chances of corrosion
(d) All of the above

7. Which of the following has maximum potential for the half-cell reaction,

$$2H^+ + 2e^- \longrightarrow H_2$$

(a) 1.0 M HCl *(b)* 1.0 M NaOH
(c) Pure water *(d)* A solution with pH = 4

8. How many moles of Pt may be deposited on cathode when 0.80 F of electricity is passed through 1.0 M solution of Pt^{4+}?
(a) 1 mole *(b)* 0.20 mole
(c) 0.40 mole *(d)* 0.80 mole

9. Which pair of electrolytes could not be distinguished by the products of electrolysis using inert electrodes.
(a) 1 M $CuSO_4$ solution, 1 M $CuCl_2$ solution
(b) 1 M KCl solution, 1 M KI solution
(c) 1 M KCl solution, 1 M NaCl solution
(d) 1 M $AgNO_3$ solution, 1 M $Cu(NO_3)_2$ solution

10. Consider the following cell reaction,

$$2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2+}(aq) + 2H_2O(l),\ E^\circ = 1.67\ V$$

At $[Fe^{2+}] = 10^{-3}$ M, $p(O_2) = 0.1$ atm and pH = 3, the cell potential at 25°C is
(a) 1.47 V *(b)* 1.77 V
(c) 1.87 V *(d)* 1.57 V

Answers

1. (a)	**2.** (b)	**3.** (c)	**4.** (d)	**5.** (a)
6. (d)	**7.** (a)	**8.** (b)	**9.** (c)	**10.** (d)

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MEDI QUEST
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NEET
SCALE UP

Mock Questions from Class XIIth syllabus with Answer key

HALF TEST 2
(XII SYLLABUS)
WITH ANSWER KEY

INSTRUCTIONS

- This test consists of 45 questions and each question is allotted 4 marks for correct response.
- Candidates will be awarded marks as stated above for correct response of each question. 1/4 marks will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
- There is only one correct response for each question. Filling up more than one response in any question will be treated as wrong response and marks for wrong response will be deducted according as per instructions.

1. Which of the following exhibit the maximum molarity in solution?
(a) 5.0 g of $CaCO_3$ in 100 mL of aqueous solution
(b) 11.7g of NaCl in 100 mL of aqueous solution
(c) 21.2 g of Na_2CO_3 in 200 mL of aqueous solution
(d) 21.3 g Na_2SO_4 in 150 mL of aqueous solution

2. Aniline and ethanamine can be distinguished by which of the following test?
(a) Hinsberg's test *(b)* Carbylamine test
(c) Nitrous acid test *(d)* All of these

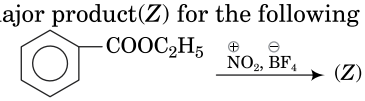
3. If degree of dissociation (α) is same for all of the following electrolytes then the maximum value of van't Hoff factor *(i)* is shown by
(a) $K_4[Fe(CN)_6]$ *(b)* $K_3[Fe(CN)_6]$
(c) $CaCO_3$ *(d)* Na_2SO_4

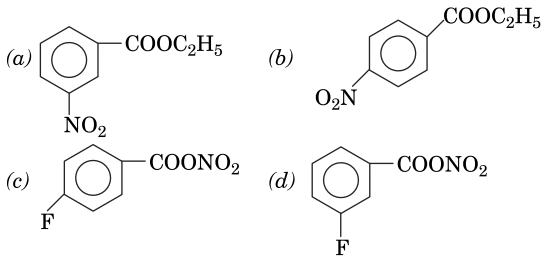
4. Identify the correct statement.
(a) Interhalogen compounds are less reactive than its elemental form
(b) Halogens (X_2) are colourless compounds
(c) The reaction of SO_2 with water and alkali is very similar to CO_2
(d) XeF_2 has sp^3d^2 hybridisation with square planar geometry

5. Total number of voids present in 1.5 moles of cubic close packing unit cells are
(a) 1.5×10^{23} *(b)* 2.7×10^{24}
(c) 1.5×10^{24} *(d)* 6.02×10^{24}

6. Which of the following reaction show maximum values for equilibrium constant at 25°C?
(a) $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$, $E^\circ_{cell} = 1.1$ V
(b) $Zn(s) + 2Ag^{+}(aq) \longrightarrow Zn^{2+}(aq) + 2Ag(s)$, $2E^\circ_{cell} = 1.56$ V
(c) $Ni(s) + 2Ag^{+}(aq) \longrightarrow Ni^{2+}(aq) + 2Ag(s)$, $2E^\circ_{cell} = 1.05$V
(d) $Ni(s) + Cu^{2+}(aq) \longrightarrow Ni^{2+}(aq) + Cu(s)$, $E^\circ_{cell} = 0.60$ V

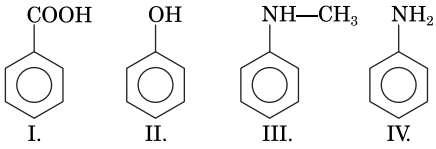
7. The major product(*Z*) for the following reaction is





8. The correct way to prevent underground iron pipe from rusting is
(a) cover the pipe with some non-conducting substance before running it below the ground
(b) sprinkle NaCl powder before running the pipe below the ground
(c) attach some magnesium blocks with the pipe through a conducting wire
(d) cover the pipe with the polythene before running it below the ground

9. The species soluble in NaOH solution is/are



(a) Only III *(b)* Only IV *(c)* I and II *(d)* III and IV

10. Which of the following is not an example of Sandmeyer's reaction?

(a) $C_6H_5\overset{+}{N}_2\bar{Cl} \xrightarrow{CuCl} C_6H_5Cl$

(b) $C_6H_5\overset{+}{N}_2\bar{Cl} \xrightarrow{CuBr} C_6H_5Br$

(c) $C_6H_5\overset{+}{N}_2\bar{Cl} \xrightarrow{CuCN} C_6H_5CN$

(d) $C_6H_5\overset{+}{N}_2\bar{Cl} \xrightarrow{HBF_4} C_6H_5F$

11. Which of the following alcohol cannot be prepared by reduction of aldehyde or ketone under normal conditions?

(a) Primary alcohol *(b)* Secondary alcohol
(c) Tertiary alcohol *(d)* None of these

12. The correct relation of the time taken (T) for a first order reaction to reduce to 12.6% of its original quantity is

(a) $T = 3 \cdot t_{1/2}$ *(b)* $T = \frac{t_{1/2}}{3}$
(c) $T = (t_{1/2})^3$ *(d)* $T = 4 \cdot t_{1/2}$

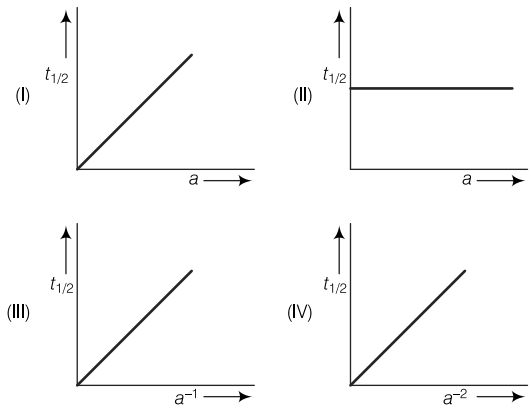
13. Which of the following gas is not poisonous in nature?

(a) Phosgene gas ($COCl_2$)
(b) Tear gas ($CCl_3 \cdot NO_2$)
(c) Carbon dioxide gas (CO_2)
(d) Mustard gas ($Cl \cdot CH_2 \cdot CH_2 \cdot S \cdot CH_2CH_2 \cdot Cl$)

14. Conductivity of a weak electrolyte

(a) increases with the dilution
(b) decreases with the dilution
(c) has no effect of dilution
(d) depends on the shape of container

15. Examine the following plots (at given temperature)



The correct representation for the relation between half-life ($t_{1/2}$) and concentration (a) for zero and first order reactions respectively are

(a) I and III *(b)* I and II *(c)* III and IV *(d)* III and II

16. In the reaction,

$$C_2H_5OH \xrightarrow{PBr_3} (X) \xrightarrow{KOH(alco.)} (Y) \xrightarrow[(ii)\ H_2O/\Delta]{(i)\ H_2SO_4} (Z)$$

Final product (Z) is

(a) $CH_2{=}CH_2$ *(b)* C_2H_5OH
(c) CH_3CHO *(d)* $C_2H_5 \cdot O \cdot C_2H_5$

17. An aliphatic amide *(A)* having molecular mass 73 is used to prepare a compound *(B)* by Hofmann bromamide degradation reaction. (*A*) and (*B*) are respectively,

(a) $OHCN\begin{matrix}CH_3\\CH_3\end{matrix}$, $C_2H_5NH_2$

(b) $OHCN\begin{matrix}CH_3\\CH_3\end{matrix}$, CH_3NH_2

(c) $C_2H_5CONH_2$, $C_2H_5NH_2$
(d) $C_2H_5CONH_2$, CH_3NH_2

18. Pure water is electrolysed using platinum electrodes. If current of 1A is passed for 1724 s at NTP, the volume of oxygen available will be

(a) 1.0 L *(b)* 0.4 L *(c)* 0.1 L *(d)* 0.2 L

19. Which of the following show least value for coordination number?

(a) $(NH_4)_2 \cdot [CoF_4]$ *(b)* $K_3[Fe(CN)_6]$
(c) $K_4[Fe(CN)_6]$ *(d)* $K_3[Co(C_2O_4)_3]$

20. Which of the following species are paramagnetic in nature?

I. $[NiCl_4]^{2-}$ II. $[Ni(CO)_4]$
III. $[Cr(NH_3)_6]^{3+}$ IV. $[Ni(CN)_4]^{2-}$

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

21. The oxoacid of sulphur in which sulphur exhibit sp^3-hybridisation is

(a) H_2SO_3 *(b)* $H_2S_2O_6$ *(c)* $H_2S_2O_7$ *(d)* All of these

22. Identify the incorrect use of noble gases.

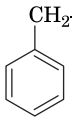
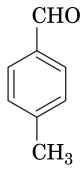
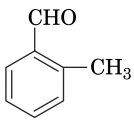
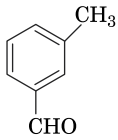
(a) Neon is used in discharge tubes and fluorescent bulbs
(b) Helium is used in filling balloons
(c) Argon is used to provide inert atmosphere in high temperature metallurgical process
(d) Xenon is mixed with the gasoline to decrease its octane number

