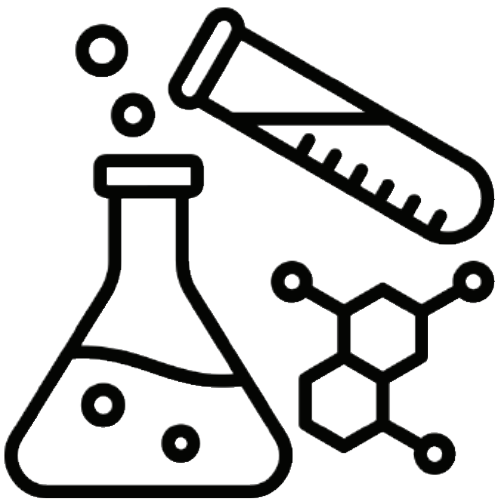
UPSC COMBINED
GEO-SCIENTIST

GEOCHEMIST

PRELIMINARY EXAMINATION

2020 to 2026

PAPER-II : CHEMISTRY



IfAS | IFAS Publications

Copyright at IFAS Publications

All rights reserved. No part of this publication or the information contained herein may be reproduced, adapted, abridged, translated, stored in a retrieval system, computer system, photographic or other systems or transmitted in any form or by any means, electronic, mechanical, optical, digital, by photocopying, recording or otherwise, without written prior permission from the publisher. Any breach will attract legal action and prosecution without further notice.

Disclaimer: While every effort has been made to avoid errors and omissions, this publication is being sold and marketed on the understanding and presumption that neither the editors (or authors) nor the publishers nor the printers would be liable in any manner whatsoever, to any person either for an error or for an omission in this publication, or for any action to be taken on the basis of this work. Any inadvertent discrepancy noted may be brought to the attention of the publisher, for rectifying it in future editions, if published.

This book contains information obtained from authentic and highly regarded sources. Reasonable efforts have been made to publish reliable data and information, but the editors and publisher cannot assume responsibility for the validity of all materials or the consequences of their use. The editors and publisher have attempted to trace and acknowledge the copyright holders of all material reproduced in this publication and apologize to copyright holders if permission and acknowledgement to publish in this form have not been obtained. If any copyright material has not been acknowledged please write and let us know so that we may rectify it.

Trademark Notice: Publications or corporate names may be trademarks, and are used only for identification and explanation in bonafide intent without intent to infringe.

Design & Published by:
IFAS Publications

Address:
Shivranjan Complex,
Someshwar Wadi, Near
Rajwada Hotel, Baner Road,
Pune 411 008.

Contact No.: **+91-960 489 7388**

Website: **https://ifasonline.com**

Price: ₹**895.00**

ISBN: **978-81-972973-3-5**

P R E F A C E

Welcome to the comprehensive guide for the **Geo-chemist Preliminary Examination**, a meticulously crafted resource designed to aid aspiring candidates in their journey towards achieving success in this prestigious examination. This book is a compilation of all the **previous years' questions (2020 to 2026)** from **Preliminary Examination**, sorted meticulously topic-wise, to provide an organized and efficient study experience.

The Combined Geo-Chemist Examination follows a three-tier pattern, ensuring a thorough evaluation of candidates' knowledge, skills, and suitability for the role. The examination stages are as follows:

Stage-I: Preliminary Examination

- The Preliminary Examination serves as a screening test for candidates aspiring to take the Main Examination (Stage-II).
- It is an objective type Computer Based Examination, comprising two papers.

Stage-II: Main Examination

- Candidates who qualify in the Preliminary Examination are eligible to appear for the Main Examination.
- Combined Geo- chemist (Main) Examination (Descriptive Type Papers)

Stage-III: Personality Test

- The final stage is the Personality Test, where candidates' suitability for the role is assessed through a series of interviews and evaluations.

This book has been structured to align with the examination pattern, offering a clear and systematic approach to preparation. Each section has a collection of previous years' questions categorized by topic. This method not only reinforces learning but also helps candidates understand the type and nature of questions that have been historically significant.

Key Features of the Book:

- **Topic-wise Sorted Questions**: All previous years' questions are organized by topic, allowing for focused and efficient study sessions.
- **Exam Pattern Insights**: Detailed information on the examination stages, providing clarity on the progression and requirements at each level.
- **Objective Type Questions**: Emphasis on the Preliminary Examination format to aid in acclimatizing to the computer-based objective type questions.

We believe that this book will serve as a valuable tool in your preparation, helping you to systematically approach the Geo-Chemist Examination with confidence and clarity. Our aim is to equip you with the knowledge and practice needed to excel at each stage of the examination process.

Wishing you the very best in your preparation and success in the examination.

Combined Geo-Scientist Examination Pattern

The CGSE exam pattern along with syllabus got changed for the examination from this year. The selection of the candidates will be based on three stages. We have described the detailed CGSE exam pattern for Preliminary and Main

Combined Geo-Scientist Examination will be conducted in three stages as follows:

1. **Stage I: Preliminary Examination**

Stream-III : Chemist		
Subject	**Duration**	**Maximum Marks**
Paper-I : General Studies	2 Hours	100 Marks
Paper-II : Chemistry	2 Hours	300 Marks
Total		**400 Marks**

2. **Stage II: Main Examination**

Stream-III : Chemist		
Subject	**Duration**	**Maximum Marks**
Paper-I : Chemistry	3 Hours	200 Marks
Paper-II : Chemistry	3 Hours	200 Marks
Paper-III : Chemistry	3 Hours	200 Marks
Total		**600 Marks**

3. **Stage III: Personality Test**
   Personality Test - **200 Marks**

Eligibility Criteria Nationality:

A CANDIDATE MUST BE EITHER:

(a) a Citizen of India, or
(b) a subject of Nepal, or
(c) a subject of Bhutan, or
(d) a Tibetan refugee who came over to India before the 1st January, 162 with the intention of permanently settling in India, or
(e) a person of Indian origin who has migrated from Pakistan, Burma, Sri Lanka or Eastern African Countries of Kenya, Uganda, the United Republic of Tanzania, Zambia, Malawi Zaire, and Ethiopia or from Vietnam with the intention of permanently settling in India.

Syllabus

Chemistry

- **Chemical periodicity:**

- Schrödinger equation for the H-atom. Radial distribution curves for 1s, 2s, 2p, 3s, 3p, 3d orbitals. Electronic configurations of multi-electron atoms.
- Periodic table, group trends and periodic trends in physical properties. Classification of elements on the basis of electronic configuration.
- IUPAC Periodic table. General characteristics of s, p, d and f block elements. Effective nuclear charges, screening effects, atomic radii, ionic radii, covalent radii. Ionization enthalpy, electron gain enthalpy and electronegativity. Group trends and periodic trends in these properties in respect of s-, p- and d-block elements. General trends of variation of electronic configuration, elemental forms, metallic nature, magnetic properties, catenation and catalytic properties, oxidation states, aqueous and redox chemistry in common oxidation states, properties and reactions of important compounds such as hydrides, halides, oxides, oxy-acids, complex chemistry in respect of s-block and p-block elements.

- C**hemical bonding and structure:**

- Ionic bonding: Size effects, radius ratio rules and their limitations. Packing of ions in crystals, lattice energy, Born-Landé equation and its applications, Born-Haber cycle and its applications. Solvation energy, polarizing power and polarizability, ionic potential, Fajan's rules. Defects in solids.
- Covalent bonding: Valence Bond Theory, Molecular Orbital Theory, hybridization. Concept of resonance, resonance energy, resonance structures.
- Coordinate bonding: Werner theory of coordination compounds, double salts and complex salts. Ambidentate and polydentate ligands, chelate complexes. IUPAC nomenclature of coordination compounds. Coordination numbers, Geometrical isomerism. Stereoisomerism in square planar and octahedral complexes.

- **Acids and bases:**

- Chemical and ionic equilibrium. Strengths of acids and bases. Ionization of weak acids and bases in aqueous solutions, application of Ostwald's dilution law, ionization constants, ionic product of water, pH-scale, effect of temperature on pH, buffer solutions and their pH values, buffer action & buffer capacity; different types of buffers and Henderson's equation.

- **Theoretical basis of quantitative inorganic analysis:**

- Volumetric Analysis: Equivalent weights, different types of solutions, normal and molar solutions. Primary and secondary standard substances.
- General principles of different types of titrations: i) acid-base, ii) redox, iii) complexometric, iv) Precipitation. Types of indicators - i) acid-base, ii) redox iii) metal-ion indicators

- **Kinetic theory and the gaseous state:**

- Kinetic theory of gases, average kinetic energy of translation, Boltzmann constant and absolute scale of temperature. Maxwell-Boltzmann distribution of speeds. Calculations of average, root mean square and most probable velocities. Page 9 of 29 Collision diameter; collision number and mean free path; frequency of binary collisions; wall collision and rate of effusion

- **Chemical thermodynamics and chemical equilibrium:**

- First law and its applications to chemical problems. Thermodynamic functions. Total differentials and state functions. Free expansion, JouleThomson coefficient and inversion temperature. Hess' law.
- Applications of Second law of thermodynamics. Gibbs function (G) and Helmholtz function (A), Gibbs-Helmholtz equation, criteria for thermodynamic equilibrium and spontaneity of chemical processes.

- **Solutions of non-electrolytes:**

- Colligative properties of solutions, Raoult's Law, relative lowering of vapour pressure, osmosis and osmotic pressure; elevation of boiling point and depression of freezing point of solvents. Solubility of gases in liquids and solid solutions.

- **Electrochemistry:**

- Cell constant, specific conductance and molar conductance. Kohlrausch's law of independent migration of ions, ion conductance and ionic mobility. Equivalent and molar conductance at infinite dilution. Debye-Hückel theory. Application of conductance measurements. Conductometric titrations. Determination of transport number by moving boundary method.

- **Basic organic chemistry:**

- Delocalized chemical bond, resonance, conjugation, hyperconjugation, hybridisation, orbital pictures of bonding sp3, sp2, sp: C-C, C-N and C-O system), bond polarization and bond polarizability. Reactive intermediates: General methods of formation, relative stability and reactivity of carbocations, carbanions and free radicals.

- **Stereochemistry:**

- Configuration and chirality (simple treatment of elements of symmetry), optical isomerism of compounds containing two to three stereogenic centres, R,S nomenclature, geometrical isomerism in compounds containing two C=C double bonds (E,Z naming), and simple cyclic systems, Newman projection (ethane and substituted ethane).

- **Types of organic reactions:**

- Aliphatic substitution reactions: SN1, SN2 mechanisms, stereochemistry, relative reactivity in aliphatic substitutions. Effect of substrate structure, Page 10 of 29 attacking nucleophile, leaving group and reaction medium and competitive reactions.
- Elimination reactions: E1, E2, mechanisms, stereochemistry, relative reactivity in aliphatic eliminations. Effect of substrate structure, attacking base, leaving group, reaction medium and competitive reactions, orientation of the double bond, Saytzeff and Hoffman rules.
- Addition reactions: Electrophilic, nucleophilic and radical addition reactions at carbon-carbon double bonds.
- Electrophilic and nucleophilic aromatic substitution: Electrophilic (halogenation, sulphonation, nitration, Friedal-Crafts alkylation and acylation), nucleophilic (simple SNAr, SN1 and aryne reactions).