23. An organic compound (Z) with molecular formula C_8H_8O show the following reactions:

I. (Z) reacts with 2, 4-DNP.
II. (Z) reduces Tollen's reagent.
III. (Z) with 50% NaOH, show Cannizzaro reaction.

IV. (Z) on oxidation with $KMnO_4$ gives 1, 2, benzene dicarboxylic acid.

Compound (Z) is

(a)  (b)  (c)  (d) 

24. Which of the following has same packing efficiency?

I. Cubic close packing

II. Body centered cubic packing

III. Hexagonal close packing

IV. Simple cubic packing

(a) I and II *(b)* I and III *(c)* II and III *(d)* II and IV

25. For the reaction,

$$2HI(g) \longrightarrow H_2(g) + I_2(g)$$

The correct expression for the decomposition of HI is

(a) $\frac{1}{2}\frac{\Delta[HI]}{\Delta t} = \frac{\Delta[H_2]}{\Delta t} = \frac{\Delta[I_2]}{\Delta t}$

(b) $-\frac{1}{2}\frac{\Delta[HI]}{\Delta t} = \frac{\Delta[H_2]}{\Delta t} = \frac{\Delta[I_2]}{\Delta t}$

(c) $-\frac{1}{2}\frac{\Delta[HI]}{\Delta t} = -\frac{\Delta[H_2]}{\Delta t} = -\frac{\Delta[I_2]}{\Delta t}$

(d) $\frac{\Delta[HI]}{\Delta t} = \frac{2\cdot\Delta[H_2]}{\Delta t} = \frac{2\cdot\Delta[I_2]}{\Delta t}$

26. Which of the following metal can be refined by zone-refining ?

(a) Zr (Zirconium) *(b)* Ti (Titanium)

(c) Ni (Nickel) *(d)* Ge (Germanium)

27. An unknown non-volatile solute having molar mass 156 g mol^{-1} is dissolved in 140.0 g of acetic acid to lower the m.p. by 2.0°C. If K_f for acetic acid is 3.9 $K\cdot kg\cdot mol^{-1}$, the mass of unknown solute dissolved in acetic acid will be

(a) 22.4 g *(b)* 5.60 g *(c)* 8.40 g *(d)* 11.20 g

28. Vapour pressure of two pure liquids (A) and (B) are 40 and 30 mm of Hg, respectively. On mixing 4 moles of (A) and 1 mole of (B), the final pressure becomes

(a) 70 mm of Hg *(b)* 10 mm of Hg

(c) 35 mm of Hg *(d)* 38 mm of Hg

29. An aliphatic saturated alkyl bromide (A) having molecular mass 123 g mol^{-1} react with KOH (alcoholic) to give a compound (B). Compound (B) on reaction with HBr give back the compound (A) (Atomic mass of Br = 80 g mol^{-1}). Compound (A) is

(a) $CH_3CH_2CH_2Br$ *(b)* $CH_3-CH_2-\underset{\displaystyle Br}{\underset{|}{C}}H-CH_3$

(c) $CH_3-\underset{\displaystyle Br}{\underset{|}{C}}H-CH_3$ *(d)* $CH_2-CH_2-CH_2-CH_3$ (Br)

30. The decreasing value of bond angles from NH_3 (107°) to SbH_3(91°) down the group-15 of the periodic table is due to

(a) increase in $bp - bp$ repulsion

(b) decrease in $lp - bp$ repulsion

(c) decrease in electronegativity

(d) increase in p-orbital character in sp^3

31. A white precipitate is formed on adding KI to $CuSO_4$ solution. It is of

(a) Cu_2I_2 *(b)* CuI_2 *(c)* Cu_2S *(d)* Cu_2SO_4

32. The correct order of increasing boiling points of the following aqueous solutions, 0.0001 M NaCl(I), 0.0001M urea (II), 0.001M $MgCl_2$ (III), 0.01M NaCl (IV) is

(a) I < II < III < IV *(b)* IV < III < II < I

(c) II < I < III < IV *(d)* III < II < IV < I

33. The method which is used to extract gold and silver is known as

(a) Thermit process

(b) Hall-Heroult-process

(c) Mac-Arthur-Forest cyanide process

(d) Baeyer's process

34. Isoelectric point is the point at which

(a) all the colloidal particles stop migration under the applied electric field

(b) double layer of charged particles starts to take place

(c) the amino acid molecules carry equal number of positive and negative charges

(d) amino acid molecules becomes charge less molecules

35. For reduction of CuO to Cu,

$\Delta G_f^\circ(CuO) = -130$ kJ/mol

$\Delta G_f^\circ(H_2O) = -230$ kJ/mol

$\Delta G_f^\circ(CO) = -160$ kJ/mol

$\Delta G_f^\circ(CO_2) = -300$ kJ/mol

On the basis of given data, the better reducing agent is

(a) hydrogen *(b)* carbon

(c) CO *(d)* All are equal

36. The term 'Kraft temperature' is related with the

(a) stability of the lattice *(b)* solvation of ions

(c) formation of micelles *(d)* magnetic nature of metals

37. On passing 1F of current through three electrolytes Ag^+, Fe^{2+} and Cr^{3+}, having molar masses 108, 56 and 52, respectively. The mass of deposited on electrodes will be (in grams)

(a) Ag^+ =108, Fe^{2+} = 56, Cr^{3+} = 52.6

(b) Ag^+ = 36, Fe^{2+} = 28, Cr^{3+} = 156

(c) Ag^+ = 36, Fe^{2+} = 52, Cr^{3+} = 156

(d) Ag^+ = 108, Fe^{2+} = 28, Cr^{3+} = 17.3

38. Inversion of sugar occurs due to
(a) geometrical isomerism shown by sugar molecules as well as by its monomers
(b) ability to rotate plane polarised light which changes on hydrolysis of sugar
(c) reducing nature of sugar
(d) cyclic structure of sugar

39. The volume (in mL) of 0.1 M $AgNO_3$ required for complete precipitation of chloride ions present in 30 mL of 0.01M solution of $[Cr(H_2O)_5Cl]Cl_2$, as silver chloride is close to
(a) 3 (b) 4 (c) 5 (d) 6

40. 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

41. During the adsorption of krypton on activated charcoal at low temperature.
(a) $\Delta H > O$ and $\Delta S < O$
(b) $\Delta H < O$ and $\Delta S < O$
(c) $\Delta H > O$ ans $\Delta S > O$
(d) $\Delta H < O$ and $\Delta S > O$

42. Which of the following statement about steel is incorrect?
(a) Process of heating a steel to redness followed by slow cooling is known as annealing
(b) Process of heating the steel to redness followed by sudden cooling is known as quenching
(c) Heating the steel at about 700 K followed by sudden cooling is known as tempering
(d) Both (a) and (b)

43. Which of the following statement is incorrect for zinc?
(a) Zinc is not considered as transition metal
(b) Zinc can only show + 2 oxidation state in its compounds
(c) Zinc belongs to d-block
(d) Enthalpy of atomisation is maximum for zinc among other members of 3d-series

44. Which of the following property about penicillin is incorrect?
(a) Penicillin is a bacteriostatic antibiotic
(b) It is a narrow spectrum antibiotic
(c) Ampicillin is the semi-synthetic modification of penicillin
(d) None of the above

45. The correct increasing order for intermolecular forces among rubber (A), terylene (B) and polythene (C) is
(a) $C < B < A$ (b) $A < C < B$
(c) $B < A < C$ (d) $C < A < B$

Answers

1. (b)	2. (c)	3. (a)	4. (c)	5. (b)	6. (b)	7. (a)	8. (c)	9. (c)	10. (d)
11. (c)	12. (a)	13. (c)	14. (a)	15. (b)	16. (b)	17. (c)	18. (c)	19. (a)	20. (a)
21. (d)	22. (d)	23. (c)	24. (b)	25. (b)	26. (d)	27. (d)	28. (d)	29. (c)	30. (c)
31. (a)	32. (c)	33. (c)	34. (c)	35. (a)	36. (c)	37. (d)	38. (b)	39. (d)	40. (c)
41. (b)	42. (c)	43. (d)	44. (a)	45. (b)					

CHEMISTRY IN action

Chemists Created Vitamin-powered Battery

Vitamins may be good for more than strong bones and healthy bodies. They might also be good for powering batteries. In the latest version of an organic flow battery, which uses carbon-based organic compounds instead of metal ions to carry charges, scientists have introduced a molecule similar to the core of vitamin B2 to carry energy.

Like other flow batteries, this one stores energy in two liquids and generates an electrical current as the liquids flow past each other, trading electrons across a membrane. Because the liquids can be housed in large tanks, these batteries have the potential to store days' worth of energy from renewable sources such as wind and sun.

The liquids typically use metals, such as vanadium, to shuttle electrons. But these metals tend to be expensive or corrosive. Organics, whether from petroleum, plants, or other places, are also good electron shuttles. Two years ago, researchers created the first organic flow battery using a compound commonly found in rhubarb. Now, the same group reports that it **has created a similar battery with alloxazine**, the backbone of B_2. If the new battery can be scaled up, it would be cheaper to produce than the metal variety, as the B_2 compound can be readily made from common starting materials at room temperature. Plus, it would be less toxic.