- **Molecular Rearrangements:**

- Acid induced rearrangement and Wagner-Meerwein rearrangements. Neighbouring group participation.

I N D E X

GEO CHEMIST		
TOPIC NO.	**PARTICULARS**	**PAGE NO.**
1	**CHEMICAL PERIODICITY**	**1**
	1.1 Schrödinger equation for the H-atom. Radial distribution curves for 1s, 2s, 2p, 3s, 3p, 3d orbitals. Electronic configurations of multi-electron atoms.	1
	1.2 Periodic table, group trends and periodic trends in physical properties. Classification of elements on the basis of electronic configuration. Modern IUPAC Periodic table.	5
	1.3 General characteristics of s, p, d and f block elements. Effective nuclear charges, screening effects, atomic radii, ionic radii, covalent radii. Ionization enthalpy, electron gain enthalpy and electronegativity.	10
	1.4 Group trends and periodic trends in these properties in respect of s-, p- and d-block elements	17
2	**CHEMICAL BONDING & STRUCTURE**	**20**
	2.1 Ionic bonding: Size effects, radius ratio rules and their limitations. Packing of ions in crystals, lattice energy, Born-Landé equation and its applications, Born-Haber cycle and its applications. Solvation energy, polarizing power and polarizability, ionic potential, Fajan's rules. Defects in solids.	20
	2.2 Covalent bonding: Valence Bond Theory, Molecular Orbital Theory, hybridization. Concept of resonance, resonance energy, resonance structures.	26
	2.3 Coordinate bonding: Werner theory of coordination compounds, double salts and complex salts. Ambidentate and polydentate ligands, chelate complexes. IUPAC nomenclature of coordination compounds. Coordination numbers, Geometrical isomerism. Stereoisomerism in square planar and octahedral complexes.	32
3	**ACIDS & BASES**	**46**
	3.1 Chemical and ionic equilibrium	46
	3.2 Strengths of acids and bases. Ionization of weak acids and bases in aqueous solutions	47
	3.3 Application of Ostwald's dilution law	50
	3.4 Ionization constants, ionic product of water, pH-scale, effect of temperature on pH, buffer solutions and their pH value	51
	3.5 Buffer action & buffer capacity; different types of buffers and Henderson's equation	55
4	**THEORETICAL BASIS OF QUANTITATIVE INORGANIC ANALYSIS**	**58**
	4.1 Volumetric Analysis: Equivalent weights, different types of solutions, normal and molar solutions. Primary and secondary standard substances.	58

	4.2 General principles of different types of titrations: i) acid-base, ii) redox, iii) complexometric, iv) Precipitation. Types of indicators - i) acid-base, ii) redox iii) metal-ion indicators	61
5	**KINETIC THEORY AND THE GASEOUS STATE**	**67**
	5.1 Kinetic theory of gases, average kinetic energy of translation, Boltzmann constant and absolute scale of temperature	67
	5.2 Maxwell-Boltzmann distribution of speeds. Calculations of average, root mean square and most probable velocities	71
	5.3 Collision diameter; collision number and mean free path; frequency of binary collisions; wall collision and rate of effusion.	76
6	**CHEMICAL THERMODYNAMICS AND CHEMICAL EQUILIBRIUM**	**80**
	6.1 First law and its applications to chemical problems.	80
	6.2 Thermodynamic functions. Total differentials and state functions.	84
	6.3 Free expansion, JouleThomson coefficient and inversion temperature. Hess' law	89
	6.4 Applications of Second law of thermodynamics. Gibbs function (G) and Helmholtz function (A), Gibbs-Helmholtz equation, criteria for thermodynamic equilibrium and spontaneity of chemical processes.	94
7	**SOLUTIONS OF NON-ELECTROLYTES**	**105**
	7.1 Colligative properties of solutions, Raoult's Law	105
	7.2 Relative lowering of vapour pressure, osmosis and osmotic pressure	107
	7.3 Elevation of boiling point and depression of freezing point of solvents	113
	7.4 Solubility of gases in liquids and solid solutions.	116
8	**ELECTROCHEMISTRY**	**120**
	8.1 Cell constant, specific conductance and molar conductance	120
	8.2 Kohlrausch's law of independent migration of ions, ion conductance and ionic mobility	124
	8.3 Equivalent and molar conductance at infinite dilution. Debye-Hückel theory	127
	8.4 Application of conductance measurements. Conductometric titrations.	134
	8.5 Determination of transport number by moving boundary method.	139
9	**BASIC ORGANIC CHEMISTRY**	**145**
	9.1 Delocalized chemical bond, resonance, conjugation, hyperconjugation, hybridisation	145
	9.2 Orbital pictures of bonding sp3, sp2, sp: C-C, C-N and C-O system), bond polarization and bond polarizability	150
	9.3 Reactive intermediates: General methods of formation, relative stability and reactivity of carbocations, carbanions and free radicals	152

10	**STEREOCHEMISTRY**	**163**
	10.1 Configuration and chirality (simple treatment of elements of symmetry), optical isomerism of compounds containing two to three stereogenic centres, R,S nomenclature	163
	10.2 Geometrical isomerism in compounds containing two C=C double bonds (E,Z naming), and simple cyclic systems, Newman projection (ethane and substituted ethane).	172
11	**TYPES OF ORGANIC REACTIONS**	**181**
	11.1 Aliphatic substitution reactions: SN1, SN2 mechanisms, stereochemistry, relative reactivity in aliphatic substitutions. Effect of substrate structure, attacking nucleophile, leaving group and reaction medium and competitive reactions.	181
	11.2 Addition reactions: Electrophilic, nucleophilic and radical addition reactions at carbon-carbon double bonds.	196
	11.3 Electrophilic and nucleophilic aromatic substitution: Electrophilic (halogenation, sulphonation, nitration, Friedal-Crafts alkylation and acylation), nucleophilic (simple SNAr, SN1 and aryne reactions).	205
12	**MOLECULAR REARRANGEMENTS**	**214**
	12.1 Acid induced rearrangement and Wagner-Meerwein rearrangements. Neighbouring group participation.	214

NUMBER OF QUESTION ASKED IN GEO CHEMIST (2020 to 2026)								
CHEMICAL PERIODICITY		**2020**	**2021**	**2022**	**2023**	**2024**	**2025**	**2026**
1	Schrödinger equation for the H-atom. Radial distribution curves for 1s, 2s, 2p, 3s, 3p, 3d orbitals. Electronic configurations of multi-electron atoms.	2	2	4	6	3	1	2
2	Periodic table, group trends and periodic trends in physical properties. Classification of elements on the basis of electronic configuration. Modern IUPAC Periodic table	2	2	2	1	2	7	6
3	General characteristics of s, p, d and f block elements. Effective nuclear charges, screening effects, atomic radii, ionic radii, covalent radii. Ionization enthalpy, electron gain enthalpy and electronegativity.	4	3	3	6	4	6	6
4	Group trends and periodic trends in these properties in respect of s-, p- and d-block elements	-	1	2	1	-	1	2

CHAPTER - 1 CHEMICAL PERIODICITY

Unit 1.1: Schrödinger equation for the H-atom. Radial distribution curves for 1s, 2s, 2p, 3s, 3p, 3d orbitals. Electronic configurations of multi-electron atoms.

- Previous Year Exam Questions -

(2020)

1. Consider the following statements regarding radial and total angular function of H-atom:

1. The radial function R(r) depends on the quantum number *n* and *l*
2. The total angular function depends only on the direction and is independent of the radial distance from the nucleus (r)

Which of the statements given above is/are correct?

(a) 1 only (b) 2 only
(c) Both 1 and 2 (d) Neither 1 nor 2

(2020)

2. Which one of the following is the correct outermost electronic configuration of representative elements?

(a) (n-1) d^{1-10} ns^{0-2} (b) $ns1^{1-2}$ ns^2 np^{1-6}
(c) (n-2) f^{1-14} (n-1) d^{0--1} ns^2 (d) ns^0

(2021)

3. The number of radial nodes for 2*s*, 3*p* and 3*d* orbitals, respectively are: J

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

(2021)

4. What fraction of the total number of electrons is in the *p*-sublevels in Iron (Fe)?

(a) 50% (b) 49%
(c) 46.15% (d) 47.82%

(2022)

5. The numbers of radial nodes, planar angular nodes and non-planar angular nodes in $3d_{z^2}, 3s \text{ and } 3p_x$ orbitals are

(a) (0, 0, 2), (2, 0, 0), (1, 1, 0) respectively
(b) (0, 2, 0), (2, 0, 0), (1, 1, 0) respectively
(c) (2, 0, 0), (2, 0, 0), (0, 1, 1) respectively
(d) (0, 2, 0), (0, 2, 0), (1, 1, 0) respectively

(2022)

6. The angular wave function for hydrogen atom depends upon the quantum number(s)

(a) n and l only (b) l and m_l only
(c) m_l only (d) l, m_l and n

(2022)

7. The total number of nodal planes possible for all the atomic orbitals with a value of principal quantum $(n) = 3$ is

(a) 8 (b) 9
(c) 11 (d) 14

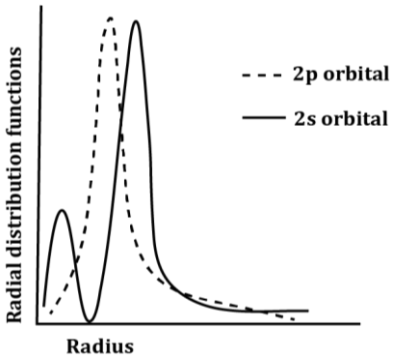
(2022)

8. The covalent radius of C atom is 0.77 Å and that of H atom is 0-37 A. What is the inter nuclear distance between C and H atoms in CH_4 molecule?

(a) 1.14 A (b) 1.20 A
(c) 1.25 A (d) 1.41 A

(2023)

9. Consider the following diagram regarding the radial distribution function for 2s and 2p orbitals:



Which one of the following statements is a correct conclusion drawn from the diagram given above?

(a) 2s electrons are less shielded than 2p electrons.
(b) 2p electrons are less shielded than 2s electrons.
(c) 2s and 2p orbitals have equal probability of closer approach to nucleus.
(d) 2s orbital electron density is at a greater distance from nucleus than that of 2p orbital.

(2023)

10. Which one of the following statements regarding wave functions is not correct?

(a) The square of the wave function gives the probability of finding the electron in the space.
(b) The angular wave function of a given type of orbital is dependent on the principal quantum number.