RAINBOW

NUCLEOPHILIC SUBSTITUTION (S_N1 AND S_N2)

Stepwise Learning and Practice through Selective Problems

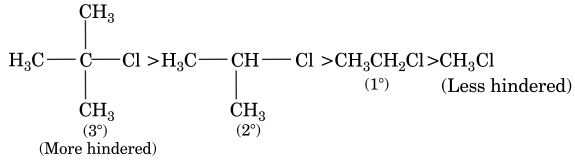
1 In S_N2 reactions, the correct order of reactivity for the following compounds CH_3Cl, CH_3CH_2Cl, $(CH_3)_2CHCl$ and $(CH_3)_3CCl$ is [JEE Main 2014]

(a) $CH_3Cl > (CH_3)_2CHCl > CH_3CH_2Cl > (CH_3)_3CCl$
(b) $CH_3Cl > CH_3CH_2Cl > (CH_3)_2CHCl > (CH_3)_3CCl$
(c) $CH_3CH_2Cl > CH_3Cl > (CH_3)_2CHCl > (CH_3)_3CCl$
(d) $(CH_3)_2CHCl > CH_3CH_2Cl > CH_3Cl > (CH_3)_3CCl$

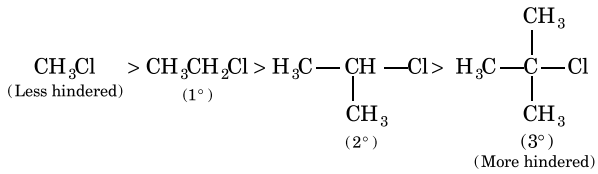
(b) ***Step I*** S_N2 reactions occurs in one step therefore, steric factor decides the rate of reactions. Write the relation between rate of S_N2 reactions and steric hindrance.

$$\text{Rate of } S_N2 \text{ reactions} \propto \frac{1}{\text{steric hindrance on carbon}}$$

Step II Arrange the given alkyl halides on the basis of steric hindrance on carbon.



Step III Reverse the order for rate of S_N2 reactions.



TRY THESE

1. Which of the following has the highest nucleophilicity?

(a) F^- *(b)* $\bar{O}H$
(c) $\bar{C}H_3$ *(d)* $\bar{N}H_2$

2. A S_N2 reaction at an asymmetric carbon of a compound always gives

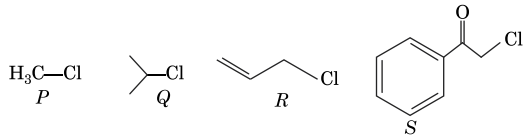
(a) an enantiomer of the substrate
(b) a product with opposite optical rotation
(c) a mixture of diastereomers
(d) a single stereoisomer

3. The correct statement regarding S_N2 reaction is

(a) the reaction mechanism involves atleast one reactive intermediate
(b) transition state is pentavalent
(c) product is formed after passing through several transition states
(d) nucleophile attack from front side on which leaving group is present

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

2 KI in acetone, undergoes S_N2 reaction with each of the following *P*, *Q*, *R* and *S*. The rates of the reaction vary as [JEE Advanced 2013]



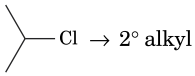
(a) $P > Q > R > S$ *(b)* $S > P > R > Q$
(c) $P > R > Q > S$ *(d)* $R > P > S > Q$

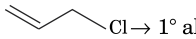
(b) ***Step I*** Acetone is an aprotic solvent, thus S_N2 reaction is favoured. Write the order of stability for S_N2 reactions.

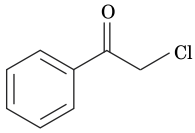
1° alkyl halide > 2° alkyl halide > 3° alkyl halide

Step II Classify each, *P*, *Q*, *R* and *S* as 1°, 2° and 3° alkyl halides.

(*P*) $CH_3—Cl \rightarrow$ 1° alkyl halide

(*Q*)  $\rightarrow$ 2° alkyl halide, rate is minimum.

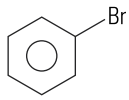
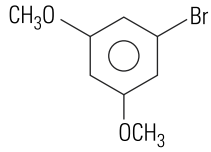
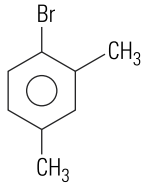
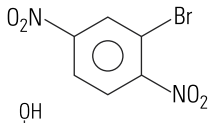
(*R*)  $\rightarrow$ 1° allylic halide but allylic 1° carbonation is resonance stabilised in S_N1 reactions.

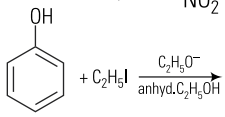
(*S*)  $\rightarrow$ 1° alkyl halide but C—Cl bond is weak hence, rate is maximum. Bond energy is decreased by electron withdrawing group [C_6H_5CO] (a case of –*I*-effect).

Step III Arrange the rate of given alkyl halides on the basis of the factors given in step II. *S* > *P* > *R* > *Q*.

TRY THESE

1. Which of the following compound is most likely to undergo a bimolecular nucleophilic substitution reaction with *aq.* NaOH?

(a) 
(b) 
(c) 
(d) 

2. The product of the following reaction is 

(a) $C_6H_5OC_2H_5$ *(b)* $C_2H_5OC_2H_5$ *(c)* $C_6H_5OC_6H_5$ *(d)* C_6H_5I

1. (d) **2.** (a)

3 The S_N1 reactivity of the following halides will be in the order.

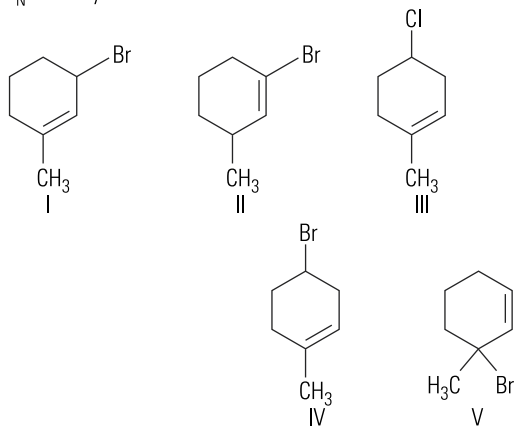
I. $(CH_3)_3CBr$ II. $(C_6H_5)_2CHBr$
III. $(C_6H_5)_2C(CH_3)Br$ IV. $(CH_3)_2CHBr$
V. C_2H_5Br

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

› ***(c)*** ***Step I*** S_N1 reactions occurs in two steps therefore, stability of intermediate, i.e. carbocation decides the rate of reactions. Write the relation between rate of S_N1 reactions and stability of carbocation.
Rate of S_N1 reaction ∝ stability of carbocation
Step II Arrange the given halides on the basis of stability of carbocation $(C_6H_5)_2\overset{+}{C}(CH_3) > (C_6H_5)_2\overset{+}{C}H > (CH_3)_3\overset{+}{C}$
$> (CH_3)_2\overset{+}{C}H > CH_3\overset{+}{C}H_2$
Step III Now, arrange the given halides on the basis of decreasing rate of S_N1 reaction.
$(C_6H_5)_2C(CH_3)Br > (C_6H_5)_2CHBr > (CH_3)_3CBr >$
(III) (II) (I)
$(CH_3)_2CHBr > C_2H_5Br$
(IV) (V)

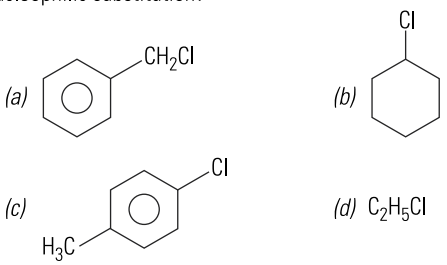
TRY THESE

1. The correct increasing order of the following with the relative rate of S_N1 solvolysis with methanol and heat will be



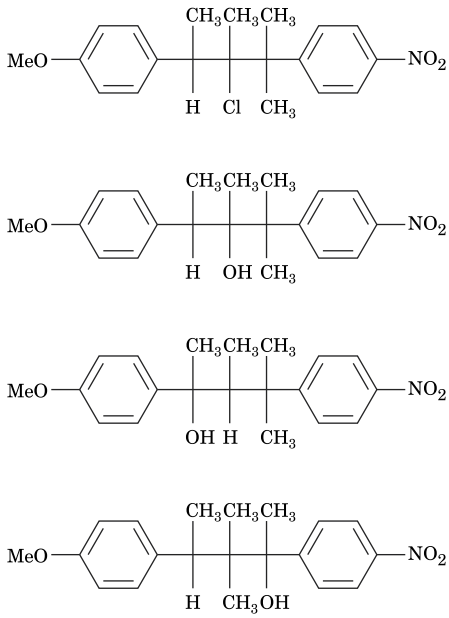
(a) III < II < IV < V < I *(b)* II < III < IV < I < V
(c) V < IV < III < II < I *(d)* II < III < IV < V < I

2. Which of the following will be the least reactive towards nucleophilic substitution?



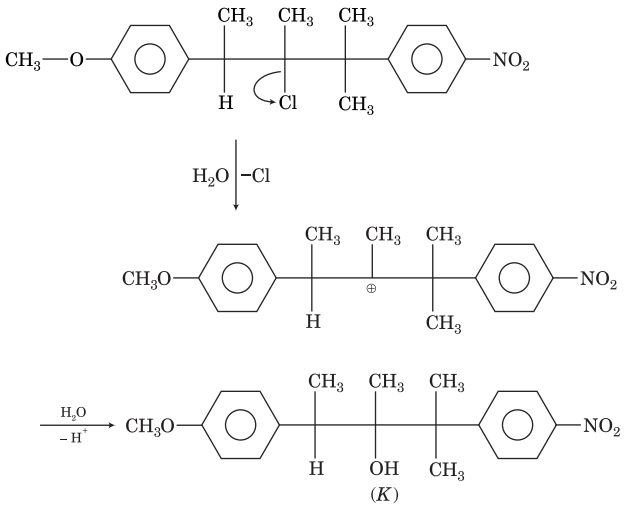
› **1.** (b) **2.** (c)

4 The following compound on hydrolysis in aqueous acetone will give [IIT JEE 2005]

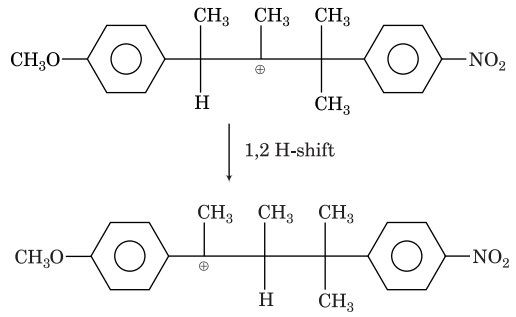


It mainly gives
(a) *K* and *L*
(b) Only *K*
(c) *L* and *M*
(d) Only *M*

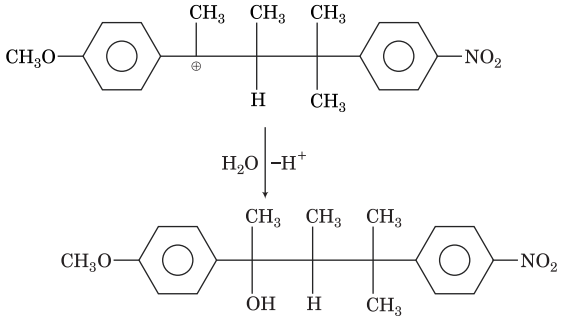
› ***(a)*** ***Step I*** Write the product by hydrolysis of the given compound through simple nucleophilic substitution.



Step II Since, the carbocation formed during Step I contains methoxy group. Hence, carbocation can undergo ~H^- shift to form stable carbocation.



Step III The finally formed carbocation undergo hydrolysis and formed the major product (*L*).



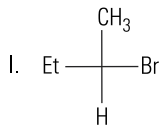
(*L*)

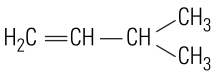
TRY THESE

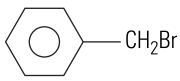
1. The alkyl halide that undergoes S_N1 reaction more readily is

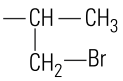
(a) ethyl bromide
(b) iso-propyl bromide
(c) vinyl bromide
(d) *t*-butyl bromide

2. Which of the following compounds will give racemic mixture by S_N1 reaction?

I. 

II. 

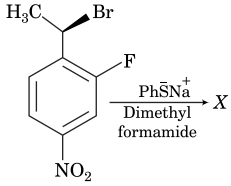
III. 

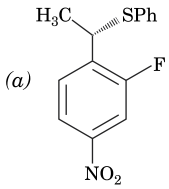
IV. 

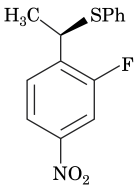
(a) Only I
(b) I and II
(c) II and III
(d) All of the above

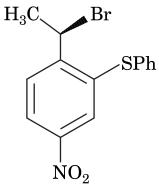
1. (d) **2.** (b)

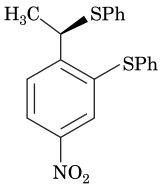
5 The major product (*X*) of the following reaction is



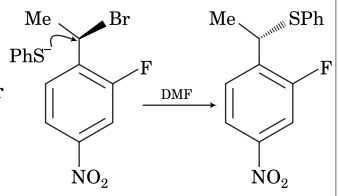
(a) 

(b) 

(c) 

(b) 

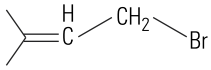
(a) ***Step I*** Identify the nature of reagents, PhS^-Na^+ and dimethyl formamide (DMF).
PhS^- is a strong nucleophile and dimethyl formamide (DMF) is a highly polar aprotic solvent.
Step II Identify whether the given reactants undergo reaction *via* S_N1 or S_N2 mechanism.
The condition as given in Step I indicates that nucleophilic substitution (S_N2) takes place at 2° benzylic place, stereochemically.
Step III Identify whether the product formed *via* inversion or retention of configuration and carry out the reaction.

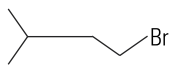


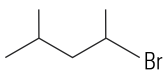
It involves inversion of configuration as it proceeds *via* S_N2 mechanism.

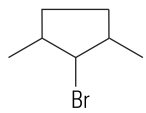
TRY THESE

1. Which one of the following alkyl bromides undergoes most rapid solvolysis in methanol solution to give corresponding methyl ether?

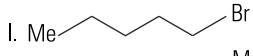
(a) 

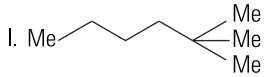
(b) 

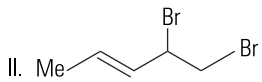
(c) 

(d) 

2. Which one of the following halides will be most reactive for S_N2 and S_N1 reaction, respectively?

I. 

I. 

II. 

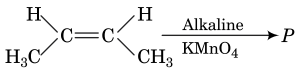
(a) I and II *(b)* II and I *(c)* I and III *(d)* Only III

1. (a) **2.** (c)

BRAIN TEASERS

To boost up your rank in JEE Main and Advanced

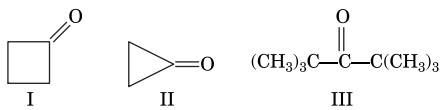
1. Which of the following statements is true for the reaction given below?



(a) *P* is a *meso* compound 2,3-butane-diol formed by *syn*-addition
(b) *P* is a *meso* compound 2,3-butane-diol formed by *anti*-addition
(c) *P* is a racemic mixture of *d*- and *l*-2,3-butane-diol formed by *syn*-addition
(d) *P* is a racemic mixture of *d*- and *l*-2,3-butane-diol formed by *anti*-addition

2. One mole crystal of a metal halide of the type *MX* with molecular weight 119 g mol^{-1} having face centred cubic structure with unit cell length 6.58 Å was recrystallised. The density of the recrystallised crystal was found to be 2.44 g cm^{-3}. The type of defect introduced during the recrystallisation is [NSEC 2016]
(a) additional M^+ and X^- ions at interstitial sites
(b) Schottky defect
(c) *F*-centre
(d) Frenkel defect

3. Arrange the following in the order of increasing value of the equilibrium constant for hydration.



I II III

(a) I < II < III *(b)* III < I < II
(c) II < I < III *(d)* II < III < I

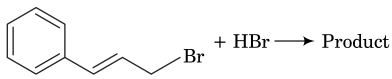
4. Vinegar is used in food preservation. The main ingredient of vinegar is acetic acid that gives it a pungent taste. A sample of vinegar has 5% *V*/*V* acetic acid. The density of acetic acid is 1.05 g mL^{-1}. Calculate the pH of the above vinegar sample (K_a for acetic acid = 1.75×10^{-5}). [INChO 2015]
(a) 3.218 *(b)* 2.407 *(c)* 4.614 *(d)* 3.718

5. Which of the following phenol is most soluble in aqueous sodium bicarbonate? [NSEC 2013]
(a) 2, 4-dihydroxyacetophenone
(b) *p*-cyanophenol
(c) 3, 4-dicyanophenol
(d) 2, 4, 6-tricyanophenol

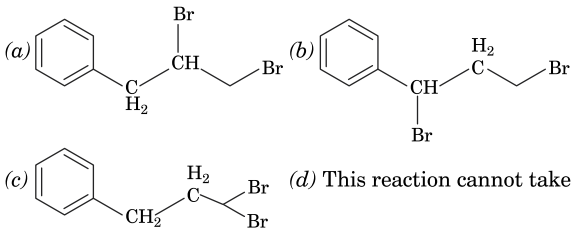
6. Which of the following salts produces the most basic solution? [NSEC 2013]
(a) $Al(CN)_3$ *(b)* $KC_2H_3O_2$ *(c)* $FeCl_3$ *(d)* KCl

7. The degree of dissociation of $Ca(NO_3)_2$ in a dilute aqueous solution containing 7g of the salt per 100 g of water at 100°C is 70 per cent. If the vapour pressure of water at 100°C is 760 mm. The vapour pressure of solution is
(a) 780.7 mm *(b)* 746.0 mm *(c)* 720.8 mm *(d)* 792.8 mm

8.



The product in the above reaction is [NSEC 2012]



(d) This reaction cannot take place

9. A DNA sample stored at 4°C was removed from the refrigerator and heated in a hot water bath with temperature increasing gradually. Which bond of the DNA molecule will break first?
(a) Phosphodiester bond *(b)* Glycosidic linkage
(c) Hydrogen bond *(d)* Covalent bond

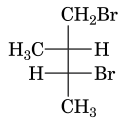
10. Saccharin ($K_a = 2 \times 10^{-12}$) is a weak acid represented by formula HSaC. If 4×10^{-4} mole of saccharin is dissolved in 200 cm^3 water of pH 3.

BRAIN TEASERS

Assuming no change in volume, calculate the concentration of SaC^- ions in the resulting solution at equilibrium.
(a) 4×10^{-10} M *(b)* 4×10^{-12} M
(c) 2×10^{-12} M *(d)* 2×10^{-10} M

11. A certain radioisotope ${}^{A}_{Z}X$ (half-life = 10 days) decays to ${}^{A-4}_{Z-2}Y$. If 1g atom of ${}^{A}_{Z}X$ is kept in sealed vessel, the helium accumulate in 20 days will be
(a) 16800 mL *(b)* 27000 mL *(c)* 18200 mL *(d)* 13200 mL

12. The *R*/*S* designation for the following stereoisomer of 1, 3 dibromo-2-methylbutane is



(a) 2*R*, 3*R* *(b)* 2*R*, 3*S* *(c)* 2*S*, 3*R* *(d)* 2*S*, 3*S*

13. The pK_a value of picric acid, acetic acid and phenol are in the order
(a) picric acid-0.4, acetic acid-4.75, phenol-10.0
(b) acetic acid-0.4, picric acid-4.75, phenol-10.0
(c) picric acid-0.4, phenol-4.75, acetic acid-10.0
(d) phenol-0.4, acetic acid-4.75, picric acid-10.0

14. The number of 'α' and 'β' particles emitted when ${}_{90}Th^{234}$ changes into ${}_{84}Po^{218}$ are, respectively
(a) 4 and 2 *(b)* 2 and 4 *(c)* 3 and 6 *(d)* 6 and 3

15. At 0°C, ice and water are in equilibrium and enthalpy change for the process, $H_2O(s) \rightleftharpoons H_2O(l)$ is 6 kJ mol^{-1}. The entropy change for the conversion of ice into liquid water is
(a) 22.61 $JK^{-1}mol^{-1}$ *(b)* 21.98 $JK^{-1}mol^{-1}$
(c) 25.32 $JK^{-1}mol^{-1}$ *(d)* 28.61 $JK^{-1}mol^{-1}$