(c) The radial function of 2s orbital is both positive and negative.
(d) The probability of finding the electron density is zero at a node in the wave function.

(2023)

11. The electronic configuration of an ion M^{3+} generated from an element with atomic number 58 is:
(a) $[Xe]4f^1\ 5d^1\ 6s^2$ (b) $[Xe]4f^1$
(c) $[Rn]5f^3\ 6d^1\ 7s^2$ (d) $[Rn]5f^2$

(2023)

12. Which one of the following rules for filling of atomic orbitals is violated in the electronic configuration $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1$?
(a) Hund's rule of maximum multiplicity
(b) Pauli's exclusion principle
(c) Aufbau principle
(d) Slater's rule

(2023)

13. The number of unpaired electrons in the ground state of Lu^{3+} ion (atomic number 71) is:
(a) Zero (b) One
(c) Two (d) Three

(2023)

14. The electronic configuration of the outermost shell of all noble gases are $ns^2\ np^6$ EXCEPT:
(a) Xe (b) Ar
(c) He (d) Ne

(2024)

15. Which among the following principal quantum numbers has/have five degenerate d-orbitals?
(a) 2 (b) 3 only
(c) 4 only (d) Both 3 and 4

(2024)

16. Which one of the following statements related to radial distribution plots for hydrogen atom is not correct?
(a) Most probable radius varies as $3s > 3p > 3d$.
(b) Most probable radius varies as $1s < 2s < 3s$.
(c) Most probable radius varies as $2p < 3p$.
(d) Most probable radius varies as $3s < 3p < 3d$.

(2024)

17. Which one of the following sets of quantum numbers represents the highest energy state?
(a) $n-4;\ l-0;\ m_1-0;\ m_s- +\frac{1}{2}$
(b) $n-3;\ l-0;\ m_1-0;\ m_s- -\frac{1}{2}$
(c) $n-3;\ l-1;\ m_1-1;\ m_s- +\frac{1}{2}$
(d) $n-3;\ l-2;\ m_1-1;\ m_s- -\frac{1}{2}$

(2025)

18. Which one of the following statements regarding hydrogen atom and other electron species is correct?
(a) For H-atom, s orbital is dependent on the radial wave function (r) only and independent of the angular wave function (0 and ϕ).
(b) For H-atom, s orbital is dependent on both the radial wave function (r) and the angular wave function (0 and ϕ).
(c) For H-atom, there is no such dependence observed for s orbital; rather, the dependence starts with involvement of p orbital.
(d) For H-atom, s orbital is dependent on the angular wave function (0 and ϕ) only and independent of the radial wave function (r).

(2026)

19. Radial distribution function does NOT depend upon
(a) Distance from the nucleus
(b) Principal quantum number
(c) Azimuthal quantum number
(d) Orientation of orbital

(2026)

20. Which one of the following statements regarding wave functions is NOT correct?
(a) Wave functions are three dimensional and contain three quantum numbers n, l and m
(b) Wave functions represent total movement of a particle over a period
(c) Probability density is interpreted as the square of wave function
(d) Wave functions should be differentiable

Answer Key									
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
(c)	(b)	(d)	(c)	(a)	(b)	(c)	(a)	(a)	(b)
11	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
(b)	(a)	(a)	(c)	(d)	(d)	(d)	(a)	(d)	(b)

EXPLANATION

1. Correct Answer is (c): The radial function depends on the quantum number n and l. The total angular function depends only on the direction and is independent of the radial distance from the nucleus (r)

2. Correct Answer is (b): This configuration represents the outermost electrons in the s and p orbitals, which is typical for the representative elements (also known as main-group elements) in the periodic table.

3. Correct Answer is (d):

$$radial\ node = n - l - 1$$

For 2S orbital; n=2, l=0

$$radial\ node = 2 - 0 - 1 = 1$$

For 3P orbital; n=3, l=1

$$radial\ node = 3 - 1 - 1 = 1$$

For 3d orbital; n=3, l=2

$$radial\ node = 3 - 2 - 1 = 0$$

4. Correct Answer is (c)

Atomic number of Fe is 26

Electronic configuration of Fe is

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$$

fraction of total number of electrons

$$= \frac{12}{26} \times 100 = 46.15\%$$

5. Correct Answer is (a):

radial node $= n - l - 1$

Radial node for $3d_{z^2}$;

radial node $= 3 - 2 - 1 = 0$

angular node $= l$

For d orbital planar angular node is = 0

Nonplanar angular node is = 2

Radial node for $3s$;

radial node $= 3 - 0 - 1 = 2$

For s orbital l value is = 0

Nonplanar angular node is 0.

Radial node for $3p_x$;

radial node$= 3 - 1 - 1 = 1$

For p orbital l value is = 1

Nonplanar angular node is 0.

6. Correct Answer is (b): The quantum numbers, l and m decide the shape of the electron cloud and its spatial orientation. They thus decide the angular wave function of the orbital.

7. Correct Answer is (c):

Principal quantum number (n)=3

Subshell present are (l)=0,1,2

As 3s, 3p,3d-orbital, number of nodal planes are;

3s orbital, no nodal plane. It is spherically symmetric orbital.

3p-orbital; it has px, py, pz orbitals where nodal planes are in yz, zx,xy-plane respectively. Total nodal planes=3

3d-orbital; it has $d_{xy}, d_{yz}, d_{xz}, d_{x^2-y^2}, d_{z^2}$ where nodal planes are in (zx,yz),(xy,xz),(xy,zx),(2-Z in between xy) planes respectively. Total nodal planes =8.

Total number of nodal planes=0+3+6=11.

8. Correct Answer is (a):

$$internulear\ distance\ of\ C\ \&H(d) = rC + rH$$
$$= 0.77 + 0.37 = 1.14A^0$$

9. Correct Answer is (a): In the diagram, the 2s orbital has a node (a region of zero electron density) at the nucleus, while the 2p orbital does not. Therefore, the electron density of the 2s orbital is concentrated further close from the nucleus compared to the 2p orbital. This means that the 2s orbital electron density is indeed at a lower distance from the nucleus than that of the 2p orbital.

10. Correct Answer is (b): This statement is not correct because the angular wave function of an orbital is dependent on the azimuthal quantum number (l) and the magnetic quantum number (m), not the principal quantum number (n). The principal quantum number primarily determines the size and energy of the orbital, while the angular wave function determines the shape and orientation of the orbital.

11. Correct Answer is (b): The element with atomic number 58 is Cerium (Ce). The electronic configuration of Cerium in its neutral state is [Xe] $4f^1$ $5d^1$ $6s^2$. When Cerium loses three electrons to form the ion M^{3+}, it will lose the two 6s electrons and one electron from the 4f orbital.

Therefore, the electronic configuration of the Ce^{3+} ion will be [Xe] $4f^1$

12. Correct Answer is (a): Hund's rule of maximum multiplicity states that electrons must occupy degenerate orbitals (orbitals with the same energy) singly as far as possible before pairing up. In the given configuration, $1s^2$ $2s^2$ $2px^2$ $2py^1$, the 2p orbitals are not filled according to Hund's rule. According to Hund's rule, the configuration should be $1s^2$ $2s^2$ $2px^1$ $2py^1$ $2pz^1$ to maximize the number of unpaired electrons in degenerate orbitals before any pairing occurs.

13. Correct Answer is (a):

Lu^{+3} electronic configuration is $[Xe]4f^{14}\ 5d^1\ 6s^2$

Lu^{+3}

$4f^{14}$ 

no. of unpaired of electron is zero.

CHAPTER - 4

THEORETICAL BASIS OF QUANTITATIVE INORGANIC ANALYSIS

Unit 4.1: Volumetric Analysis: Equivalent weights, different types of solutions, normal and molar solutions. Primary and secondary standard substances.

- Previous Year Exam Questions -

(2020)

1. What will be the value of mole fraction of the solute in 1.00 mol aqueous solution?

(a) 1.7700 (b) 1.7770
(c) 0.0180 (d) 0.0344

(2020)

2. Equivalent weight of $K_2Cr_2O_7$ in acidic medium will be:

(atomic weight of K = 39, Cr = 52 and O = 16)

(a) 294 / 2 (b) 294 / 3
(c) 294 / 6 (d) 294

(2020)

3. Which one of the following is a primary standard substance?

(a) $KMnO_4$ (b) $K_2Cr_2O_7$
(c) $Na_2S_2O_3$ (d) NaOH

(2021)

4. The molarity of concentrated commercial HCl with 36 % (w/w) HCl and density 1.19 g/cm^3 is close to:

(a) 11.7 M (b) 10.6 M
(c) 11.2 M (d) 11.5 M

(2021)

5. Which one of the following primary standard is usually used to standardize KOH by titration?

(a) Potassium acid phthalate
(b) Sulphuric acid
(c) Hydrochloric acid
(d) Nitric acid

(2022)

6. 25 mL of H_2SO_4 solution requires 48.75 mL of 0.02 M NaOH for complete titration. What will be the molarity of H_2SO_4?

(a) 0.0201 M (b) 0.0161 M
(c) 0.0180 M (d) 0.0195 M

(2022)

7. In which one of the following titrimetric analyses, AgNO3 is used as a primary standard?

(a) Acid-base titration
(b) Complexometric titration
(c) Precipitation titration
(d) Redox titration

(2023)

8. Specific gravity of a solution is defined as:

(a) Ratio of mass of a solution to the mass of an equal volume of water
(b) Ratio of molarities of two solutions
(c) Ratio of normalities of two solutions
(d) Ratio of volumes of two solutions

(2023)

9. Which one of the following statements regarding Ammonium Ferrous Sulphate is not correct?

(a) Its composition is constant.
(b) Its aqueous solutions tend to undergo hydrolysis.
(c) It contains considerable amount of Fe3+ owing to aerial oxidation.
(d) Its standard solution can be prepared by direct weighing.

(2023)

10. Which one among the following compounds does not form primary standard solution?

(a) Na_2CO_3
(b) $NaOH$
(c) ZnO
(d) Potassium hydrogen phthalate

(2025)

11. Which one of the following will not make an acidic buffer solution?

(a) 100 mL 0.1 N CH_3COOH (aq) + 25 mL 0.4 N NaOH (aq)
(b) 100 mL 0.1 N CH_3COOH (aq) + 25 mL 0.3 N NaOH (aq)
(c) 100 mL 0.1 N CH_3COOH (aq) + 25 mL 0.2 N NaOH (aq)
(d) 100 mL 0.1 N CH_3COOH (aq) + 25 mL 0.1 N NaOH (aq)

(2025)

12. In quantitative volumetric analysis for the iodometric determination of copper, what will be the required amount of $CuSO_4 \cdot 5H_2O$ for preparing 100 mL of N/40 standard solution?