16. In a nitration experiment, 10 g of benzene gives 13.2 g of nitrobenzene. The percentage yield of nitrobenzene is
(a) 62.7% *(b)* 88.9% *(c)* 26.7% *(d)* 83.5%

17. A decapeptide (molecular weight 796 $gmol^{-1}$) on complete hydrolysis gives glycine (molecular weight 75 $gmol^{-1}$), alanine and phenyl alanine. Glycine contributes 47% to the total weight of the hydrolysed products. The number of glycine units present in the decapeptide is
(a) 4 *(b)* 3 *(c)* 6 *(d)* 5

18. You are provided with two solutions of non-volatile solute *A* and *B* with the molar mass ratio $\left(\frac{M_A}{M_B}\right)$ of $\frac{1}{3}$. 5% (by weight) aqueous solution was prepared for both *A* and *B* and ratio of the freezing point depression is $\frac{(\Delta T_f)_A}{(\Delta T_f)_B}$ of the solutions. If you mixed two solutions to prepare two new solutions S_1 and S_2, considering the mixing ratio being 2 : 3 and 3 : 2 by volume for S_1 and S_2, respectively. The ratio $\frac{(\Delta T_f)_{S_1}}{(\Delta T_f)_{S_2}}$ will be
(a) 11/9 *(b)* 9/11 *(c)* 23/16 *(d)* 16/23

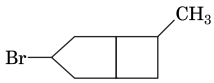
19. A student dissolved a silver coin of weight 5.82 g in nitric acid. When he/she added sodium chloride to the solution, all the silver is precipitated as AgCl. The AgCl precipitate weighs 7.20 g. The percentage of silver in the coin will be
(a) 84.2% *(b)* 78.1% *(c)* 81.6% *(d)* 93.1%

20. Which of the following observation indicates colligative properties? [NSEC 2016]
I. A 0.5 M NaBr solution has a higher vapour pressure than 0.5 M $BaCl_2$.
II. A 0.5 M NaOH solution freezes at a lower temperature than pure water.
III. Pure water freezes at a higher temperature than pure ethanol.
(a) Only I *(b)* Only II *(c)* Only III *(d)* I and II

21. The maximum amount of CH_3Cl that can be prepared from 20 g of CH_4 and 10 g of Cl_2 by the following reaction, $CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$, is (Assuming that no other reaction is taking place).
(a) 3.625 mole *(b)* 0.365 mole *(c)* 0.141 mole *(d)* 1.41 mole

22. An aqueous solution containing 28% by mass of a liquid *A*(mol. mass = 140 g mol^{-1}) has a vapour pressure of 160 mm at 37°C. The vapour pressure of the pure liquid *A* (vapour pressure of water at 37°C is 150 mm) will be
(a) 280 mm *(b)* 348 mm *(c)* 390 mm *(d)* 360 mm

23. The correct IUPAC name of the following compound is [NSEC 2012]



(a) 2-bromo-5-methylbicyclo [5.4.0] heptane
(b) 3-bromo-7-methylbicyclo [3.2.0] heptane
(c) 3-bromo-6-methylbicyclo [3.2.0] heptane
(d) 2-methyl-6-bromobicyclo [2.3.0] heptane

24. The factor by which the rate of first order reaction is increased for a temperature rise of 10°C from 25°C to 35°C. If the energy of activation is 35 kcal mol^{-1} will be
(a) 7.212 *(b)* 8.123 *(c)* 6.812 *(d)* 9.214

25. An enzyme working at pH 4.5 became inactive when treated with a hydrophobic surfactant. The enzyme may be
(a) cytosolic
(b) extracellular
(c) peripheral membrane bound
(d) integral membrane bound

Answers

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

TARGET CBSE 2017

TEST DRIVE

Comprehensive Simulator Test Series for JEE Main & Advanced

BOARD EXAM

(PAPER ONE PREP UP)

Typical Questions with Crispy Solutions

HALF TEST 1

(XII SYLLABUS) WITH SOLUTIONS

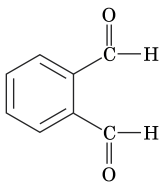
INSTRUCTIONS

- All questions are compulsory.
- Question numbers 1 to 5 are very short answer type questions and carry 1 mark each.
- Question numbers 6 to 10 are short answer type I questions and carry 2 marks each.
- Question numbers 11 to 22 are also short-answer type II questions and carry 3 marks each.
- Question numbers 23 is a value based type question and carry 4 marks.
- Question numbers 24 to 26 are long-answer type questions and carry 5 marks each.
- Use log tables, if necessary. Use of calculators is not allowed.

Very Short Answer Type Questions [1 Mark]

1. Why does Frenkel defect not change the density of AgCl crystals?

2. Write the IUPAC name of the given compound.



3. What happens when ethyl chloride is treated with aqueous KOH?

4. Give an example where physisorption changes to chemisorption with rise in temperature?

5. $Pb(NO_3)_2$ on heating gives a brown gas which undergoes dimerisation on cooling. Identify the gas. [All India 2016]

Short Answer Type I Questions [2 Marks]

6. The rate law for the reaction,

$CH_3COOC_2H_5 + H_2O \xrightarrow{H^{\oplus}} CH_3COOH + C_2H_5OH$

is $\frac{dx}{dt} = k[CH_3COOC_2H_5][H_2O]^0$

What would be the effect on the rate if

(i) concentration of $CH_3COOC_2H_5$ is doubled?

(ii) concentration of H_2O is doubled?

7. 18 g glucose, $C_6H_{12}O_6$ (molar mass = 180 g mol^{-1}) is dissolved in 1 kg of water in a sauce pan. At what temperature will this solution boil?

(K_b for water = 0.52 K kg mol^{-1}, boiling point of pure water = 373.15 K). [Delhi 2013]

8. Write the chemical equations involved in the following reaction:

(i) Etard reaction

(ii) Hell-Volhard-Zelinsky reaction

9. (i) Write the IUPAC name of $[Co(H_2NCH_2CH_2NH_2)_3]_2(SO_4)_3$

(ii) $[Co(CN)_6]^{3-}$ and $[CoF_6]^{3-}$ both are octahedral complexes. Then, what is the difference between the two?

10. Write the structures of the following compounds.

(i) BrF_3 (ii) XeF_4

OR

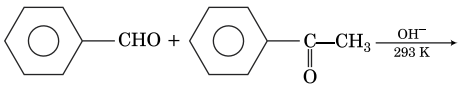
What happens when

(i) SO_2 gas is passed through on aqueous solution of Fe^{3+} salt? [All India 2016]

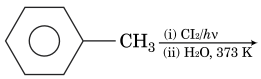
(ii) XeF_4 reacts with SbF_5?

Short Answer Type II Questions [3 Marks]

11. Write the final product(s) in each of the following reactions:

(i) 

(ii) $CH_3—CH_2—C\equiv N \xrightarrow[(ii)\ H_3O^+]{(i)\ C_6H_5MgBr/ether}$

(iii) 

12. How do you convert

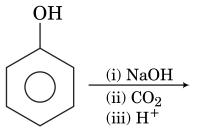
(i) phenol to benzyl alcohol?

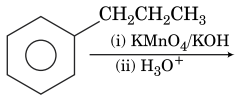
(ii) acetaldehyde to butane-1, 3-diol?

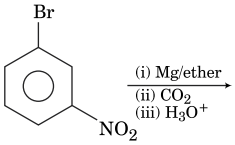
(iii) acetone to propene?

OR

Write the major product(s) in the following reactions.

(i) 

(ii) 

(iii) 

13. (i) Deficiency of which vitamin causes night blindness?

(ii) Name the base that is found in nucleotide of RNA only.

(iii) Glucose on reaction with HI gives *n*-hexane. What does it suggest about the structure of glucose? [All India 2014]

14. (i) Name the method used for refining of zirconium.

(ii) The reduction of a metal oxide is easier if the metal formed is in liquid state at the temperature of reduction. Why?

(iii) What is the role of cryolite in the metallurgy of aluminium.

15. Give reason for the following.

(i) Halogens are strong oxidising agent.

(ii) Noble gases form compounds with fluorine and oxygen only.

(iii) HF is the weakest acid among hydrohalo acids inspite of the fact that fluorine is most electronegative.

16. (i) Write the IUPAC name of the complex $[Cr(NH_3)_4Cl_2]Cl$.

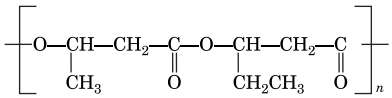
(ii) What type of isomerism exhibited by the complex $[Co(en)_3]^{3+}$? (en = ethane -1, 2-diamine).

(iii) Why $[NiCl_4]^{2-}$ is paramagnetic but $[Ni(CO)_4]$ is diamagnetic? [Delhi 2014]

17. An element *X* crystallises in body-centred cubic structure. If the edge length of the cell is 1.5×10^{-10} m and density is 15.5 g cm^{-3}. Calculate the atomic mass of this element.

18. (i) How does vulcanisation change the character of natural rubber?

(ii) Identify the monomers in the following polymer



(iii) Natural rubber can be stretched and exhibit elastic properties. Why?

19. 1.00 g of a non-electrolyte solute when dissolved in 50 g of benzene lowered the freezing point of benzene by 0.40 K. Find the molar mass of the solute. (K_f for benzene = 5.12 K kg mol^{-1}] [All India 2013]

20. Give reason for the following

(i) Reactivity of $—NH_2$ group gets reduced in acetanilide.

(ii) Aniline does not undergo Friedel-Craft's reaction.