Reactions are:

$$2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2$$
$$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$$

(Molecular weight of $CuSO_4 \cdot 5H_2O = 159.6$ g/mol)
(a) 0.19 g (b) 0.29 g
(c) 0.39 g (d) 0.49 g

(2025)

13. Consider the following characteristics for a primary standard substance:
1. The substance has high formula weight.
2. The substance is 100% pure with very less impurity of only 0.01 to 0.02%.
3. The substance is stable indefinitely at room temperatures.
4. The substance is involved in a reaction for which equilibrium is far right to obtain a very sharp end point.

The above statements are correct for which one of the following pairs of substances?
(a) Na_2CO_3 and $KMnO_4$ (b) $C_2H_2O_4$ and $KMnO_4$
(c) $C_2H_2O_4$ and $K_2Cr_2O_7$ (d) $KH_2C_2O_4$ and H_2SO

(2026)

14. Which one of the following equations is used to get molarity (M) of a standard solution?
(a) $M = \frac{\text{Weight of solute in gm}}{\text{Molecular weight of solute}} \times \frac{1000}{\text{Volume of solution (mL)}}$
(b) $M = \frac{\text{Weight of solute in } gm}{\text{Equivalent weight of solute}} \times \frac{1000}{\text{Volume of solution (mL)}}$
(c) $M = \frac{\text{Volume of solute (mL)}}{\text{Molecular weight of solute}} \times \frac{1000}{\text{Weight of solution } (gm)}$
(d) $M = \frac{\text{Volume of solute (mL)}}{\text{Equivalent weight of solute}} \times \frac{1000}{\text{Weight of solution } (gm)}$

(2026)

15. Despite of being obtained in high purity, sodium thiosulphate is unsuitable as a primary standard. This is because:
1. CO_2 present in ordinary distilled water may decompose it
2. It can be decomposed by bacterial action
3. It decomposes upon exposure to light

Select the correct answer using the code given below:
(a) 1 and 2 only (b) 1 and 3 only
(c) 2 and 3 only (d) 1,2 and 3

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

EXPLANATIONS

1. Correct Answer is (c):
1 mol present in 1000kg water

$$\frac{1000}{18} = 55.55\ moles\ of\ solvent$$

$$x_{solute} = \frac{no.\ of\ moles\ of\ solute}{total\ moles\ of\ solute}$$

$$\frac{1}{55.55} = 0.0180$$

2. Correct Answer is (c):

$$equivalent\ weigh = \frac{molecular\ weight}{n - factor}$$

Molar mass of K2Cr2O7
2(39)+2(52)+7(16)=78+104+112=294
So,
Molar mass=294
Reduction half-reaction:
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$
One mole of K_2Cr2O_7 gains 6 electrons.
Therefore,
n-factor=6
Molecular weight of $K_2Cr_2O_7$ is 294

$$equivalent\ weigh = \frac{294}{6}$$

3. Correct Answer is (b):
The primary standard is a compound of sufficient purity from which standard solutions of known normalities can be prepared by direct weighing of it and diluting to a defined volume of solution. Potassium Dichromate $K_2Cr_2O_7$ is suitable to be used as a primary standard. It cannot be obtained in every pure form. It readily reacts with any traces of organic material or any other reducing substance in water.

4. Correct Answer is (a):
Let total volume is 1000mL=1L
Total mass of solution= 1190g
Mass of HCl= $\frac{36}{100} \times 1190$

$$moles\ of\ HCl = \frac{36 \times 1190}{100 \times 36.5}$$

So, $molarity = \frac{36 \times 1190}{100 \times 36.5} = 11.73M$

5. Correct Answer is (a):
The primary standard is a compound of sufficient purity from which standard solutions of known normalities can be prepared by direct weighing of it and diluting to a defined volume of solution.
To standardize KOH**,** a primary standard acid is preferred.
- Potassium acid phthalate (KHP)

- Pure, stable, non-hygroscopic
- High molar mass
- Monoprotic acid
- Commonly used as a primary standard for standardizing NaOH and KOH solutions

- Sulphuric acid Not a primary standard
- Hydrochloric acid Volatile; not a primary standard
- Nitric acid Not a primary standard

6. Correct Answer is (d):

$$M_1V_1(H_2SO_4) = M_2V_2(NaOH)$$
$$M_1 \times 25 = 0.02 \times 48.75$$
$$M_1\ 25 = 0.975$$
$$M_1 = 0.039$$
$$\frac{M_1}{n}$$

n is a n- factor of H_2SO_4

$$molarity(M) = \frac{0.039}{2}$$

$$= 0.0195M$$

7. Correct Answer is (c):

Precipitation titration $AgNO_3$ is used as a primary standard.

Silver nitrate is used as a **primary standard in precipitation titrations**, especially in argentometric methods.

- $AgNO_3$ reacts with halides (Cl^-, Br^-, I^-) to form insoluble precipitates like AgCl.
- This makes it ideal for **precipitation (precipitimetry) titrations**.

Checking options:

- (a) Acid–base titration → uses acids/bases, not $AgNO_3$
- (b) Complexometric titration → uses EDTA
- (c) Precipitation titration → uses $AgNO_3$
- (d) Redox titration → uses oxidants/reductants like $KMnO_4$

8. Correct Answer is (a):

The specific gravity of a solution is defined as: Ratio of mass of a solution to the mass of an equal volume of water.

9. Correct Answer is (c):

It contains a considerable amount of Fe^{3+} owing to aerial oxidation.

This is not correct. Ammonium ferrous sulfate primarily contains Fe^{2+}. Although Fe^{2+} can be oxidized to Fe^{3+} upon exposure to air, this does not happen significantly in the solid state or in freshly prepared solutions.

10. Correct Answer is (b):

A primary standard must be pure, stable, non-hygroscopic, and have a definite composition.

Let's check:

- **Na_2CO_3** Primary standard (pure, stable, non-hygroscopic)
- **NaOH** Not a primary standard (hygroscopic, absorbs CO_2 from air, composition changes)
- ZnO Can be used as a primary standard in some analyses (stable solid oxide)
- Potassium hydrogen phthalate (KHP) Excellent primary standard (pure, stable, non-hygroscopic)

11. Correct Answer is (a):

An acidic buffer forms only when after neutralization:

- some weak acid (CH_3COOH) remains, and
- its conjugate base (CH_3COO^-) is formed,

but no excess strong base remains**.**

Reaction:

$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$

Step 1: Moles of CH_3COOH in all cases

100 mL×0.1 N=0.010 eq

Step 2: Moles of NaOH in each case (25 mL)

(a) 0.4N⇒0.4×0.025=0.010eq

(b) 0.3N⇒0.00750 eq

(c) 0.2N⇒0.0050 eq

(d) 0.1N⇒0.00250 eq

Step 3: Check each case

(a) 0.010 acid = 0.010 base → complete neutralization

Only salt remains → NOT an acidic buffer

(b), (c), (d)

Acid is in excess → acid + conjugate base present → acidic buffer formed

Final answer:

(a) 100 mL 0.1 N CH_3COOH + 25 mL 0.4 N NaOH

12. Correct Answer is (c):

In iodometric estimation:

Step 1: Determine n-factor of Cu^{2+}

From reaction:

$2Cu^{2+} \rightarrow I_2 \rightarrow 2S_2O_3^{2-}$

Each Cu^{2+} ultimately corresponds to 1 electron change equivalent**,** so:

- n-factor of Cu^{2+} **=** 1

So:

Equivalent weight of CuSO4·5H2O=159.6

Step 2: Normality given

$$N = \frac{1}{40} = 0.025$$

Volume = 100 mL = 0.1 L

Step 3: Use formula

Weight=N×Eq. wt×V

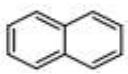
CHAPTER - 9 BASIC ORGANIC CHEMISTRY

Unit 9.1: Delocalized chemical bond, resonance, conjugation, hyperconjugation, hybridisation

- Previous Year Exam Questions -

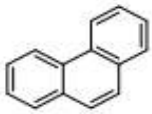
(2020)

1. Which one of the following structures is non-aromatic?

(a) 

(b) 

(c) 

(d) 

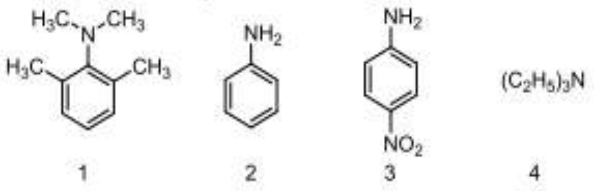
(2020)

2. The o/p-directing effect of methyl group in electrophilic substitution reaction of toluene is due to:

(a) Inductive effect
(b) Hyperconjugation effect
(c) Resonance effect
(d) Electrometric effect

(2020)

3. The relative order of basicity of following amines is

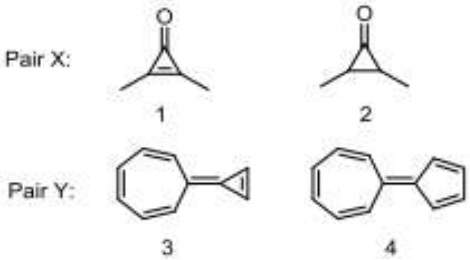


1 2 3 4

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

(2020)

4. Which molecule in each of the following pairs has a higher dipole movement?

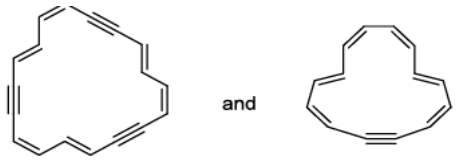


1 2 3 4

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

(2021)

5. The total number of delocalized pi-electrons in compounds I and II are:

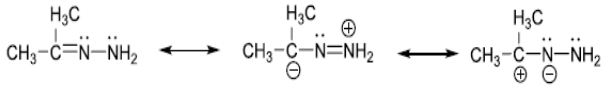


I II

(a) 18 and 14 respectively
(b) 24 and 16 respectively
(c) 16 and 12 respectively
(d) 22 and 14 respectively

(2021)

6. Rank the following structures in order of increasing contribution to the resonance hybrid:

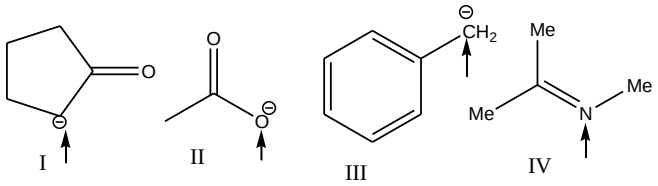


I II III

(a) II < I < III (b) III < II < I
(c) III < I < II (d) I < II < III

(2021)

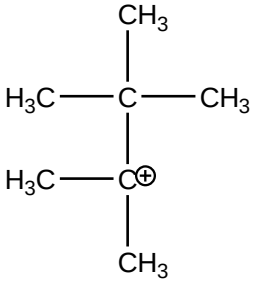
7. Which of the following indicated atoms in each species has sp^2-hybridization?