(iii) Bromination of aniline at room temperature gives 2, 4, 6-tribromoaniline instantaneously

21. Define the following terms.

(i) Lyophobic colloids (ii) Peptisation

(iii) Hardy-Schulze rule

22. A solution is prepared by dissolving 10 g of non-volatile solute in 200 g of water. It has a vapour pressure of 31.84 mm of Hg at 308 K. Calculate the molar mass of the solute (vapour pressure of pure water at 308 K = 32 mm of Hg). [All India 2015]

Value Based Type Question [4 Marks]

23. Annu works in a company. She is stressed due to his hectic schedule. Rani, her friend, comes to know that she has started taking sleeping pills without consulting the doctor. Rani requests Annu to stop this practice and takes her to a yoga centre. With regular Yoga sessions, Annu is now a happy and relaxed girl.

After reading the above passage, answer the following questions.

(i) Write the value shown by Rani.

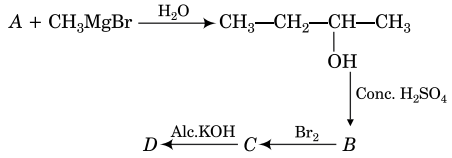
(ii) Which class of drugs is used in sleeping pills?

(iii) Why is it not advisable to take sleeping pills without consulting with the doctor?

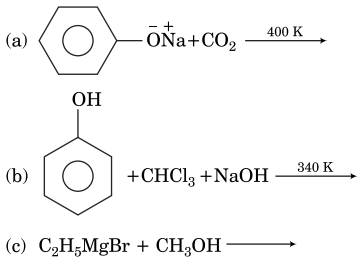
(iv) Give an example of drug used to treat mood changes and depression.

Long Answer Type Questions [5 Marks]

24. (i) Write the structural formula of the organic compounds *A*, *B*, *C* and *D* in the following sequence of reactions:



(ii) Complete the following equations and name the products formed.



OR

(i) Ethereal solution of an organic compound '*A*' when heated with Mg give '*B*'. *B* on treatment with ethanal followed by acid hydrolysis gave 2-propan-2-ol. Identify the compound '*A*' and identify '*B*'.

(ii) How will you distinguish between the following pairs by chemical reactions?

(a) CH_3OH and C_2H_5OH

(b) propan-1-ol and 2-methyl propan-2-ol

(c) Ethanol and propan-1-ol

25. (i) For a cell,

$Ag(s) \mid AgNO_3(0.01\ M) \parallel AgNO_3(1.0\ M) \mid Ag(s)$

(a) Calculate the emf of the cell at 25°C

(b) Write the net cell reaction

(c) Will the cell generate emf when two concentrations become equal.

(ii) The emf of a cell corresponding to the reaction.

$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(0.1M) + H_2(g, 1\ atm)$

is 0.28 V at 25°C.

Write the half-cell reactions and calculate the pH of the solution at the hydrogen electrode.

$E^\circ_{Zn^{2+}/Zn} = -0.76\ V,\ E^\circ_{H^+/H_2} = 0\ V.$

OR

(i) How long will it take for an electric current of 0.15 A to deposit all the copper from 500 mL of 0.15 M copper sulphate solution.

(ii) (a) Predict whether F_2 and Na will react with one another. Give reason

$E^\circ_{F_2/F^-} = +2.87\ V,$

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

(b) What do you mean by cell constant?

26. (i) Account for the following,

(a) Mn shows the highest oxidation state of +7 with oxygen but with fluorine, it shows the highest oxidation state of + 4.

(b) Cr^{2+} is a strong reducing agent.

(c) Cu^{2+} salts are coloured while Zn^{2+} salts are white.

(ii) Complete the following equations :

(a) $2MnO_2 + 4KOH + O_2 \xrightarrow{\Delta}$

(b) $Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow$

OR

The element of 3*d*-transition series are given as

Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn

Answer the following.

(i) Write the element which shows maximum number of oxidation states. Give reason.

(ii) Which element has the highest melting point?

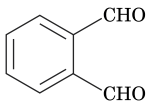
(iii) Which element shows only +3 oxidation state?

(iv) Which element is a strong oxidising agent in +3 oxidation state and why? [All India 2016]

Answers with Explanation

1. In Frenkel defect, smaller ion is dislocated from its normal site to an interstitial site, i.e. no ion is missing from the lattice. Hence, the density remain same.

2.



IUPAC name → Benzene-1, 2-dicarbaldehyde

3. Bimolecular nucleophilic substitution (S_N2) reaction occurs.

$C_2H_5Cl + KOH(aq) \longrightarrow C_2H_5OH + KCl$

4. Adsorption of H_2 on finely divided nickel (physisorption) involves weak van der Waal's forces. When temperature is increased, hydrogen molecules dissociate into hydrogen atoms, form chemical bonds with the metal atoms at the surface (chemisorption).

5. NO_2 gas, reactions involved are given as below:

$$2Pb(NO_3)_2 \xrightarrow{\Delta} 2PbO + \underset{\text{(Brown gas)}}{4NO_2} + O_2$$

$$2NO_2 \xrightarrow{\text{On cooling}} N_2O_4$$

6. The given reaction is an example of pseudo first order.

(i) If concentration of $CH_3COOC_2H_5$ is doubled then the rate of reaction will also get doubled.

(ii) In the given rate equation, the term $[H_2O]$ can be taken as constant, hence there is no effect on rate on changing the concentration of H_2O.

7. Given, $w_{solvent}$ = Weight of H_2O = 1 kg

w_{solute} = Weight of $C_6H_{12}O_6$ = 18 g.

T_b° = 373.15 K

K_b = 0.52 K kg mol^{-1}

M_{solute} = Molar mass of glucose = 180 g mol^{-1}

$$\Delta T_b = \frac{K_b \times 1000 \times w_{solute}}{M_b \times w_{solvent}}$$

$$\Delta T_b = \frac{(0.52) \times 1000 \times 18}{180 \times 1000} = 0.052 \text{ K}$$

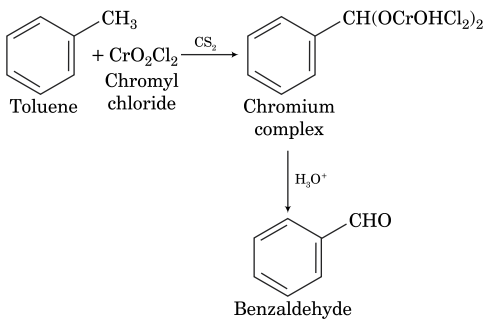
As we know that,

$\Delta T_b = T_b - T_b^\circ$

$\Rightarrow$ $0.052 = T_b - 373.15$

$\Rightarrow$ $T_b = 373.15 + 0.052 = 373.202$ K

8. (i)



(ii) $R—CH_2COOH \xrightarrow[(ii)\ H_2O]{(i)\ X_2 /\ \text{Red P}} R—\underset{\displaystyle X}{\underset{|}{CH}}—COOH$

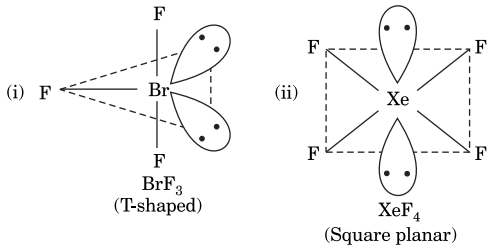
α-halocarboxylic acid

where, X = Cl, Br

9. (i) $[Co(H_2NCH_2CH_2NH_2)_3]_2(SO_4)_3$ is named as *tris* (ethane-1, 2-diammine) cobalt (III) sulphate.

(ii) $[Co(CN)_6]^{3-}$ is an inner orbital or low spin complex involving the hybridisation, d^2sp^3 while $[CoF_6]^{3-}$ is an outer orbital or high spin complex involving sp^3d^2-hybridisation.

10.



OR

(i) SO_2 gas reduces Fe^{3+} to Fe^{2+}

$SO_2 + 2Fe^{3+} + 2H_2O \longrightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$

(ii) XeF_4 reacts with covalent pentafluoride (SbF_5) to form an adduct.

$XeF_4 + SbF_5 \longrightarrow XeF_4 \cdot SbF_5$ or $[XeF_3^+][SbF_6^-]$

TARGET CBSE 2017

TEST DRIVE

Comprehensive Simulator Test Series for JEE Main & Advanced

BOARD EXAM

(PAPER TWO SCALE UP)

Typical Questions without Solutions

HALF TEST 2 (XII SYLLABUS) UNSOLVED

INSTRUCTIONS

- All questions are compulsory.
- Questions number 1 to 5 are very short answer type questions and carry 1 mark each.
- Questions 6 to 10 are short answer type I questions and carry 2 marks each.
- Question number 11 to 22 are also short answer type II questions and carry 3 marks each.
- Question number 23 is a value based type questions and carry 4 marks.
- Question number 24 to 26 are long-answer type questions and carry 5 marks each.
- Use log table, if necessary. Use of calculators is not allowed.

Very Short Answer Type Questions [1 Mark]

1. Give the IUPAC name of the following compounds.
(i) $[Ag(NH_3)_2][Ag(CN)_2]$ (ii) $[Co(NH_3)_5SCN]Cl_2$

2. Which compound is used for smoke screens and Holme's signals?

3. A compound formed by elements X and Y, crystallises in the cubic structure, where Y atoms are at the corners of a cube and X atoms are at alternate faces. What is the formula of the compound?

4. Why aniline doesn't undergo Friedel-Crafts reaction?
[All India 2011, Delhi 2008]

5. Write the two examples of reversible colloids.

Short Answer Type I Questions [2 Marks]

6. Among 0.1 M glucose, 0.15 M urea and 0.2 M sucrose solutions.
(i) Which solution exhibit lowest freezing point and highest boiling point?
(ii) Which solution contains highest number of particles in their solution?

7. Why special methods are used to prepare HBr and HI?

8. Define homoleptic and heteroleptic complexes.

9. The reaction, $A \rightarrow B$ follows first order kinetics. The time taken for 0.8 mole of A to produce 0.6 mole of B is 1 h. Calculate the time required for the conversion of 0.9 mole of A to 0.675 mole of B ?

10. (i) Explain Libermann's nitroso reaction.
(ii) Which of the following compounds will react faster in S_N1 reaction with the hydroxide ion.
CH_3CH_2Cl or $C_6H_6CH_2Cl$?

OR

Give, simple chemical tests to distinguish between the following pair of compounds.
(i) Benzaldehyde and acetophenone.
(ii) Pentan-2-one and pentan-3-one.
[All India 2012, 2013]

Short Answer Type II Questions [3 Marks]

11. CsBr crystallises in a body-centred cubic lattice with unit cell length of 436.6 pm. Given, that the atomic mass of Cs = 133 u and that of Br = 80 u and Avogadro's number is 6.02×10^{23} mol^{-1}. Calculate the density of CsBr.

12. A first order reaction takes 40 min for 30% decomposition. Calculate $t_{1/2}$ for this reaction.
(Given, log 1.428 = 0.1548)

13. Explain the following.
(i) Charge on colloidal particles
(ii) Kraft temperature (iii) Coagulating value

14. (i) Define the terms, froth stabilisers and depressants.
(ii) Give the reaction of Mac-Arthur Forest cyanide process.
(iii) Explain the thermite process.

15. Calculate the vapour pressure of a solution at 100°C containing 3 g of cane sugar in 33 g of water.
(Atomic weight of C = 12, H = 1, O = 16)

16. (i) Write chemical reaction which is used for distinguishing between thiosulphate and sulphite.
(ii) Sulphur has a greater tendency for catenation than oxygen. Why?
(iii) Which compound is used in manufacturing of nitrocellulose membrane?

17. Write short notes on the following reactions.
(i) Stephen (ii) Fittig (iii) Wurtz-fittig

18. (i) Why we do not use $CaCl_2$ (anhydrous) to get dry CH_3OH or C_2H_5OH?
(ii) Sodium metal can be used to dry diethyl ether but not for ethanol. Why?
(iii) Arrange the following compounds in increasing order of acidic strength.
$(CH_3)_2CHCOOH$, $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$.

19. How will you convert
(i) methanamine into ethanamine?
(ii) hexane-1-nitrile to 1-aminopentane?
(iii) methanol to ethanoic acid?

20. Write short notes on
(i) poly β-hydroxybutyrate-co-β-hydroxy valerate (PHBV).
(ii) nylon-2-nylon-6.
(iii) bakelite

21. (i) D-glucose only used in cold drinks but not in hot drinks. Justify.
(ii) Why sucrose is called 'invert sugar'.
(iii) Aldose react with Benedict's solution and phenyl hydrazine but not with $NaHSO_3$ or Schiff's reagent, why?

22. (i) Draw the geometrical isomers of
$[Pt(NH_3)py(NH_2—OH)(NO_2)]^+$
(ii) Anhydrous $CuSO_4$ is white while hydrated $CuSO_4$ is blue. Why?

Value Based Type Questions [4 Marks]

23. Ramu, a domestic helper of Mrs. Swati fainted while mapping the floor. Mrs. Swati immediately took him to the nearby hospital where, he was diagnosed with 'Pernicious anaemia'. The doctor prescribe an iron rich diet and multivitamins supplement to him. Mrs. Swati helped him financially to get the medicines. After sometime, Ramu was diagnosed to be normal.

Answer the following questions based on the above given passage.
(i) Name the vitamin whose deficiency causes 'Pernicious anaemia'.
(ii) Give an example of a fat soluble vitamin.
(iii) Write down the components of iron rich diet?
(iv) What values are shown by Mrs. Swati?

Long Answer Type Questions [5 Marks]

24. Calculate the standard emf, standard free energy change and equilibrium constant for the following redox reaction taking place in a galvanic cell at 25°C

$$Cu(s) + Cl_2(g) \rightleftharpoons Cu^{2+}(aq) + 2Cl^-(g)$$

OR

Molten aluminium chloride is electrolysed with a current of 0.5 A to produce 27.0 g of aluminium.
(i) How many gram equivalent of aluminium were produced?
(ii) How many gram atom of aluminium were produced?
(iii) How many electrons were consumed?
(iv) What is the number of Faraday of electricity?
(v) How long will the electrolysis take place?

25. Assign reason for the following.
(i) Copper (I) ion is not known in aqueous solution.
(ii) Transition metals and their compounds generally exhibit a paramagnetic behaviour.
(iii) $E^\circ_{M^{2+}/M}$ values are not regular for first row transition metal (3*d* series).
(iv) Mn^{3+} is a good oxidising agent.
(v) Nitrogen is much less reactive than phosphorus.

OR

(i) Zn^{2+} salts are white whereas Cu^{2+} salts are blue. Explain.
(ii) How is potassium dichromate prepared? Write only equations.
(iii) Give two applications of transition elements.
(iv) Complete the following reactions by replacing *A*, *B*, *C* and *D*.
(a) $Ag_2S + 4NaCN + 2O_2 \longrightarrow B + C$
(b) $2Ag + 4HNO_3 \longrightarrow A + 2NO_2 + D$

26. (i) A compound has two isomers (*A*) and (*B*) having formula $C_5H_{10}O$. Compound (*A*) on treatment with aqueous NaOH gives 2, 2-dimethyl propan-1-ol and 2,2-dimethyl propanoic acid salt. Compound (*B*) on treating with aqueous NaOH gives 3-hydroxy-2-propyl heptanol. What are (*A*) and (*B*)?
(ii) Give the chemical tests to distinguish between,
(a) methylamine and dimethylamine
(b) propanol and propanone.

OR

(i) Give the preparations of ketones
(a) from benzene (b) from nitriles.
(ii) Write the structures of products of the following reactions.
(a) $CH_3—C\equiv CH \xrightarrow{Hg^{2+},\ H_2SO_4} (P)$
(b) $R—CHOH \xrightarrow{Cu/573K} (P)$
(c) $CH_3COCH_3 + 4HI \xrightarrow[423\ K]{Red\ P} (P)$

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FUN ARCADE

Amedeo Avogadro

(09/08/1776-09/07/1856)

The full name of Amedeo Avogadro was **Lorenzo Romano Amedeo Carlo Avogadro di Quaregna e di Cerreto** was born on 9 August 1776 in Turin, Piedmont-Sardinia Italy into a noble family. He received a classical education in humanities, earned a doctorated in law in 1796 at the age of twenty, and practiced law for the next ten years. Around this time he grew increasingly interest in physics and mathematics and began studying these subjects. At that time, he put forth the hypothesis that "equal volumes of gases under the same conditions of pressure and temperature contain the same number of particles". Trained as a lawyer, Avogadro turned to the study of science and spent most of his career as chair of mathematical physics at Turin. Although he published widely on subjects in physics and chemistry, he was most famous for building on the work of French chemist **Joseph Louis Guy-Lussac** (1778-1850). Although his work was largely ignored during his lifetime, by the 1880's it was universally accepted.

Thanks to Stanislao Cannizzaro, who created a table of atomic weights based on Avogadro's work. Later physicists and chemists determined the value of "Avogadro's Number" the number of gas molecules in one mole as $\mathbf{6.022 \times 10^{23}}$, two years after Avogadro's death. Amedeo Avogadro died aged 79 on July 9th 1856 in Turin. He was buried in the cemetery of Quaregna.

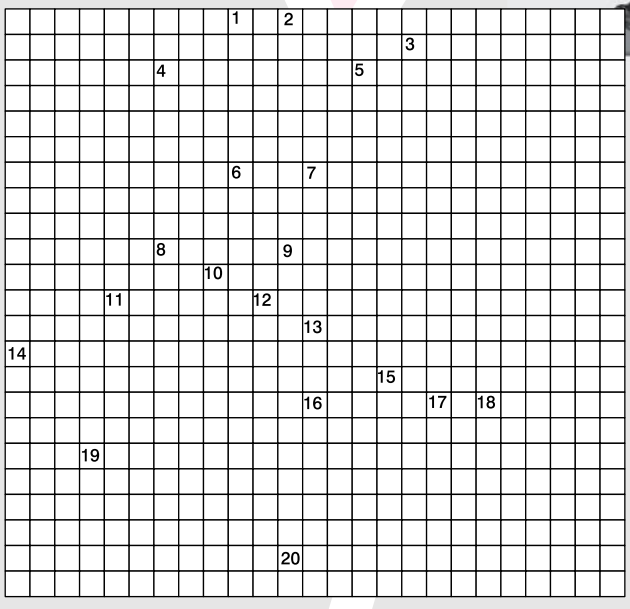
CROSSWORD

ACROSS

3. Covalent bonds are directional in nature hence covalent compounds exhibit ..... . (9)
4. An almost non-crystalline form of quartz or hydrated silica used as gemstone. (4)
6. In TLC technique amino acids may be detected by spraying the plate with ..... . (9)
9. The number of waves per second passing at a given point which is denoted by *v*. (9)
11. A process of heating organic compound in the absence of oxygen. (9)
13. The number of electron pairs shared by an atom of an element in the formation of covalent compound. (9)
14. The boiling point of acetic acid is more than that of ethyl alcohol even though both are associated by hydrogen bonds because acetic acid exist as ..... . (5)
16. A volumetric method used for the estimation of oxidising agent (e.g. $CuSO_4$, $K_2Cr_2O_7$) which liberate I_2 from acidified KI solution. (9)
19. A furnance for making bricks, ceramics and used for heating chalk to form lime and CO_2. (4)
20. A very hard natural form of silica, used for knife edge of balances and in ornamentals. (5)

DOWN

1. When Lassaigne's filtrate is acidify with nitric acid and mixed with silver nitrate, formation of precipitate indicates the presence of ..... (7)
2. 1, 1, 2, 2 chloro ethane or acetylene tetrachloro is called ..... (7)
3. A protein hormone that is secreted by the islets of langerhans in the pancreas. (7)
5. A compound of boron with a more electropositive element. (6)
7. A chemical substance that absorbs moisture from atmosphere. (11)
8. Substance containing calcium carbonate secreted by various marine animals. (5)
10. Addition of ozone to acetylene gives ozonide which on hydrolysis with Zn and water gives ..... (7)
11. The graph showing the relation between b.p. and number of carbon atom is a ..... (8)
12. The arrangement obtained by splitting of electromagnetic radiation into its component wavelength when passed through a prism is called. ..... (8)
15. A mineral containing phosphates of cerium, thorium and other rare earths, containing some occluded helium. (8)
17. Naturally occurring alloy of gold and silver (up to 45% Ag.) (8)
18. A glass vessel or a metallic vessel in which distillation takes place. (6)



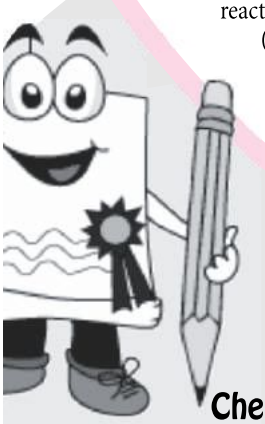
PUZZLES TO PUZZLE YOU

1. The inactivation of a viral preparation in a chemical bath is found to be a first-order reaction.
   (i) Calculate the rate constant for the viral inactivation if in the beginning 1.5% of the virus is inactivated per minute. Also, calculate the time required for
   (ii) 50% inactivation
   (iii) 80% inactivation of the virus.