I II III IV

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

8. The total number of hyper conjugative structures possible for the following carbocation is:



(a) 3 (b) 1
(c) 4 (d) 12

(2022)

9. Which one of the following statements is not true about the molecules I and II?

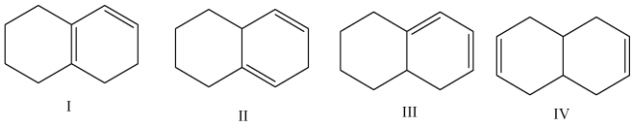


I II

(a) The structures of I and II are simply two resonance forms of the same molecule.
(b) The structures of I and II represent different molecules.
(c) I and II are non-aromatic in nature.
(d) The dianions of I and II are aromatic in nature.

(2022)

10. Rank the following dienes in order of increasing heat of hydrogenation:

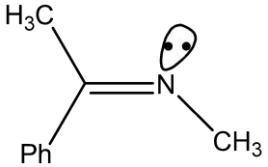


I II III IV

(a) I<I<I<II`
(b) IV<II<I< III
(c) III<I<IV < II
(d) I< III < II < IV

(2022)

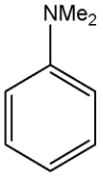
11. The hybridization of nitrogen present in the following imine is

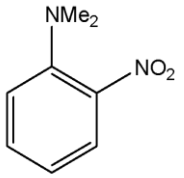


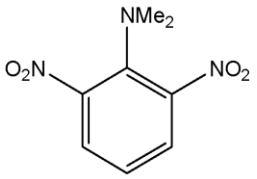
(a) sp^3
(b) sp^2
(c) sp
(d) sp^3d

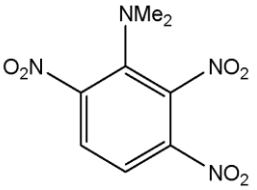
(2023)

12. Which one of the following compounds is most stabilized by resonance?

a) 

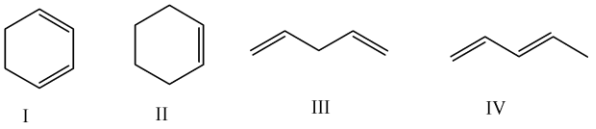
c) 

b) 

d) 

(2023)

13. The correct order of heats of hydrogenation among the following alkenes (when hydrogenation is carried out in the presence of a platinum catalyst) is:



I II III IV

(a) I < II < IV < III
(b) II < IV < I < III
(c) II < I < IV < III
(d) I < II < III < IV

(2024)

14. Consider the following statements regarding structures of naphthalene and biphenylene:

(1) The $C1-C2$ bond order is more than $C2-C3$ bond in naphthalene.
(2) The $C2-C3$ bond order is more than $C1-C2$ bond in naphthalene.
(3) The C1-C2 bond order is more than C2-C3 bond in biphenylene.
(4) The $C2-C3$ bond order is more than C1-C2 bond in biphenylene.

Which of the statements given above are correct?

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

(2024)

15. The correct order of increasing acid strength of the given carboxylic acids is

(a) 4-acetylbenzoic acid < 4-cyanobenzoic acid < 4-hydroxybenzoic acid < benzene-1,4-dicarboxylic acid
(b) 4-hydroxybenzoic acid < 4-acetylbenzoic acid < 4-cyanobenzoic acid < benzene-1,4-dicarboxylic acid
(c) 4-hydroxybenzoic acid < benzene1,4-dicarboxylic acid < 4-acetylbenzoic acid < 4-cyanobenzoic acid
(d) 4-cyanobenzoic acid < 4-acetylbenzoic acid < benzene-1,4dicarboxylic acid < 4-hydroxybenzoic acid

(2025)

16. How many resonating structures are possible for $CO_3^{2-?}$

(a) 2
(b) 3
(c) 4
(d) 5

(2025)

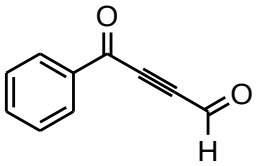
17. Which one of the following represents the correct increasing order of reactivity towards electrophilic attack among indicated compounds?

(a) $CH_2 = CNHO_2 < CH_2 = \overset{+}{N}H(CH_3)_3 < CH_2 = CH_2 < CHCH_3 < CH_2 = CHBr < CH_2 = CHOCH_3$
(b) $CH_2 = \overset{+}{N}H(CH_3)_3 < CH_2 = CHNO_2 < CH_2 = CH_2 < CH_2 < CHBr < CH_2 = CHCH_3 < CH_2 = CHOCH_3$
(c) $CH_2 = CHNO_2 < CH_2 = \overset{+}{N}H(CH_3)_3 < CHBr < CH_2 = CH_2 = CH_2 = CHCH_3 < CH_2 = CHOCH_3$

(d) $CH_2 = \overset{+}{N}H(CH_3)_3 < CH_2 = CHNO_2 < CH_2 = CHBr < CH_2 = CH_2 < CH_2 = CHOCH_3 < CH_2 = CHCH_3$

(2026)

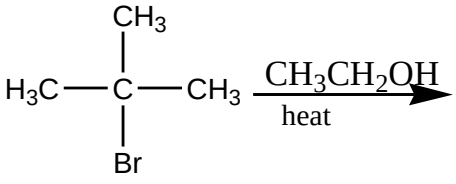
18. The types of hybridization exhibited by the carbon atoms in the given compound are



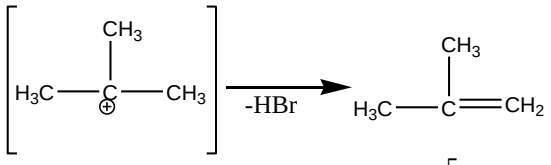
(a) sp^2 and sp^3 only (b) sp^2 and sp only
(c) sp and sp^3 only (d) sp, sp^2 and sp^3

(2026)

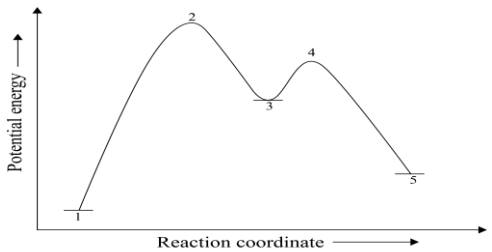
19. A potential energy diagram is shown below for the E1 mechanism of indicated reaction



1



3 5



By applying Hammond's postulate to the potential energy diagram for this reaction, which one of the following statements is correct?

(a) The structure of transition state 2 is more carbocation-like than transition state 4
(b) The structure of transition state 2 is less carbocation-like than transition state 4
(c) The structure of transition state 2 resembles 1 more than it resembles 3
(d) The structure of transition state 4 resembles 5 more than it resembles 3

Answer Key									
1	2	3	4	5	6	7	8	9	10
(c)	(b)	(b)	(b)	(a)	(b)	(d)	(a)	(a)	(d)
11	12	13	14	15	16	17	18	19	
(b)	(c)	(b)	(b)	(a)	(b)	(c)	(b)	(a)	

EXPLANATIONS

1. Correct Answer is (c):

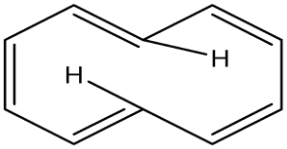
A compound is aromatic if it satisfies all conditions of aromaticity (Hückel's rule)**:**

The molecule must be a ring system (atoms arranged in a closed loop).

All atoms in the ring must lie in the same plane (or nearly planar), allowing proper orbital overlap.

The ring must have a continuous system of p-orbitals, meaning:

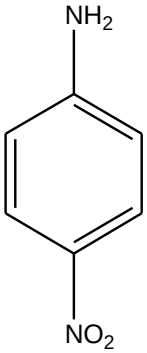
- alternating double and single bonds, or
- lone pairs/charges that contribute to conjugation



Hydrogen repel each other and loose planarity, it is non-aromatic.

2. Correct Answer is (b): In toluene, the methyl group releases electrons towards the benzene ring partly due to inductive effect and mainly due to hyperconjugation. Thus the reactivity of the ring towards electrophilic substitution increases and the substitution is directed at ortho and para positions to the methyl group.

3. Correct Answer is (b):

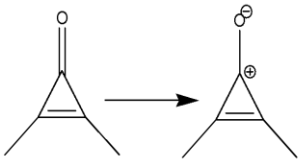


NO_2 is electron withdrawing group it shows –I effect. Lone pair of nitrogen not available for donation. Hence, less basic.

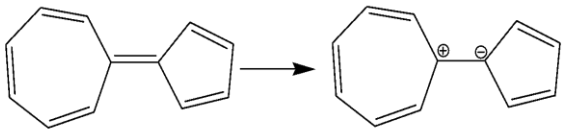
$N(C_2H_5)_2$

lone pair of nitrogen easily available to accept hydrogen.

4. **Correct Answer is (b):**



Aromatic compound



Aromatic compound

5. **Correct Answer is (a):** In compounds I there is 9 double bonds present, pi electrons is $9 \times 2 = 18$. Triple bond does not take part in delocalization. In compounds II there is 7 double bonds present, pi electrons is $7 \times 2 = 14$.

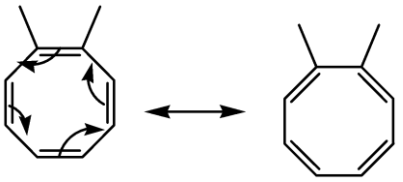
6. **Correct Answer is (b):** More electronegative element has negative charge. Opposite charges near to each other.

- Complete Octets vs. Incomplete Octets**:** Structures where all atoms have a complete valence shell (8 electrons) are significantly more stable than those with incomplete octets.
- **Structure I (Most Stable):**
  All atoms have complete octets.
  It is entirely neutral with no charge separation.
  Highest contribution.
- Structure II (Intermediate Stability):
- The double bond shifts to form
  $$C^{-}N = NH_2^{+}$$
- It is less stable than **I** due to charge separation, but much more stable than **III** .
- **Structure III (Least Stable):**
- The positively charged carbocation (C^{+}) has only 3 single bonds and no lone pairs, leaving it with an incomplete octet (only 6 valence electrons).
- Lowest contribution.

7. **Correct Answer is (d):** Delocalized pi electron in all these compound, and the hybridization of these compound is sp^2.
   (C=O). To maximize stability through resonance ($C^{-} - C = O \leftrightarrow C = C - O^{-}$) the lone pair must reside in a p-orbital. Therefore, this carbon rehybridizes from sp^3 to sp^2 **Species II (Acetate Ion Oxygen):**
   The negatively charged oxygen ($O^{-}\ \pi\ -$) -system of the carbonyl bond $O^{-} - C = O \leftrightarrow O = C - O^{-}$. For effective resonance overlap, the oxygen atom adopts **(sp^2)** hybridization.
   Species III (Benzyl Carbanion):
   The negatively charged carbon ($C^{-}H_2$) is adjacent to a benzene ring. Its lone pair is in resonance with the aromatic (π)-system of the phenyl ring. To allow this delocalization, the carbon atom adopts a planar geometry **sp^2** hybridization.
   Species IV (Imine Nitrogen):
   The nitrogen atom is part of a carbon-nitrogen double bond (C=N). It has a steric number of 3 (1 double bond + 1 single bond + 1 lone pair), which inherently gives it a trigonal planar geometry and **(sp^2)** hybridization.