2. A bottle of milk stored at 30°C sours in 36 hours and if stored in a refrigerator at 5°C sours after one week. Assuming the rate constant to be inversely related to the souring time, estimate the activation energy of chemical reaction involved in the souring reaction.

3. 10 g of a sample of bleaching powder was extracted with water and the solution made upto one litre. 25 mL of this solution were added to 50 mL of N/14 ferrous ammonium sulphate solution containing enough sulphuric acid. After the reaction was completed, the whole mixture requires 22 mL of $KMnO_4$ solution containing 2.271 g of $KMnO_4$ per litre for complete oxidation. Calculate the percentage of available chlorine in the sample of bleaching powder.

4. A white crystalline solid (*A*) swells up on heating and gives violet coloured flame on burning. Its aqueous solution gives the following reactions.
   (i) White ppt. with $BaCl_2$ insoluble in acids.
   (ii) With excess of NH_4OH, white gelatinous ppt. is produced which dissolves in NaOH and reappears on addition of NH_4Cl.
   (iii) It gives yellow ppt. with sodium cobalt nitrite solution.
   Identify (*A*) giving equations involved.



November 2016 issue Answers

(Crossword)

1,5 C	10 O	2 M	B	U	S	T	3 I	O	N	17 D		6 A	
O	X	O								I		N	
R	I	N					16 P	L	A	S	T	I	15 C
R	D	O		9 D		11,12 C	A	K	E	T		O	A
O	A	M		I		A				I		N	T
S	T	4 E	20 L	E	C	T	19 R	O	N	L		7 G	A
I	I	R	E	S		I	E			L		A	L
O	O		A	E		O	T			A		S	Y
N	N		C	L		N	E			T		O	S
			H				N			I		L	T
			I				T			O		I	
			N			8 O	I	L		N		N	
			G				O	18 C	A	L	X	E	
13 R	E	A	C	T	I	O	N	14 P	E	T	R	O	L

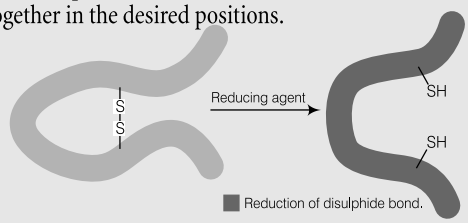
Puzzles to Puzzle you

1. 7.9×10^7 g CaO
2. 1.766% Cl^- by mass
3. $CH_3—\overset{\overset{O}{\|}}{C}—CH_2CH_3$
4. 3.9×10^{-9}

Chemical Connect

Waving and Straightening of Hair

- If you ever visit a salon for permanent waving or straightening of your curly hair.
- Keratin is a fibrous protein of hair that does have a predominantly α-helix structure.
- Keratin is completely insoluble in cold or hot water; it is not attached by proteolytic enzymes (i.e. enzymes that break apart, protein molecules).
- The great stability of keratin results from the numerous disulphide bonds of crystine.
- The peptide chains of keratin are arranged approximately equal amounts of antiparallel and parallel pleated sheets, in which the peptide chains are linked to each other by hydrogen bonds between the carbonyl and imino groups.
- The disulphide bonds are primarily responsible for the shape of the hair, whether straight or curly.
- In either permanent waving or straightening, the hair is first treated with a reducing agent that cleaves some of the —S—S— bonds.
- Reducing agents, such as 2-mercaptoethanol ($HOCH_2CH_2SH$), can break the —S—S— disulphide bonds, reducing them to —SH groups.
- The treatment allows the molecules to lose their rigid orientations and become flexible.
- The hair is then set into the desired shape by using curlers or rollers and an oxidising agent is applied.
- The oxidising agent reverses the preceding reaction forming new disulphide bonds, which now hold the molecules together in the desired positions.



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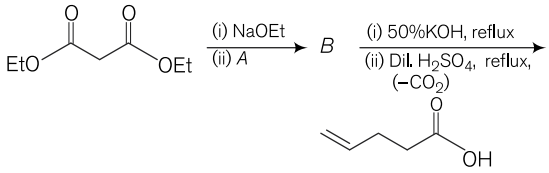
JUST SOLVE & SEND KNOWLEDGE COEFFICIENT QUIZZER (NO. 25)

1. Cobalt (II) chloride hexahydrate, dissolves readily in water to give a red solution. If we use this solution as an ink, we can write secret messages on paper. The writing is not visible when the water evaporates from the paper. When the paper is heated, however, the message can be read. Why?

2.



Identify *A* and *B*.

3. Name the product of elimination in the conversion of acyl chloride bearing acidic proton adjacent to carboxyl functional group into an amide.

4. A certain compound on burning in air produces three oxides. Out of these, one oxide turned lime water milky, the second one turned anhyd. $CuSO_4$ blue and third formed a solution of pH = 9. What are the constituents of compounds?

5. A slice of banana weighing 2.7 g was burned in oxygen in a bomb calorimeter and produced a temperature rise of 3.05 K. In the same calorimeter, the combustion of 0.316 g of benzoic acid produced a temperature rise of 3.24 K. $\Delta_C U$ for benzoic acid is $-3251\,kJ\,mol^{-1}$. If the average mass of a banana is 125 g, how much energy in kilo joule can be obtained on average from a banana?

Fill in the Blanks

6. ^{210}Pb decays into ^{206}Pb in a pathway involving two β-emissions followed by an α-emission. The intermediate isotopes are …… .

7. The class of organic reaction which do not require any solvent and neither they proceed *via* formation of intermediate is …… .

8. CS_2 readily undergoes insertion reactions introducing …… group in between a metal-nitrogen bond and also in some other bonds.

9. The ratio of …… in teeth provides a means of determining where a person might have lived at the time of their teeth formed.

10. The structure of α-boron consists of …… linked by B—B bonds and it is a regular polyhedron with 12 vertices and 20 triangular faces.

KNOWLEDGE Coefficient Quizzer (No. 25)

Write your answers on separate sheets and send to us along with this coupon

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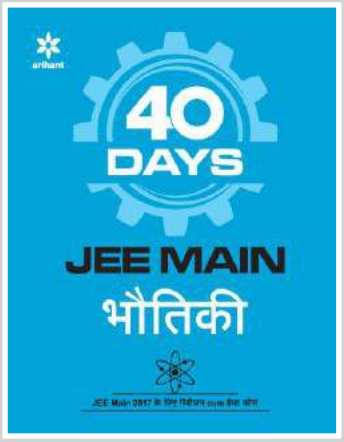

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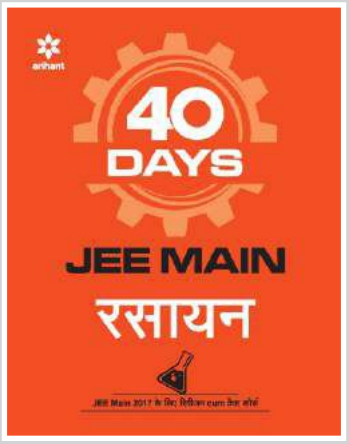

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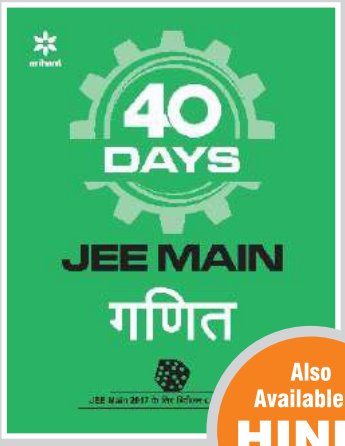

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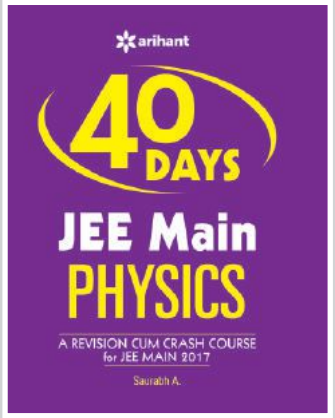

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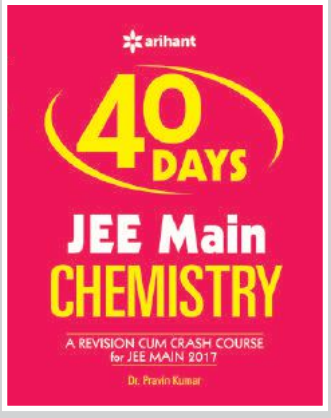

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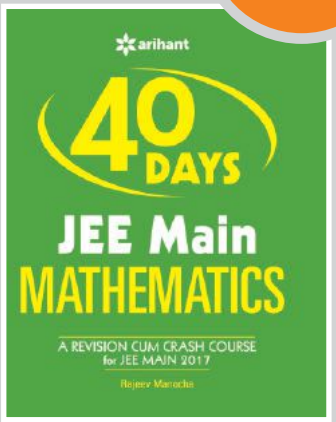

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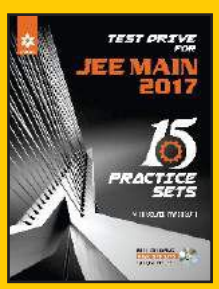

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