8. **Correct Answer is (a):** The carbon next to carbocation is called alpha carbon and hydrogen present on that carbon is alpha hydrogen. There are 3 hyper conjugate H-atoms in this carbocation that are contributing to the hyperconjugation.

9. **Correct Answer is (a)**:

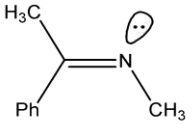


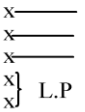
resonance form

The structures of I and II represent same molecules.

10. **Correct Answer is (d):** More is the stability lesser will be heat of hydrogenation.
$$heat\ of\ hydrogenation \propto \frac{1}{stability}$$

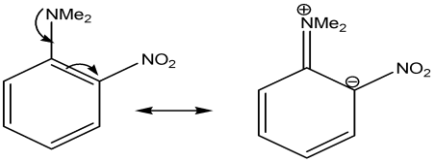
11. **Correct Answer is (b):**





2 bond pair and 1 lone pair
hybridisation is sp^2

12. **Correct Answer is (c):**

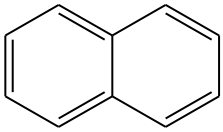


NO2 is electron withdrawing group it stabilised by negative charge.

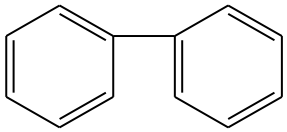
13. Correct Answer is (b): Heat of hydrogenation inversely proportional to the stability.

More is the stable compound lesser will be heat of hydrogenation.

14. Correct Answer is (b):



Naphthalene



Biphenyl

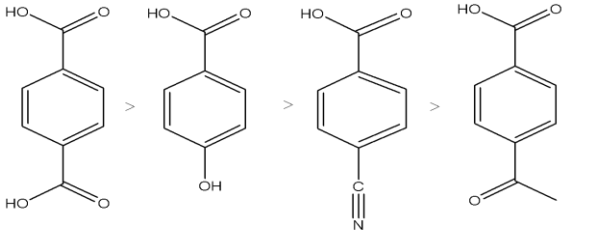
The C1-C2 bond order is more than the C2-C3 bond in naphthalene.

Correct, due to delocalization in the fused rings.

The C2-C3 bond order is more than the C1-C2 bond in biphenylene.

Correct, due to the stability of the benzene ring compared to the four-membered ring.

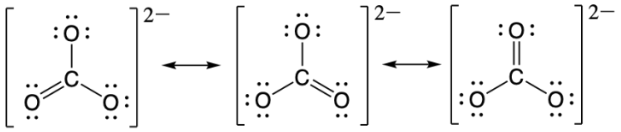
15. Correct Answer is (a):



Benzene 1,4 Di-Carboxylic Acid | 4-Hydroxy benzoic acid | 4-cyano benzoic acid | 4-Acetyl Benzoic acid

Electron-withdrawing groups (EWGs) increase acid strength by stabilizing the conjugate base through inductive and resonance effects. Electron-donating groups (EDGs) decrease acid strength by destabilizing the conjugate base.

16. Correct Answer is (b):



there are **3 possible resonating structures** for CO_3^{2-}

17. Correct Answer is (c):

EDG increase rate of electrophilicity increase

EWG increase rate of electrophilicity decrease

$$CH_2 = CHNO_2 < CH_2 = CH\overset{+}{N}(CH_3)_3 < CHBr < CH_2 = CH_2 = CH_2 = CHCH_3 < CH_2 = CHOCH_3$$

18. Correct Answer is (b):

The full structure is: Ph–CO–C≡C–CHO

Hybridization of Each Carbon:

Carbon	Type	Hybridization
6 carbons of benzene ring	Aromatic	sp^2
C=O (ketone carbonyl)	Double bond	sp^2
–C≡C– (two carbons)	Triple bond	sp
–CHO (aldehyde carbon)	Double bond	sp^2

Conclusion:

The compound contains only sp^2 and sp hybridized carbons.

- sp^2: benzene carbons, ketone C=O, aldehyde CHO
- sp: the two triple bond carbons (C≡C)
- sp^3: None present

Therefore, the correct answer is b)

19. Correct Answer is (a):

Transition State 2 (between 1 and 3):

- The energy barrier **1→2** is **large** (endergonic step, high activation energy)
- TS2 is **close in energy to intermediate 3** (carbocation)
- ∴ TS2 is **carbocation-like** (resembles **3**)

Transition State 4 (between 3 and 5):

- The energy barrier **3→4** is **small** (exergonic step, low activation energy)
- TS4 is **close in energy to intermediate 3** (carbocation)
- ∴ TS4 is **also carbocation-like**, but the barrier is smaller

Comparing TS2 vs TS4:

- TS2 lies **much higher above 1** than TS4 lies above 3
- TS2 is **more carbocation-like** than TS4 (TS2 is closer in energy to 3 relative to its preceding minimum)

"The structure of transition state 2 is more carbocation-like than transition state 4"

- Step 1→3 is **highly endothermic** → late TS → more resembles carbocation **3**
- Step 3→5 is **exothermic** → early TS → less carbocation-like

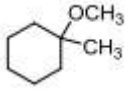
CHAPTER - 11 TYPES OF ORGANIC REACTIONS

Unit 11.1: Aliphatic substitution reactions: SN1, SN2 mechanisms, stereochemistry, relative reactivity in aliphatic substitutions. Effect of substrate structure, attacking nucleophile, leaving group and reaction medium and competitive reactions.

- Previous Year Exam Questions -

(2020)

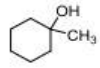
1. Consider the following compound



Which one of the following substrate seats is the best for synthesizing above compound?

(a) CH_3I + 

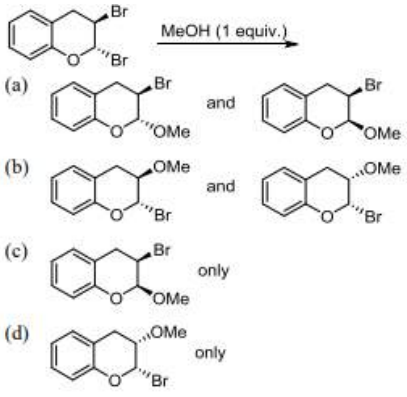
(b) CH_3ONa + 

(c) CH_3OH + 

(d) CH_3I + 

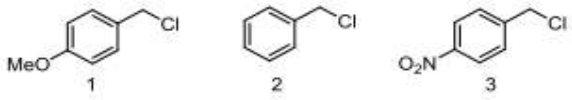
(2020)

2. The major products formed in the following reaction is/are:



(2020)

3. The relative order of reactivity of the following chlorides in SN1 reaction is:

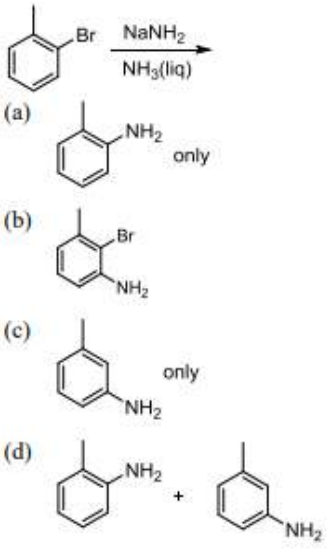


(a) 2>1>3 (b) 3>2>1

(c) 1>2>3 (d) 1>3>2

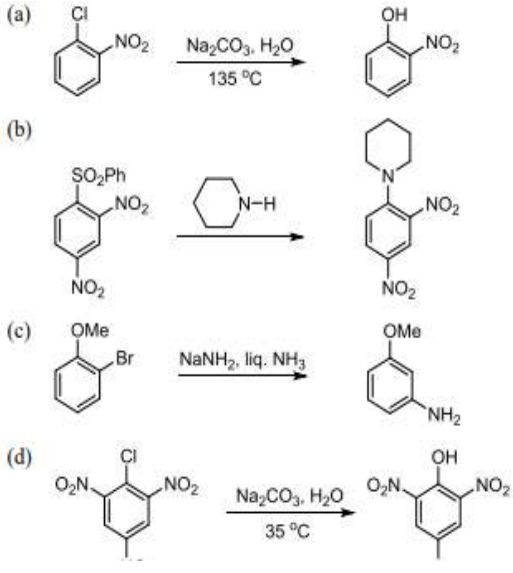
(2020)

4. The major product formed in the reaction is/are:



(2020)

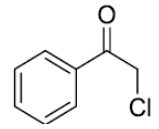
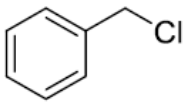
5. Which of the following reaction is NOT an example of ipso-substitution?

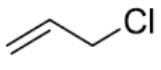
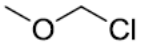


(2021)

6. Which one of the following chlorides undergoes a fastest S_N2 reaction with KI in acetone

Indicate the order of reactivity of HX in the following reaction:

(a)  (b) 

(c)  (d) 

(2021)

7. Indicate the order of reactivity of HX in the following reaction:

$$ROH + HX \rightarrow RX + H_2O$$

(a) I > HBr > HCl (b) HCl > HBr > HI

(c) HBr > HI > HCl (d) HBr > HCl > HI

(2021)

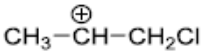
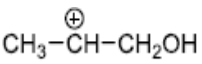
8. Which one of the following alkenes will react most rapidly with concentrated sulphuric acid?

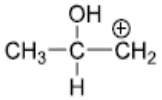
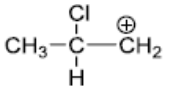
(a) $H_2C{=}CH_2$ (b) $(CH_3)_2C{=}CH_2$

(c) $Cl_2C{=}CCl_2$ (d) $F_3CCH{=}CHCH_3$

(2021)

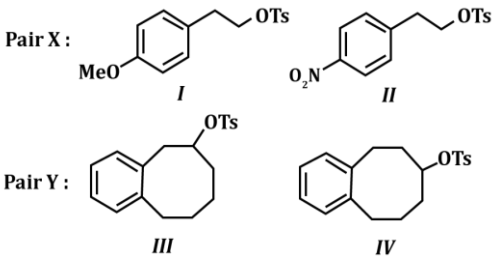
9. The regioselective electrophilic addition of HOCl with propene proceeds through:

(a)  (b) 

(c)  (d) 

(2022)

10. Which of the following substrates will be more reactive in Solvolysis conditions using formic acid in Pair X and Pair Y respectively?

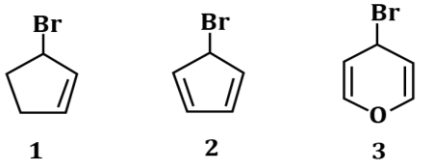


(a) I and III (b) I and IV

(c) II and III (d) II and IV

(2022)

11. The relative order of reactivity of the following bromides in SN 1 reaction is

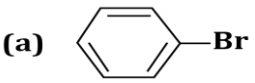
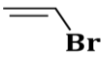


(a) 3>2>1 (b) 2>3>1

(c) 3>1>2 (d) 2>1>3

(2022)

12. Which one of the following compounds would react most readily by S_N2 mechanism?

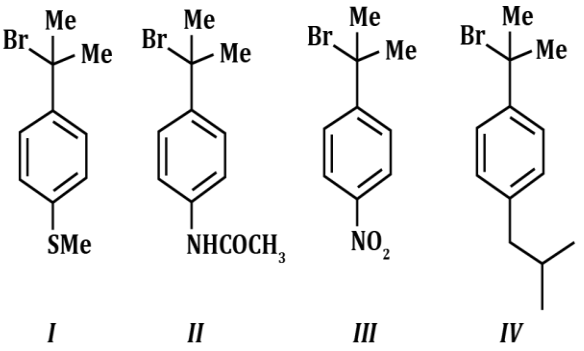
(a)  (b) 

(c) 

(d) None of the above

(2022)

13. Rank the following alkyl bromides from most reactive to least reactive in a Solvolysis reaction using aqueous acetone:

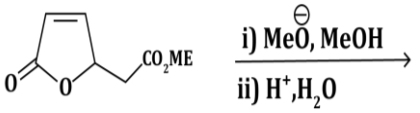


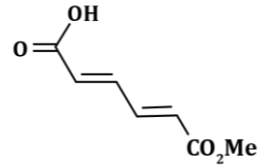
(a) II > IV>I> III (b) I>II>IV> III

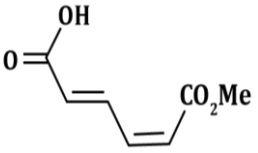
(c) III>IV> II>I (d) III > IV>I> II

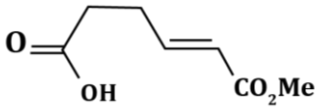
(2022)

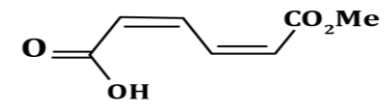
14. The major product formed in the following reaction sequence is



(a) 

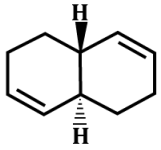
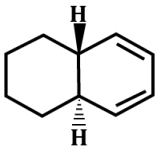
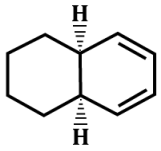
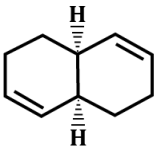
(b) 

(c) 

(d) 

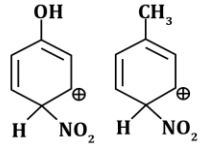
(2022)

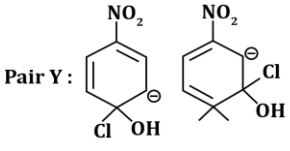
15. An unknown compound with molecular formula $C_{10}H_{14}$ decolorizes bromine in carbon tetrachloride. When treated with warm, concentrated potassium permanganate, this compound gives cis-cyclohexane-1,2-dicarboxylic acid and oxalic acid. The structure for the unknown compound is

(a) 
(b) 
(c) 
(d) 

(2022)

16. Which is the most stable intermediate in the following Pair X and Pair Y respectively?

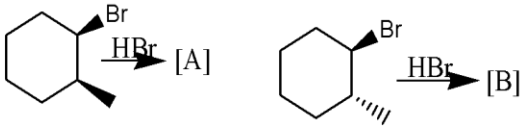
Pair X : 
I *II*

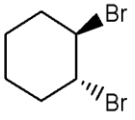
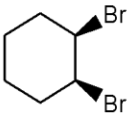
Pair Y : 
III *IV*

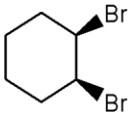
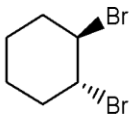
(a) I and III
(b) I and IV
(c) II and III
(d) II and IV

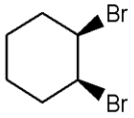
(2023)

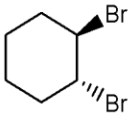
17. The major products [A] and [B] formed in the following reactions are:



a) [A]=  [B]= 

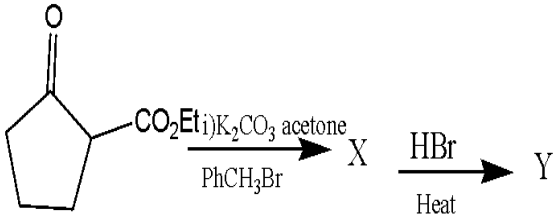
b) [A]=  [B]= 

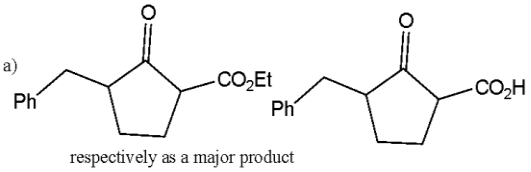
c) [A]=[B] 

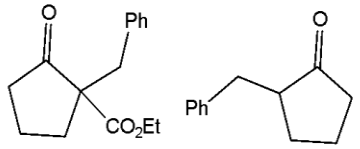
d) [A]=[B] 

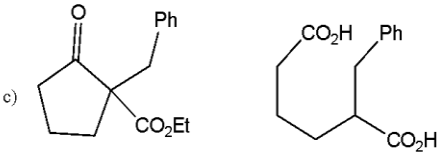
(2023)

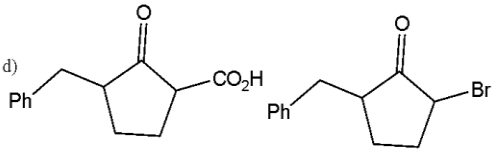
18. In the given reaction sequence, products X and Y are:



a) 
respectively as a major product

b) 
respectively as a major product

c) 
respectively as a major product

d) 
respectively as a major product

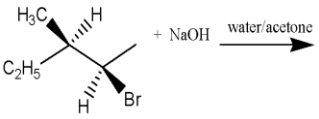
(2023)

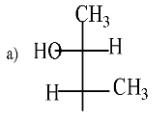
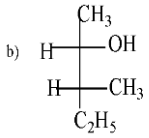
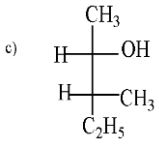
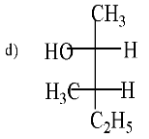
19. Deprotection of phenyl methyl ether with HI goes via:

(a) SN^2 attack at sp^3 carbon
(b) SN^1 attack at sp^2 carbon
(c) SN^2 attack at sp^2 carbon
(d) SN^1 attack at sp^3 carbon

(2023)

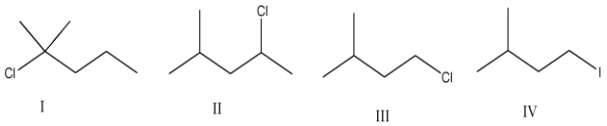
20. The product formed in the following reaction is:



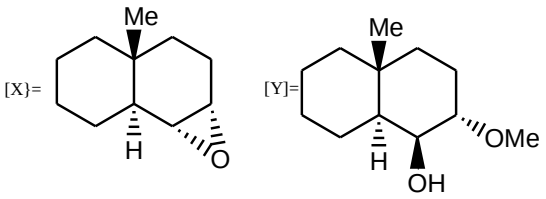
a) 
b) 
c) 
d) 

(2023)

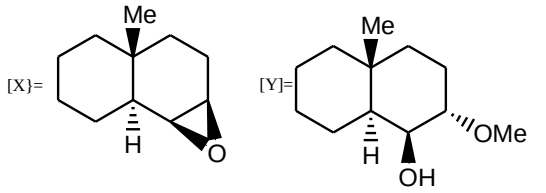
21. The correct order of reactivity of the following alkyl halides in SN2 reaction is:


I II III IV

(a) IV> III > II > I
(b) I > III > II > IV
(c) IV > III > I > II
(d) II > I > IV > III



(c)



(d)

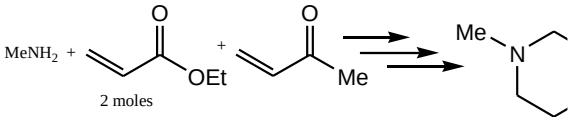
(2026)

51. Which one of the following alkyl bromides will give exclusively one terminal mono-substituted alkene upon dehydro-bromination by an E2 process?

(a) 3-bromo-3-methylpentane
(b) 3-bromo-2-methylpentane
(c) 2-bromo-2,3-dimethylbutane
(d) 2-bromo-3,3-dimethylbutane

(2026)

52. The total number of 1,4 -addition reactions involved in the synthesis of target molecule [X] using the indicated starting material is/are

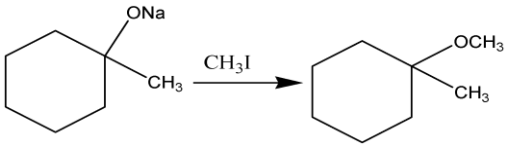


(a) One (b) Two
(c) Three (d) Four

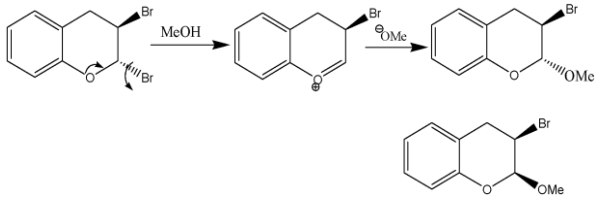
Answer Key									
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
(a)	(a)	(c)	(d)	(c)	(a)	(a)	(b)	(a)	(a)
11	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
(c)	(d)	(b)	(c)	(c)	(a)	(d)	(b)	(a)	(b)
21	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**
(a)	(a)	(b)	(b)	(d)	(c)	(b)	(b)	(b)	(a)
31	**32**	**33**	**34**	**35**	**36**	**37**	**38**	**39**	**40**
(a)	(b)	(d)	(b)	(c)	(c)	(d)	(a)	(b)	(a)
41	**42**	**43**	**44**	**45**	**46**	**47**	**48**	**49**	**50**
(d)	(c)	(a)	(a)	(a)	(a)	(b)	(b)	(b)	(a)
51	**52**								
(d)	(c)								

EXPLANATION

1. Correct Answer is (c):



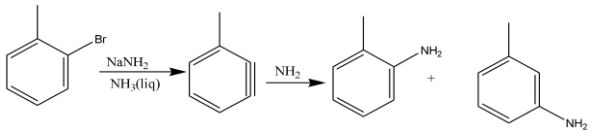
2. Correct Answer is (a):



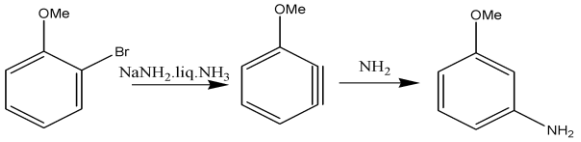
3. Correct Answer is (c): In SN^1 reaction carbocation is formed. Electron donating group stabilised carbocation and electron withdrawing group destabilised carbocation.

OMe is electron donating group it stabilise carbocation. NO_2 is electron withdrawing group it destabilised the carbocation.

4. Correct Answer is (d):



5. Correct Answer is (c): A position which is already occupied by a non-hydrogen substituent in an aromatic ring is called. ipso position (Latin: ipso, on itself), the attack on this position is called ipso attack (or ipso addition), and the aromatic substitution in which a substituent already present is replaced is called ipso substitution.



6. Correct Answer is (a): In compound (b), (c) and (d) carbocation is more stable, SN^1 reaction is more preferred than SN^2.

The strongly electron-withdrawing carbonyl carbon pulls electron density away from the (α)- carbon via the inductive effect. This drastically increases its partial positive charge (δ), making it highly electrophilic and reactive towards the incoming iodide (I^-) nucleophile.

7. Correct Answer is (a): Reactivity of iodine is grater than Br and Cl.

The reaction of an alcohol with a hydrogen halide ($ROH + HX \rightarrow RX + H_2O$) depends directly on two main properties of the acid: **acid strength** and **nucleophilicity of the halide ion**.

1. **Bond Dissociation Energy & Acid Strength:** As you move down the halogen group ($Cl \rightarrow Br \rightarrow I$) the atomic size increases. This lengthens the (H-X) bond and drastically

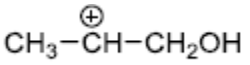
reduces its bond dissociation energy. Because the (H-Ibond is the weakest, it cleaves the most easily, making HI the strongest acid among them to protonate the alcohol ($ROH \rightarrow ROH_2^+$).

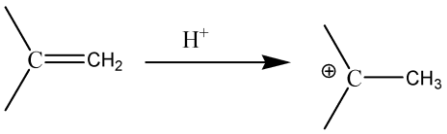
2. **Nucleophilicity:** The iodide ion (I^-) is larger and more polarizable than\(\text{Br^- and Cl^-)

Combining both factors yields the definitive reactivity trend:

HI >HBr>HCl>HF

8. Correct Answer is (b):

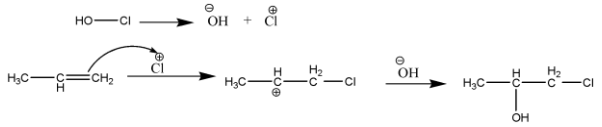




Carbocation is more stable.

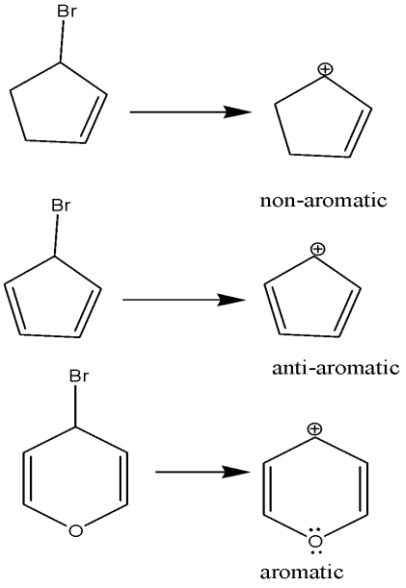
- This is a tertiary (3^0) carbocation , highly stabilized by the powerful electron-donating inductive effect (+I) and 9 hyperconjugative hydrogens .

9. Correct Answer is (a):



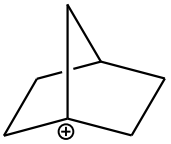
10. Correct Answer is (a): after solvolysis carbocation is form, electron donating group stabilized cation and electron withdrawing group destabilized cation. OMe and Ph is electron donating group it stabilized cation.

11. Correct Answer is (c):



Stability order: aromatic > non-aromatic > anti-aromatic

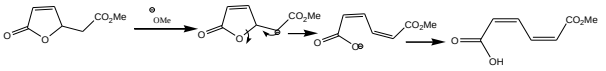
12. Correct Answer is (d): at sp^2 carbon SN^2 reaction does not occur.



bridgehead carbocation
not stable

13. Correct Answer is (b): in a solvolysis reaction cation is formed, electron donating group stabilized cation. Here SMe donate more electron to the benzene.

14. Correct Answer is (d):



15. Correct Answer is: (c)

Molecular Formula: C10H14 suggests a bicyclic or branched structure with double bonds or rings.

Decolorizes Bromine: This indicates the presence of double bonds or aromatic rings.

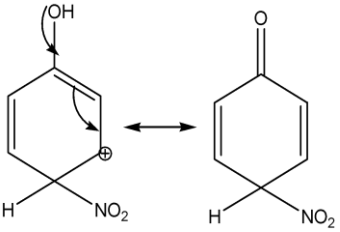
Reaction with Potassium Permanganate: Potassium permanganate (KMnO4) oxidizes organic compounds. The formation of cis-cyclohexane-1,2-dicarboxylic acid and oxalic acid suggests the presence of a structure that can be oxidized to these specific products.

Structure Determination:

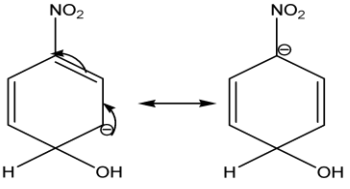
- The compound must contain a structure that can be oxidized to produce cis-cyclohexane-1,2-dicarboxylic acid. This structure involves a cyclohexane ring with two carboxylic acid groups in the cis configuration.

The presence of methyl groups (C10H14) and the specific oxidation products point towards cis-1,2-dimethylcyclohexane as the compound.

16. Correct Answer is (a):

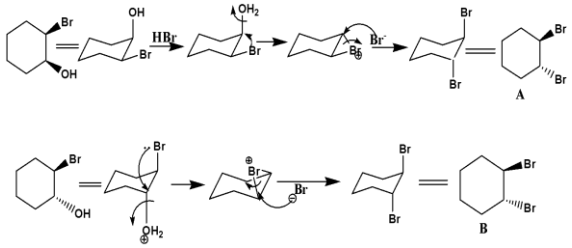


Mesomeric effect of OH group stabilized cation.

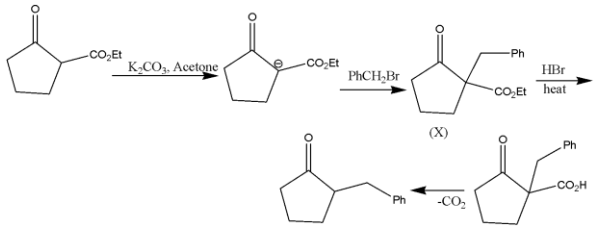


NO_2 is electron withdrawing group it stabilized negative charge.

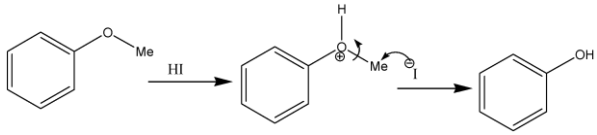
17. Correct Answer is (d):



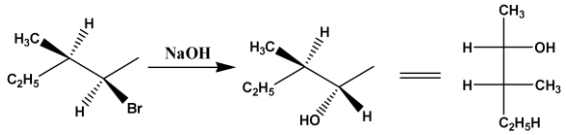
18. Correct Answer is (b):



19. Correct Answer is (a):



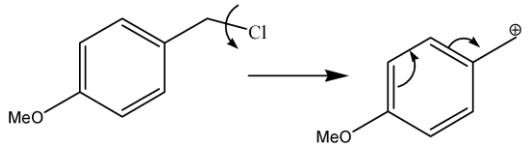
20. Correct Answer is (b):



21. Correct answer is (a): Leaving group tendency of iodine is greater than chlorine hence IV > III.

Secondary carbon is more preferred than tertiary carbon for SN^2 reaction. Tertiary carbon is more preferred for SN^1 reaction.

22. Correct Answer is (a):



OMe is electron donating group it stabilised carbocation.

23. Correct Answer is (b):

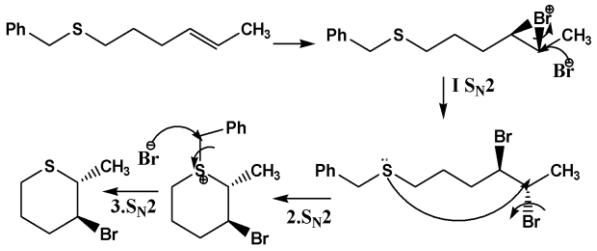
III (pyridyl) would be the least reactive due to the strong electron-withdrawing effect of the nitrogen.

I (benzyl) would be more reactive than III but less reactive than IV and II.

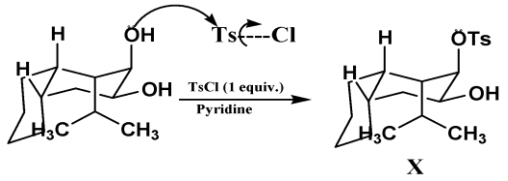
IV (furyl) would be more reactive than I but less reactive than II due to the moderate electron-donating effect of oxygen.

II (thienyl) would be the most reactive due to the strong electron-donating effect of sulfur.

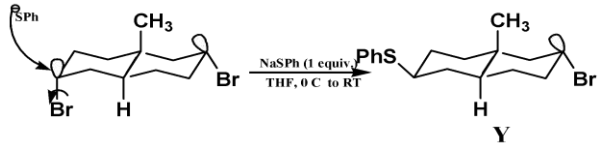
24. Correct Answer is (b):



25. Correct Answer is (d):

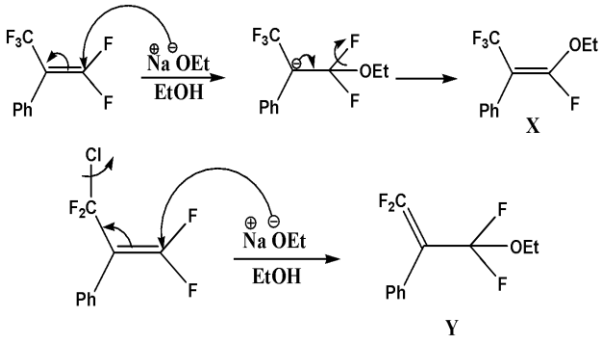


In first reaction tosylation of axial OH group take place



In second reaction substitution at equatorial position of bromine group

26. Correct Answer is (c):



In case of X product Fluorine is not good leaving group & in Y product Chlorine is good leaving group

27. Correct Answer is (b):

Compound IV (Bromo cyclohexane) : Least steric hindrance due to the larger ring size

Compound I (Bromo cyclopentane): More steric hindrance than IV but less than III.

Compound III (Bromo cyclobutane): More steric hindrance and ring strain than I.